Chapter 12
Solutions

12.1 Ideal solutions

Solutions are arguably the most important kind of system studied by chemical engineers, whether in large chemical processing or cellular-level molecular phenomena. The simplest model of a solution is the so-called ideal solution.

An ideal solution is defined by the following properties:

1) Species of the components are non-interacting. In other words, there are no energetic interactions between molecules of different species.

2) At constant temperature and pressure, there is an ideal entropy of mixing that contributes to the total entropy, due to the presence of different components.

3) Ideal solutions are valid in the very dilute limit, where there is one major component and the concentrations of all other species are very small.

In order to develop a thermodynamic model of ideal solutions, we will first evaluate the entropy of mixing. A simple model is sufficient to describe how the entropy changes when two species are mixed. Consider a two component system:

Here, we assume every particle sits on a lattice site. Though the lattice certainly does not represent the molecular structural features of real liquids, our final expression for the entropy of mixing will be insensitive to its use. Initially, the particles on the lattice are separated by an impermeable wall. There is just one configuration for this state and thus the entropy is zero. If we remove the wall, and allow the particles to mix randomly, the number of arrangements of $N_A$ “A” particles and $N_B$ “B” particles is given by how many ways there are to place $N_A$ particles in the $N_A + N_B$ sites:
In the second line, we applied Stirling’s approximation. Taking the logarithm to get the entropy,

\[ \Omega_{\text{mix}}(N_A, N_B) = \frac{(N_A + N_B)!}{N_A! N_B!} \approx \frac{(N_A + N_B)^{N_A+N_B}}{N_A^{N_A} N_B^{N_B}} \]

\[ = \left( \frac{N_A}{N_A + N_B} \right)^{-N_A} \left( \frac{N_B}{N_A + N_B} \right)^{-N_B} \]

(12.1)

In the second line, we applied Stirling’s approximation. Taking the logarithm to get the entropy,

\[ \Delta S_{\text{mix}}(N_A, N_B) = -N_A k_B \ln x_A - N_B k_B \ln x_B \]

\[ = -N k_B (x_A \ln x_A + x_B \ln x_B) \]

(12.2)

where \( x_A \) and \( x_B \) are the mole fractions of A and B particles, respectively, and \( N \) is the total number of molecules. We use \( x_i \) here, rather than \( y_i \) as we did for ideal gases, to indicate we are in the solution phase. We can easily generalize this expression to a system of \( M \) components:

\[ \Delta S_{\text{mix}}(N_1, N_2, \ldots, N_M) = -N k_B \sum_i x_i \ln x_i \]

(12.3)

This expression gives the ideal entropy of mixing. It is also interesting to note that it is the same entropy of mixing we found for ideal gas mixtures. In an ideal solution, this entropy of mixing contributes to the thermodynamic properties of the mixture at constant temperature and pressure. This means that it augments the Gibbs free energy:

\[ G(T, P, N_1, N_2, \ldots, N_M) = \sum_i G_i(T, P, N_i) - T \Delta S_{\text{mix}}(N_1, N_2, \ldots, N_M) \]

\[ = \sum_i G_i(T, P, N_i) + N k_B T \sum_i x_i \ln x_i \]

(12.4)

Here, the first term on the RHS is just the sum of the Gibbs free energies of each of the components in the pure state, at the same temperature and pressure. Since the components don’t interact, these free energies can just be summed directly. The second term on the RHS is the entropy of mixing times the temperature. By taking the \( T \)-derivative of the mixture free energy, it is easy to see that this results in the linear addition of \( \Delta S_{\text{mix}} \) to pure component entropies:
To derive the chemical potentials of each component, we take the \( N_i \)-derivative of the free energy. Note that the chemical potentials, in general, depend on the whole composition of the system, described here using \( \{x\} \):

\[
\mu_i(T, P, \{x\}) = \left( \frac{dG}{dN_i} \right)_{T, P, N_j \neq i} + T \left( \frac{dS_{\text{mix}}}{dN_i} \right)_{T, P, N_j \neq i}
\]

(12.6)

After some simplification,

\[
\mu_i(T, P, \{x\}) = \mu_i^*(T, P) + k_B T \ln x_i
\]

(12.7)

Here, the notation \( \mu_i^*(T, P) \) indicates the chemical potential of pure component \( i \). Therefore, in an ideal solution, the chemical potential of each species is augmented by the quantity \( k_B T \ln x_i \) relative to the pure phase. Moreover, the chemical potential of a species \( i \) depends only on the mole fraction of \( i \), and not the other compositions in the system.

The ideal solution chemical potential comes from a simple model, and it is just an approximation to real systems, capturing only mixing entropy effects. It is typically valid for a component in the limit \( x \to 1 \). Sometimes, however, this approximation is also used at the opposite conditions, where a component is very dilute. This changes the significance of the quantity \( \mu_i^*(T, P) \):

- **Component \( i \) is nearly pure (\( x_i \to 1 \))**: In this case, \( \mu_i^*(T, P) \) gives the usual chemical potential we would expect if we just had a system of pure \( i \) at \( T \) and \( P \).

- **Component \( i \) is very dilute (\( x_i \ll 1 \))**: In this case, \( \mu_i^*(T, P) \) gives the chemical potential of a hypothetical state of pure \( i \) at \( T \) and \( P \) in an infinitely dilute state. This state is unrealizable, and here it is best to think of \( \mu_i^*(T, P) \) as just a constant term in a Taylor expansion of the chemical potential about \( x_i \).

We will avoid using the second convention above because it can be confusing. Instead, we will apply the ideal solution chemical potentials, as often as possible, to the dominant components in solutions where \( x \) is very close to one.
This expression for the chemical potential is central to many problems involving solutions that are in equilibrium with other phases. At equilibrium, the chemical potentials of a component must be equal in different phases, if that component can be transferred between the phases. At constant temperature and pressure, therefore, a general strategy for solving problems involving solutions is to equate the chemical potentials in each phase. Below we discuss several applications of this approach.

12.2 Raoult’s law

Consider a mixture that is at a coexistence temperature and pressure such that there is equilibrium between a vapor and liquid phase. This is often the case, for example, in distillation. Here, we will consider both phases to be ideal:

\[
\begin{array}{c}
\text{ideal gas mixture} \\
T, P \\
\text{ideal solution}
\end{array}
\]

For each component, there must be equality of chemical potentials in the two phases at equilibrium:

\[\mu_{i,G} = \mu_{i,L}\]  \hspace{1cm} (12.8)

If we substitute the ideal solution and ideal gas chemical potentials, we get:

\[\mu_{i,G}^0(T) + k_B T \ln P_i = \mu_{i,L}^*(T, P) + k_B T \ln x_i\]  \hspace{1cm} (12.9)

where \(P_i\) is the partial pressure of component \(i\). After a little rearrangement, we obtain:

\[P_i = x_i \exp\left(\frac{\mu_{i,L}^* - \mu_{i,G}^0}{k_B T}\right)\]  \hspace{1cm} (12.10)

In order to remove the chemical potentials, we consider the behavior as \(x_i \to 1\), that is, as we approach pure component \(i\):

\[P_i^{\text{vap}} = \exp\left(\frac{\mu_{i,L}^* - \mu_{i,G}^0}{k_B T}\right)\]  \hspace{1cm} (12.11)
Here, $P_i^0$ denotes the vapor pressure of pure component $i$, i.e. the vapor-liquid equilibrium pressure at the same temperature. We know this because the equation signifies the equality of chemical potentials of the pure components when $x_i = 1$, which means pure vapor-liquid equilibrium. If we move away from $x_i = 1$, to good approximation, the exponential term involving chemical potentials remains approximately constant, to zeroth order. Therefore, we can rewrite a general relationship between composition and partial pressure as:

$$P_i = x_i P_i^{\text{vap}}$$  \hspace{1cm} (12.12)

This important relationship is known as Raoult’s Law, and it says that the partial pressure of a component in a gas mixture above a solution is given by the mole fraction in the solution times the vapor pressure. Raoult’s law is typically valid near the pure-component limit, where $x_i$ is very close to 1. This is because the ideal solution model works best for near-pure systems, and because the exponential involving the chemical potentials does not vary much near $x_i = 1$.

### 12.3 Boiling-point elevation

Consider a liquid in equilibrium with its vapor phase at its boiling temperature, at constant pressure. A small amount of solute is dissolved in the liquid:

What happens to the boiling point temperature? Here, we compute the change in $T_B$ using the ideal solution model, which will be asymptotically valid in the limit of an infinitely dilute amount of solute. We will assume that none of the solute is present in the vapor phase.

Recall that, at phase equilibrium, the chemical potentials of a component are equal in all of the phases present. For the case in which no solute is present, we have

$$\mu_{G,\text{solute}}^*(T_B, P) = \mu_{L,\text{solute}}^*(T_B, P)$$  \hspace{1cm} (12.13)
Where the “**” superscripts indicate the pure phase chemical potentials. Upon addition of solute to the solvent, we have instead

$$\mu_{G,\text{solvent}}^*(T_B', P) = \mu_{L,\text{solvent}}^*(T_B', P, x_{\text{solvent}}) \quad (12.14)$$

where $T_B'$ is the new temperature at which the chemical potentials are equal, i.e., the new boiling temperature. From here on out, we will drop the “solvent” subscript, though it will be understood that the un-subscripted chemical potentials and mole fractions are those of the solvent and not the solute. Substituting the ideal solution chemical potential for the liquid phase:

$$\mu_{G}^*(T_B', P) = \mu_{L}^*(T_B', P) + k_B T_B' \ln x \quad (12.15)$$

Another way to write this is:

$$\Delta \mu(T_B', P) = k_B T_B' \ln x \quad (12.16)$$

where $\Delta \mu(T_B', P) \equiv \mu_{G}^*(T_B', P) - \mu_{L}^*(T_B', P)$

That is, $\Delta \mu$ is the difference in solvent chemical potential between the pure gas and liquid. Clearly, $\Delta \mu$ equals zero at the original boiling temperature. It is finite, however, at $T_B'$.

We would like to relate the chemical potentials at $T_B'$ to those at $T_B$. For pure phases, we have the thermodynamic identity

$$\frac{d(\mu/T)}{dT} = -\frac{h}{T^2} \quad (12.17)$$

Taking this equation for each of the liquid and gas phases, and subtracting, we can write

$$\frac{d(\Delta \mu/T)}{dT} = -\frac{\Delta h}{T^2} \quad (12.18)$$

where $\Delta h$ is the enthalpy difference between the pure gas and liquid phases. For small changes in temperature, $\Delta h$ can be considered constant, equal to the heat of vaporization at $T_B$. Therefore, we can integrate this expression to get the change in chemical potential between two temperatures:

$$\frac{\Delta \mu(T_B', P)}{T_B'} - \frac{\Delta \mu(T_B, P)}{T_B} = \Delta h_{\text{vap}} \left( \frac{1}{T_B} - \frac{1}{T_B'} \right) \quad (12.19)$$

But since $\Delta \mu(T_B, P) = 0$ due to the pure-phase equilibrium at $T_B$, we have

$$\Delta \mu(T_B', P) = \Delta h_{\text{vap}} \left( 1 - \frac{T_B'}{T_B} \right) \quad (12.20)$$

Substituting this expression for $\Delta \mu$ back into the chemical potential equality, we have
\[
\Delta h_{\text{vap}} \left(1 - \frac{T'_B}{T_B}\right) = k_B T'_B \ln x
\]  

(12.21)

After a little rearranging, we finally find

\[
T'_B = T_B \left(1 + \frac{k_B T_B}{\Delta h_{\text{vap}}} \ln x\right)^{-1}
\]  

(12.22)

In the limit of very small additions of solute, we can use two approximations:

- \( \left(1 + \frac{k_B T_B}{\Delta h_{\text{vap}}} \ln x\right)^{-1} \approx 1 - \frac{k_B T_B}{\Delta h_{\text{vap}}} \ln x \)
- \( \ln x = \ln(1 - x_{\text{solute}}) \approx -x_{\text{solute}}. \)

These are both just Taylor expansions around the point \( x = 1. \) The final result is:

\[
T'_B \approx T_B \left(1 + \frac{k_B T_B}{\Delta h_{\text{vap}}} x_{\text{solute}}\right) \quad (x_{\text{solute}} \ll 1)
\]  

(12.23)

Thus, as solute is added, the boiling point temperature increases since \( \Delta h_{\text{vap}} \) is positive and the term in parenthesis is greater than one. This expression might also be used to estimate the value of \( \Delta h_{\text{vap}} \) by measuring changes in the boiling point temperature of a substance with small additions of a solute.

### 12.4 Freezing point depression

Consider a liquid solution in equilibrium with a pure crystal phase of the solvent. This would be the case, for example, if we mixed salt into a glass of ice water. The derivation for the change in melting temperature \( T_M' \) with solute concentration proceeds almost identically to the one above, starting with

\[
\Delta \mu(T_M', P) = k_B T \ln x \quad (x_{\text{solute}} \ll 1)
\]  

(12.24)

where \( \Delta \mu(T_M', P) \equiv \mu^*_X(T_M', P) - \mu^*_L(T_M', P) \)

Here, the subscript \( X \) indicates the crystal phase. The final result is:

\[
T_M' \approx T_M \left(1 - \frac{k_B T_M}{\Delta h_{\text{freeze}}} x_{\text{solute}}\right) \quad (x_{\text{solute}} \ll 1)
\]  

(12.25)

Where \( \Delta h_{\text{freeze}} \) is the enthalpy of freezing, greater than zero. Therefore, the addition of solute lowers the melting point, since the term in parenthesis will be less than one.
12.5 Osmotic pressure

Consider an experiment where a solution is divided into two cells by a semi-permeable membrane that allows solvent to pass, but not to solute:

In the left cell, there is no solute but instead pure solvent. On the right hand side, a solution is present with both solute and solvent. At equilibrium, the following conditions apply:

- The temperatures of the two sides must be the same, since energy can freely move between the two systems. Each side is also at equilibrium with the environment temperature $T$.
- Because solvent can freely move from one side to another, the solvent chemical potential on the left must equal that on the right.
- The pressure at the top of each column must be the same as that of the environment pressure $P$. The pressures at the bottom can be calculated from $P + \rho g z$ where $g$ is the gravitational constant and $h$ is the height of the liquid.
- The two sides cannot exchange volume with each other, due to the fixed position of the membrane. Therefore, in general, there can be a difference in pressure between the sides at the location of the membrane. That means the heights of the liquids on each side can be different.

In fact, as we will show here, the solute dissolved on the right-hand side of this apparatus will cause solvent to move from left to right, such that the height of liquid on the right is greater than that of the left. The greater liquid on the right means the pressure at the bottom is greater on the right hand side. This pressure difference is called the osmotic pressure.
The equality of solvent chemical potentials on each side leads to:

$$\mu^*(T, P_L) = \mu(T, P_R, x)$$  \hspace{1cm} (12.26)

where $P_L$ and $P_R$ are the left and right pressures, respectively, and subscripts for the solvent have been omitted for simplicity. Substituting the ideal solution chemical potential:

$$\mu^*(T, P_L) = \mu^*(T, P_R) + k_B T \ln x$$  \hspace{1cm} (12.27)

The two pure-component chemical potentials differ only in the pressures at which they are evaluated. Recall that

$$\frac{d\mu}{dP} = \nu$$  \hspace{1cm} (12.28)

For liquids, the molar volume $\nu$ changes very little with small changes in pressure. Thus assuming $\nu$ constant, we can integrate this expression to get

$$\mu^*(T, P_L) - \mu^*(T, P_R) \approx \nu (P_L - P_R)$$  \hspace{1cm} (12.29)

Substituting into the equation for equalities of chemical potentials:

$$\nu (P_L - P_R) = k_B T \ln x$$  \hspace{1cm} (12.30)

Here we define the pressure difference as $\Pi \equiv P_R - P_L$. This is the osmotic pressure. We can easily measure it from the difference in heights of the two sides, using $\Pi = \rho g \Delta z$ where $\Delta z = z_R - z_L$. Using the osmotic pressure we find,

$$\Pi = -\frac{k_B T}{\nu} \ln x$$  \hspace{1cm} (12.31)

For dilute solutions, we can write $\ln x = \ln (1 - x_{\text{solute}}) \approx -x_{\text{solute}}$, so that

$$\Pi = \frac{k_B T}{\nu} x_{\text{solute}}$$  \hspace{1cm} (12.32)

Expanding out $\nu$ and $x$:

$$\Pi = k_B T \frac{N_{\text{solvent}}}{V} \left( \frac{x_{\text{solute}}}{N_{\text{solute}} + N_{\text{solvent}}} \right)$$

$$\approx k_B T \frac{N_{\text{solvent}}}{V} \left( \frac{x_{\text{solute}}}{N_{\text{solvent}}} \right)$$

$$= k_B T \rho_{\text{solute}}$$  \hspace{1cm} (12.33)

Typically we don’t know the molar concentration, but we know the mass of solute originally added to the solution on the right hand side. Therefore $\rho_{\text{solute}} = c_{\text{solute}}/M_{\text{solute}}$, where $c_{\text{solute}}$ is the concentration of solute in mass per volume, and $M_{\text{solute}}$ gives its molecular weight. Finally,
The remarkable significance of this osmotic pressure equation is it provides a way to measure the molecular weight of a solute: a mass of solute can be dissolved into the solvent and the osmotic pressure measured from the height difference $\Delta z$. Knowing $c_{\text{solute}}$ from the initial mass dissolved and the volume of the container, $M_{\text{solute}}$ can be solved. In fact, this is one of the most common ways of measuring molecular weight.

Note that the ideal solution model and the approximations used in this derivation depend on the dilute limit. Typically the osmotic pressure is measured at different values of $c_{\text{solute}}$ and the slope at low dilutions is used to estimate the molecular weight.

\[ \Pi = \frac{k_B T c_{\text{solute}}}{M_{\text{solute}}} \]  

**12.6 Binary mixing with interactions**

What happens if we can’t treat a solution as consisting of non-interacting components? What if the interactions become important?

Here, we will derive a very simple model of interacting solutions based on the lattice model described above. This can be considered a slight extension of the ideal solution where we now accommodate not only the entropy of mixing, but the energy of mixing as well. This is sometimes called a **regular solution**.

Let’s say $N_A$ “A” particles mix with $N_B$ “B” particles, similar to the example described above. Now let’s assume that when two A particles are next to each other, they experience a pairwise energy in the amount $w_{AA}$. Similarly, two B particles interact with an energy $w_{BB}$ and an A and a B particle interact with energy $w_{AB}$.

If we knew exactly the lattice configuration of A’s and B’s, we could sum up all of the kinds of interactions to find the exact energy of the system. Here, instead, we use the **mean field approximation** to compute an average energy. This is the same basic technique we
used to model the lattice gas. Essentially, we assume the particles are well-mixed such that the composition of A and B molecules around any one lattice site is just equal to the overall composition of those components. In reality, differences in energetic interactions will give rise to differences in local compositions, but we will ignore those for now.

Let’s examine the local composition around any one lattice site (or particle):

- average number of A particles = \( zN_A/N \)
- average number of B particles = \( zN_B/N \)

where \( z \) is the number of neighbors to a lattice site (six for three dimensions). Now consider all of the A particles:

- On average, there are \( \frac{1}{2} \times N_A \times zN_A/N \) total A-A contacts. The half accounts for the fact that we don’t want double-count the A-A interactions.
- On average, there are \( N_A \times zN_B/N \) total A-B contacts. We don’t have a half here because we can’t double count the interactions if we always start with an A particle and go to a B particle.

Similarly, for the B particles:

- On average, there are \( \frac{1}{2} \times N_B \times zN_B/N \) total B-B contacts.
- On average, there are \( N_B \times zN_A/N \) total A-B contacts. This is identical to the previous result.

Since we know how many of each kind of contact there are, and we also know the energies of these contacts, we can compute the total energy:

\[
E_{\text{mix}} = \frac{zN_A^2}{2N}w_{AA} + \frac{zN_B^2}{2N}w_{BB} + \frac{zN_A zN_B}{N}w_{AB}
\]  \hspace{1cm} (12.35)

Rewriting in terms of mole compositions:

\[
E_{\text{mix}} = zN \left( \frac{w_{AA}}{2}x_A^2 + \frac{w_{BB}}{2}x_B^2 + w_{AB}x_A x_B \right)
\]  \hspace{1cm} (12.36)

We want to see how this energy is different from the unmixed state, pure A and pure B in separate containers. For the unmixed system, we just have that the total number of AA and BB contacts are proportional to the number of particles, times the number of neighbors:

\[
E_{\text{unmixed}} = zN_A w_{AA} + zN_B w_{BB} = zN (w_{AA}x_A + w_{BB}x_B)
\]  \hspace{1cm} (12.37)

Taking the difference and simplifying using \( x_B = 1 - x_A \), we find after some algebra,

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where we have defined the new quantity $\chi_{AB}$:

$$\chi_{AB} = \frac{Z}{k_BT} \left( w_{AB} - \frac{w_{AA} + w_{BB}}{2} \right)$$ \hspace{1cm} (12.39)$$

This is called the exchange parameter. It measures how different AB interactions are from the AA and BB interactions. If all of the interactions among the components are the same, then $\chi_{AB} = 0$ and there is no energy of mixing.

We now return to the Gibbs free energy expression for this binary mixture. Accounting for both the energy and entropy of mixing, we find

$$G(T, P, N_A, N_B) = G_A(T, P, N_B) + G_B(T, P, N_B) - T\Delta S_{mix}(N_A, N_B) + \Delta E_{mix}(N_A, N_B)$$ \hspace{1cm} (12.40)$$

Simplifying,

$$G = G_A + G_B + Nk_BT [x_A \ln x_A + (1 - x_A) \ln(1 - x_A)] + x_A(1 - x_A)Nk_BT\chi_{AB}$$ \hspace{1cm} (12.41)$$

Here, $G_A$ and $G_B$ are the pure-component free energies. The new term added to the right is due to the energy of mixing. This equation suggests several scenarios:

- $\chi_{AB} = 0$: This just recapitulates the ideal solution model, and energetics are not a factor in solution behavior.
- $\chi_{AB} < 0$: AB interactions are more favorable than AA and BB interactions. This creates a scenario favorable for mixing. Therefore the energy term lowers the free energy.
- $\chi_{AB} > 0$: It is energetically more favorable for A particles to be in contact with other A particles, and for B particles to be near B particles. Thus if the $\Delta E_{mix}$ term grows large enough compared to the $T\Delta S_{mix}$ term, there could be an increase in the free energy upon mixing. The system might therefore phase separate in order to reduce the total free energy.

Here is a diagram of the free energy function for a positive $\chi_{AB}$:
From this diagram, we can see that in the region between the compositions \(x_A^I\) and \(x_A^{II}\), the free energy increases. In fact, if the total system concentration lies between these two values, it is always favorable for the system to spontaneously phase separate into two regions, one with composition \(x_A^I\) and another with composition \(x_A^{II}\). The horizontal tangent line (orange) gives the free energy of the phase-separated region. In this model, the compositions of the two phases are symmetric around \(x_A = 1/2\). This is due to the simplicity of the model, but in general is not the case for real solutions.

The exchange parameter \(\chi_{AB}\) that comes from this model is therefore a simple metric describing the mixing compatibility of two substances A and B. It is frequently used in the study of polymer mixtures, where effective exchange parameters can be measured in a variety of ways, such as solubility and light scattering experiments.

### 12.7 Nonideal solutions, in general

For solutions whose properties deviate substantially from ideality, corrections are usually treated by introducing an activity coefficient \(\gamma\) into the expression for the component chemical potentials:

\[
\mu_i(T, P, x_1, x_2, \ldots) = \mu_i^*(T, P) + k_B T \ln[\gamma_i(T, P, x_1, x_2, \ldots)x_i]
\]  

(12.42)

This approach is reminiscent of the technique used for imperfect gases, where a fugacity was introduced as a fictitious "corrected" pressure. Again, \(\mu_i^*\) is the pure-phase chemical potential. The activity coefficient for each component, \(\gamma_i\), is in general dependent on the state condition, i.e., the temperature, pressure, and all of the compositions. Notice that this complicates the way the component chemical potentials \(\mu_i\) depend on the solution composition.
To completely specify $\gamma_i$, one needs to have a convention for its limiting behavior. Unfortunately, there are two conventions frequently used, which tends to be confusing. Those conventions are:

- $\gamma_i \to 1$ as $x_i \to 1$. That is, as component $i$ becomes the dominant component, the activity returns the ideal solution behavior. That means that $\mu_i^*$ is the pure phase chemical potential for component $i$.

- $\gamma_i \to 1$ as $x_i \to 0$. In other words, as component $i$ becomes infinitely dilute, the activity returns ideal solution behavior. That means that $\mu_i^*_{\text{in}}$ is the pure phase chemical potential for component $i$ in the hypothetical limit of infinite dilution.

Thus, depending on this convention is used, the significance of the pure-phase chemical potential will change. It is therefore important to carefully keep note of the convention being used.

There are, in fact, many models for activities of solutions. These are simply functionalities (equations with parameters) for the activity coefficients. Many of these have been derived from statistical-mechanical theory. From your undergraduate thermodynamics course, you may be familiar with the Margules, van Laar, Redlich/Kister, NRTL, UNIQUA, UNIFAC, and Wilson models. We won’t discuss any particular model of activities in more detail, since these are just parameterizations and do not bring new physics to the table.

### 12.8 Gibbs-Duhem relation

We have found that it is often the case that relationships exist between different thermodynamic variables and their derivatives. Maxwell relations are good examples. Here, we show that similar relationships exist between composition variables in mixtures.

Recall first the Gibbs free energy for a mixture, given in integrated form:

$$G(T,P,N_1,N_2,\ldots,N_M) = \sum_i N_i \mu_i(T,P,\{x\})$$

Where $\{x_i\} = \{x_1, x_2, \ldots, x_N\} = \{N_1/N, N_2/N, \ldots, N_M/N\}$ and $N$ is the total number of particles. The Gibbs phase rule states that, for a single-phase system, $M + 1$ intensive variables completely specify the state of the system. These could be $T$, $P$, and $(M - 1)$ composition variables $x_i$. One composition variable is redundant, since it could always be found using $\sum_i x_i = 1$.

We now show that the composition variables are also related by changes in the thermodynamic properties. The equation above gives the integrated form of $G$. Remember,
this can be derived using Euler’s theorem since \( G \) is extensive in the values \( N_i \). Take the total differential:

\[
dG = \sum_i N_i d\mu_i + \mu_i dN_i \quad (12.44)
\]

Consider also the differential form of the Gibbs free energy, given from the Legendre transform of the energy:

\[
dG = -SdT + VdP + \sum_i \mu_i dN_i \quad (12.45)
\]

Subtracting the two equations, we find

\[
-SdT + VdP = \sum_i N_i d\mu_i \quad (12.46)
\]

This important relationship is called the **Gibbs-Duhem equation**. It shows that differential changes in the temperature, pressure, and chemical potentials of a mixture are all interrelated. Of particular interest are the conditions of constant temperature and pressure, for which \( dT = 0 \) and \( dP = 0 \):

\[
\sum_i N_i d\mu_i = 0 \quad \text{(constant } T, P) \quad (12.47)
\]

For a binary mixture of just two components, we can write

\[
N_1 d\mu_1 + N_2 d\mu_2 = 0 \quad (12.48)
\]

Taking the derivatives with respect to the mole fraction of the first component:

\[
N_1 \frac{d\mu_1}{dx_1} + N_2 \frac{d\mu_2}{dx_1} = 0 \quad (12.49)
\]

\[
N_1 \frac{d\mu_1}{dx_1} + N_2 \left( \frac{d\mu_2}{dx_2} \right) \left( \frac{dx_2}{dx_1} \right) = 0
\]

Simplifying using \( x_1 + x_2 = 1 \) and dividing through by \( N \):

\[
x_1 \left( \frac{d\mu_1}{dx_1} \right)_{T,P} = x_2 \left( \frac{d\mu_2}{dx_2} \right)_{T,P} \quad (12.50)
\]

Thus in a binary mixture, the changes in chemical potentials with composition are strictly related. Clearly this relation is satisfied by an ideal solution, for which \( d\mu_i / dx_i = k_B T / x_i \). For a nonideal solution,

\[
x_1 \left( \frac{d\ln \gamma_1}{dx_1} \right)_{T,P} = x_2 \left( \frac{d\ln \gamma_2}{dx_2} \right)_{T,P} \quad (12.51)
\]
This equation is often very useful in an experimental setting. If the activity of one component in a binary solution is known as a function of composition, this gives a mechanism for computing the activity of the other, by integrating from a reference state (infinite dilution or pure phase).

The **Gibbs-Duhem** relation places constraints on the way in which chemical potentials in a multicomponent system can vary in relation to each other.

### 12.9 Partial molar quantities

Often we are interested in the way in which solution properties change with the amount of each component present. The way we express changes of properties with composition is through a **partial molar** quantity. For any total extensive quantity $X$, like the entropy, volume, or free energy, the partial molar quantity for component $i$ is defined by:

$$\bar{X}_i = \left( \frac{dX}{dN_i} \right)_{T,P,\text{all } N_j \neq i}$$

This equation simply says that a partial molar quantity for $i$ measures the change in a property when the number of moles $N_i$ is varied, holding fixed the amounts of all of the other components. Note also that:

- $\bar{X}_i$ is **intensive**, since $X$ and $N_i$ are both extensive.
- The derivative is at constant $N_j \neq N_i$, which is **not** the same thing as a derivative at constant composition (since changing $N_i$ affects all of the other mole fractions).
- $\bar{X}_i$ is a function of $T, P$, and all the $N_i$.

Because the original quantity $X$ is extensive, it obeys the relationship $X(T, P, \lambda N_1, \lambda N_2, \ldots) = \lambda X(T, P, N_1, N_2, \ldots)$. We can therefore use Euler’s theorem to show:

$$X = \sum_i N_i \left( \frac{dX}{dN_i} \right)_{T,P,\text{all } N_j \neq i}$$

This means that the total quantity $X$ is just the particle-weighted sum of the partial molar quantities:

$$X = \sum_i N_i \bar{X}_i$$

Now we examine some specific partial molar quantities. The partial molar Gibbs free energy is just the chemical potential:
\[ \bar{G}_i = \left( \frac{dG}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} \]

\[ = \mu_i \tag{12.55} \]

This just comes directly from the differential form of \( G \). Next, we consider the partial molar entropies and volumes:

\[ \bar{S}_i = \left( \frac{dS}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} \quad \bar{V}_i = \left( \frac{dV}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} \tag{12.56} \]

Recall that \( dG = -SdT + VdP - \sum \mu_j dN_j \). Therefore, we can use Maxwell relations to convert the entropy and volume derivatives into chemical potential derivatives:

\[ \bar{S}_i = -\left( \frac{d\mu_i}{dT} \right)_{T,\text{all } N_j} \quad \bar{V}_i = \left( \frac{d\mu_i}{dP} \right)_{T,\text{all } N_j} \tag{12.57} \]

Notice that the derivatives are now taken with all mole amounts held constant, i.e., at constant composition. We can now easily find the partial molar enthalpy:

\[ \bar{H}_i = \left( \frac{dH}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} \]

\[ = \left( \frac{d(G + TS)}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} \]

\[ = \left( \frac{dG}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} + T \left( \frac{dS}{dN_i} \right)_{T,P,\text{all } N_{j\neq i}} \tag{12.58} \]

\[ = \mu_i - T \left( \frac{d\mu_i}{dT} \right)_{T,\text{all } N_j} \]

We can re-express the two terms as a single temperature derivative:

\[ \bar{H}_i = -T^2 \left( \frac{d(\mu_i/T)}{dT} \right)_{P,\text{all } N_j} \tag{12.59} \]

You may notice the similarities between the derivatives of the partial molar quantities and the derivatives of intensive thermodynamic variables in pure systems. Consider, for example, that a single-component system has \( h = -T^2(d(\mu/T)/dT)_P \). The analogy with pure systems can help you remember the partial molar relationships. Keep in mind, however, that the partial molar derivatives are performed at constant amounts of the other components in the system.

The considerations above show that, in general, we can write for the chemical potential of one component in a mixture as:
\[ d\mu_i = -S_i dT + \sum_{j=1}^{M-1} \left( \frac{d\mu_i}{dx_j} \right)_{T,P,all \ x_{k\neq j}} dx_j \]  \hspace{1cm} (12.60)

That is, the chemical potential is expressed as function of \( S_i, V_i, \) and \((M - 1)\) mole fractions, since the last mole fraction is redundant \((\sum x_i = 1)\). All of these independent variables are intensive.

**EXAMPLE 12.1**

*Calculate the partial molar volume of a nonideal solution modeled with an activity coefficient.*

For this problem, recall that

\[ \mu_i(T, P, x_1, x_2, ...) = \mu_i^*(T, P) + k_B T \ln[y_i(T, P, x_1, x_2, ...)x_i] \]

Using the expression for \( \bar{V}_i \) derived above,

\[ \bar{V}_i = \left( \frac{d\mu_i}{dT} \right)_{T, all N_j} = \left( \frac{d\mu_i^*}{dT} \right) + k_B T \left( \frac{d\ln y_i}{dT} \right)_{T, all N_j} \]

But the first term applies to a system of pure component \( i \), and is therefore the molar volume of pure \( i \) at the same temperature and pressure. Thus,

\[ \bar{V}_i = v_i + k_B T \left( \frac{d\ln y_i}{dT} \right)_{T, all N_j} \]

This equation provides a way to estimate the pressure dependence of the activity coefficient: one can measure the volume of the solution \( V \) as a function of \( N_i \) and take a derivative to measure \( \bar{V}_i \). The \( v_i \) term is just the volume per particle of pure \( i \) at the same temperature and pressure. Therefore, the activity coefficient derivative is given by:

\[ \left( \frac{d\ln y_i}{dT} \right)_{T, all N_j} = \frac{(\bar{V}_i - v_i)}{k_B T} \]

This equation could be used to reconstruct the value of the activity coefficient between two different pressures.

### 12.10 Constraints along mixture phase boundaries

For the situation in which two mixture phases are in equilibrium, the expression for the chemical potential can be used to derive relationships analogous to the Clapeyron equation. In other words, we can determine how the thermodynamic state changes as we move along a phase boundary.

Consider that we have a binary system of components A and B at vapor-liquid equilibrium. Mole fractions in the liquid phase are denoted \( x_A \) and \( x_B = 1 - x_A \), and those
in the gas phase are \( y_A \) and \( y_B = 1 - y_A \). According to the Gibbs phase rule, the number of variables required to completely specify the (intensive) state of the system is 2 components - 2 phases + 2 = 2 degrees of freedom. These could be the temperature and pressure, for example. Therefore, the phase boundary is two-dimensional.

At equilibrium, we must have equality of chemical potentials of each component in the gas and liquid phases:

\[
\mu_A^l = \mu_A^G \\
\mu_B^l = \mu_B^G
\]  

(12.61)

If we stay on the phase boundary, then a change in state conditions must maintain this equality. Therefore, along the phase boundary:

\[
d\mu_A^l = d\mu_A^G \\
d\mu_B^l = d\mu_B^G
\]  

(12.62)

Substituting the chemical potentials above:

\[
-S_A^l dT + V_A^l dP + \left(\frac{d\mu_A^l}{dx_A}\right)_{T,P} dx_A = -S_A^G dT + V_A^G dP + \left(\frac{d\mu_A^G}{dy_A}\right)_{T,P} dy_A
\]

\[
-S_B^l dT + V_B^l dP + \left(\frac{d\mu_B^l}{dx_B}\right)_{T,P} dx_B = -S_B^G dT + V_B^G dP + \left(\frac{d\mu_B^G}{dy_B}\right)_{T,P} dy_B
\]  

(12.63)

Here, we are leaving off the overbars in the partial molar quantities for clarity.

Next we perform a little trick. We multiply the top equation by \( x_A \), the bottom by \( x_B \), and add them together. We also use the fact that \( dx_B = -dx_A \) and \( dy_B = -dy_A \), since the mole compositions must sum to one in each phase. After a little bookkeeping, the final result is:

\[
-[x_A(S_A^G - S_A^l) + x_B(S_B^G - S_B^l)]dT + [x_A(V_A^G - V_A^l) + x_B(V_B^G - V_B^l)]dP
\]

\[
+ x_A \left(\frac{d\mu_A^l}{dy_A}\right)_{T,P} - x_B \left(\frac{d\mu_B^l}{dy_B}\right)_{T,P} \right] dy_A
\]

\[
- \left[ x_A \left(\frac{d\mu_A^l}{dx_A}\right)_{T,P} - x_B \left(\frac{d\mu_B^l}{dx_B}\right)_{T,P} \right] dx_A = 0
\]  

(12.64)

Let’s simplify the notation by defining \( \Delta S_I \) as the difference in partial molar enthalpies in the two phases, \( \Delta S_I \equiv S_I^G - S_I^l \). We’ll do a similar thing for the volume. Thus we get:
Now, the derivatives of the chemical potentials with respect to composition in each phase are not independent, but related by Gibbs-Duhem relations:

\[
\begin{align*}
y_A \left( \frac{d\mu_A}{dy_A} \right)_{T,P} &= y_B \left( \frac{d\mu_B}{dy_B} \right)_{T,P} \\
x_A \left( \frac{d\mu_A}{dx_A} \right)_{T,P} &= x_B \left( \frac{d\mu_B}{dx_B} \right)_{T,P}
\end{align*}
\] (12.66)

Substituting these expressions into the above equation, we find that the last term in brackets vanishes. The penultimate term in brackets simplifies such that the final equation reads:

\[
\begin{align*}
- [x_A\Delta S_A + x_B\Delta S_B]dT + [x_A\Delta V_A + x_B\Delta V_B]dP + \left[ x_A - x_B \frac{y_A}{y_B} \right] \left( \frac{d\mu_A}{dy_A} \right)_{T,P} dy_A
\end{align*}
\] (12.67)

This equation relates differential changes in \(T\), \(P\), and \(y_A\) along the phase boundary. We could have also derived a similar equation for changes in \(T\), \(P\), and \(x_A\), using the same approach but multiplying the initial chemical potential equality equations by \(y_A\) and \(y_B\) before adding them.

There are three differentials here. If we make changes in two variables, such as \(P\) and \(T\), the change in the other variable is completely specified. This should make sense, since as we found earlier, there are only two degrees of freedom for this binary, two-phase equilibrium.

This Clapeyron-like equation can be manipulated to show specific variances. For example, at constant pressure \((dP = 0)\), we can show that the variation between temperature and composition must obey:

\[
\begin{align*}
\left( \frac{dT}{dy_A} \right)_{P,\text{phase boundary}} &= \frac{\left[ x_A - x_B \frac{y_A}{y_B} \right] \left( \frac{d\mu_A}{dy_A} \right)_{T,P}}{x_A\Delta S_A + x_B\Delta S_B}
\end{align*}
\] (12.68)

This equation has important implications for phase diagrams. Consider the following diagram for a binary mixture:
How does this phase diagram work? At a given temperature $T_0$, one first considers the overall mole fraction of A in the system, $z_A$. Locating this point on the phase diagram, if it lies inside one of the coexistence regions, the system will spontaneously phase separate into liquid and gas phases. The compositions of these phases are given by the point at which the temperature intersects the phase boundaries. The amounts of the phases can be found by a mass balance on A: $N_{tot}z_A = N_Gy_A + N_Lx_A$ with $N_{tot} = N_G + N_L$.

Now consider the point on this curve which is a minimum. This is an azeotrope since the gas and liquid phases have equal composition, $x_A = y_A$. That means that distillation isn’t a viable separation technique at this point since there is no enrichment of one component in the vapor relative to the liquid. For an azeotrope, the differential equation derived above shows that the phase boundary must have zero slope at this point:

$$\left(\frac{dT}{dy_A}\right)_{P,\text{phase boundary}} = \left[\frac{x_A - x_B}{x_B} \frac{y_A}{y_B} \left(\frac{d\mu_A^G}{dy_A}\right)_{T,P}\right] \frac{x_A\Delta S_A + x_B\Delta S_B}{x_A\Delta S_A + x_B\Delta S_B} = 0 \tag{12.69}$$

Therefore, there are thermodynamic constraints on the forms that phase diagrams can take for mixtures. Similar constraints here could be shown at constant temperature or constant composition, rather than constant pressure as we examined here.