Because a lot of chemistry occurs in mixtures (solutions e.g.) or produces a mixture, chemists really need to consider the thermodynamics of mixtures. Fortunately the partial molar quantities—in particular the concept thermodynamic potential—are the key that unlocks that door.

### Partial Quantities and Scaling

Let’s consider a rather odd process: scaling. We have a system of a certain size and we reduce its size stepwise from $\lambda=1$ to $\lambda=0$, e.g. take half of it, throw the other half away and keep repeating the process. Say, the system has two components, initially $n_1$ moles of component 1 and $n_2$ moles of component 2. These number will change as $\lambda$ changes:

\[
[dn_1=n_1d\lambda]
\]
\[
[dn_2=n_2d\lambda]
\]

The Gibbs free energy is an extensive variable that will be affected the same way:

\[
[dG = Gd\lambda]
\]

At constant $(T)$ and $(P)$ we can also write:

\[
[dG = -SdT + VdP + \mu_1dn_1+\mu_2dn_2]
\]

So:

\[
[dG = \mu_1dn_1+\mu_2dn_2]
\]
\[
[Gd\lambda= \mu_1n_1d\lambda+\mu_2n_2d\lambda]
\]

If we integrate this from 0 to 1 (or 1 to 0, it does not matter) we get

\[
[\int_0^1 Gd\lambda= \int_0^1 \mu_1n_1d\lambda+\int_0^1 \mu_2n_2d\lambda]
\]
\[
[G=\mu_1n_1+\mu_2n_2]
\]

By the same argument we have:

\[
[V=V_{\text{bar,1}}n_1+V_{\text{bar,2}}n_2]
\]

where $V_{\text{bar,2}}$ is the partial molar volume for component two. These partial molar volumes are generally a function of composition (and $P,T$) and have been tabulated for a number of liquid systems. They allow us to calculate the real volume of a binary mixture. Volumes are generally speaking not strictly additive. This fact is typically ignored in volumetric analysis and the use of molarities. Fortunately the deviations are often negligible in dilute solutions.
For phase diagrams molarity is not a very suitable quantity to use for concentration. Usually we work with mole fractions or molalities (no volume measure!).

Gaseous Mixtures

Gases can always mix in any ratio and mixtures are typically pretty ideal unless compressed heavily and brought to low temperatures. The only exception is if the gases react (e.g., HCl and NH₃). Apart from that gas molecules experience little interaction from each other and therefore it does not matter much whether the 'each' and the 'other' are different molecules or not. The total pressure can be computed by adding the partial pressures of the two components

$$P_{\text{total}} = P_1 + P_2 \label{PreDalton}$$

Liquid Mixtures

There are binary liquid systems that are fully miscible and are said to be ideal solutions. However, we have to realize that the situation is very different in liquids than in gases. The liquid molecules typically experience strong interactions from their neighbors. For the solution to be ideal the interactions must remain equally strong when the neighbor is not identical. This means it must chemically be very similar. Often liquid binaries are not ideal. The next nearest thing are regular solutions. Even these systems can display phase segregation and limited mutual solubilities at low temperatures. Many liquid-liquid binaries diverge from ideality even more than the regular solutions and many of them are hardly miscible at all.

<table>
<thead>
<tr>
<th>Solution/mixture</th>
<th>Interactions</th>
<th>Miscibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ideal gas</td>
<td>none</td>
<td>complete</td>
</tr>
<tr>
<td>Ideal liquid</td>
<td>strong but similar</td>
<td>complete</td>
</tr>
<tr>
<td>Regular liquid</td>
<td>strong, modestly dissimilar</td>
<td>not always complete</td>
</tr>
<tr>
<td>Real liquid</td>
<td>often strongly dissimilar</td>
<td>partial or none</td>
</tr>
</tbody>
</table>

Table 24.1.1: Solutions

Solid Mixtures

What we said about liquid binaries is even more so for solids. Immiscibility is the rule, miscibility the exception. Even totally miscible systems like electrum (the alloys of silver and gold) are certainly not ideal.
Another point of practical (kinetic rather than thermodynamic) importance is that even if two compounds are able to form a homogenous solid solution, it usually takes heating for prolonged periods to actually get them to mix because solid diffusion is typically very slow. Nevertheless solid solubility is an important issue for many systems particularly for metal alloys. Two molecular solids, e.g. organic compounds, of which the molecules differ vastly in shape, size, polarity and or hydrogen bonding typically have negligible mutual solid solubility. The latter fact is frequently exploited in organic chemistry to purify compounds by recrystallization.

Note

Solid solutions are relatively infrequent and never ideal

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**Ideal liquid/Ideal Gas Phase Diagrams**

When mixing two liquids they typically have different boiling points, one being more volatile than the other. The vapor pressure of a component scales simply with the equilibrium vapor pressure of the pure component. In the gas phase, *Dalton’s law* is applicable

\[
y_i = \frac{P_i}{P_{\text{total}}} \quad \text{(Dalton)}
\]

This is a consequence of the fact that ideal gases do not interact. The latter implies that the total pressure is simply the sum of the partial ones.

\[
P_{\text{total}} = \sum_{i}^N P_i
\]

If the liquid solution is ideal, then the vapor pressure of both components follows *Raoult’s law* that says that the equilibrium vapor pressure above the mixture is the equilibrium pressure of the pure component times the mole fraction.

\[
P_i = x_i P^*_i \quad \text{(Raoult)}
\]

- \(P_i\) is the vapor pressure of component \(i\) in the mixture
- \(P^*_i\) is equilibrium vapor pressure of the pure component \(i\).
- \(x_i\) is the mole fraction of \(i\) component in the liquid phase.

Values for pure components are typically indicated by adding an asterisk * superscript.
The idea behind Raoult's law is that if the interactions are similar that it is a matter of chance which component sits at the interface at a given moment. The equilibrium vapor pressure has to do with the probability that a molecule takes off from the interface depends on both its volatility and how many of them cover the surface we have to multiply \(P^*_i\) with \(x_i\).

Note: Applicability of Raoult's Law

Raoult's law seldom holds completely, which is more applicable if the two components are almost chemically identical like two isomers, e.g., 1-propanol and 2-propanol.

The Pressure Phase Diagram

If we assume that temperature is constant we can plot the total pressure for both Dalton and Raoult's laws versus composition (of gas: \(y_1\) and liquid: \(x_1\) on the same axis).

Liquid Phase:

\[
P_{\text{total}} = P_1 + P_2 = x_1P^*_1 + x_2P^*_2 = x_1P^*_1 + (1-x_1)P^*_2 = P^*_2 - x_1(P^*_2 - P^*_1) \tag{liquidus}
\]

Clearly this is a straight line going from \(P^*_2\) at \(x=0\) to \(P^*_1\) at \(x=1\).

However the composition of the vapor in equilibrium with a liquid at a given mole fraction \(x\) is different than that of the liquid. So \(y\) is not \(x\). If we take Dalton's law (Equation \(\ref{Dalton}\)) and substitute Raoult's Law (Equation \(\ref{Raoult}\)) in the numerator and the straight line in the denominator we get:

\[
y_1 = \frac{x_1P^*_1}{P^*_2 - x_1(P^*_2 - P^*_1)} \tag{vaporus1}
\]

Exercise

Suppose \(P^*_1 = 50\) Torr and \(P^*_2 = 25\) Torr. If \(x_1 = 0.6\) what is the composition of the vapor?

We can rearrange Equations \(\ref{liquidus}\) and \(\ref{vaporus1}\) to plot the total pressure as function of \(y_1\):

\[
P_{\text{total}} = \frac{P^*_1P^*_2}{P^*_1 + (P^*_2 - P^*_1)y_1} \tag{vaporus2}
\]

This is clearly not a straight line.
As you can see when we plot both lines we get a diagram with three regions. At high pressures we just have a liquid. At low pressures we just have a gas. In between we have a phase gap or two phase region. Points inside this region represent states that the system cannot achieve homogeneously. The horizontal tie-line shows which two phases coexists. I used the same 25 and 50 Torr values for the pure equilibrium pressures as in the question above. If you try to make a system with overall composition $x$ and impose a pressure that falls in the forbidden zone you get two phases: a gaseous one that is richer in the more volatile component and a liquid one that is poorer in the volatile component than the overall composition would indicate.

### The Temperature Phase Diagram

Note that the question: what phase do we have when? is really a function of both $P$ and $T$, so that if we want to represent all our knowledge in a diagram we should make it a three dimensional picture. This is not so easy to draw and not easy to comprehend visually either. This is why we usually look at a 2D cross section of the 3D space.

The above diagram is isothermal: we vary $P$, keeping $T$ constant. It is however more usual (and easier) to do it the other way around. We keep pressure constant (say 1 bar, that's easy) and start heating things up isobarically.

The boiling points of our mixtures can also be plotted against $x$ (the liquid composition) and $y$ (the gaseous one) on the same horizontal axis. Again because in general $y$ is not equal $x$ we get two different curves. Neither of them are straight lines in this case and we end up with a lens-shaped two phase region.
What happens to a mixture with a given overall composition $x=x_1$ when it is brought to a temperature where it boils can be seen at the intersection of a vertical line (an isopleth) at $x_{\text{overall}}$ and a horizontal one (an isotherm) at $T_{\text{boil}}$. If the intersection points in inside the two phase region a vapor phase and a liquid phase result that have a different composition from the overall one. The vapor phase is always richer in the more volatile component (the one with the lowest boiling point, on the left in the diagram). The liquid phase is enriched in the less volatile one.

**The Lever Rule**

How much of each phase is present is represented by the arrows in the diagram. The amount of liquid is proportional to the left arrow, the amount of gas to the right one (i.e. it works crosswise). The composition of the liquid in equilibrium with the vapor is:

$$\frac{x_2}{x_{2}^*} = \frac{n^{\text{liq}}_2}{n^{\text{liq}}_{1+2}}$$

$$x_{2}^*n^{\text{liq}}_{1+2} = n^{\text{liq}}_2$$

The composition of the vapor is:

$$\frac{y_2}{y_{2}^*} = \frac{n^{\text{gas}}_2}{n^{\text{gas}}_{1+2}}$$

$$y_{2}^*n^{\text{gas}}_{1+2} = n^{\text{gas}}_2$$

The overall composition is:
\[ x_{all} = \frac{n^{liq+gas}_2}{n^{liq+gas}_{1+2}} \]
\[ x_{all}^*n^{liq+gas}_{1+2} = n^{gas}_2+n^{liq}_2 \]
\[ x_{all}^*n^{liq+gas}_{1+2} = y_2^*n^{gas}_{1+2}+x_2^*n^{liq}_{1+2} \]
\[ x_{all}^*n^{gas}_{1+2}+x_{all}^*n^{liq}_{1+2} = y_2^*n^{gas}_{1+2}+x_2^*n^{liq}_{1+2} \]

Thus:
\[ \frac{n^{liq}_{1+2}}{n^{gas}_{1+2}} = \frac{y_2-x_{all}}{x_{all}-x_2} \]

**Distillation**

The difference in composition between the gas and the liquid can be exploited to separate the two components, at least partially. We could trap the vapor and cool it down to form a liquid with a different composition. We could then boil it again and repeat the process. Each time the vapor will be more enriched in the volatile phase whereas the residual liquid is more enriched in the less volatile one. This process is known as *distillation*. In practice the process is done on a fractionation column which makes it possible to have a series of vapor-liquid equilibria at once.

A good degree of purity can be reached this way, although 100% purity would take an infinite number of distillation steps.