Phase Equilibrium: Fugacity and Equilibrium Calculations

- Relate the fugacity and the chemical potential (or the partial molar Gibbs free energy)
- Use the fugacity coefficient to calculate the vapor phase fugacity
- Use the activity coefficient to calculate the liquid (or solid) phase fugacity
- Identify conditions when a liquid or solid mixture would form an ideal solution
- Explain when Lewis-Randall versus Henry ideal solution reference states are appropriate
- Use the Gibbs-Duhem equation to relate activity coefficients in a mixture
- Perform bubble-point and dew point calculations
- using Raoult's Law
- using complete fugacity relations (assuming known fugacity coefficients and activity coefficients)
- Draw and read Txy and Pxy diagrams for VLE
- Use Henry's Law to calculate VLE for gases dissolved in liquids

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FEC: Definition of Fugacity

Fugacity

We have already established that all of the property relations that are used for the pure-species Gibbs free energy, G, also are applicable for the partial molar Gibbs free energy. Specifically, we are interested right now in the fact that:

$$\left(\frac{\partial \bar{G}_i}{\partial P}\right)_{T,n_i} = \bar{V}_i$$

If we have a closed, isothermal system then T and n_i are *actually* constant (rather than being *held* constant mathematically as in a partial differential) so that this relation becomes:

$$\frac{d\bar{G}_i}{dP} = \bar{V}_i$$

This relation is useful because, in order to obtain a *value* for $\bar{G}_i$ we need to calculate it relative to some other value (i.e., a reference state).

If we consider the simplest case that we can think of, that is an ideal gas, we can rearrange, substitute and integrate

$$\int d\bar{G}_i = \int \bar{V}_i dP = \int \frac{RT}{P} dP = RT \int \frac{dP}{P}$$

$$\bar{G}_i - \bar{G}_i^o = \mu_i - \mu_i^o = RT \ln\left[\frac{P}{P^o}\right]$$

where the $_o$ values refer to whatever the reference state is chosen to be.

There are two issues with this:

- there is not a simple choice of what the reference state should be
- at low (zero) pressure the $\ln$ term goes to $-\infty$

To alleviate these problems, mixture equilibrium relations are not built using the partial molar Gibbs free energy (or chemical potential) but instead with a construct proposed by Lewis.

The **fugacity** of species i in a mixture, $\hat{f}_i$, is defined in the following way:

$$\bar{G}_i - \bar{G}_i^o = \mu_i - \mu_i^o = RT \ln\left[\frac{\hat{f}_i}{\hat{f}_i^o}\right]$$

where the $_\wedge$ denotes the mixture value (as opposed to a pure-species value which would not have the hat).

Note that the utility of this definition lies in the fact that the reference state can be chosen somewhat arbitrarily and, in practice, has very convenient "values" that differ by situation (i.e., vapor, liquid, solid). Also, since f is not *actually* a pressure (even though it has units of pressure), we no longer have the $\ln$ issues.

NOTE:

While we will not rigorously prove it, it is straight-forward to show that the following equations are equivalent:

$$\mu_L = \mu_v$$

$$\hat{f}_i^L = \hat{f}_i^v$$

Henceforth, all phase equilibrium will be based on the fugacity version of this relation.

OUTCOME:

Relate the fugacity and the chemical potential (or the partial molar Gibbs free energy).

FEC: Vapor-phase Fugacity

Vapor-Phase Fugacity

The reference state to choose in calculating the vapor-phase fugacity is particularly simple: an ideal gas mixture. In this way, the denominator in our fugacity definition becomes the partial pressure of an ideal gas at the pressure of interest (P_{tot}).

$$\mu_i - \mu_i^o = RT \ln\left[\frac{\hat{f}_i}{y_i P_{tot}}\right]$$

NOTE:

At low pressures the fugacity approaches that of an ideal gas. That is, it approaches the partial pressure of the species of interest, which is why we write our reference fugacity as $\hat{f}_i^o = y_i P_{tot}$.

Using this expression, we can define the deviation of the vapor from its ideal reference.

DEFINITION:

The **fugacity coefficient**, $\hat{\varphi}_i$ is defined as the ratio of the species fugacity in the vapor mixture to the ideal gas reference state:

$$\hat{\varphi}_i = \frac{\hat{f}_i}{y_i P_{tot}}$$

If one were interested in **calculating** this fugacity coefficient at a given pressure P_{tot} (and a temperature of interest), we would integrate between a low pressure (where the vapor will behave ideally) and the pressure of interest.

$$\int_{P_{low}}^{P} \bar{V}_i dP = RT \ln[\hat{\varphi}_i]$$

When a vapor is behaving ideally, the fugacity coefficient, $\hat{\varphi}_i$, becomes equal to 1. This is easy to see by recalling the above expression:

$$\int_{P_{low}}^{P} \bar{V}_i dP = RT \ln[\hat{\varphi}_i]$$

If the gas behaves ideally, the integral becomes zero (because the pressure to achieve ideal behavior approaches P).

OUTCOME:

Use the fugacity coefficient to calculate the vapor phase fugacity.

FEC: Liquid-phase Fugacity

Liquid-Phase Fugacity

$$\mu_i - \mu_i^o = RT \ln\left[\frac{\hat{f}_i}{f_i^o}\right]$$

For a liquid, a reference state (f_i^o) of an ideal gas is a poor choice. Instead, we choose what is called an ideal solution.

DEFINITION:

*An **ideal solution** is a solution where all of the intermolecular interactions are essentially the same. The two ways that this could be accomplished is:*

- having any composition of mixture with components that are molecularly similar
- having a very dilute (or very concentrated) solution

In both of these cases the intermolecular interactions are the same.

OUTCOME:

Identify conditions when a liquid or solid mixture would form an ideal solution.

The two choices of reference state for the liquid phase fugacity are therefore:

- Lewis-Randall State: a state where a-a type interactions are dominant. This would be the choice for both (all) components in a molecularly similar mixture or the concentrated component in a concentrated/dilute mixture
- Henry State: a state where the a-b type interactions are dominant. This would be the choice for the dilute component in a concentrated/dilute mixture

OUTCOME:

Explain when Lewis-Randall versus Henry ideal solution reference states are appropriate.

Lewis-Randall

For an a-a dominant ideal solution (Lewis-Randall solution), the proper choice of reference state is the pure-species fugacity $\hat{f}_i^{\,o} = x_i f_i$ (Note the lack of a hat.) As we will see, under certain conditions this can reduce to the saturation pressure of the pure substance.

$$\mu_i - \mu_i^o = RT \ln\left[\frac{\hat{f}_i}{x_i f_i}\right]$$

Henry

For an a-b dominant ideal solution (Henry solution), the proper choice of reference state is the so-called Henry's constant for the species $\hat{f}_i^{\,o} = x_i \mathcal{H}_i$. This quantity can be found tabulated in a variety of places.

$$\mu_i - \mu_i^o = RT \ln\left[\frac{\hat{f}_i}{x_i \mathcal{H}_i}\right]$$

For both reference states, it is convenient to define a new quantity ...

DEFINITION:

*The **activity coefficient**, γ_i is defined as the ratio of the species fugacity in the liquid mixture to the ideal solution reference state fugacity:*

$$\gamma_i = \frac{\hat{f}_i}{\hat{f}_i^{\,o}}$$

L-R: $\gamma_i = \dfrac{\hat{f}_i}{x_i f_i}$

Henry: $\gamma_i = \dfrac{\hat{f}_i}{x_i \mathcal{H}_i}$

OUTCOME:

Use the activity coefficient to calculate the liquid (or solid) phase fugacity.

FEC: Solving Equilibrium Problems

Vapor-Liquid Equilibrium

Using our new criterion for vapor-liquid equilibrium (or any phase equilibrium):

$$\hat{f}_i^{\,v} = \hat{f}_i^{\,L}$$

and combine it with our definitions of the fugacity and the activity coefficients:

$$\hat{\varphi}_i = \frac{\hat{f}_i^{\,v}}{y_i P_{tot}} \text{ and } \gamma_i = \frac{\hat{f}_i^{\,L}}{x_i f_i^{\,o}}$$

By rearranging these quantity definitions:

$$y_i \hat{\varphi}_i P_{tot} = x_i \gamma_i f_i^{\,o}$$

OUTCOME:

Use the fugacity coefficient to calculate the vapor phase fugacity

Ideal Gases vs Ideal Solutions

Since we will be using ideal gases (which we are already familiar with) as a reference for gas phase fugacities and ideal solutions for liquid phase fugacities, it is useful to examine the similarities and differences between the two.

NOTE

*An **ideal gas** is one whose molecules occupy no volume and have no intermolecular interactions. It is generally assumed that gases at low pressure approximate this behavior.*

NOTE

*An **ideal solution** is one whose molecules exhibit essentially the same intermolecular interactions between all constituents. It is generally assumed that liquid mixtures that are highly concentrated (dilute) or mixtures of molecularly-similar materials approximate this behavior.*

These ideal mixtures exhibit no change in intermolecular interactions upon mixing, so we can conclude the following:

ideal gas	ideal solution
$\Delta v_{mix}^{ig} = 0$	$\Delta v_{mix}^{is} = 0$
$\Delta h_{mix}^{ig} = 0$	$\Delta h_{mix}^{is} = 0$
$\Delta s_{mix}^{ig} = -R\sum_i y_i \ln[y_i]$	$\Delta s_{mix}^{is} = -R\sum_i x_i \ln[x_i]$
$\Delta g_{mix}^{ig} = RT\sum_i y_i \ln[y_i]$	$\Delta g_{mix}^{is} = RT\sum_i x_i \ln[x_i]$

We can expand the Δg_{mix} as:

$$\Delta g_{mix}^{ig} = \sum_i (\bar{g}_i - g_i)^{ig} = RT\sum_i y_i \ln[y_i]$$

$$\Delta g_{mix}^{is} = \sum_i (\bar{g}_i - g_i)^{is} = RT\sum_i x_i \ln[x_i]$$

If we consider the Δg_{mix} on a component-by-component basis, we can write:

$$(\bar{g}_i - g_i)^{ig} = RT \ln[y_i]$$

$$(\bar{g}_i - g_i)^{is} = RT \ln[x_i]$$

Rearranging and recalling the definition of μ:

$$\mu_i^{ig} = \bar{g}_i^{ig} = g_i^{ig} + RT \ln[y_i]$$

$$\mu_i^{is} = \bar{g}_i^{is} = g_i^{is} + RT \ln[x_i]$$

FEC: Raoult's Law

Raoult's Law

Raoult's Law is a special case of the general vapor-liquid equilibrium expression(s):

$$\hat{f}_i^L = \hat{f}_i^v$$

$$\mu_i^L = \mu_i^v$$

$$x_i \gamma_i f_i^o = y_i \hat{\varphi}_i P_{tot}$$

DEFINITION

Raoult's Law is based on the assumptions that the vapor phase behaves as an ideal gas, while the liquid phase behaves as a (Lewis-Randall) ideal solution.

From the combination of these equations and assumptions, we will start with the following:

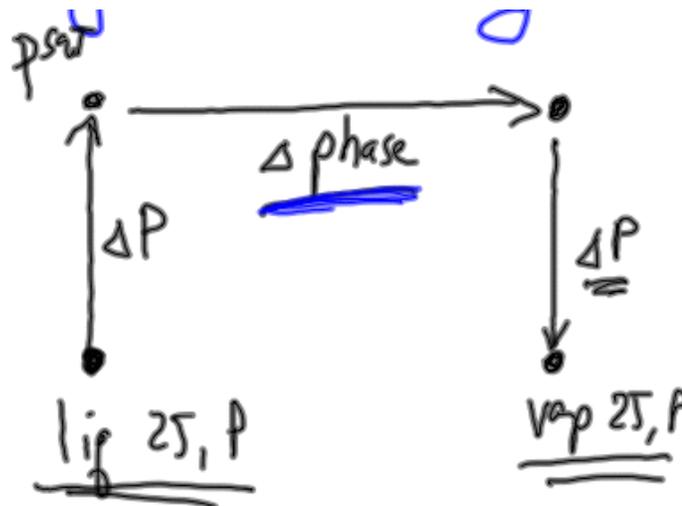$$\mu_i^{ig} = \mu_i^{is}$$

From our previous discussion we can replace these terms to yield the following:

$$\mu_i^{ig} = g_i^{ig} + RT \ln[y_i] = g_i^{is} + RT \ln[x_i] = \mu_i^{is}$$

Rearranging gives:

$$g_i^{ig} - g_i^{is} = RT \ln\left[\frac{x_i}{y_i}\right]$$

The left hand side of this equation requires us to take a three step path in order to evaluate the change in g:

- ΔP from liquid at T and P to liquid at T and P^{sat}
- change of phase
- ΔP from vapor at T and P^{sat} to vapor at T and P

The Δg from each of these steps is respectively:

$$\Delta g_i = g_i^{ig} - g_i^{is} = v_L(P^{sat} - P) + 0 + RT \ln\left[\frac{P}{P^{sat}}\right]$$

NOTE

Two of three of these expressions comes from the relation that $\left(\frac{\partial g}{\partial P}\right) = v$, while the third simply recognizes that there is no Δg associated with a simple phase change.

If we further assume that our system is at low enough pressure, P, that

$$v_L(P^{sat} - P) \approx 0$$

our expression reduces to:

$$g_i^{ig} - g_i^{is} = RT \ln\left[\frac{P}{P^{sat}}\right] = RT \ln\left[\frac{x_i}{y_i}\right]$$

Which can be simplified and rearranged to yield Raoult's Law:

$$y_i P = x_i P_i^{sat}$$

NOTE

The value of $P = P_{tot}$, so this expression is a simple case of the general one at the top except with both activity coefficient (γ_i) and fugacity coefficient ($\hat{\varphi}_i$) equal to 1 (their idealized values). Finally, we also assume that the pure species fugacity (under L-R conditions) is given as P^{sat}, which holds true for low pressure problems.

OUTCOME

Perform bubble-point and dew point calculations using Raoult's Law

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FEC: Phase Equilibrium Calculations

Bubble and Dew Point Calculations

If we need to know any combination of two of the following: concentration of phase "1" (say, liquid), concentration of phase "2" (say, vapor), T of system, P of system, we can start from the phase equilibrium condition

$$\hat{f}_i^\alpha = \hat{f}_i^\beta \text{ for any two (or more!) generic phases, or}$$

$$\hat{f}_i^L = \hat{f}_i^v \text{ specifically for vapor-liquid equilibrium, which gives}$$

$$x_i \gamma_i f_i^{oL} = y_i \hat{\varphi}_i P_{tot}$$

In order to use this equation, we need to know expressions for the fugacity and activity coefficients, as well as models/values for the reference fugacity of the liquid phase.

While the following procedure can be easily modified to relax these simplifications, it is instructive to examine how to use this equation for a system that satisfies Raoult's Law (i.e., one that has an ideal gas vapor phase and liquid mixture that acts as a (L-R) ideal solution), so:

$$x_i P_i^{sat} = y_i P_{tot}$$

Bubble Point

Recall that we can use the Antoine (or Clausius-Clapeyron) Equation in order to get P_i^{sat} in terms of T. Therefore, if we know T and the liquid phase composition we have three unknowns in a binary mixture: y_1, y_2, and P_{tot}. Luckily, we can also write three equations:

$$x_1 P_1^{sat} = y_1 P_{tot}$$

$$x_2 P_2^{sat} = y_2 P_{tot}$$

$$y_1 + y_2 = 1$$

NOTE

Recall that T can be used to explicitly calculate P^{sat} for each component.

If we add the first two equations and combine this with the third, we get:

$$x_1 P_1^{sat} + x_2 P_2^{sat} = (y_1 + y_2) P_{tot} = P_{tot}$$

This can easily be solved for P_{tot} and then P_{tot} can be plugged into either of the first two equations to yield y_1 and y_2.

Dew Point

If, instead, we know P_{tot} and the vapor phase composition we now have five unknowns in a binary mixture: x_1, x_2, P_1^{sat}, P_2^{sat} and T. Luckily, we can also write five equations (explicitly counting the Antoine equations now):

$$x_1 P_1^{sat} = y_1 P_{tot}$$

$$x_2 P_2^{sat} = y_2 P_{tot}$$

$$P_1^{sat} = \exp\left[A_1 - \frac{B_1}{T - C_1}\right]$$

$$P_2^{sat} = \exp\left[A_2 - \frac{B_2}{T - C_2}\right]$$

$$x_1 + x_2 = 1$$

NOTE

*Recall that T is **not** the boiling temperature of either species. Instead, it is the system temperature of interest (so it is the same in the 3rd and 4th equations).*

If we rearrange the first two equations to isolate x_i on the left and *then* add them together, we get:

$$x_1 + x_2 = 1 = y_1 \frac{P_{tot}}{P_1^{sat}} + y_2 \frac{P_{tot}}{P_2^{sat}}$$

Plugging in the Antoine equations into the P_i^{sat} relations on the right we get an equation with T as the only unknown:

$$1 = y_1 \frac{P_{tot}}{\exp\left[A_1 - \frac{B_1}{T - C_1}\right]} + y_2 \frac{P_{tot}}{\exp\left[A_2 - \frac{B_2}{T - C_2}\right]}$$

Once we identify T from this equation, we can plug it into the two P_i^{sat} relations and use those results in the first two equations to yield x_1 and x_2.

OUTCOME

Perform bubble-point and dew point calculations using Raoult's Law

Small variations of these procedures would be used if we knew values or expressions for $\hat{\varphi}_i$ and γ_i, rather than assuming that they were equal to 1 (ideal). Also, a similar procedure would be used for equilibrium between phases other than vapor and liquid (for example, liquid and liquid or even multiple phases).

OUTCOME

Perform bubble-point and dew point calculations using complete fugacity relations (assuming known fugacity coefficients and activity coefficients)

FEC: Gibbs-Duhem and Modeling for Activity Coefficients

Gibbs-Duhem and the Activity Coefficient

Recall that the Gibbs-Duhem equation relates partial molar properties. Here we are specifically interested in applying this to the partial molar Gibbs free energy (or chemical potential), so:

$$0 = \sum_i n_i d[\bar{G}_i] = \sum_i n_i d\mu_i$$

Recalling the definition of fugacity ($\mu_i - \mu_i^o = RT \ln[\frac{\hat{f}_i}{\hat{f}_i^o}]$) and the fact that our reference values are *constants*, we can plug them into this equation to get:

$$0 = \sum_i n_i d\mu_i = \sum_i n_i d[\ln(\hat{f}_i)]$$

Using the expression for a liquid phase fugacity ($\hat{f}_i = x_i \gamma_i f_i^o$) we get:

$$0 = \sum_i n_i d[\ln(\hat{f}_i)] = \sum_i n_i \left[d[\ln(x_i)] + d[\ln(\gamma_i)] + d[\ln(f_i^o)] \right]$$

Again, we recall that our reference fugacity (f_i^o) is a constant (so that derivative goes to zero) and that the sum of the x_i's is *also* a constant (1!) leads us to the fact that the *sum* of those derivatives must be zero, so we can reduce this to:

$$0 = \sum_i n_i [d[\ln(\gamma_i)]$$

which is essentially the Gibbs-Duhem relation applied to activity coefficients.

NOTE

*We did **not** mention whether we were considering Henry or Lewis-Randall states as our reference point because it does not matter! In fact, this equation holds true even if we have a mixture of reference states (that is, we choose Henry for some components and Lewis-Randall for others).*

Now that we know that activity coefficients must be related to each other, we can list the known qualities of activity coefficients:
• they must (collectively) satisfy the G-D relation

- they must approach a value of 1 when the solution approaches conditions that would behave in the same manner as the ideal solution reference

IMPORTANT

This second quality sounds complex, but it simply means that the activity coefficient for the concentrated component must approach 1 as the composition of that component approaches 1 (provided that we chose a Lewis-Randall or "everyone is like me" reference state for that component). Similarly, the activity coefficient should approach 1 for a Henry reference state component as that component's composition goes to zero (because a Henry reference state is like saying "no one is like me").

Margules and other activity coefficient correlations

Provided that empirical correlations satisfy these two conditions, they are valid models for activity coefficient dependence on composition.

DEFINITION

One of the most common correlations for activity coefficients is the Margules model. The "two suffix" version has only 1 fitting parameter and looks (for a binary mixture) like

$\ln(\gamma_1) = A x_2^2$ *and* $\ln(\gamma_2) = A x_1^2$

The "three suffix" version has 2 fitting parameters so it can now accomodate differing "infinite dilution" behavior for the two components and looks (for a binary mixture) like

$\ln(\gamma_1) = x_2^2[A_{12} + 2(A_{21} - A_{12})x_1]$ *and* $\ln(\gamma_2) = x_1^2[A_{21} + 2(A_{12} - A_{21})x_2]$
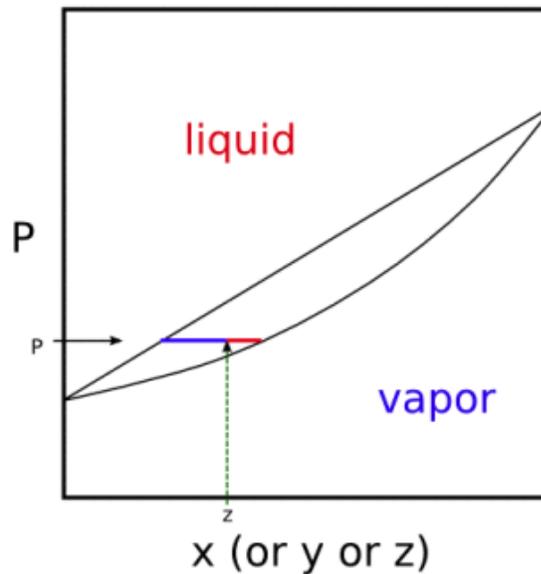
OUTCOME

Use the Gibbs-Duhem equation to relate activity coefficients in a mixture

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FEC: Pxy (Phase) Diagrams

Pxy Diagrams

We often use Pxy and/or Txy diagrams to determine the compositions in VLE problems, but where do they come from?

For simplicity, let's start with Raoult's law for a binary mixture

$$x_1 P_1^{sat} = y_1 P_{tot}$$

$$x_2 P_2^{sat} = y_2 P_{tot}$$

We would like to write the pressure, P_{tot} as a function of the liquid composition. So we add these two equations together:

$$x_1 P_1^{sat} + x_2 P_2^{sat} = (y_1 + y_2) P_{tot} = P_{tot}$$

which we can simplify to:

$$P_{tot} = x_1 P_1^{sat} + (1-x_1) P_2^{sat} = P_2^{sat} + x_1 (P_1^{sat} - P_2^{sat})$$

Which we can plot as a straight line showing the liquid composition (see above). Similarly, to get the pressure as a function of the vapor phase composition, we solve our equation for x_i and then add them to get:

$$x_1 + x_2 = 1 = y_1 \frac{P_{tot}}{P_1^{sat}} + y_2 \frac{P_{tot}}{P_2^{sat}}$$

Solving for P_{tot} gives:

$$P_{tot} = \frac{1}{\frac{y_1}{P_1^{sat}} + \frac{y_2}{P_2^{sat}}}$$

which can be simplified to:

$$P_{tot} = \frac{1}{\frac{y_1}{P_1^{sat}} + \frac{1-y_1}{P_2^{sat}}}$$

This yields the curved line denoting the vapor phase composition (above).

NOTE:

This procedure is not fundamentally different for the case when the fugacity and/or activity coefficients are non-ideal (i.e., not 1), except that they often depend on composition as well so that our "lines" become more curved.

Tie Lines
DEFINITION:

Tie lines are the name given to lines that bridge the "coexistence space" in a phase diagram. In the example above the lens-shaped region between the line and the curve is a "no mans land" that separates the vapor phase compositions from the liquid phase compositions. The bi-colored line is an example of a tie line.

Tie lines are useful because the are graphical examples of a material balance. For example, write two balance equations for the binary mixture depicted here:

$$x_1 L + y_1 V = z_1 M$$

$$M = L + V$$

Here z_1 depicts the "total" composition considering both phases at once and M is the total mass in the system (again, considering both phases at once). Combining these equations gives:

$$x_1 L + y_1 V = z_1(V + L) = z_1 V + z_1 L \text{ or (rearranged)}$$

$$L(x_1 - z_1) = V(z_1 - y_1)$$

Rearranging one last time shows that the ratio of the line segment lengths is equal to the ratio of the amount of material in both phases.

$$\frac{L}{V} = \frac{(z_1 - y_1)}{(x_1 - z_1)}$$

NOTE:

The line segments are "backwards". That is, the red line (on the right) shows the relative amount of liquid (which is found to the left of the lens region), while the blue line (on the left) corresponds to the relative amount of vapor (which is found on the left of the lens shaped region).

OUTCOME:

Draw and read Txy and Pxy diagrams for VLE

FEC: Henry's Law

Henry's Law

Henry's Law is a special case of the general vapor-liquid equilibrium expression(s):

$$x_i \gamma_i f_i^o = y_i \hat{\varphi}_i P_{tot}$$

DEFINITION

Henry's Law is based on the assumptions that the vapor phase behaves as an ideal gas, while the component of interest in the liquid phase behaves as a (Henry) ideal solution. This would be a valid assumption if that component was very dilute or if it had much stronger interactions with the other mixture components than it does with itself.

From the combination of these equations and assumptions, we can replace these terms to yield the following:

$$x_i \, \mathcal{H}_1 = y_i P_{tot}$$

NOTE

The left hand side of this "law" is a particularly good assumption for components that are above their critical temperature. Examples would include "gases" (as opposed to vapors) like nitrogen, oxygen, etc. at room temperature.

OUTCOME

Use Henry's Law to calculate VLE for gases dissolved in liquids