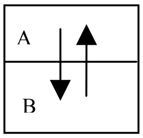
Vapor Liquid Equilibrium (VLE): **10.213** **04/29/02**
A Guide Spring 2002 YT

Here is a somewhat more systematic approach to VLE. There will not be much derivation from first principle. I suggest that you go through the derivation done in lecture notes or the textbook, once you are comfortable with the material here. They hopefully will make more sense then.

Fugacity

We use fugacity to represent equilibrium because fugacity is directly related to Gibbs free energy G (see eqn 11.30 in textbook). In an equilibrium between two phases A and B, $G_i^A = G_i^B$ (the G's of component *i* in both phases are the same). Since *f* is directly related to G, we can also say $\hat{f}_i^A = \hat{f}_i^B$. You can think of fugacity as "tendency to escape":

$\hat{f}_i^A = \hat{f}_i^B$: the tendency of *i* to escape A phase = the tendency of *i* to escape B phase



So for vapor-liquid equilibrium, besides saying that $G_i^L = G_i^V$, we can also say:

$$\boxed{\hat{f}_i^V = \hat{f}_i^L}$$

The hats as usual indicate that we are dealing with mixtures. Our task now is to get expressions for these fugacities.

Vapor fugacity

Pure Vapor

We learned for pure vapor:

$$\boxed{f_i^V(T,P) = \phi_i(T,P)P}$$

Note the missing hat (because this is for pure component). Here ϕ_i is the fugacity coefficient for pure component *i*, a measure of deviation from ideal gas behavior. How do we calculate this ϕ_i? Several methods:

1) $\ln\phi = \dfrac{G^R}{RT}$ if G^R/RT is known

2) $\ln\phi = \int_0^P (Z-1)\dfrac{dP}{P}$ if Z is given as Z = f(P,T), e.g. $Z = 1 + B'(T)/P$

3) $\ln\phi = (\ln\phi)^0 + \omega(\ln\phi)^1$ using generalized correlation tables; good if Z is not given as some function

Vapor Mixture

Now we want a more general expression for the fugacity: the fugacity in gas mixtures, not just a pure gas. The fugacity of a component i in the vapor phase is:

$$\boxed{\hat{f}_i^V(T,P) = \hat{\phi}_i(T,P)P_i = \hat{\phi}_i(T,P)y_iP} \qquad (1)$$

Again, the "hats" indicate mixture. How do we get $\hat{\phi}_i$? It's not the same as the pure fugacity coefficient. We didn't cover this in class but the method the textbook offers is to use the virial EOS with a mixing rule (p. 393-5 and 398). For now, just keep in mind that $\hat{\phi}_i$ (for a component in mixture) is not calculated the same way as ϕ_i (for a pure substance).

Liquid Fugacity

Pure Liquid

We learned in class:

$$\boxed{f_i^L(T,P) = \phi_i^{sat}(T,P_i^{sat})P_i^{sat}\exp\left[\frac{V_i^L(P-P_i^{sat})}{RT}\right]} \qquad (2)$$

Liquid Solution

Fugacity of liquid solution has to be defined somewhat differently. The reason for not using the same formulation as gas is that there is no good easy model for ϕ for liquid mixtures. Thus we turn to the concept of activity coefficient γ. We use activity coefficient to relate the fugacity of the pure species to that in a mixture by:

$$\hat{f}_i^L = \gamma_i x_i f_i^L$$

Once again, the hat indicates mixture and no hat indicates pure component. γ_i is the deviation from ideal case. For ideal solution, $\gamma_i = 1$.

Plugging in the pure liquid fugacity eqn (2), we get the general expression for liquid fugacity in mixture:

$$\boxed{\hat{f}_i^L = \gamma_i x_i \phi_i^{sat} P_i^{sat} \exp\left[\frac{V_i(P-P_i^{sat})}{RT}\right]} \qquad (3)$$

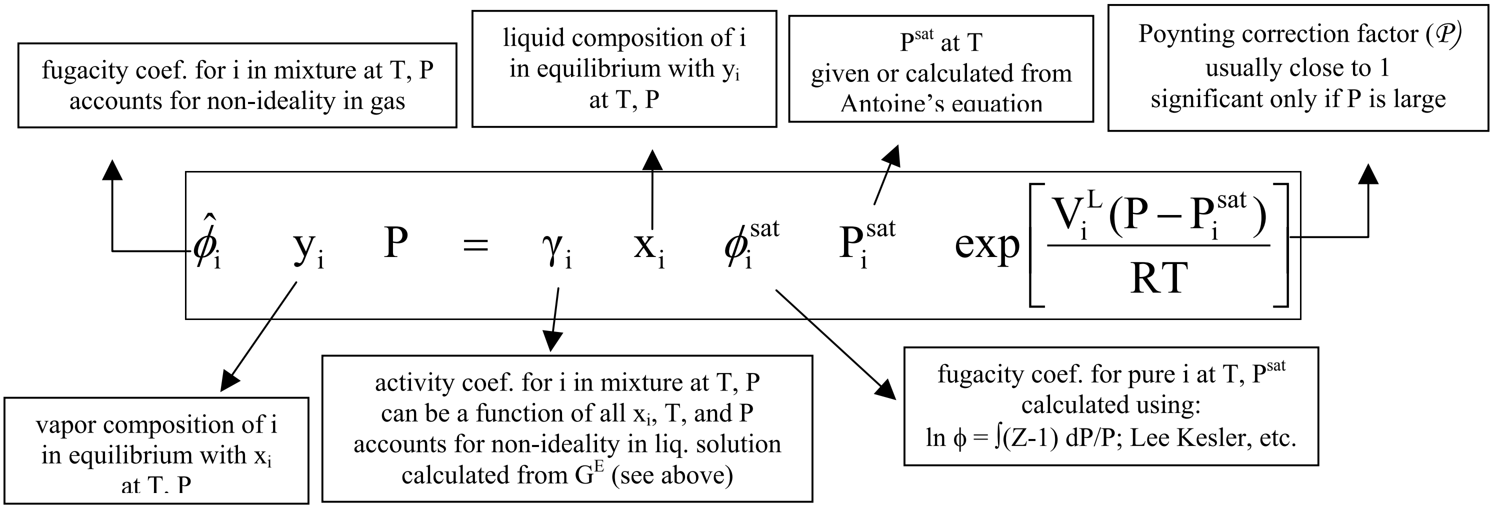
ϕ_i^{sat} is calculated from one of the 4 methods given in the "Vapor fugacity" section for the pure i (not mixture). How does one obtain γ_i? This is normally measured in experiment and then fitted to give some expression for G^E. This is useful because:

$$\ln\gamma_i = \frac{\overline{G}_i^E}{RT} = \frac{1}{RT}\left[\frac{\partial(nG^E)}{\partial n_i}\right]_{T,P,n_{j\neq i}}$$

Recall that there are other ways to calculate partial molar properties from G^E. For binary, there is the "graphical method". Then there is also Gibbs-Duhem equation. These all should give the same result.

Putting Them Together

If we equate the fugacity of liquid and vapor in mixture ($\hat{f}_i^V = \hat{f}_i^L$) from (2) and (3), the general expression for VLE:



$$\hat{\phi}_i \quad y_i \quad P \quad = \quad \gamma_i \quad x_i \quad \phi_i^{sat} \quad P_i^{sat} \quad \exp\left[\frac{V_i^L(P-P_i^{sat})}{RT}\right]$$

Special cases

($\mathcal{P}$ = Poynting correction factor)

1) ideal gas, ideal liq. solution, low P:
   $\phi = 1$, $\gamma = 1$, $\mathcal{P} = 1$ $y_i P = x_i P_i^{sat}$ (Raoult's Law)

2) ideal gas, non-ideal liq. solution, low P:
   $\phi = 1$, $\mathcal{P} = 1$ $y_i P = \gamma_i$xiPisat (modified Raoult's Law)

3) non-ideal gas and liq. solution, moderate P:
   $\mathcal{P} = 1$ $\hat{\phi}_i y_i P = \gamma_i x_i \phi_i^{sat} P_i^{sat}$

4) only one component in V or L:
   use the pure vapor (2) or pure liquid (3) fugacity expressions