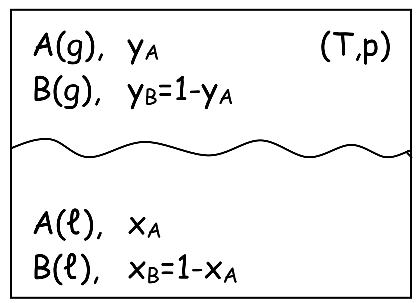
5.60 Thermodynamics & Kinetics
Spring 2008

Two-Component Phase Equilibria II
Ideal and Non-Ideal Solutions

How do we use liquid-gas binary mixture phase diagrams?

We use them to find the compositions of the gas and liquid phases at coexistence.

Consider again our typical system:



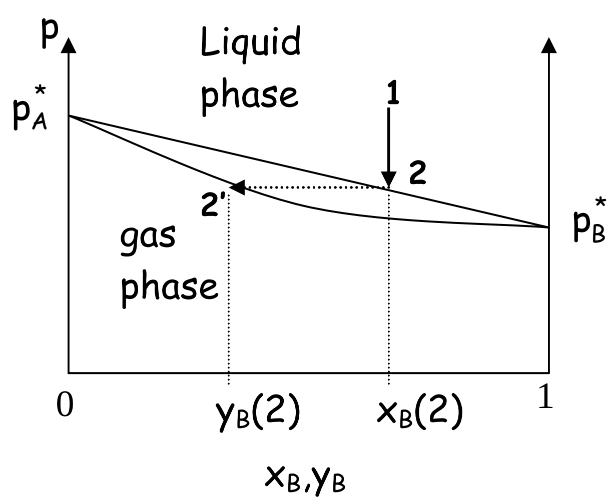
Here <u>A is more volatile than B</u> (for constant T, $p_A^* > p_B^*$).

Suppose start at point "1" in the pure liquid phase.

As we decrease the pressure, we eventually reach "2" on the coexistence line.

The system now consists of a liquid phase and a very small amount of gas phase.

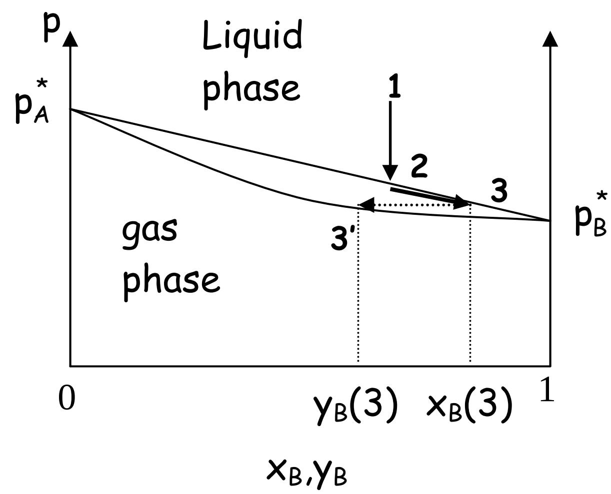
The composition of the liquid phase at this point is $x_B(2)$.



To find out the composition of the gas phase, we have to switch to the coexistence line that is described by y_B, keeping p the same. That is point 2'. The composition of the gas phase is then given by

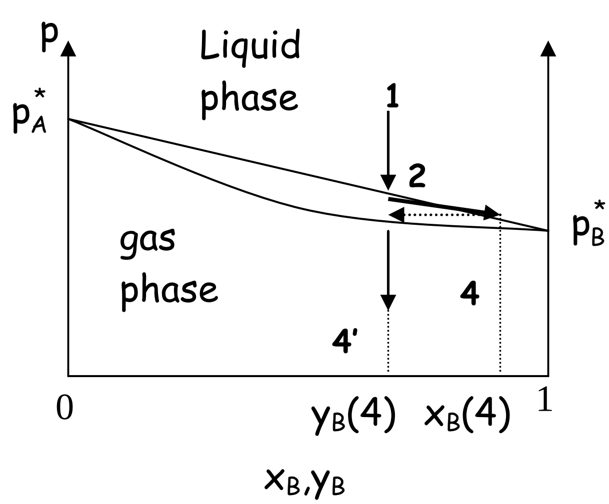
$y_B(2)$. Note here that $y_B(2)<x_B(2)$, the gas phase is "rich" in the more volatile component.

We don't have to stop changing the pressure when we reach "2" in the diagram above.



If we keep decreasing the pressure to "3," we stay on the coexistence line as long as there are two phases around and the compositions in the liquid and gas phases can be read off at $x_B(3)$ and $y_B(3)$.

Note that this increases the fraction of B in the liquid phase, enriching the liquid phase in the less volatile component.



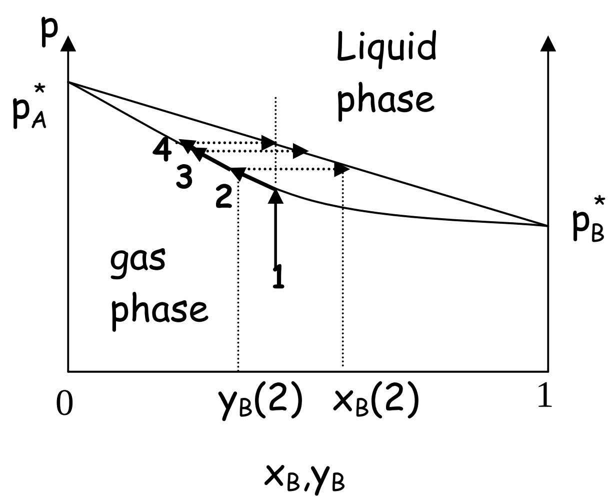
We stay on the coexistence line as pressure decreases until $y_B(4)=x_B(1)$.

Then the composition in the gas phase is the same as what it was at "1". There is then no more liquid left, and we continue down the phase diagram into the pure gas phase.

Lever Rule

How can you determine the quantities in each phase?

What is the number of moles in solution and gas at (2) and (3)?



n_A, n_B ≡ total # moles of A, B
n_g, n_ℓ ≡ total # moles of gas, liq

At (1): pure gas
$n_A = y_A(1)n_g(1) = y_A(1)n_{total}$

At (2): gas-liq mixture
$n_A = y_A(2)n_g(2) + x_A(2)n_\ell(2)$

$\Rightarrow \quad y_A(2)n_g(2) + x_A(2)n_\ell(2) = y_A(1)n_{total} = y_A(1)[n_g(2) + n_\ell(2)]$
$\quad [y_A(1) - y_A(2)]\, n_g(2) = [x_A(2) - y_A(1)]\, n_\ell(2)$

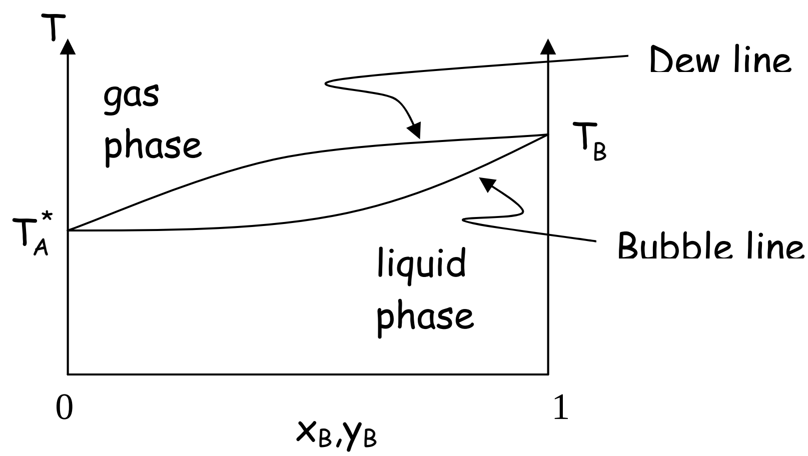
$\Rightarrow$ Ratio of gas to liq is $\dfrac{n_g(2)}{n_{liq}(2)} = \dfrac{x_A(2) - y_A(1)}{y_A(1) - y_A(2)}$ ratio of "lever arms"

So if $x_A(4) = y_A(1) \Rightarrow n_g(4) = 0 \quad \Rightarrow$ no more gas!

T-x Diagrams

Instead of T being fixed as in the diagrams above, we can keep p fixed. The same kind of phase diagrams can be generated, with (T,x_B) or (T,y_B) as the independent variables:

Let's keep A more volatile that B ($T_A^* < T_B^*$)



And the arguments for the pressure-composition diagrams now apply to these Temperature-composition diagrams as well.

Temperature-composition diagrams explain distillation.

Ideal Solutions:

Solutions that obey Raoult's law are called "ideal" solutions.
What does that imply about the chemical potential?

At coexistence: $\mu_A(\ell,T,p) = \mu_A(g,T,p_A)$

Assuming Ideal Gas: $\mu_A(g,T,p_A) = \mu_A^{o}(g,T) + RT\ln p_A$

So… $\mu_A(\ell,T,p) = \mu_A^{o}(g,T) + RT\ln p_A$

If the system were <u>pure</u> A, then

$$\mu_A^{*}(\ell,T,p) = \mu_A^{o}(g,T) + RT\ln p_A^{*}$$

So for the mixture: $\mu_A(\ell,T,p) = \mu_A^{*}(\ell,T,p) + RT\ln \dfrac{p_A}{p_A^{*}}$

But Raoult's says that $p_A = x_A p_A^{*}$

Finally then, for an <u>ideal solution</u>:

$$\boxed{\mu_A(\ell,T,p) = \mu_A^{*}(\ell,T,p) + RT\ln x_A}$$

Chemical potential "A" in mixture

Chemical potential "A" in pure liquid

Mole fraction of "A" in mixture

Looks just like a mixture of ideal gases except that the g's are replaced by ℓ's.

Note that $\boxed{\mu_A(\ell,T,p)(\text{Mixture}) \le \mu_A^{*}(\ell,T,p)(\text{Pure})}$