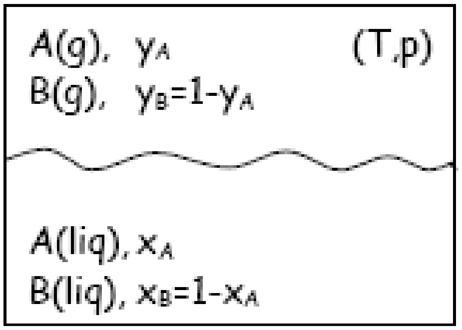
5.60 Thermodynamics & Kinetics
Spring 2008

Two-Component Phase Equilibria

Goal: Understand & predict effects of mixing of substances on vapor pressure, boiling point, freezing point, etc.

Binary liquid-gas mixtures (non-reacting):



Total # of variables: 4

(T, p, x_A, y_A)

Constraints due to coexistence: 2

$\mu_A(\ell) = \mu_A(g)$

$\mu_B(\ell) = \mu_B(g)$

independent variables $F = 4 - 2 = 2$

Only 2! e.g. knowing (T,p) uniquely determines the compositions in the liquid & gas phases

Generalization: **Gibbs phase rule** gives # independent variables needed to describe a multi-component system where different phases coexist in equilibrium

$$\boxed{F = C - P + 2}$$

F ≡ # degrees of freedom (independent variables)
C ≡ # components
P ≡ # phases

How do we get this?

Suppose a system has C components and P phases.
What are all the variables?
First, T and p.

Then in each phase "α", each component is specified by its mole fraction, with the constraint that $\sum_{i=1}^{C} x_i^{(\alpha)} = 1$.

So the composition of each phase is specified by (C – 1) variables.
With P phases, we have P(C – 1) variables.
Including T and p, the total # variables is P(C – 1) + 2.

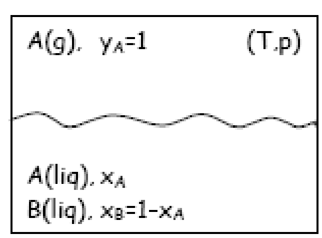
Now add constraints due to phase equilibria:
Chemical potential of each component is the same in all the phases.
e.g. for component "i", $\mu_i^{(1)} = \mu_i^{(2)} = \ldots \mu_i^{(P)} \Rightarrow$ P – 1 constraints
For C components, it's C(P – 1) constraints altogether

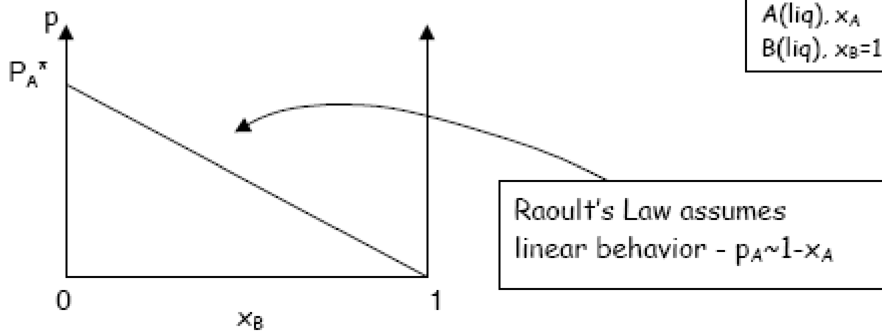
So total # independent variables is F = P(C – 1) + 2 - C(P – 1)
F = C – P + 2 Gibbs phase rule

For 1-component system: F = 3 – P
P = 1 $\Rightarrow$ F = 2 Can vary freely in (T,p) plane
P = 2 $\Rightarrow$ F = 1 Can vary along coexistence curve T(p)
P = 3 $\Rightarrow$ F = 0 No free variables at triple point (T_t,p_t)
P = 4 $\Rightarrow$ Impossible! Can't have 4 phases in equilibrium

Raoult's Law and Ideal Solutions

"A" is a volatile solvent (e.g. water)
"B" is a nonvolatile solute (e.g. antifreeze)



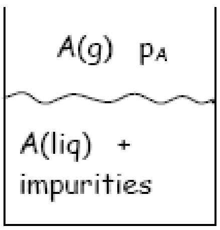


$p_A^* \equiv$ vapor pressure of pure A at temperature T

Raoult's Law assumes a linear dependence
Solvent and solute do not interact, like in mixture of ideal gases

$$\boxed{p_A = x_A p_A^*} = (1-x_B)p_A^*$$

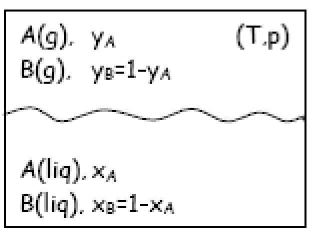
Application: Vapor pressure lowering (our first "colligative" property)

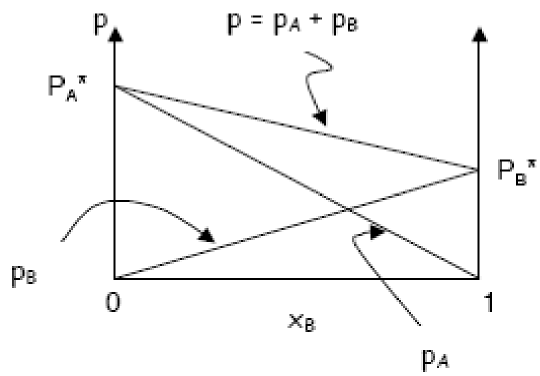


$$p_A^* - p_A = p_A^* - x_A p_A^* = (1 - x_A)p_A^* = x_B p_A^* > 0$$

So $p_A < p_A^*$
Vapor pressure is lowered in the mixture

Now let's consider both A and B volatile





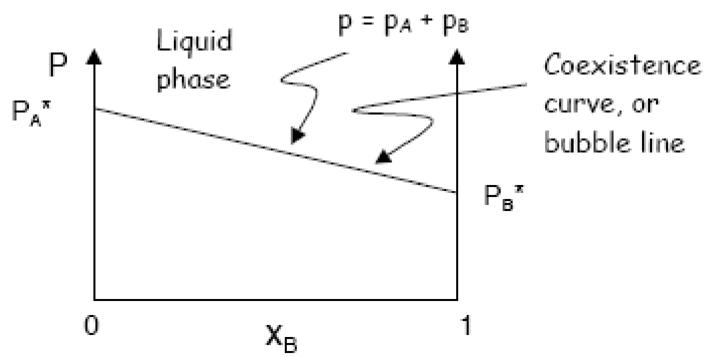
$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^*$$

$$p = p_A + p_B = x_A p_A^* + x_B p_B^*$$

$$(x_A + x_B = 1)$$

"Ideal" solutions ≡ both components obey Raoult's Law

The diagram above shows the composition of the liquid phase
It does not provide information about the gas phase composition



The gas phase is described by y_A or y_B. If T and x_A are given, then y_A and y_B are fixed (by Gibbs phase rule). That is, if T and the composition of the liquid phase are known, then the composition of the gas phase is determined.

So how do we get y_A?

$p_A = y_A p$ (Dalton's Law)

$p_A = x_A p_A^*$ and $p_B = x_B p_B^* = (1 - x_A) p_B^*$ (Raoult's Law)

$$y_A = \frac{p_A}{p} = \frac{p_A}{p_A + p_B} = \frac{x_A p_A^*}{x_A p_A^* + (1 - x_A) p_B^*}$$

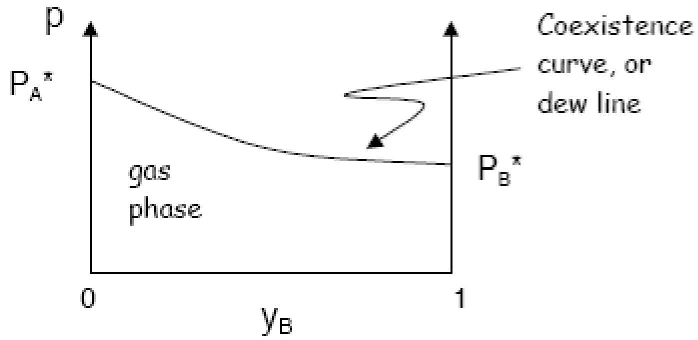
$$y_A = \frac{x_A p_A^*}{p_B^* + (p_A^* - p_B^*) x_A}$$

Inverting this expression $\Rightarrow$ $x_A = \dfrac{y_A p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$

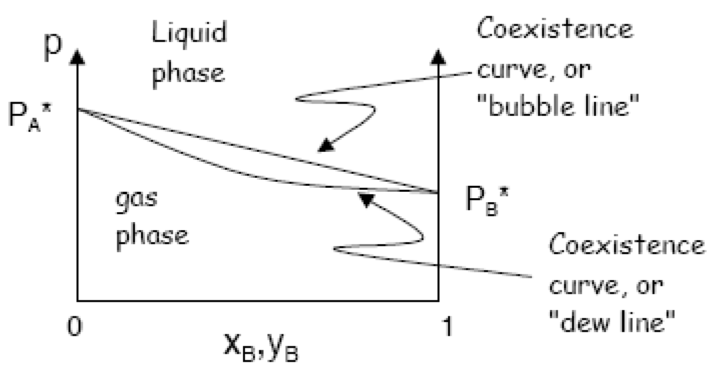
Combining these two results $\Rightarrow$ $p = \dfrac{p_A}{y_A} = \dfrac{x_A p_A^*}{y_A}$

or $p = \dfrac{p_A^* p_B^*}{p_A^* + (p_B^* - p_A^*) y_A}$

This is summarized in the following diagram:



Combining both diagrams into one plot:



This allows us to see the compositions of both liquid and gas phases

If we know the composition of one phase at a given T, we can determined the composition of the other phase from the diagram