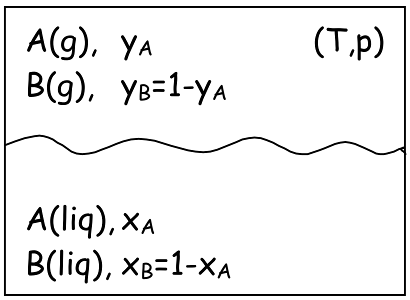
Two-Component Phase Equilibria

Goal: To understand and predict the effect mixing substances has on properties such as 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

$\mu_A(liq)=\mu_A(g)$

$\mu_B(liq)=\mu_B(g)$

The number of independent variables (degrees of freedom) in the system is

$$F = 4 - 2 = 2$$

There are only 2 independent variables. For example, knowing (T, p) uniquely determines the compositions in the liquid and gas phases.

We can generalize this.

Gibbs phase rule: Gives the number of independent variables needed to describe a multi-component system where different phases coexist in equilibrium

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

where F is the number of degrees of freedom (independent variables), C and P are the number of components and the number of phases, respectively.

Josiah Willard Gibbs

How do we get this?

Suppose we have a system that has C components and P phases.

Before putting in the constraint of phase equilibrium, to describe the system, we first specify T and p. Then in each phase "α", each of the C components is described by its mole fraction $x_i^{(\alpha)}$, with the constraint that

$$\sum_{i=1}^{C} x_i^{(\alpha)} = 1$$

So the composition of each phase is described by (C-1) variables. With P phases, we require P(C-1) variables. Adding T and p, describing the system then requires P(C-1)+2 variables.

Now let's add the constraints of equilibrium: The chemical potential of a component must be the same in all the phases.

So, for component "i" for example, $\mu_i^{(1)} = \mu_i^{(2)} = \ldots = \mu_i^{(P)}$. This is P-1 constraints. Since there are C components, the total number of constraints as a result of phase equilibrium is C(P-1).

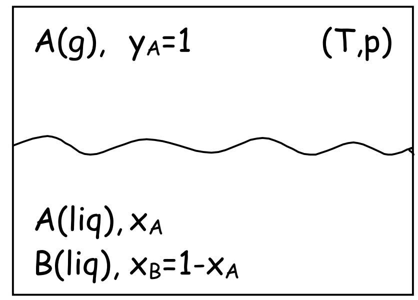
So the total number of independent variables (F) is
F = P(C-1)+2-C(P-1) = <u>C-P+2</u>, the Gibbs' phase rule.

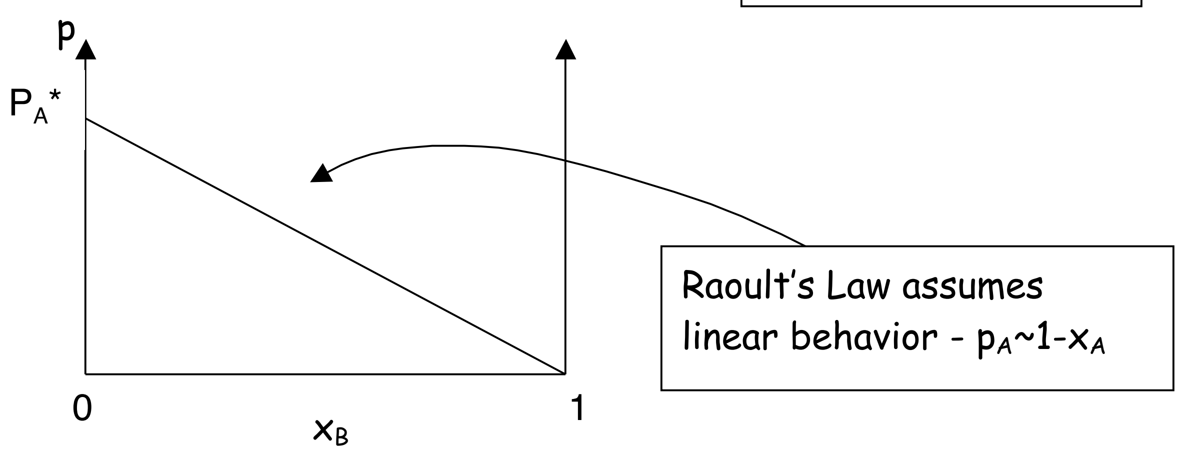
Implication of Gibbs' phase rule for a one-component system:

P=1 $\rightarrow$ F=2 (T,p) defines a coexistence plane
P=2 $\rightarrow$ F=1 T(p) defines a coexistence line
P=3 $\rightarrow$ F=0 T_t,p_t uniquely defines a triple point
P=4 $\rightarrow$ F=-1 IMPOSSIBLE!

Raoult's Law and Ideal Solutions:

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



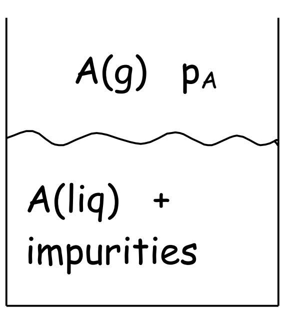


p_A^* is the vapor pressure of <u>pure</u> A at temperature T.

<u>Raoult's law</u> assumes linear dependence (solute and solvent do not interact, like mixture of ideal gases):

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

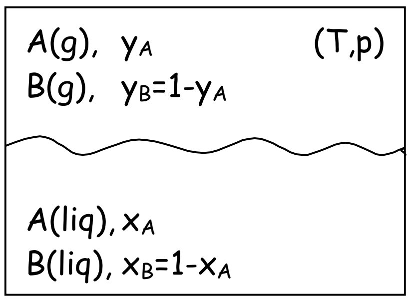
<u>Application: Vapor pressure lowering</u> (our first "colligative" property)

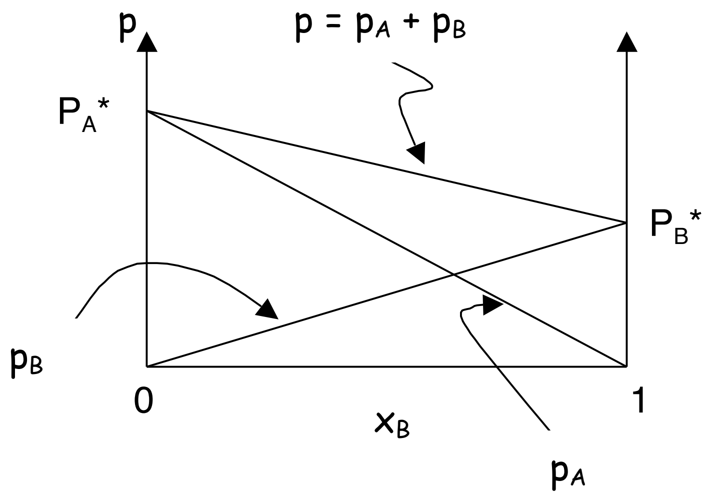


$$p_A^* - p_A = p_A^* - x_A p_A^* = (1 - x_A)p_A^* = x_B p_A^* \quad > 0$$

$$\text{So} \quad p_A < p_A^*$$

Let's now have <u>both A and B volatile</u>





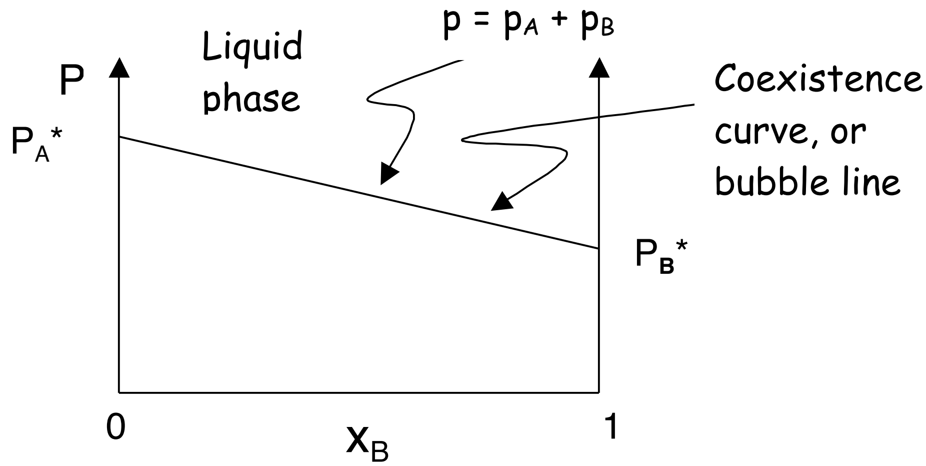
$$p_A = x_A p_A^* \quad \text{and} \quad p_B = x_B p_B^*$$

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

$$(x_A + x_B = 1)$$

Solutions where both components obey Raoult's Law are called "ideal"

Note: The diagram above described the composition of the <u>liquid phase</u>. It does <u>not</u> provide any information about the composition of the gas phase.



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 the Gibbs phase rule). That is, if T and the composition of the liquid phase are known, then the composition of the gas phase is automatically 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)

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

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

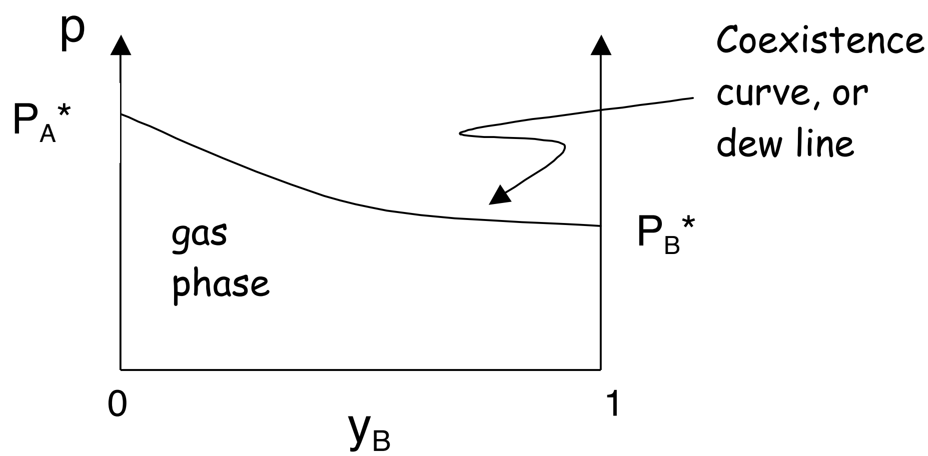
And by inverting the equation,

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

Putting these last two equations together:

$$p = \frac{p_A}{y_A} = \frac{x_A p_A^*}{y_A} \quad or \quad p = \frac{p_A^* p_B^*}{p_A^* + \left(p_B^* - p_A^*\right) y_A}$$

This is summarized in the following diagram:



And combining both phase diagrams into one plot: