

Recapitulation and today's lecture

Last time, we introduced molar and partial molar quantities and we found that Gibbs free energy has a unique characteristic: the molar quantity of Gibbs free energy is equal to the partial molar quantity of Gibbs free energy. This characteristic was used to deduce the Gibbs-Duhem relations. We also showed that for a multiple-phase system by using equilibrium conditions and Gibbs-Duhem relations, how the Gibbs phase rule is developed.

Today, we will discuss *very important* graphical constructions that determines the equilibrium composition of phases in equilibrium and the chemical potentials of each independent species—the *common tangent construction*. We will also show phase diagrams can be obtained through the common tangent construction while varying the temperature. In addition, we will also introduce the ideal solution and different models of ideal solutions.

The Origin of Common Tangent Construction

A useful graphical construction can be utilized for extracting values of chemical potentials:

Consider that the molar free energy of a solution is plotted as follows:

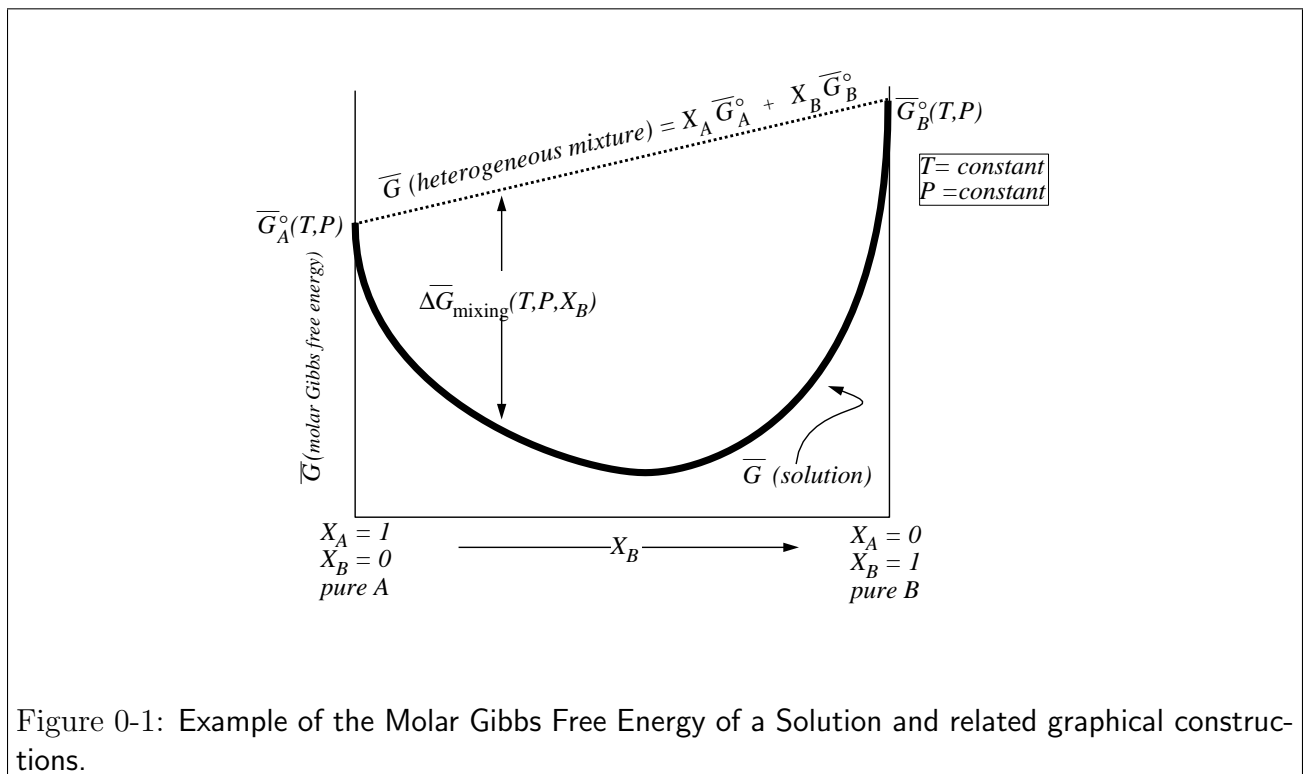


Figure 0-1: Example of the Molar Gibbs Free Energy of a Solution and related graphical constructions.

It would be particularly useful to obtain the chemical potentials of each species in solution as a function of composition. This relationship can be determined as follows:

Starting with an expression for the molar free energy of the solution being a weighted sum of the chemical potentials:

$$\bar{G}_{\text{sol}} = X_A \mu_A + X_B \mu_B$$

$$d\overline{G_{sol}} = X_A d\mu_A + X_B d\mu_B + \mu_A dX_A + \mu_B dX_B$$

$d\overline{G_{sol}}$ becomes when using $dX_B = -dX_A$.

$$d\overline{G_{sol}} = X_A d\mu_A + X_B d\mu_B + (\mu_B - \mu_A) dX_B$$

and recall that

$$0 = \vec{\mathcal{E}} \cdot d\vec{\mathcal{I}} \quad (0 = \vec{X} \cdot d\vec{\mu})$$

thus,

$$\frac{\partial \overline{G_{sol}}}{\partial X_A} = \mu_A - \mu_B$$

similarly,

$$\frac{\partial \overline{G_{sol}}}{\partial X_B} = \mu_B - \mu_A$$

Multiplying $\partial \overline{G}/\partial X_B$ by X_B and subtracting it from $\overline{G_{sol}}$:

$$\overline{G_{sol}} - X_B \frac{\partial \overline{G_{sol}}}{\partial X_B} = X_A \mu_A + X_B \mu_B - (X_B \mu_B - X_B \mu_A) = \mu_A \quad (1)$$

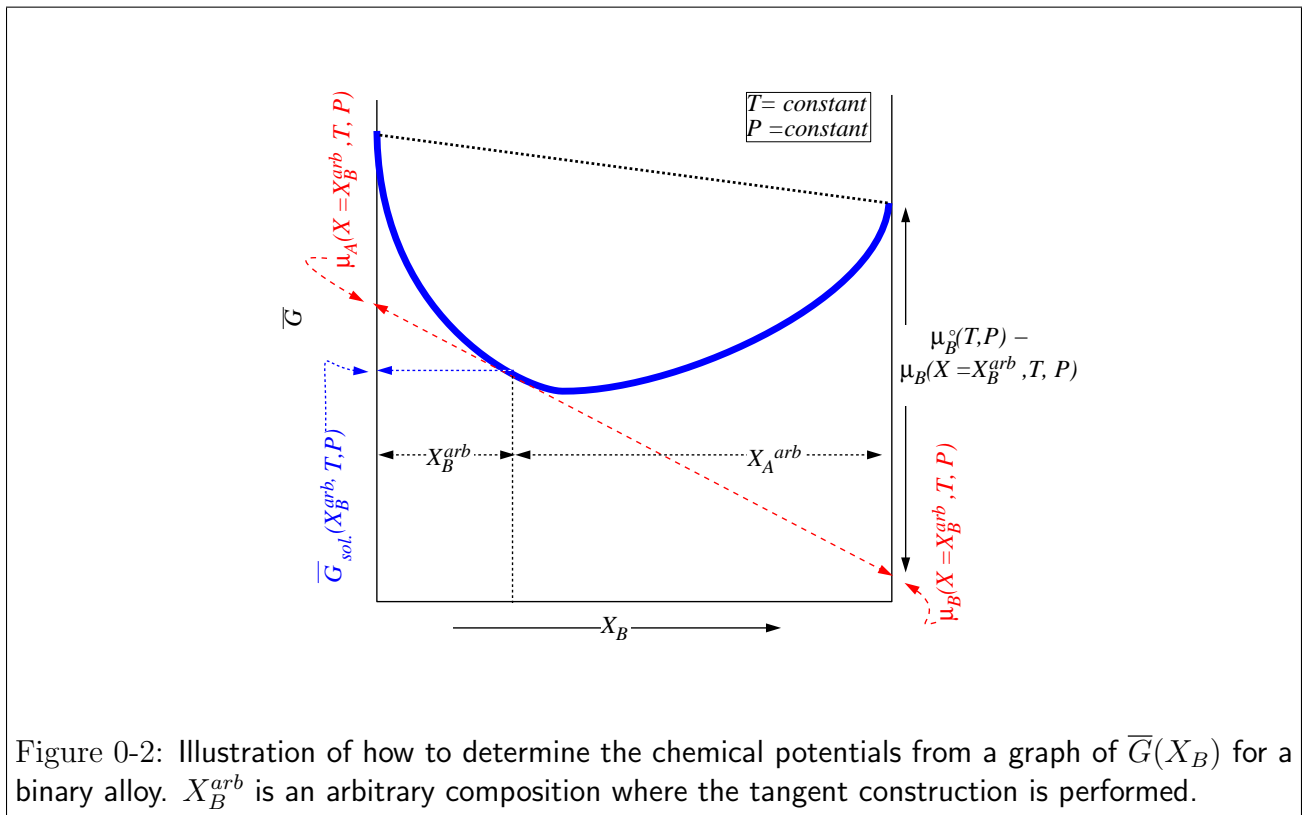
or

$$\begin{aligned} \mu_A &= \overline{G_{sol}} + X_B \frac{\partial \overline{G_{sol}}}{\partial X_A} \\ &= \boxed{\overline{G_{sol}} - X_B \frac{\partial \overline{G_{sol}}}{\partial X_B}} \end{aligned} \quad (2)$$

similarly,

$$\begin{aligned} \mu_B &= \overline{G_{sol}} + X_A \frac{\partial \overline{G_{sol}}}{\partial X_B} \\ &= \boxed{\overline{G_{sol}} - X_A \frac{\partial \overline{G_{sol}}}{\partial X_A}} \end{aligned} \quad (3)$$

These equations can be interpreted with the following figure.



Here is the important thing to remember for ever for constructions like the above: *Each point on the solution curve has a tangent: the chemical potentials of each species are given by the intersection of that tangent with the pure axis for that species. At the temperature and pressure for which the curve is drawn, T and P , the chemical potentials $\mu_A(X, P, T)$ and $\mu_B(X, P, T)$ are thus determined.*

Phase Diagram Construction

To calculate the equilibrium condition between several phases, the condition that the chemical potential of each component μ_i is the same in each phase. The graphical construction for chemical potential can be used to obtain this condition—this condition will be called the “common tangent” condition.

Suppose another curve corresponding to another phase that can also form a solution of A - B is considered. Below, another graphical construction will be demonstrated that will determine the properties of stable phases.

Consider two phases; to fix our ideas let one curve be the molar Gibbs free energy as a function of composition at constant pressure and temperature be for a *solid* solution. Another curve for the liquid solution will be added:

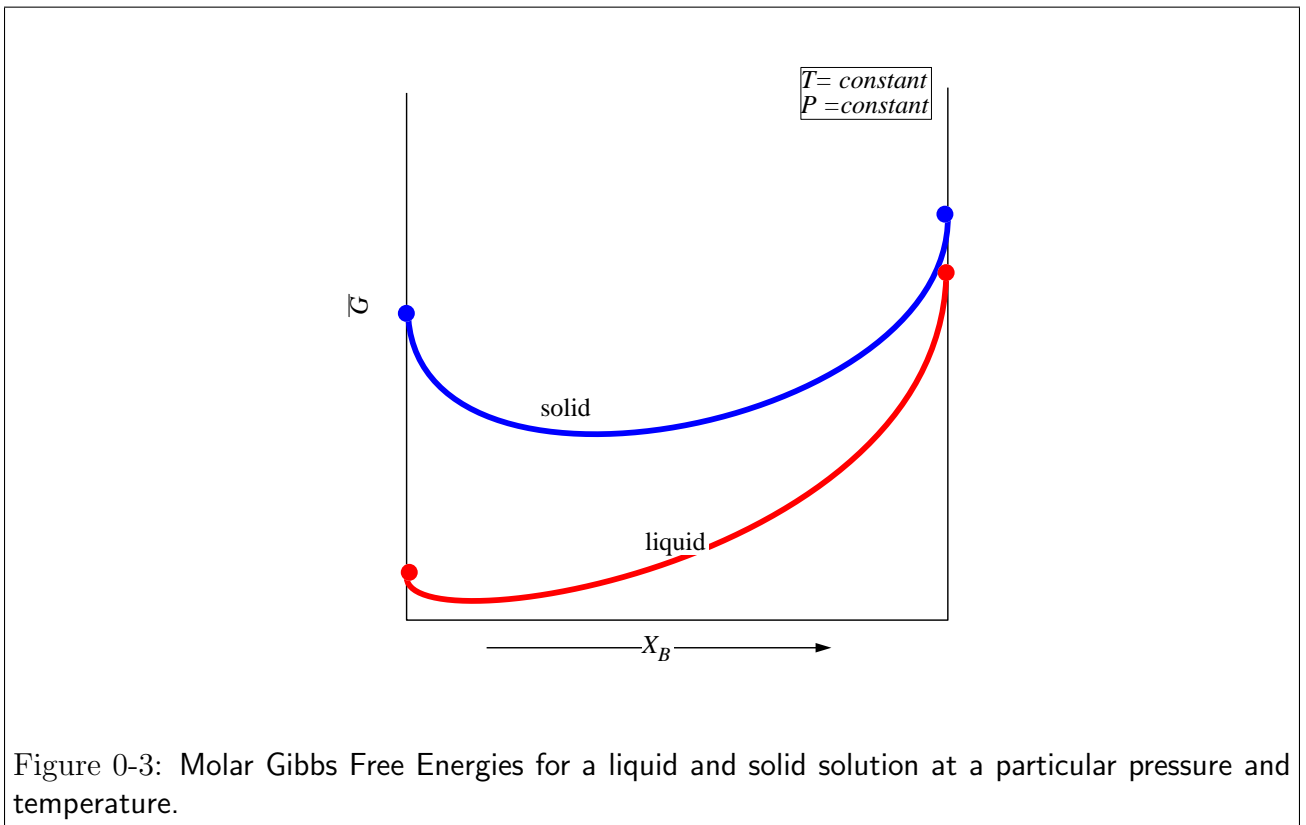


Figure 0-3: Molar Gibbs Free Energies for a liquid and solid solution at a particular pressure and temperature.

Consider the effect of lowering the temperature slightly.

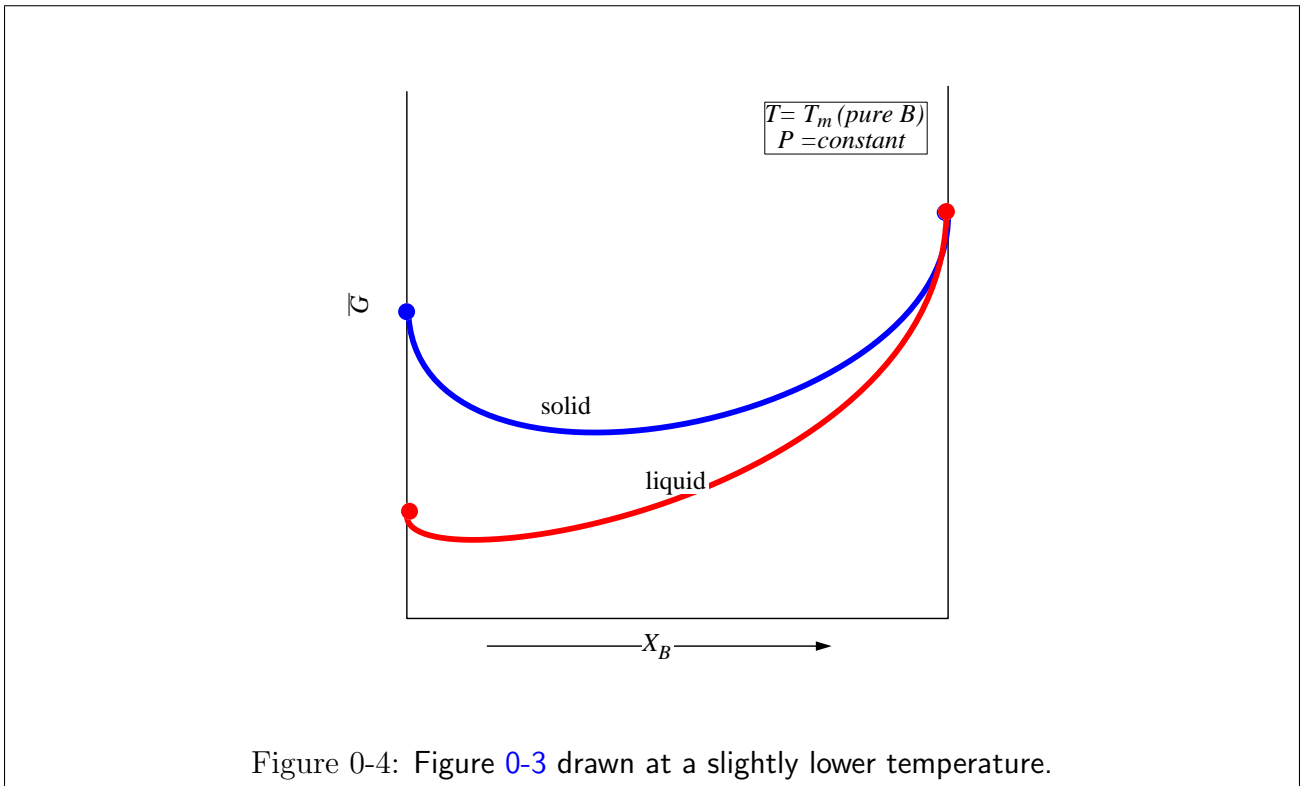
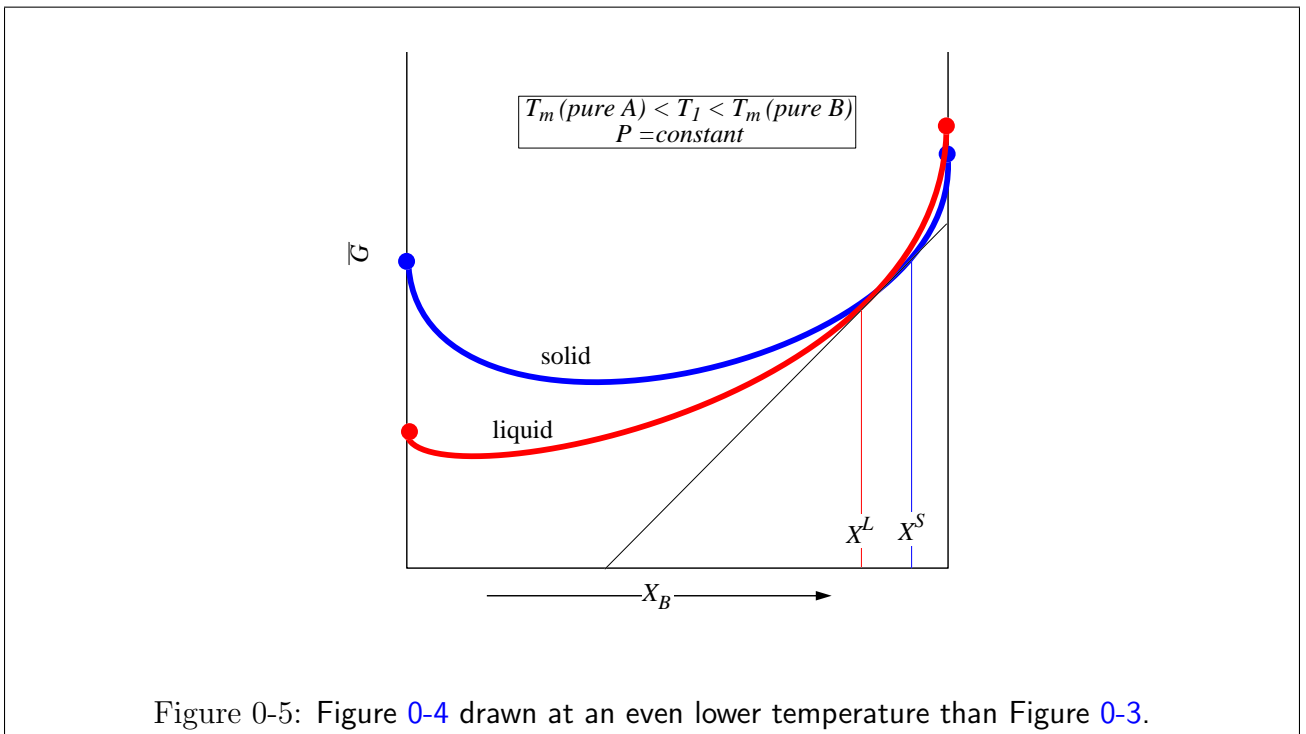
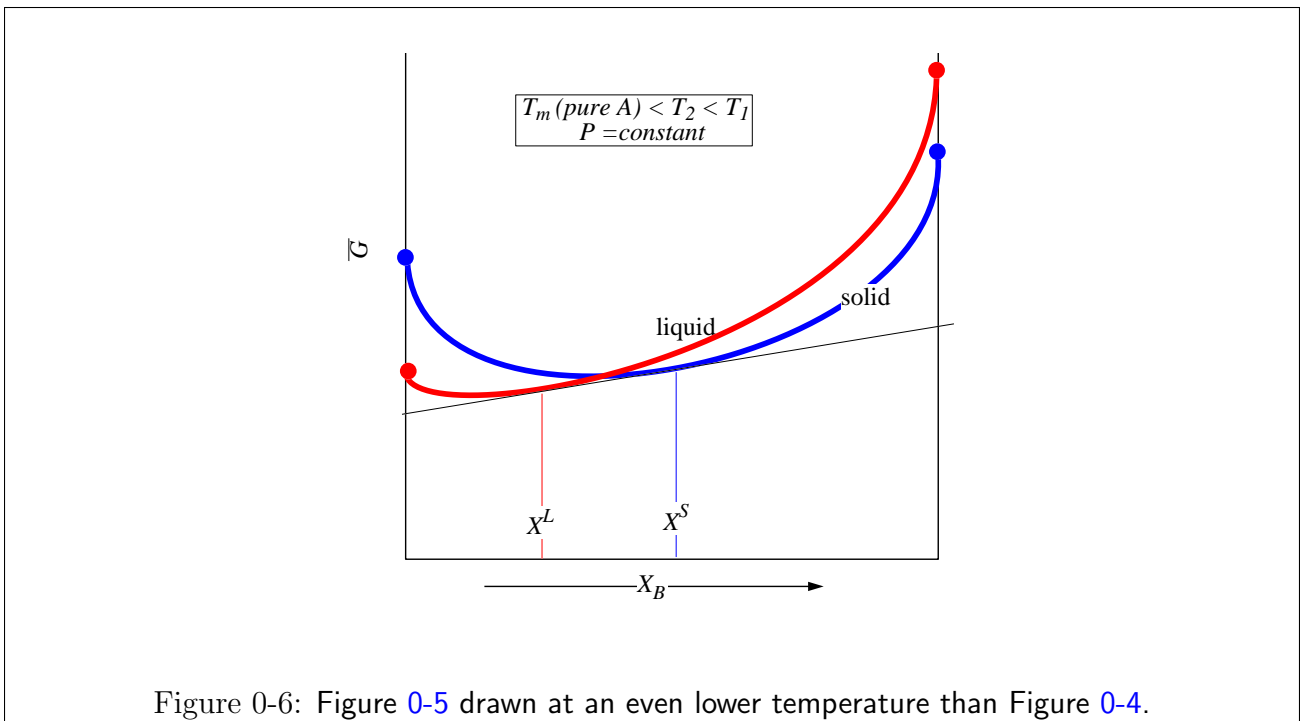


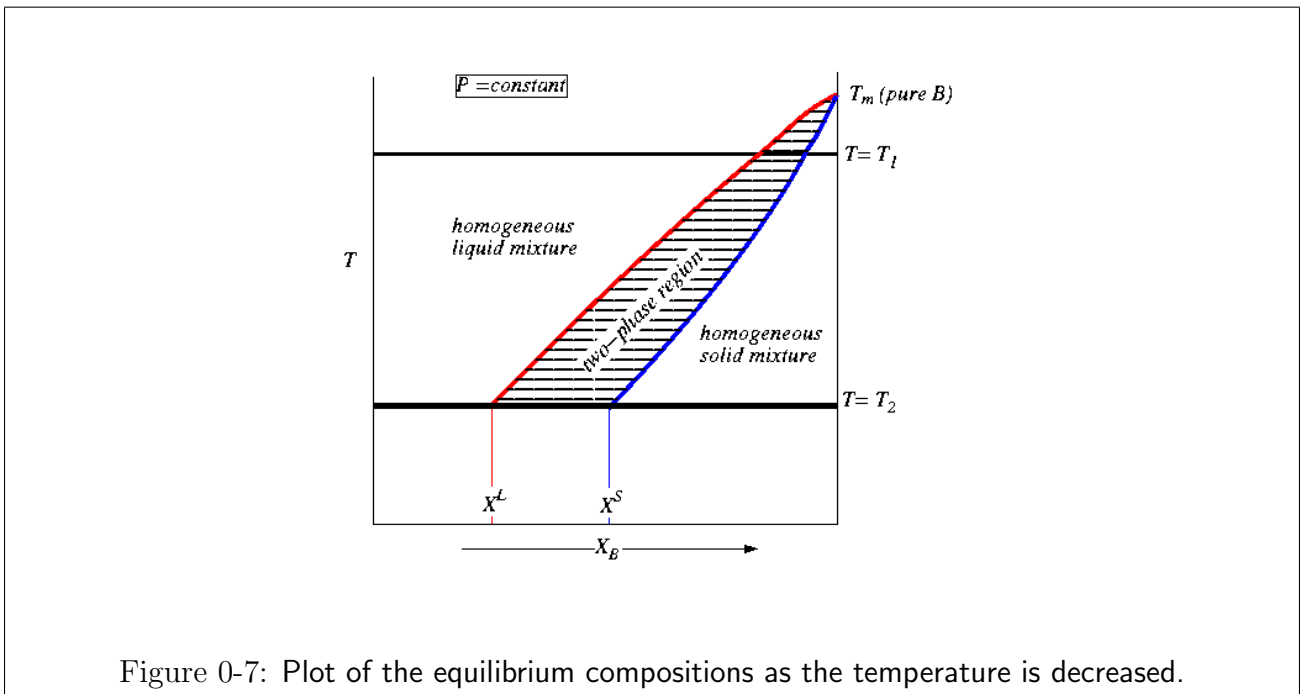
Figure 0-4: Figure 0-3 drawn at a slightly lower temperature.



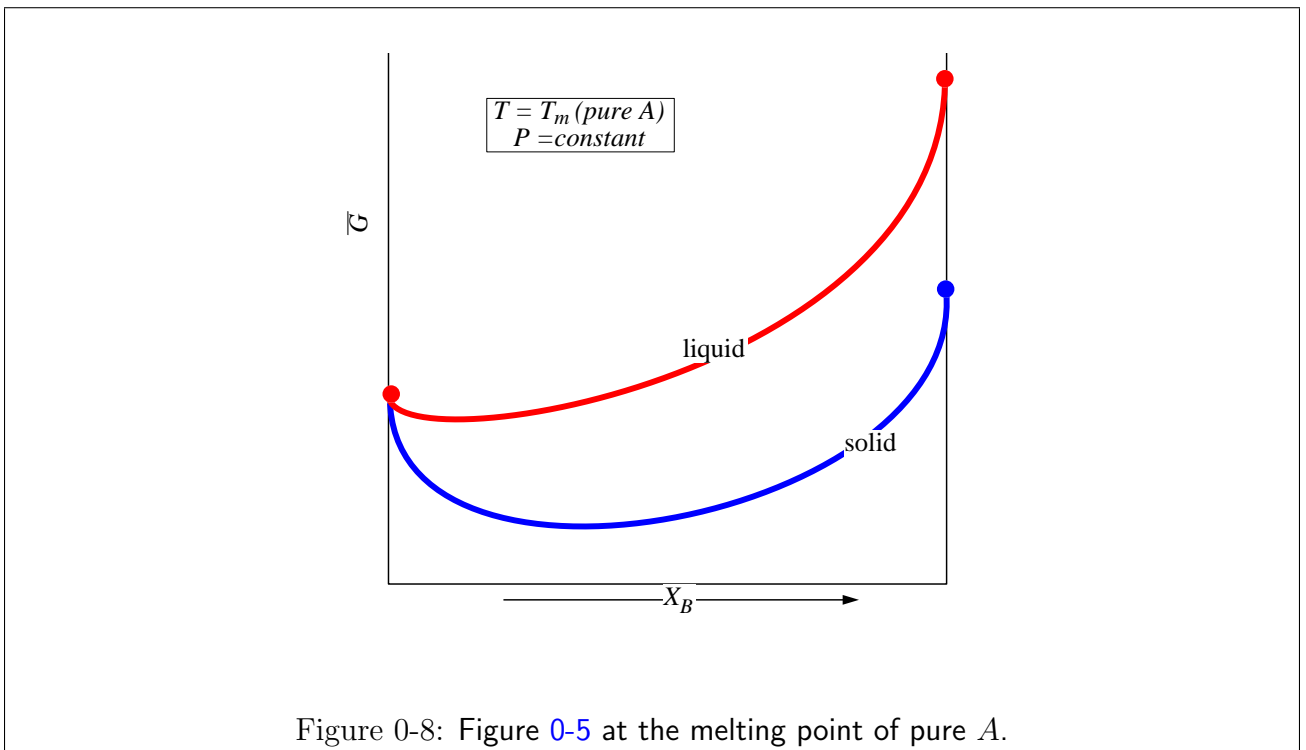
Question: Which combination is the most stable in Figure 0-5? (Hint: Consider that at equilibrium $\mu_A^{\text{liquid}} = \mu_A^{\text{solid}}$ and $\mu_B^{\text{liquid}} = \mu_B^{\text{liquid}}$)

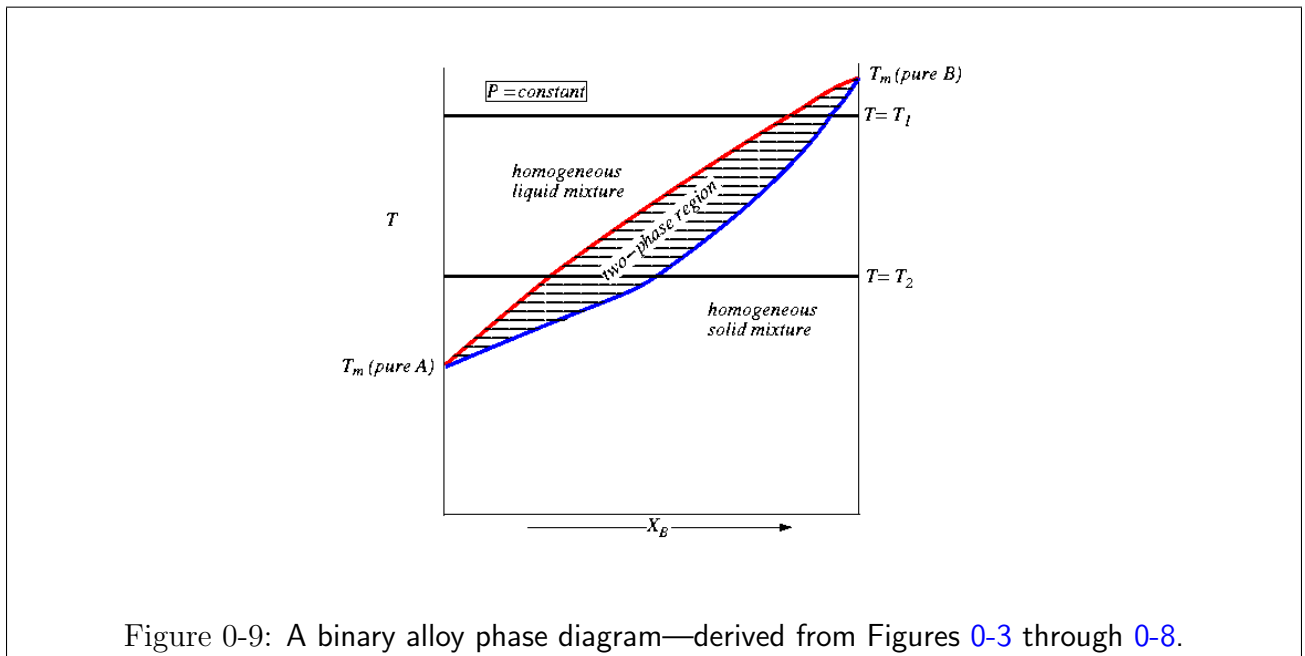
If the temperature in Figure 0-5 is decreased a little further:





Lowering it to the melting point of pure A





The Lever Rule

The equilibrium condition, that the chemical potentials of components must have equal values in all phases, indicates that at equilibrium compositions that have the same tangent (*i.e.*, a *common tangent*).

Consider the region of lines that lies inside the common tangent point in Figure 0-5, a mixture of $f^{\text{liquid}} G^{\text{sol liquid}}(X_L, T, P) + f^{\text{solid}} G^{\text{sol solid}}(X_S, T, P)$ has lowest value of \bar{G} where f^{liquid} is the fraction of the system that is liquid and f^{solid} fraction of system that is solid.

$$f^{\text{solid}} + f^{\text{liquid}} = 1$$

This corresponds to a diagram that maps stable compositions of phase mixtures:

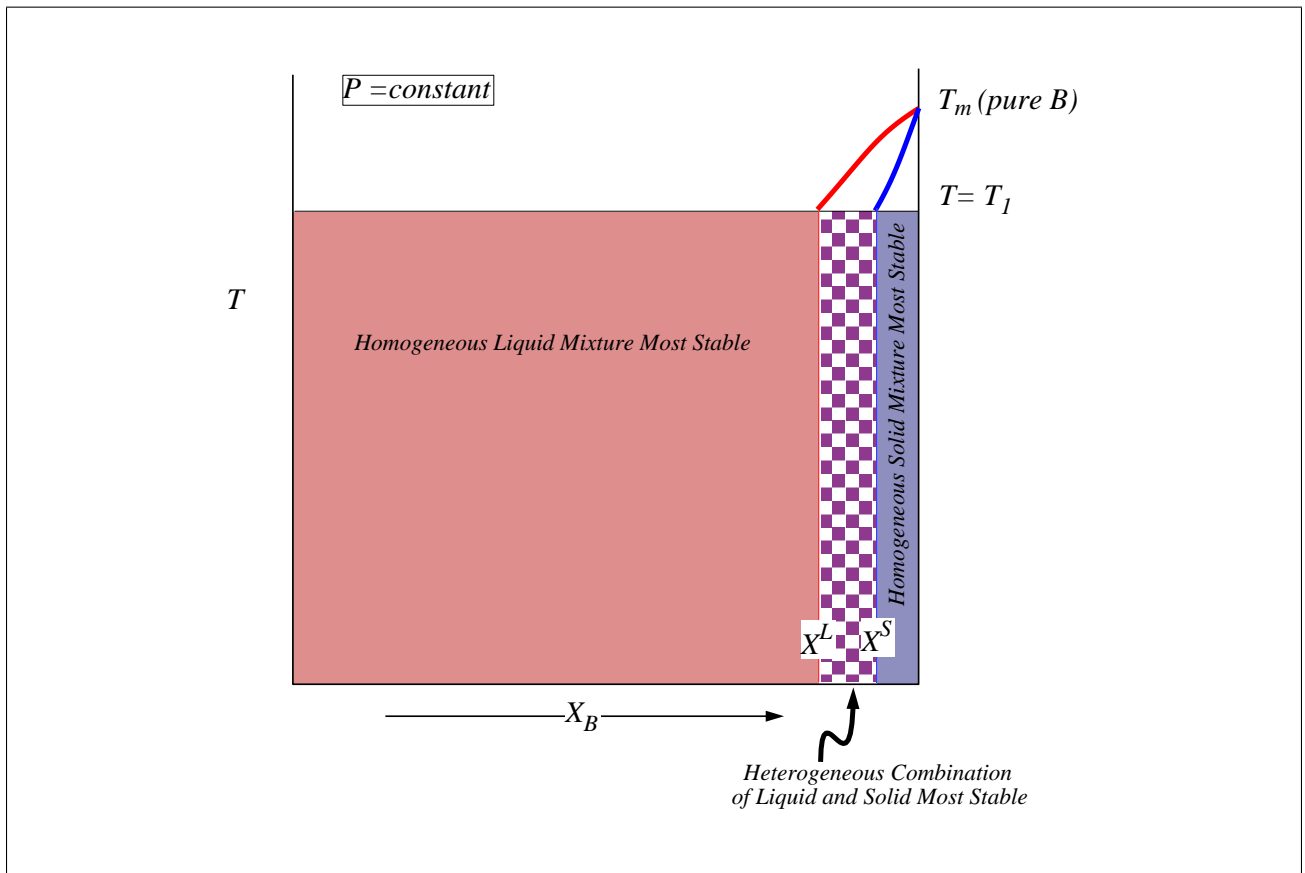


Figure 0-10: Construction of the equilibrium values of the compositions resulting from the lowest free energy in Figure 0-5.

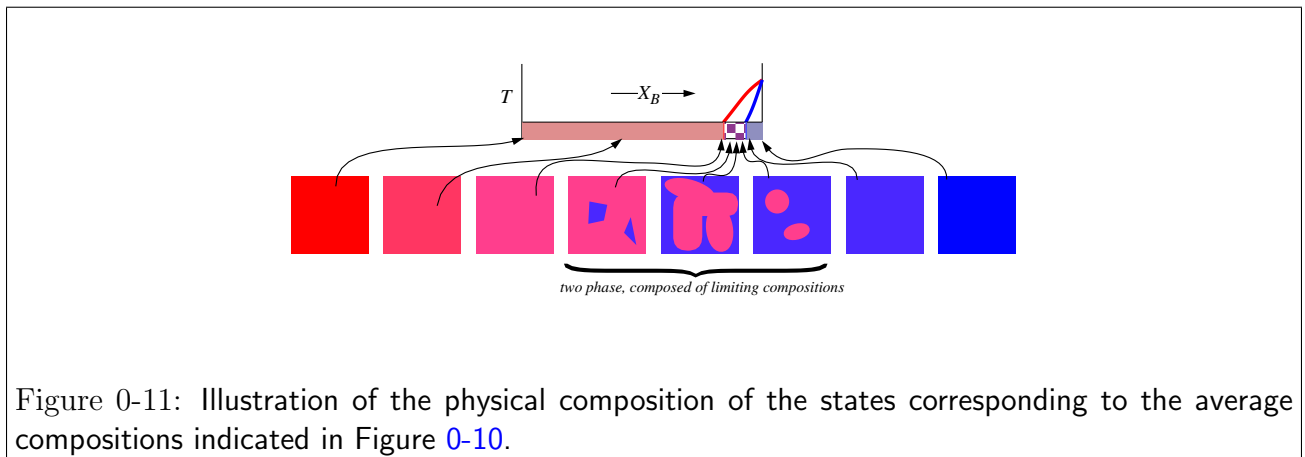


Figure 0-11: Illustration of the physical composition of the states corresponding to the average compositions indicated in Figure 0-10.

There is a range of “average compositions” at $T < T_M^B$ in which the system has as its most stable form a mixture of liquid at composition X_L and solid at composition X_S . The fractions of f^{liquid} and f^{solid} come from the requirements that the average composition is given by:

$$\begin{aligned} \langle X \rangle &= X^{\text{liquid}} f^{\text{liquid}} + X^{\text{solid}} f^{\text{solid}} \\ &= X^{\text{liquid}} f^{\text{liquid}} + X^{\text{solid}} (1 - f^{\text{liquid}}) \end{aligned} \quad (4)$$

or, for the general case where the two phases in equilibrium are α and β :

$$f^\alpha = \frac{X^\beta - \langle X \rangle}{X^\beta - X^\alpha} \quad \text{and} \quad f^\beta = \frac{\langle X \rangle - X^\alpha}{X^\beta - X^\alpha} \quad (5)$$

equation (5) is called the lever rule:

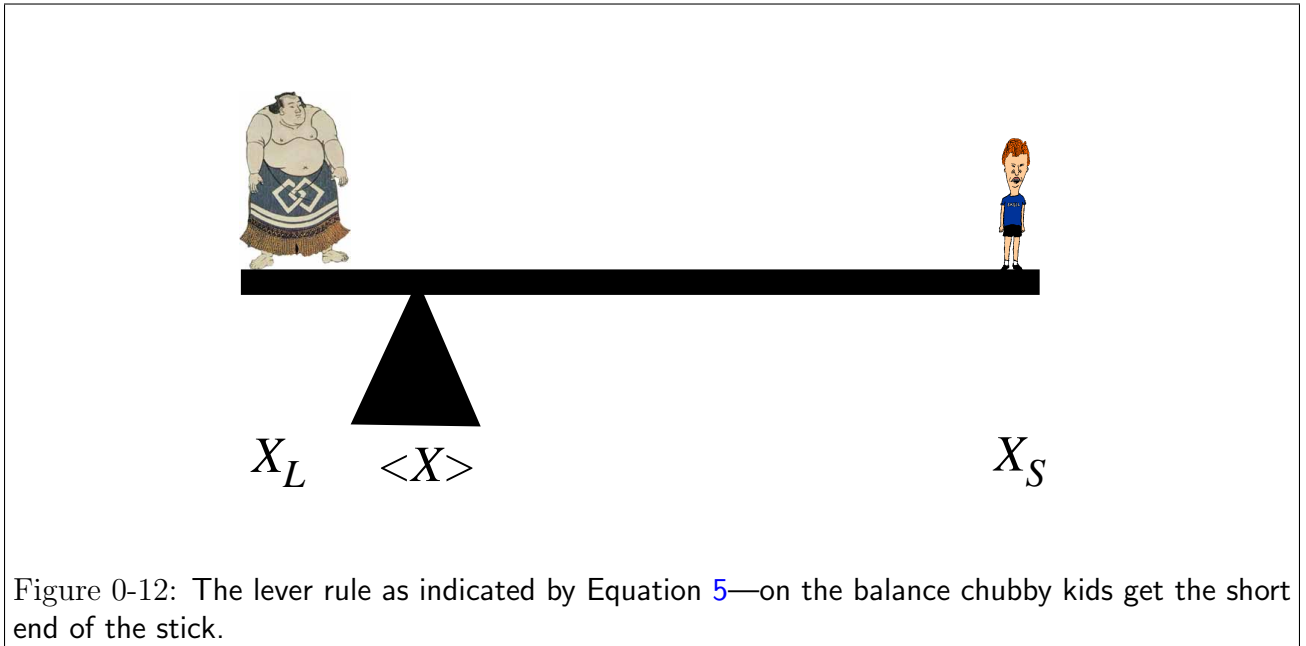


Figure 0-12: The lever rule as indicated by Equation 5—on the balance chubby kids get the short end of the stick.

The Origin of Ideal Solutions

It has been shown that if several phases are in equilibrium with each other, then the chemical potential of any chemical species will be the same in each phase. Therefore, if we can calculate the chemical potential in *some* phase we know its value in *any other* phase that is in equilibrium with it. A clever approach would be to determine the chemical potential in the phase where it is most simple to calculate. It is particularly simple to calculate the chemical potential in an ideal gas mixture. In this manner, the determination of chemical potential in any phase can be determined by finding the ideal gas mixture that is equilibrium with it.

We begin by applying the condition that applies for equilibrium to a single phase mixture of ideal gases at constant pressure and temperature.

To apply equilibrium condition:

$$dG = \sum_{i=1}^C \mu_i dN_i = 0 \quad (6)$$

to an ideal gas, an expression for the Gibbs free energy associated with each component is calculated.

Consider that we have a quantity of a pure ideal gas in a closed system ($dN_i = 0$). As we shown previously, the chemical potential is the molar free energy of the gas: $\mu_i = \bar{G}_i$, thus

$$d\mu_i = d\bar{G}_i = \bar{S}_i dT + \bar{V}_i dP \quad (7)$$

If we integrate the differential for the chemical potential, we can calculate the chemical potential in some arbitrary state relative to that in some other defined reference state. We want to know the chemical potential at a temperature T and pressure P , relative to a reference state of the gas at the same temperature (T) and a reference pressure P^{ref} . Integrating the expression above:

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

$$\int_{reference}^{current} d\mu_i = \Delta\mu_i = \mu_i(T, P_i) - \mu_i^0(T) = \int_{P^{ref}}^P RT \frac{dP}{P} \quad (8)$$

$$\mu_i(T, P_i) - \mu_i^0(T) = RT \ln \frac{P_i}{P^{ref}}$$

$$\begin{aligned} \mu_i(T, P_i) &= \mu_i^0(T) + RT \ln \frac{P_i}{P^{ref}} \\ &= \mu_i^0(T) + RT \ln \frac{P_i P^{total}}{P^{ref} P^{total}} \end{aligned} \quad (9)$$

$$\boxed{\mu_i(T, P_i) = \mu_i^0(T) + RT \ln \frac{P^{total}}{P^{ref}} + RT \ln X_i} \quad (10)$$

where in an ideal gas, the ratio of partial pressure to the total pressure $P_i/P^{total} = X_i$.

if we take P^{total} to be some standard state (i.e. STP) then P_i/P^{total} is the partial pressure of the gaseous species i with respect to that standard state.

Models of Ideal Solution

There are various models for the chemical potential in a solution; the simplest is the ideal gas.¹

The following are definitions that will be used when we discuss solution behavior, but are useful to introduce in the context of ideal gases.

An Ideal Gas Mixture

$$\boxed{\mu_i(T, P_i) = \mu_i^0(T) + RT \ln \frac{P_i}{P^0}} \quad (11)$$

$$\boxed{\mu_i(T, X_i) = \mu_i^0(T) + RT \ln X_i}$$

An Ideal Solution In an “ideal solution,” the system is made slightly more complicated by allowing chemical potential to become a function of pressure.

$$\boxed{\mu_i(T, P, X_i) = \mu_i^0(T, P) + RT \ln X_i} \quad (12)$$

¹An ideal single gas: $\mu(P, T) = \mu^0(T) + RT \ln P/P^0$. Note, you will often see formulae like $\mu = \mu^0 + RT \ln P$, you know that P cannot have units—so a convenient $P^0 = 1$ has been picked.

A General Solution In the general case, a new term (the activity a_i) is introduced to generalize the dependence on concentration:

$$\boxed{\mu_i(T, P, X_i) = \mu_i^0(T, P) + RT \ln a_i} \quad (13)$$

a_i is called the “activity of species i ”—it is a “generalized composition.” Factoring out the X_i :

$$a_i = \gamma_i X_i \quad (14)$$

γ_i is called an activity coefficient. In the most general case.

Further Discussion of Ideal Solution Behavior

Recall, the *ideal solution* was defined for the case where the chemical potential of *each* component is a linear function of the logarithm of its mole fraction:

$$\mu_i^{IS}(T, P, X_i) = \mu_i^{0,IS}(T, P) + RT \ln X_i$$

recall that $\bar{G}^{IS} = \sum_{i=1}^C X_i \mu_i$, which implies that (for a binary solution):

$$\begin{aligned} \bar{G}^{IS} &= X_1 \mu_1 + X_2 \mu_2 = X_1 (\mu_1^{0,IS} + RT \ln X_1) + X_2 (\mu_2^{0,IS} + RT \ln X_2) \\ \bar{G}^{IS} &= \sum_{i=1}^2 X_i \mu_i^{0,IS} - (-R)T \sum_{i=1}^2 X_i \ln X_i \\ \bar{G}^{IS} &= \bar{H}^{IS} - T \bar{S}^{IS} \\ \bar{H}^{IS}(T, P, X_i) &= \sum_{i=1}^2 X_i \mu_i^{0,IS}(T, P), \quad \bar{S}^{IS}(X_i) = R \sum_{i=1}^2 X_i \ln X_i \end{aligned} \quad (15)$$

which does give the qualitative features that are drawn in Figures 0-1 and 0-2.

One might wonder why such a simple form of the molar Gibbs free energy of solution would be used for condensed phases, since this is the form that was derived from ideal gases.

One condition of equilibrium is that the chemical potential in each phase must be equal. Therefore if the vapor phase above a condensed phase is in equilibrium then:

$$\mu_i^{sol} = \mu_i^{vap}$$

Considering an ideal gas as the vapor (another assumption):

$$\mu_i^{0,IS}(T, P) + RT \ln X_i = \mu_i^{0,IG}(T) + RT \ln P_i \quad (16)$$

The second term it is what we derived for the ideal solution:

$$\frac{P_i}{X_i} \equiv \gamma_i^{IS} = \exp\left[-\frac{\mu_i^{0,IG}(T) - \mu_i^{0,IS}(T, P)}{RT}\right] \quad (17)$$

where γ_i^{IS} is independent of X_i .

Limiting Solution Behavior: Henry's and Raoult's Laws

It can be shown that the ideal solution represents the limiting behavior of very dilute solutions. The question may be posed: "In what cases can we expect the activity to depend only on composition?"

Consider a very dilute solution of B in A :

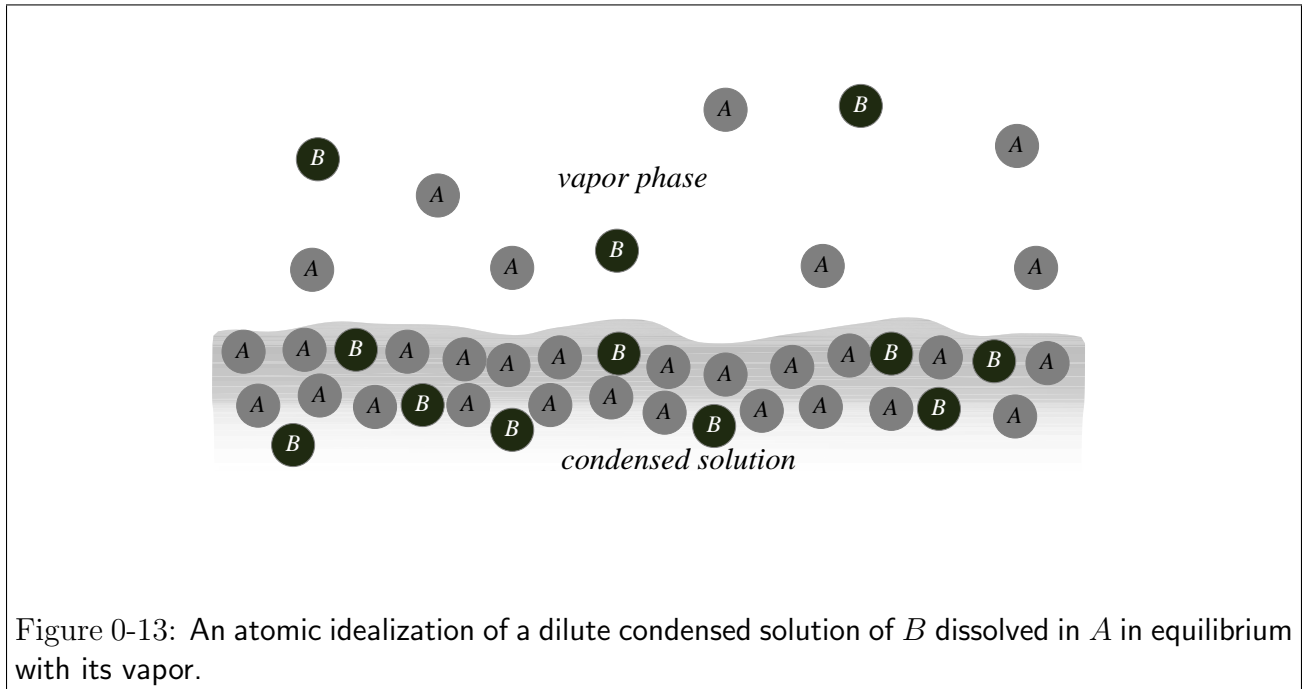


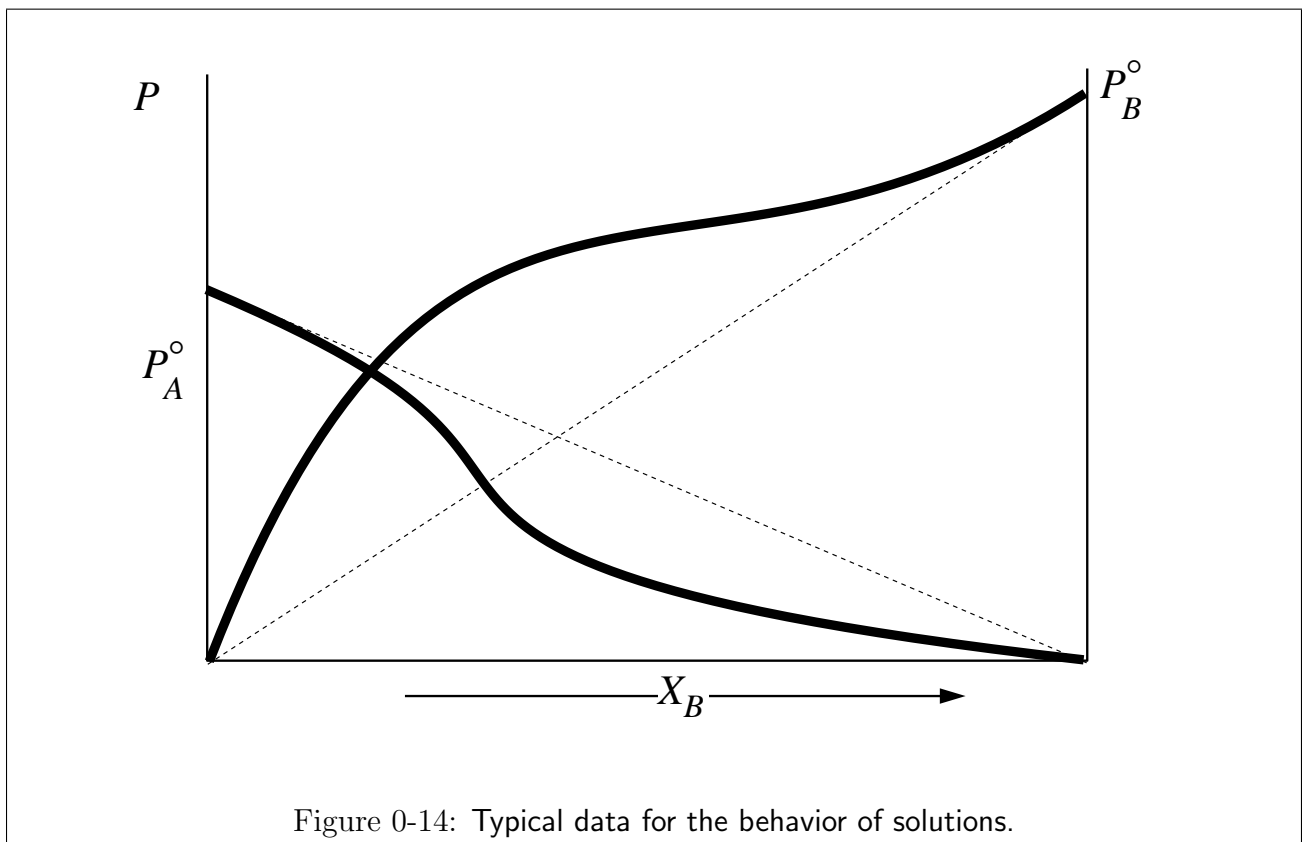
Figure 0-13: An atomic idealization of a dilute condensed solution of B dissolved in A in equilibrium with its vapor.

Each time an A comes out of solution, it does so mostly without any influence of B . It is as if it does so as in a pure solution.

Each time a B comes out of solution, it does so entirely under the influence of the surrounding A atoms; it is as if it does so from pure A .

So one can expect very concentrated, or very dilute solutions to behave ideally.

Typically, the data look like the following:



One gets as limiting behavior:
Raoult's Law:²

$$\gamma_i \rightarrow 1 \quad \text{as} \quad X_i \rightarrow 1 \quad (\text{Raoult's Law}) \quad (18)$$

and Henry's law:

$$\gamma_i \rightarrow \gamma_i^{IS} = \text{constant} \quad \text{as} \quad X_i \rightarrow 0 \quad (\text{Henry's Law}) \quad (19)$$

²Raoult's = really pure = really simple