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Dec. 09 2002: Lecture 31:

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## Solution Thermodynamics

Last Time

**Other Types of Phase Diagrams**

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**Models for Solutions**

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**Limiting Behavior for Dilute and nearly Pure Solutions**

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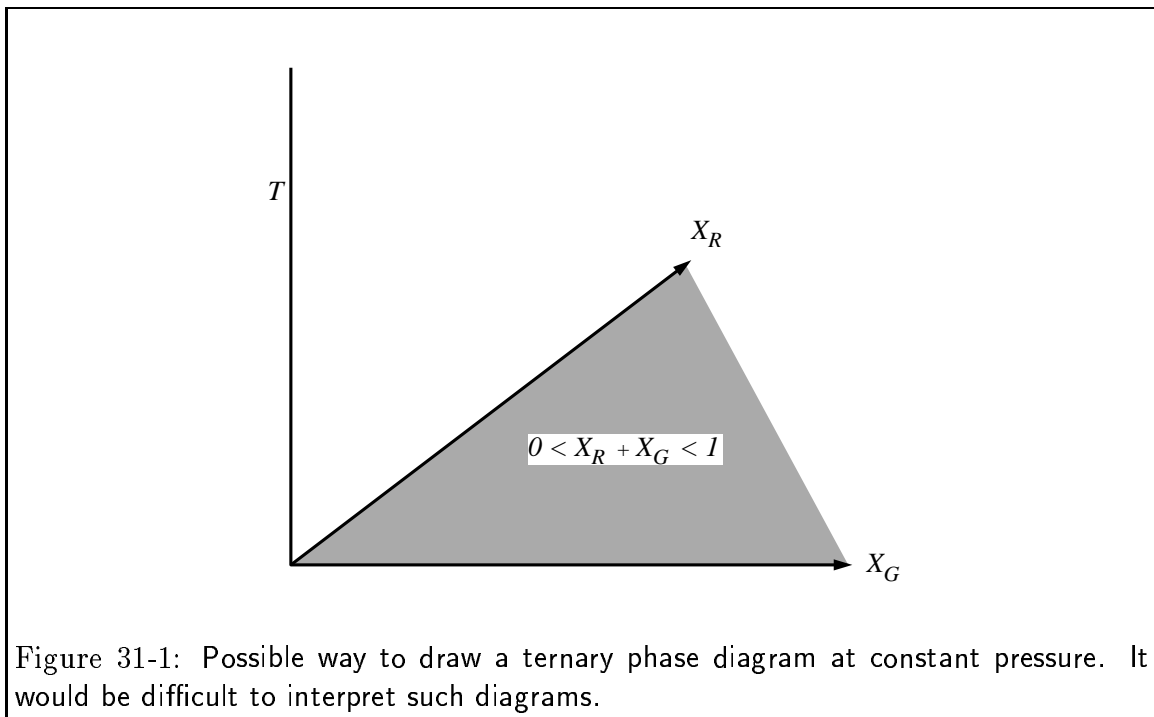
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## Ternary Phase Diagrams

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Phase diagrams have been constructed for the case of one component ( $P$ - $T$  diagrams for a pure material), and for two component systems ( $T$ - $X_B$  diagrams drawn at constant pressure). Each time a new component is added, another intensive variable must be held constant if the phase diagram is to be drawn in two-dimensions.

For ternary systems, there are three components. Let the three components be denoted by  $R$ ,  $G$ , and  $B$ . Because,  $X_R + X_G + X_B = 1$ , the system can be represented by two components, say  $X_R$ , and  $X_G$ , and the phase diagram could be represented in the following coordinate system:



Question: what is the maximum number of phases that can be in equilibrium at one point in Figure 31-1?

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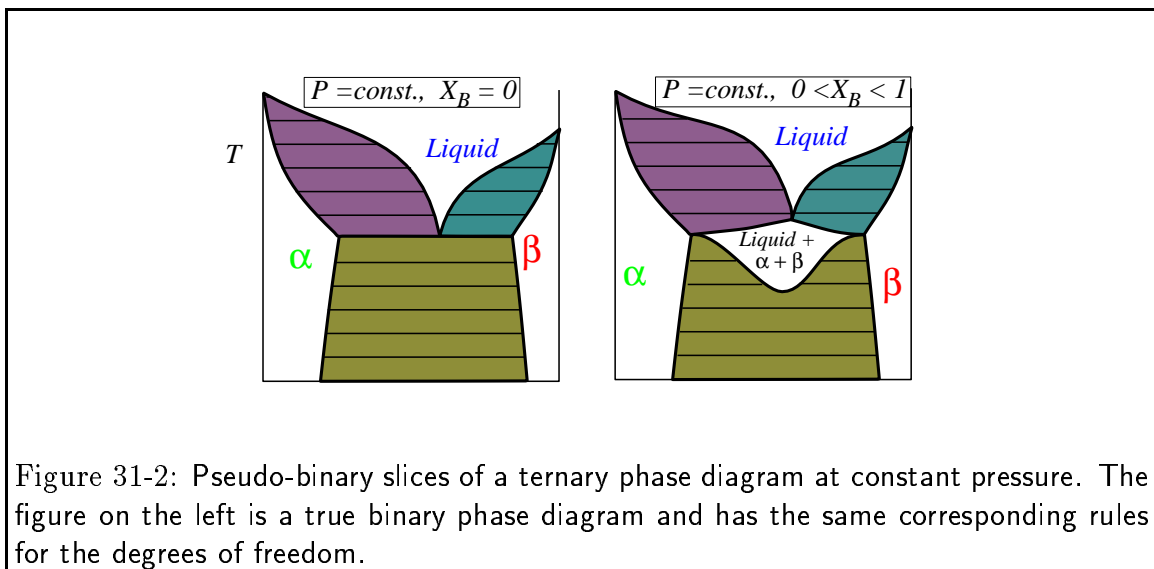


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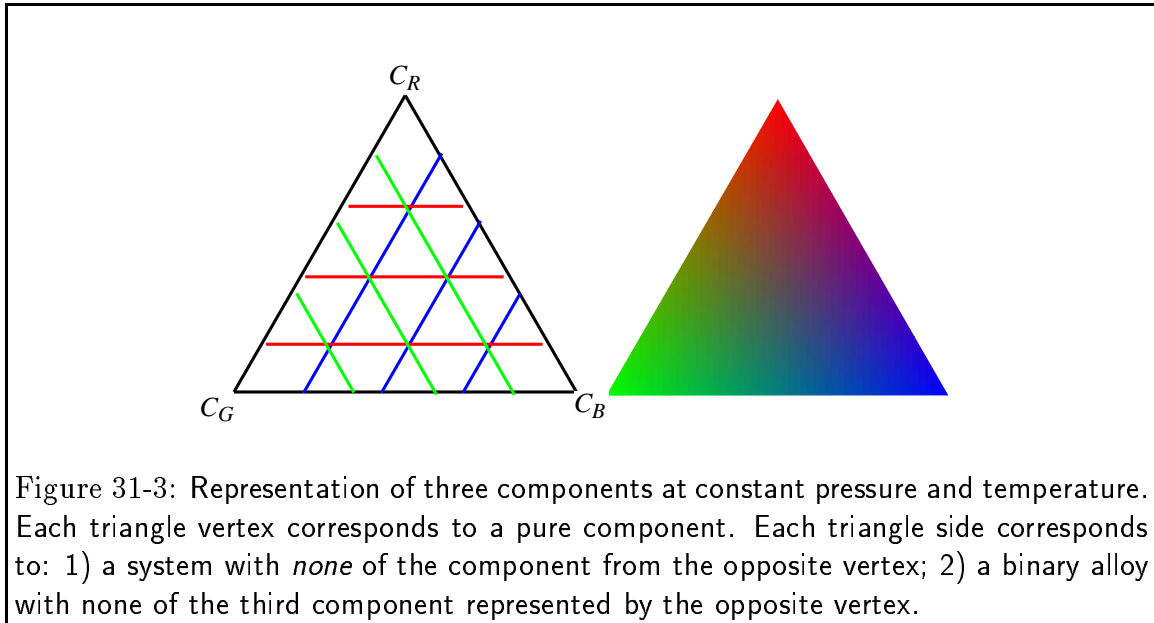


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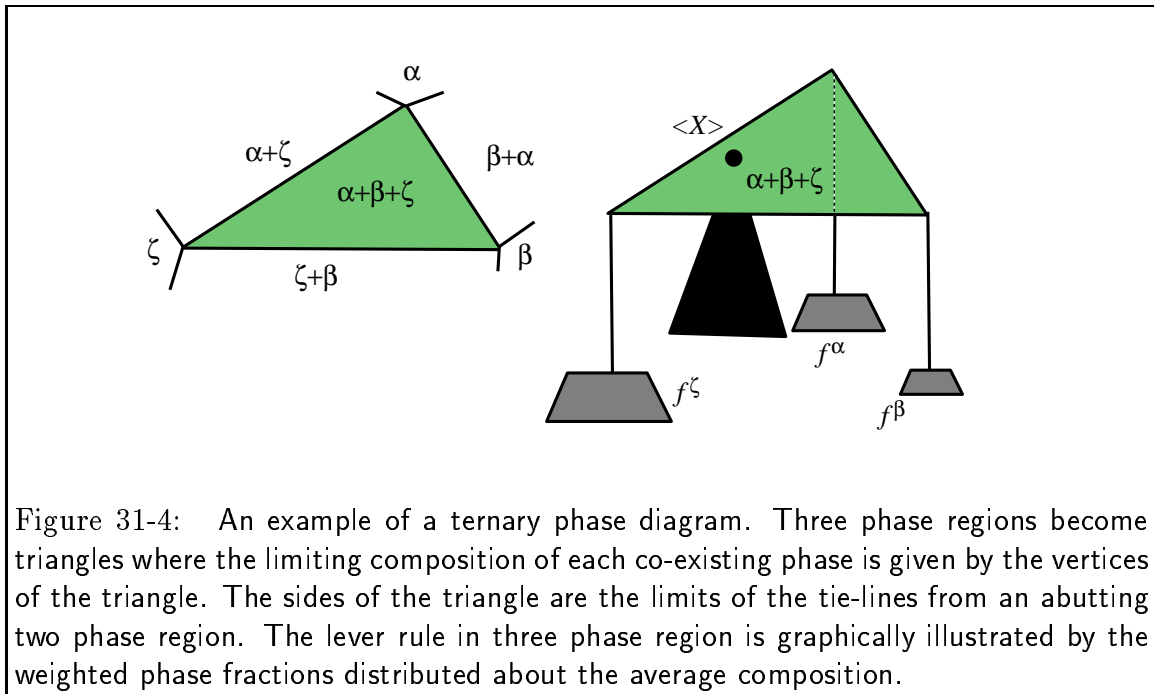
It may be possible to represent such a diagram in two dimensions by taking slices at constant composition, for instance:

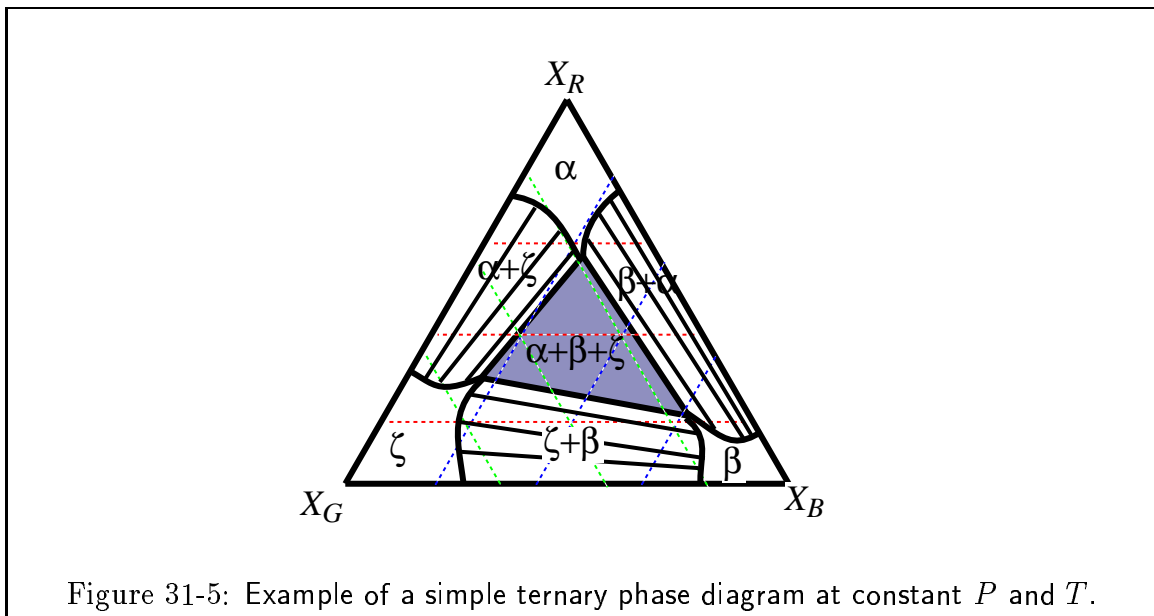


Ternary phase diagrams are traditionally drawn at constant pressure and temperature—and the following scheme is used to represent all three components:



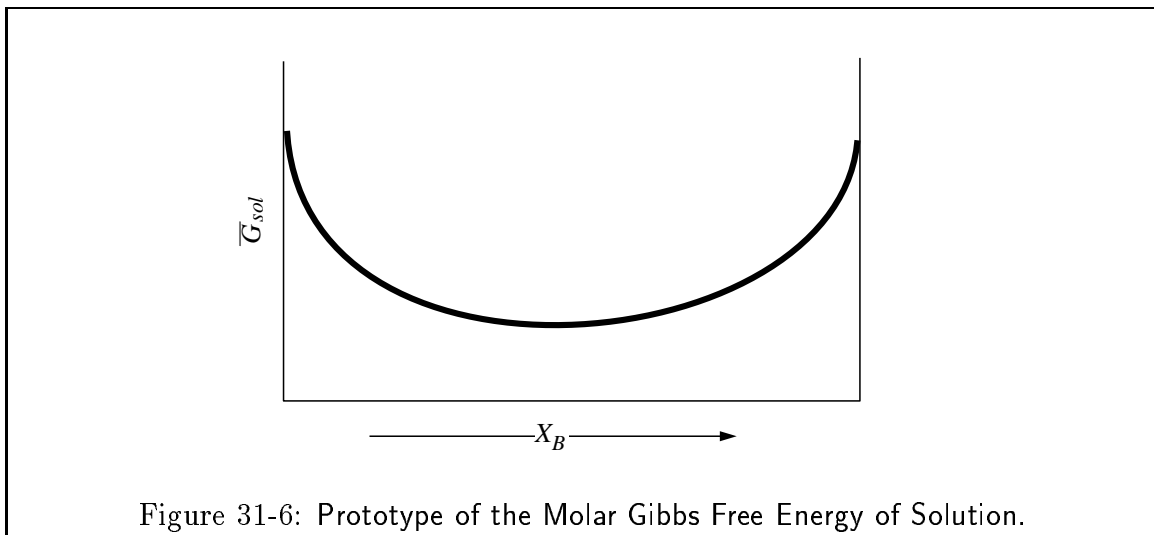
For example, a ternary phase diagram may look something like this:





### Solution Free Energies that Generate Phase Diagrams

For the construction of phase diagrams, plausible forms of the free energy of solution have been utilized without discussion of their derivation. For instance,



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

$$\mu_i^{IS}(T, P, X_i) = \mu_{i_0}^{IS}(T, P) + RT \log X_i \quad (31-1)$$

which implies that:

$$\begin{aligned} \overline{G^{\text{total}}^{\mathcal{IS}}}(T, P) &= \sum_{i=1}^C X_i \mu_{i_0}^{\mathcal{IS}}(T, P) - (-R)T \sum_{j=1}^C X_j \log X_j \\ &= \overline{H^{\text{total}}^{\mathcal{IS}}} - T \overline{S^{\text{total}}^{\mathcal{IS}}} \end{aligned} \quad (31-2)$$

which does give the qualitative features that are drawn in Figure 31-6.

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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:

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

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

$$\mu_{i_0}^{\mathcal{IS}}(T, P) + RT \log X_i = \mu_{i_0}^{\mathcal{IG}}(T) + RT \log P_i \quad (31-3)$$

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

$$\frac{P_i}{X_i} \equiv \gamma_i^{\mathcal{IS}} = e^{-\left[\frac{\mu_{i_0}^{\mathcal{IG}}(T) - \mu_{i_0}^{\mathcal{IS}}(T, P)}{RT}\right]} \quad (31-4)$$

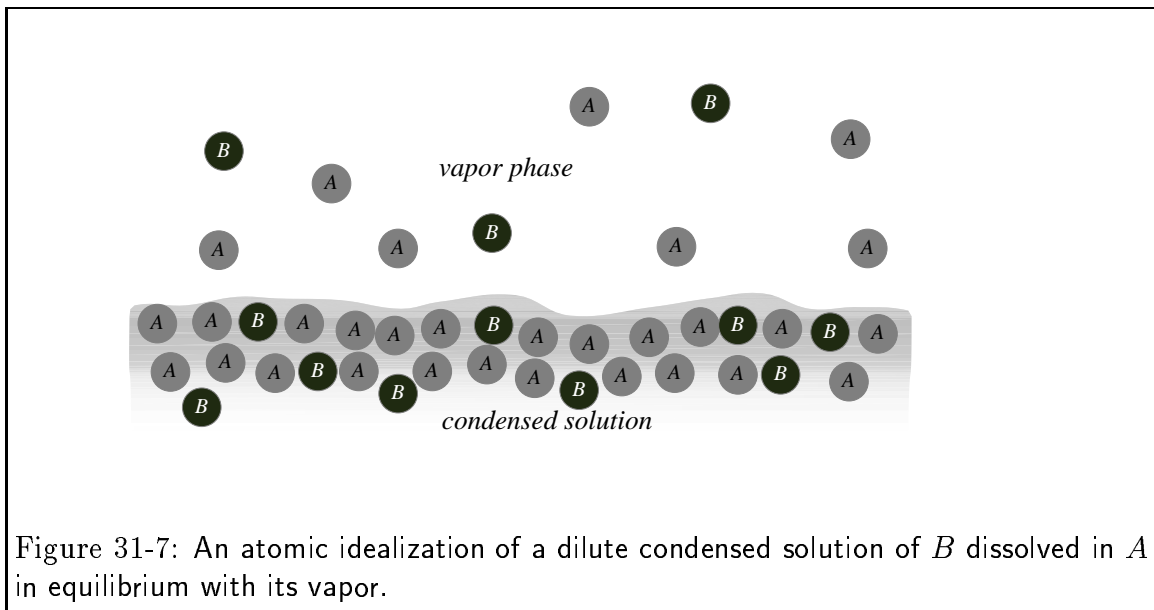
where  $\gamma^{\mathcal{IS}}$  is independent of  $X_i$ .

## Limiting Solution Behavior

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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?”

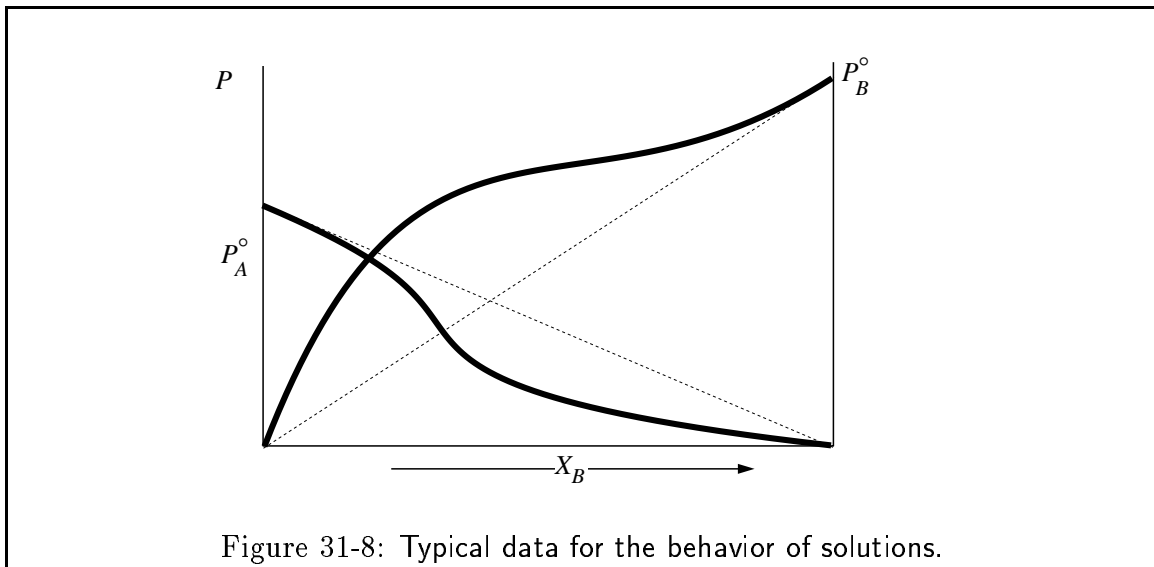
Consider a very dilute solution of  $B$  in  $A$ :



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:<sup>30</sup>

$$\gamma_i \rightarrow 1 \quad \text{as} \quad X_i \rightarrow 1 \quad (\text{Raoult's Law}) \quad (31-5)$$

<sup>30</sup>Raoult's = really pure = really simple

and Henry's law:

$$\gamma_i \rightarrow \gamma_i^{\text{IS}} = \text{constant} \quad \text{as} \quad X_i \rightarrow 0 \quad (\text{Henry's Law}) \quad (31-6)$$

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