4/1/2013 Lecture 15 Binary Mixtures

I. Mixture: system with multiple distinguishable particles

They can be:

a. homogeneous: mixed at the atomic scale (solution)

b. heterogeneous: mixing not possible for all values (E, T, V, N)

ex: oil + water → phase separation (refra to Chemical) phases not solid like gas

What determines the equilibrium state of a mixture?

⇒ minimization of free energy

\[ F = U - TS \quad \Rightarrow \quad \Delta F = \Delta U - T \Delta S \]

Helmholtz (F) used for mixtures at fixed P and fixed V.

Otherwise we need to use Gibbs: \[ G = U + TS + PV \]

II. Binary Mixtures: only two types of molecules: A and B

N particles \( N_B = \# \) mol type B \( \rho = \frac{N_B}{N} \) (\% B)

\( N = N_A + N_B \)

\( N_A = \# \) mol type A \( 1 - \rho = \frac{N_A}{N} \) (\% A)
• Phase diagram has a new dimension $x$ in comparison with single component phase diagram.

• Interactions between particles will drive the phase transitions. Let's analyze this in a simplistic way:

  “Bond energies” $\rightarrow$ $E$ of interaction between particles $\frac{U_{AA}}{U_{AB}}$ $\rightarrow$ $E_{bond}$

  Coordination number “$p$” $\rightarrow$ # of neighbors $\frac{U_{AB}}{U_{BB}}$

$\rightarrow$ Let's compute total interaction energies per particle $\Rightarrow$ $U_n = \text{interaction energy per A atom}$

$U_A = \frac{p(1-x)U_{AA} + pX \cdot U_{AB}}{\# \text{ of neighbors}}$

$\text{Number of B neighbors}$

$\text{That are A type}$

$\text{Weight}$

$U_B = p \cdot U_{BB} + p(1-x) \cdot U_{BA}$

$\text{Weight That are A type for a B atom}$

$V = \frac{1}{2} \left[ N_A \cdot U_A + N_B \cdot U_B \right]$ 

Energy requires pairs, $k^2$ to avoid double counting.

$V = \frac{1}{2} \left[ N(1-x) \cdot U_A + N \cdot U_B \right] = \frac{1}{2} \left[ N(1-x) \cdot \left[ p(1-x) \cdot U_{AA} + p \cdot x \cdot U_{AB} \right] + N \cdot x \cdot \left[ p \cdot U_{BB} + (1-x) \cdot U_{BA} \right] \right]$

$= \frac{NP}{2} \left[ (1-x)^2 \cdot U_{AA} + x^2 \cdot U_{BB} + 2x(1-x) \cdot U_{AB} \right]$
III. Ideal and non-ideal mixtures.

**Ideal**: All molecules (A and B) have same size. Also all interaction energies are equal. \((U_{AA} = U_{AB} = U_{BB} = U)\) \[\text{Ideal} = \frac{N P}{2} U \Rightarrow \text{No dependence on } X\]

**Non-ideal (Real)**: Interaction energies are very different (water vs. oil, dipoles vs. van der Waals interactions).

\(\Rightarrow\) very non-ideal \(\Rightarrow\) unlike molecules are less attracted than like molecules \(\Rightarrow U_{AB} > U_{AA} = U_{BB}\)

Mixing A & B increases total energy \((U\text{ inc excave down})\)
IV. Entropy of a Binary Mixture: Let's make a grid in our total volume, \( N \) sites (\( N \) molecules in total). Can we have \( A \) or \( B \) type, \( N = N_A + N_B \). How many ways of ordering? \( \Rightarrow \) This is like a two level system.

\[
\frac{N!}{N_A!N_B!(N-N_B)!} = \frac{N!}{N!} \]

\[
S \propto \ln \frac{N_A!N_B!(N-N_B)!}{N!} = \ln \frac{N(N-N_B)}{N_N_B} + N_B \ln N_B = \ln \left( \frac{N-N_B}{N} \right) - N_B \ln \left( \frac{N_B}{N} \right) = -N \left[ (1-x) \ln (1-x) + x \ln(x) \right]
\]

(Same result can be obtained in problem 2.37)

\[
S = S_{\text{max}} \quad \Rightarrow \quad \frac{\partial S}{\partial x} \mid_{x=0} = x=1 \quad \text{Entropy of mixing}
\]

Same result can be obtained from ST : \( \Delta S = N_A k_B \ln \left( \frac{v_i}{v_f} \right) = -N_B k_B \ln \left( \frac{N_B}{N} \right) = -N k_B \ln \frac{N_B}{N} \)

\[
\Delta S = \Delta S_A + \Delta S_B = -N k_B \left[ x \ln x + (1-x) \ln (1-x) \right]
\]
Free energy of mixtures (We use $\Delta F = \Delta U - T \Delta S$, fixed $T$, $P$, constant)

a) Ideal mixture \( \Rightarrow U = U(x) = U_0 \)

\[ \text{F remains constant up to all Times} \]

\[ \text{if we prepare a mixture at Temp = T and x, it will remain homogeneous at all T. In such a system a phase separation would imply an increase in F \Rightarrow not allowed.} \]

Free energy over curve (of any) of e.g. mixtures of 2 gases always homogenous of unmixed combination, \( F_{ps}(x) = xF + (1-x)F_m \)

\[ V = \frac{N}{2} \left[ (1-x)^2 U_{AA} + x^2 U_{BB} + 2x(1-x)U_{AB} \right] \]

\[ S = Nk_B \left[ (1-x) \ln(1-x) + x \ln x \right] \]

\[ F(x) = U(x) - TS(x) \]

\[ x \]

\[ U \]

\[ S \]
Target between initial and final state.

\[ T < T_c \quad \text{and} \quad F_p < F_p^* \quad \xrightarrow{\text{dissoc.}} \quad T_c: \text{largest } T \text{ where } Z \text{ minima appear.} \]

\( x < x_1 \quad F_p > F \Rightarrow \text{homogeneous solution.} \)

\( x > x_2 \quad F_p > F \Rightarrow \text{homog.} \)

up to \( x_1 \) of B dissolves in A

\( x > x_2 \) of A dissolves in B

\( x_1 < x < x_2 \) : \( F_p < F \) phase separation.

System becomes unstable against macroscopic phase separation (same instability that we saw in solid-gas theory, but now \( z \) is function of \( x \), not \( V \)). When system is cooled below \( T_c \), it separates into two spatially separated mixtures (one at ratio \( x_1 \) and one at ratio \( x_2 \)).

\( \Rightarrow \) Solubility gaps: Combined free energies of the combined spatially separate mixtures in below homogeneous mixture.
heterogeneous mixture
(2 separate liquid-solid phases).

$T > T_c \Rightarrow$ miscibility gap vanishes.

VI Melting + mixing add a phase change \( \Rightarrow \) Next lecture

VII chemical potential of mixtures:

$$\mu = \frac{\partial F}{\partial x}$$

the variable \( x \) plays the same role for mixing that \( V \) plays in liquid-gas systems, while \( n \) plays the role that pressure plays in big-gas systems.

\( \mu(x) \) looks like \( P(V) \) in the vdW gas.

\[ \mu(x) \]

\[ \frac{d\mu}{dx} < 0 \Rightarrow \text{instability region} \]