A. Regular Solutions: A Simple Example of a Real Solution

- The simplest non-ideal solution model that works beyond the Henry’s Law model is the regular solution model. The basic assumption of the simplest regular solution model is that when components A and B mix, they mix randomly.
- If that is the case, the for both the simple regular and ideal binary solution
  \[ \Delta S_{\text{MIX}} = -R \left( \chi_A \ln \chi_A + \chi_B \ln \chi_B \right) > 0 \]  
  (17.1)
- If mixing is not random then the entropy will deviate from this expression.
- Ideal solution always form when components are mixed. To show this start with
  \[ \Delta G_{\text{MIX}} = \Delta H_{\text{MIX}} - T \Delta S_{\text{MIX}} \]  
  (17.2)
- Recall for an ideal solution...
  \[ \Delta H_{\text{MIX}} = 0 \]  
  (17.3)
- Given 17.1 -17.3 we conclude
  \[ \Delta G_{\text{MIX}} = -T \Delta S_{\text{MIX}} = RT \left( \chi_A \ln \chi_A + \chi_B \ln \chi_B \right) < 0 \]  
  (17.4)
- To construct a regular solution model we recall an ideal solution is a solution where all interactions between solution components are equal. In a solution composed of two components A and B, call the interaction between two A molecules, \( \varepsilon_{AA} \), between 2 B molecules \( \varepsilon_{BB} \), and between an A and a B \( \varepsilon_{AB} \). If these three interaction energies are equal, the solution is ideal. If they are not the same, the solution’s thermodynamic behavior is non-ideal.
- Suppose we imagine mixing \( N_A \) molecules A with \( N_B \) molecules B to form a solution. The solution can be imagined as \( N_A \) A molecules and \( N_B \) B molecules arranged on a lattice:

  
  \[
  \begin{array}{ccccccc}
  \end{array}
  \]

  
  \[
  \begin{array}{ccccccc}
  A & B & B & A & A \\
  B & B & A & B & A \\
  B & B & A & B & B \\
  \end{array}
  \]

  
  \[
  \begin{array}{ccccccc}
  \end{array}
  \]

  
  - The energy of such a solution now depends on the number of AA interactions \( N_{AA} \), BB interactions \( N_{BB} \), and AB interactions \( N_{AB} \). In general the energy is
  \[ U(A,B) = N_{AA} \varepsilon_{AA} + N_{AB} \varepsilon_{AB} + N_{BB} \varepsilon_{BB} \]  
  (17.5)
- This lattice-based theory of solutions is sometimes called regular solution theory. A regular solution is non-ideal but the interactions between molecules are weak, and all molecules are about the same size.
An important number in the theory of regular solutions is the number of sides for a particular lattice position. This can be imagined to be the number of neighbors a A or B molecules has and in this simple lattice model the number is Z for A and B. The number of neighbors around \( N_A \) molecules is therefore \( ZN_A \) and can be expressed in terms of the number of AA and AB contacts \( N_{AA} \) and \( N_{AB} \):

\[
ZN_A = 2N_{AA} + N_{AB} \quad (17.6)
\]

A similar expression exists for the number of neighbors around \( N_B \) B molecules:

\[
ZN_B = 2N_{BB} + N_{AB} \quad (17.7)
\]

Now we solve for \( N_{AA} \) and \( N_{BB} \) and put the results into the energy equation:

\[
U(A, B) = N_{AA} \varepsilon_{AA} + N_{AB} \varepsilon_{AB} + N_{BB} \varepsilon_{BB}
\]

\[
= \left( \frac{ZN_A - N_{AB}}{2} \right) \varepsilon_{AA} + \left( \frac{ZN_B - N_{AB}}{2} \right) \varepsilon_{BB}
\]

\[
= \left( \frac{Z \varepsilon_{AA}}{2} \right) N_A + \left( \frac{Z \varepsilon_{BB}}{2} \right) N_B + \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) N_{AB}
\]

\[
(17.8)
\]

The only quantity in this equation that we do not know in general is \( N_{AB} \), because the number of AB contacts depends on the specific arrangement of A and B molecules on the lattice. But we can get this number using statistics. The probability that a given A molecule has a B neighbor is:

\[
p_B = \frac{N_B}{N_A + N_B} = \frac{N_B}{N} \quad (17.9)
\]

The number of AB contacts is there the number of neighbors around \( N_A \) A molecules, times the probability that any of those neighbors is a B molecule:

\[
N_{AB} = ZN_A p_B = \frac{ZN_A N_B}{N} \quad (17.10)
\]

The energy equation is now:

\[
U(A, B) = \left( \frac{Z \varepsilon_{AA}}{2} \right) N_A + \left( \frac{Z \varepsilon_{BB}}{2} \right) N_B + \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \left( \frac{ZN_A N_B}{N} \right)
\]

\[
= \left( \frac{Z \varepsilon_{AA}}{2} \right) N_A + \left( \frac{Z \varepsilon_{BB}}{2} \right) N_B + \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \left( \frac{Z N_A N_B}{N} \right)
\]

\[
= \left( \frac{Z \varepsilon_{AA}}{2} \right) N_A + \left( \frac{Z \varepsilon_{BB}}{2} \right) N_B + wRT \left( \frac{N_A N_B}{N} \right)
\]

\[
(17.11)
\]

i.e. \( w = \frac{Z}{RT} \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \)

The energy equation has three parts which we write as:
\[ U(A, B) = \left( \frac{Z\varepsilon_{AA}}{2} \right) N_A + \left( \frac{Z\varepsilon_{BB}}{2} \right) N_B + wRT \left( \frac{N_A N_B}{N} \right) \]
\[ = U(A) + U(B) + \Delta U_{\text{MIX}}(A, B) \quad (17.12) \]

- The first two terms are the energies of the separated components. The third term arises from the mixing of the components:

\[ \Delta U_{\text{MIX}} = wRT \left( \frac{N_A N_B}{N} \right) \quad (17.13) \]

- Recall also that \( \Delta H = \Delta U + \Delta (PV) \approx \Delta U \) if pressure and volumes are kept constant for the solution. Then for a regular solution:

\[ \Delta H_{\text{MIX}} \approx \Delta U_{\text{MIX}} = wRT \left( \frac{N_A N_B}{N} \right) \quad (17.14) \]

- Notice that \( w = \frac{Z}{RT} \left( \varepsilon_{AB} - \frac{\varepsilon_{AA} + \varepsilon_{BB}}{2} \right) \) can be positive or negative. So if \( w < 0 \) the mixing is exothermic and if \( w > 0 \) the mixing is endothermic.

- Now we want the chemical potential for a solute in a regular solution. Because \( \Delta U_{\text{MIX}} \approx \Delta H_{\text{MIX}} \) then \( \Delta A_{\text{MIX}} \approx \Delta G_{\text{MIX}} \). The Helmholtz (Gibbs) energy of mixing is obtained from:

\[ \Delta G_{\text{MIX}} \approx \Delta A_{\text{MIX}} = \Delta U_{\text{MIX}} - T\Delta S_{\text{MIX}} = wRT \left( \frac{N_A N_B}{N} \right) + RT \left( N_A \ln \chi_A + N_B \ln \chi_B \right) \]
\[ = wNRT \chi_A \chi_B + NRT \left( \chi_A \ln \chi_A + \chi_B \ln \chi_B \right) \]
\[ \therefore \frac{\Delta A_{\text{MIX}}}{NRT} = \chi_A \ln \chi_A + \chi_B \ln \chi_B + w\chi_A \chi_B = \chi_A \ln \chi_A + (1 - \chi_A) \ln (1 - \chi_A) + w\chi_A (1 - \chi_A) \]
\[ (17.15) \]

- Clearly the first two terms in the equation correspond to the Helmholtz energy of mixing for an ideal solution (i.e. \( w = 0 \)). The third term represents deviations from ideality. We can get the chemical potential for A or B by differentiating with respect to \( N_A \) or \( N_B \). Start with

\[ \mu_A - \mu_A^0 = \left( \frac{\partial A_{\text{MIX}}}{\partial N_A} \right)_{V,T,N_B} \approx \left( \frac{\partial G_{\text{MIX}}}{\partial N_A} \right)_{P,T,N_B} \]
\[ = \frac{\partial}{\partial N_A} \left[ RT \left( \frac{N_A}{N_A + N_B} \right) + N_B \ln \left( \frac{N_B}{N_A + N_B} \right) + wRT \left( \frac{N_A N_B}{N_A + N_B} \right) \right] \]
\[
\begin{align*}
\frac{\partial}{\partial N_A} \left( N_A \ln N_A + N_B \ln N_B - (N_A + N_B) \ln (N_A + N_B) \right) + wRT \left( \frac{N_B}{N_A + N_B} - \frac{N_A N_B}{(N_A + N_B)^2} \right) \\
= RT \left( \ln N_A + 1 - \ln (N_A + N_B) \right) + wRT \left( \frac{N_B^2}{(N_A + N_B)^2} \right) = RT \ln \chi_A + wRT \chi_B^2
\end{align*}
\]

(17.16)

- It is a lot of calculus but the result is simple and gives the activity coefficients for A and B:

\[
\mu_A - \mu_A^0 = RT \ln \chi_A + wRT \chi_B^2 = RT \ln \chi_A + RT \ln \gamma_A
\]

\[
\therefore \ln \gamma_A = w\chi_B^2
\]

Similarly:

\[
\mu_B - \mu_B^0 = RT \ln \chi_B + wRT \chi_A^2 = RT \ln \chi_B + RT \ln \gamma_B
\]

\[
\therefore \ln \gamma_B = w\chi_A^2
\]

- We can also consider deviations from ideal behavior produced by properties of the regular solution. The Helmholtz energy can be divided into two parts: a part that represents ideal solution behavior \( \Delta A^{\text{ideal}}_{\text{mix}} \) and a second part that contains \( w \) and represents non-ideal conditions. This non-ideal part is sometimes called the excess Helmholtz energy \( \Delta A^E_{\text{mix}} \):

\[
\Delta A_{\text{mix}} = \Delta A^{\text{ideal}}_{\text{mix}} + \Delta A^E_{\text{mix}} = NRT \left( \chi_A \ln \chi_A + \chi_B \ln \chi_B \right) + N\Delta \varepsilon_{\chi_A \chi_B}
\]

where:

\[
\Delta \varepsilon = Z \left( \frac{\varepsilon_{AB} - \varepsilon_{AA} + \varepsilon_{BB}}{2} \right) = wRT
\]

(17.18)

- Once you have an expression for \( \Delta A_{\text{mix}} \) you can get an expression for the entropy, enthalpy, and heat capacity for regular solutions:

\[
\Delta S_{\text{mix}} = -\frac{\partial \Delta A_{\text{mix}}}{\partial T} = \Delta S^{\text{ideal}}_{\text{mix}} + \Delta S^E_{\text{mix}} = -NR \left( \chi_A \ln \chi_A + \chi_B \ln \chi_B \right) - N\chi_A\chi_B \frac{\partial \Delta \varepsilon}{\partial T}
\]

(17.19)

where again there is a part of the entropy that is the ideal entropy of mixing, which assumes random mixing, and a second part that represents non-ideal conditions. This non-ideal part is called the excess entropy of mixing \( \Delta S^E_{\text{mix}} \).

- The enthalpy of mixing is easy to get from the fact that the volume is assumed to not change much upon mixing. So for constant volume and pressure

\[
\Delta H_{\text{mix}} = \Delta U_{\text{mix}} + \Delta (PV) = \Delta U_{\text{mix}} = \Delta A_{\text{mix}} + T\Delta S_{\text{mix}}
\]

\[
= N\chi_A\chi_B \left( \Delta \varepsilon - T \frac{\partial \Delta \varepsilon}{\partial T} \right)
\]

(17.20)
Note the enthalpy of mixing is entirely dependent on non-ideal effect as it must be because for ideal solutions $\Delta H_{\text{MIX}}=0$.

- The heat capacity at constant pressure is also easy to get:
  
  $$\Delta C_{p,\text{MIX}} = \left( \frac{\partial \Delta H_{\text{MIX}}}{\partial T} \right)_p = -N \chi_A \chi_B T \frac{\partial^2 \Delta \varepsilon}{\partial T^2}$$

- Again, the heat capacity of mixing for a regular solution, which is derived from the enthalpy of mixing, depends entirely on non-ideal effects.