University of Washington
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Lecture 17 8/06/14

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

$$\Delta S_{MIX} = -R\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) > 0 \tag{17.1}$$

- 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

$$\Delta G_{MIX} = \Delta H_{MIX} - T\Delta S_{MIX} \tag{17.2}$$

- Recall for an ideal solution...

$$\Delta H_{MIX} = 0 \tag{17.3}$$

- Given 17.1 -17.3 we conclude

$$\Delta G_{MIX} = -T\Delta S_{MIX} = RT\left(\chi_A \ln \chi_A + \chi_B \ln \chi_B\right) < 0 \tag{17.4}$$

- 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, ε_{AA}, between 2 B molecules ε_{BB}, and between an A and a B ε_{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:

$$\begin{array}{ccc} A & A & A \\ A & A & A \\ A & A & A \end{array} + \begin{array}{cccc} B & B & B & B \\ B & B & B & B \\ B & B & B & B \\ B & B & B & B \end{array} \rightarrow \begin{array}{ccccc} A & B & B & A & A \\ B & B & A & B & A \\ B & B & A & B & B \\ B & A & A & B & B \\ B & B & B & A & B \end{array}$$

- 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
- $$U\left(A,B\right) = N_{AA}\varepsilon_{AA} + N_{AB}\varepsilon_{AB} + N_{BB}\varepsilon_{BB} \tag{17.5}$$
- 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}:

- $$ZN_A = 2N_{AA} + N_{AB} \tag{17.6}$$

- A similar expression exists for the number of neighbors around NB B molecules:

- $$ZN_B = 2N_{BB} + N_{AB} \tag{17.7}$$

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

$$\begin{aligned}U\left(A,B\right) &= N_{AA}\varepsilon_{AA} + N_{AB}\varepsilon_{AB} + N_{BB}\varepsilon_{BB}\\ &= \left(\frac{ZN_A - N_{AB}}{2}\right)\varepsilon_{AA} + N_{AB}\varepsilon_{AB} + \left(\frac{ZN_B - N_{AB}}{2}\right)\varepsilon_{BB}\\ &= \left(\frac{Z\varepsilon_{AA}}{2}\right)N_A + \left(\frac{Z\varepsilon_{BB}}{2}\right)N_B + \left(\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)N_{AB}\end{aligned} \tag{17.8}$$

- The only quantity in this equation that we do not know in general is N_{AB}, because the number of AB contacts depends of 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:

$$p_B = \frac{N_B}{N_A + N_B} = \frac{N_B}{N} \tag{17.9}$$

- 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;

$$N_{AB} = ZN_A p_B = \frac{ZN_A N_B}{N} \tag{17.10}$$

- The energy equation is now:

$$\begin{aligned}U\left(A,B\right) &= \left(\frac{Z\varepsilon_{AA}}{2}\right)N_A + \left(\frac{Z\varepsilon_{BB}}{2}\right)N_B + \left(\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)N_{AB}\\ &= \left(\frac{Z\varepsilon_{AA}}{2}\right)N_A + \left(\frac{Z\varepsilon_{BB}}{2}\right)N_B + \left(\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)\left(\frac{ZN_A N_B}{N}\right)\\ &= \left(\frac{Z\varepsilon_{AA}}{2}\right)N_A + \left(\frac{Z\varepsilon_{BB}}{2}\right)N_B + wRT\left(\frac{N_A N_B}{N}\right)\\ &\text{i.e. } w = \frac{Z}{RT}\left(\varepsilon_{AB} - \frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)\end{aligned} \tag{17.11}$$

- The energy equation has three parts which we write as:

$$U\left(A,B\right)=\left(\frac{Z\varepsilon_{AA}}{2}\right)N_A+\left(\frac{Z\varepsilon_{BB}}{2}\right)N_B+wRT\left(\frac{N_AN_B}{N}\right) \qquad (17.12)$$
$$=U\left(A\right)+U\left(B\right)+\Delta U_{MIX}\left(A,B\right)$$

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

$$\Delta U_{MIX}=wRT\left(\frac{N_AN_B}{N}\right) \qquad (17.13)$$

- Recall also that that $\Delta H=\Delta U+\Delta\left(PV\right)\approx\Delta U$ if pressure and volumes are kep constant for the solution. Then for a regular solution:
- $$\Delta H_{MIX}\approx\Delta U_{MIX}=wRT\left(\frac{N_AN_B}{N}\right) \qquad (17.14)$$
- 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 $\Delta U_{MIX}\approx\Delta H_{MIX}$ then $\Delta A_{MIX}\approx\Delta G_{MIX}$. The Helmholtz (Gibbs) energy of mixing is obtained from:

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

- 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

$$\mu_A-\mu_A^0=\left(\frac{\partial A_{MIX}}{\partial N_A}\right)_{V,T,N_B}\approx\left(\frac{\partial G_{MIX}}{\partial N_A}\right)_{P,T,N_B}$$
$$=\frac{\partial}{\partial N_A}\left(RT\left(N_A\ln\left(\frac{N_A}{N_A+N_B}\right)+N_B\ln\left(\frac{N_B}{N_A+N_B}\right)\right)+wRT\left(\frac{N_AN_B}{N_A+N_B}\right)+\right)$$

$$= RT\frac{\partial}{\partial N_A}\left(N_A\ln\left(N_A\right)+N_B\ln\left(N_B\right)-\left(N_A+N_B\right)\ln\left(N_A+N_B\right)\right)+wRT\left(\frac{N_B}{N_A+N_B}-\frac{N_AN_B}{\left(N_A+N_B\right)^2}\right)$$

$$= RT\left(\ln\left(N_A\right)+1-1-\ln\left(N_A+N_B\right)\right)+wRT\left(\frac{N_B^2}{\left(N_A+N_B\right)^2}\right)=RT\ln\chi_A+wRT\chi_B^2$$

(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: (17.17)

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

$$\therefore \ln\gamma_B=w\chi_A^2$$

- 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 ΔA_{MIX}^{ideal} and a second part that contains w and represents non-ideal conditions. This non-ideal part is sometimes called the excess Helmholtz energy ΔA_{MIX}^{E}:

$$\begin{aligned}&\Delta A_{MIX}=\Delta A_{MIX}^{ideal}+\Delta A_{MIX}^{E}=NRT\left(\chi_A\ln\chi_A+\chi_B\ln\chi_B\right)+N\Delta\varepsilon\chi_A\chi_B\\&where:\quad \Delta\varepsilon=Z\left(\varepsilon_{AB}-\frac{\varepsilon_{AA}+\varepsilon_{BB}}{2}\right)=wRT\end{aligned} \qquad (17.18)$$

- Once you have an expression for ΔA_{MIX} you can get an expression for the entropy, enthalpy, and heat capacity for regular solutions:

- $$\Delta S_{MIX}=-\frac{\partial\Delta A_{MIX}}{\partial T}=\Delta S_{MIX}^{ideal}+\Delta S_{MIX}^{E}=-NR\left(\chi_A\ln\chi_A+\chi_B\ln\chi_B\right)-N\chi_A\chi_B\frac{\partial\Delta\varepsilon}{\partial T} \qquad (17.19)$$

  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-deal conditions. This non-ideal part is called the excess entropy of mixing ΔS_{MIX}^{E}.

- 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

$$\begin{aligned}\Delta H_{MIX}&=\Delta U_{MIX}+\Delta\left(PV\right)=\Delta U_{MIX}=\Delta A_{MIX}+T\Delta S_{MIX}\\&=N\chi_A\chi_B\left(\Delta\varepsilon-T\frac{\partial\Delta\varepsilon}{\partial T}\right)\end{aligned} \qquad (17.20)$$

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

- The heat capacity at constant pressure is also easy to get: $\Delta C_{P,MIX} = \left(\frac{\partial \Delta H_{MIX}}{\partial T}\right)_P = -N\chi_A\chi_B T\frac{\partial^2\Delta\varepsilon}{\partial T^2}$
- Again, the heat capacity of mixing for a regular solution, which is derived from the enthalpy of mixing, depends entirely on non-ideal effects.