

**University of Washington  
Department of Chemistry  
Chemistry 452/456  
Summer Quarter 2014**

---

Lecture 14 8/01/14  
ERD 8.1-8.3

### A. Thermodynamics of Solutions

A basic construct in the biological sciences is a solution of a macromolecule. The macromolecule is usually some type of biopolymer (i.e. protein, nucleic acid, carbohydrate, etc.). The macromolecular solution is composed of several components...

- Solvent (usually water)
- Macromolecular solute
- Ions (including counterions for the biopolymer if it is charged, and components of the buffer)
- Ligands: small molecules that bind to the macromolecule as part of its function or whose binding affects the function of the macromolecule.

Understanding the properties of a macromolecular solution is a basic endeavor in the biological sciences. The principles of thermodynamics can be used in such studies and free energy calculations are an important feature of the thermodynamic approach.

- The study of the components of a solution...and specifically the free energy of the solution, begin, interestingly enough, with the study of the vapor over the solution. It is assumed that for each component, the vapor is in equilibrium with the dissolved form.

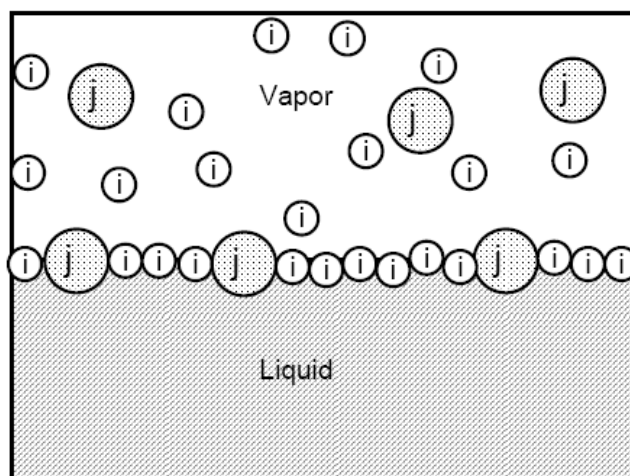


Figure 1 There is a tendency for molecules in the solution (e.g. water and volatile solutes) to “escape” to the vapor phase (i.e. vaporization) and there is also a tendency for molecules in the vapor phase to enter the solution. At equilibrium these tendencies are in balance.

## B. Simple Models for Solutions of Non-electrolytes: Ideal Solution

A non-electrolyte is an uncharged species. We will talk about electrolyte solutions later . For now the components of the solution will be assumed to be uncharged, i.e. non-electrolytes. Two simple models exist for non-electrolyte solutions: the ideal solution and the Henry's Law solution.

- Ideal solutions: Ideal solutions are solutions in which all interactions between all components are equivalent. If an ideal solution is composed of two components, referred to as A and B, the AA, BB, and AB interactions are all the same.
  - Because the components of an ideal solution have equivalent interactions, the enthalpy of mixing the components together is zero...

$$\Delta\bar{H}_{mix} = \frac{\Delta H_{mix}}{n} = 0 \quad (14.1)$$

where  $n_A + n_B = n$

- The molar entropy of mixing  $n_A$  moles of component A with  $n_B$  moles of component B into an ideal solution is

$$\Delta\bar{S}_{mix} = \frac{\Delta S_{mix}}{n} = -R(\chi_A \ln \chi_A + \chi_B \ln \chi_B) \quad (14.2)$$

- where  $\chi_A$  and  $\chi_B$  are the mole fractions of A and B, respectively.
- Finally, for an ideal solution
 
$$\Delta\bar{G}_{mix} = \Delta\bar{H}_{mix} - T\Delta\bar{S}_{mix} = 0 - T\Delta\bar{S}_{mix} = RT(\chi_A \ln \chi_A + \chi_B \ln \chi_B)$$
- The free energy of the  $i$ th components of the (ideal) vapor above the solution obeys the equation derived above...

$$\mu_i(v) = \mu_i^0 + RT \ln \left( \frac{P_i}{P_i^0} \right) \quad (14.3)$$

- In equation 14.3, the reference state is a vapor mixture with chemical potential  $\mu_i^0$  where the partial pressure of component  $i$  is:  $P_i^0 = 1 \text{ bar} = 1.00 \times 10^5 \text{ Pa}$
- If the vapor and dissolved component  $i$  are in equilibrium the chemical potentials are equal so that...

$$\mu_i(\ell) = \mu_i(v) = \mu_i^0 + RT \ln \left( \frac{P_i}{P_i^0} \right) \quad (14.4)$$

- Now consider component  $i$  in the pure state. Again assuming in the pure state the vapor and dissolved species are in equilibrium equation 14.2 becomes:

$$\mu_i^*(\ell) = \mu_i^*(v) = \mu_i^0 + RT \ln \left( \frac{P_i^*}{P_i^0} \right) \quad (14.5)$$

- In equation 14.5 the asterisk indicates the pure state chemical potential. Note we can still use the same reference state as in equation 14.3. Now we can subtract equation 14.5 from 14.4...

$$\mu_i(\ell) - \mu_i^*(\ell) = \mu_i^0 + RT \ln\left(\frac{P_i}{P_i^0}\right) - \mu_i^0 + RT \ln\left(\frac{P_i^*}{P_i^0}\right) \quad (14.6)$$

$$\therefore \mu_i(\ell) = \mu_i^*(\ell) + RT \ln\left(\frac{P_i}{P_i^*}\right)$$

- Equation 14.6 is the chemical potential of the  $i$ th component in the liquid phase and this expression involves the partial pressure of component  $i$  in the vapor phase. We have yet to relate the chemical potential of component  $i$  in the solution to its mole fraction. To do this note Equation 14.3 can be rewritten:

$$\mu_i(v) - \mu_i^0 = +RT \ln\left(\frac{P_i}{P_i^0}\right) \quad (14.7)$$

- Now the chemical potential difference on the left of 14.7 is the reversible work required to take a mole of component  $i$  from a vapor mixture where  $P_i^0 = 1 \text{ bar}$  to a vapor mixture where the partial pressure is  $P_i$ . By analogy the reversible work required to take a mole of component  $i$  from the pure liquid state to a solution where its mole fraction is  $\chi_i$  has the form

$$\mu_i(\ell) - \mu_i^*(\ell) = +RT \ln \chi_i \quad (14.8)$$

Equating 14.6 and 14.8 we get the ideal solution equation of state:

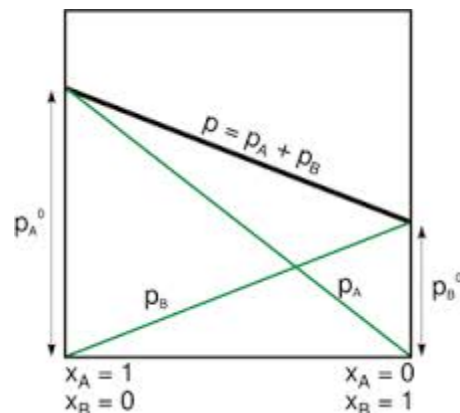
$$\chi_i = \frac{P_i}{P_i^*} \quad (14.9)$$

- Equation 14.9 is also called Raoult's Law. Both components of an ideal solution can be varied from mole fractions of 0 to 1. The distinction between solvent and solute does not really exist.
- Equation 14.8 and its consequence 14.9 imply that the only physical property of an ideal solution associated with a given component is its mole fraction. This arises because in an ideal solution, interactions between all solution components are assumed to be the same.
- Assume a solution has two components A and B. Then the vapor above the solution has total pressure  $P_T$  given by:

$$P_T = P_A + P_B = \chi_A P_A^* + \chi_B P_B^* = \chi_A P_A^* + (1 - \chi_A) P_B^* \quad (14.10)$$

- Figure 2 shows a plot of  $P_A$ ,  $P_B$  and  $P = P_A + P_B$  as functions of  $x_A$  and  $x_B$ . The linear form of all three plots is characteristic of ideal solution behavior.

Figure 2: Composite plots of  $P_A$ ,  $P_B$ , and  $P = P_A + P_B$  from equation 14.10.



- Example: Benzene  $C_6H_6$  and toluene  $C_7H_8$  form an ideal solution when mixed. Calculate the enthalpy change  $\Delta H_{mix}$ , entropy change  $\Delta S_{mix}$ , and free energy change  $\Delta G_{mix}$  when 39 grams of benzene are mixed at a constant temperature of 300K with 92 grams of toluene.

Solution:

$$\text{moles } C_6H_6 = (39 \text{ g})(1 \text{ mole} / 78 \text{ g}) = 0.5 \text{ moles}$$

$$\text{moles } C_7H_8 = (92 \text{ g})(1 \text{ mole} / 92 \text{ g}) = 1.0 \text{ moles}$$

$$\text{mole fraction } C_6H_6 = \chi_b = \frac{0.5 \text{ moles}}{1.5 \text{ moles}} = 0.33$$

$$\text{mole fraction } C_7H_8 = \chi_t = \frac{1.0 \text{ moles}}{1.5 \text{ moles}} = 0.66$$

$$\Delta H_{mix} = 0$$

$$\begin{aligned} \Delta \bar{S}_{mix} &= -R(\chi_b \ln \chi_b + \chi_t \ln \chi_t) = -(8.31 \text{ J} / \text{moles} \cdot \text{K})(0.33 \ln(0.33) + 0.66 \ln(0.66)) \\ &= 5.31 \text{ J} / \text{mole} \cdot \text{K} \end{aligned}$$

$$\Delta S_{mix} = (1.5 \text{ moles}) \Delta \bar{S}_{mix} = 7.98 \text{ J} / \text{K}$$

$$\Delta G_{mix} = -T \Delta S_{mix} = -(300 \text{ K})(7.98 \text{ J} / \text{K}) = -2393 \text{ J}$$

## B. The Lever Rule

- An application of Raoult's Law is in the prediction of vapor liquid compositions at equilibrium.
- Suppose we have two components in a solution in equilibrium with its vapor. Figure three shows the total pressure above the solution as a function of  $x_2$ , the mole fraction of component 2 in solution (lower curve) and  $y_2$  the mole fraction of 2 in the vapor phase (upper curve)

- To clarify we give expressions for vapor and solution composition in terms of these two mole fractions. Assuming  $P_T = P_1 + P_2$ : the vapor composition is

$$P_2 = y_2 P_T \text{ where } y_2 = \frac{n_2^v}{n_1^v + n_2^v} = \frac{n_2^v}{n^v} \quad (14.11)$$

- The solution composition is given by Raoult's Law

$$P_2 = x_2 P_2^* \text{ where } x_2 = \frac{n_2^\ell}{n_1^\ell + n_2^\ell} = \frac{n_2^\ell}{n^\ell} \quad (14.12)$$

- Figure 3 shows a plot of total pressure  $P_T$  as a function of  $x_2$  (lower curve) and  $y_2$  (upper curve). At point A the pressure is high and both components are in the liquid form. As the pressure is lowered vapor appears when the upper curve is

encountered. At point B both components are vaporized . For total pressures between the two curves, liquid and vapor are in equilibrium.

- We define the total mole fraction of component 2:

$$Z_2 = \frac{n_2^v + n_2^\ell}{n_v + n_\ell} \quad (14.13)$$

- We combine equations 14.11 and 14.12 with 14.13:

$$Z_2(n_v + n_\ell) = n_2^v + n_2^\ell = y_2 n_v + x_2 n_\ell \quad (14.14)$$

- We rearrange equation 14.14 to get the so-called lever rule;

$$n_v(y_2 - Z_2) = n_\ell(Z_2 - x_2) \quad (14.15)$$

*or ...  $n_v \ell_\beta = n_\ell \ell_\alpha$*

Figure 3; Pressure composition curve for an ideal solution.. The upper curve is

$$P_T = P_1 + P_2 = x_1 P_1^* + x_2 P_2^*$$

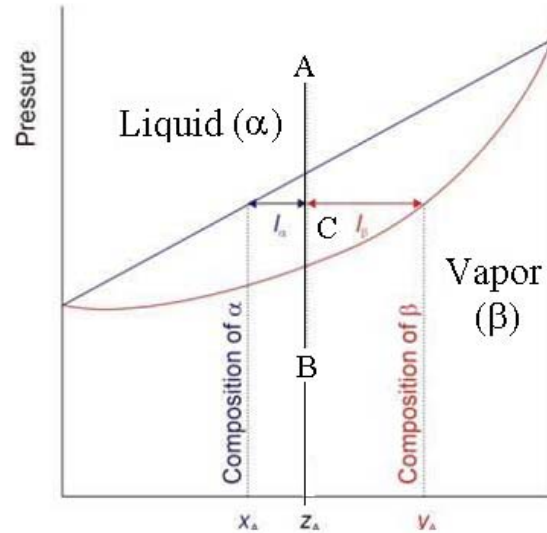
$$= x_1 P_1^* + (1 - x_1) P_2^* = P_2^* + (P_1^* - P_2^*) x_1$$

The lower curve is:

$$y_1 = \frac{P_1}{P_T} = \frac{x_1 P_1^*}{P_2^* + (P_1^* - P_2^*) x_1}$$

$$\therefore x_1 = \frac{y_1 P_2^*}{P_1^* + (P_2^* - P_1^*) y_1}$$

$$\therefore P_T = P_2^* + (P_1^* - P_2^*) x_1 = \frac{P_1^* P_2^*}{P_1^* + (P_2^* - P_1^*) y_1}$$



- At point C the mole fraction of 2 in both phases is given by equation 14.13. If a horizontal line is drawn from C, the intersection with the vapor line gives the vapor mole fraction  $y_2$ . The intersection with the liquid line gives the liquid mole fraction  $x_2$ . This horizontal line is called a tie line.
- Equation 14.15 is called the lever rule because it is analogous to the mechanical equilibrium equation for a lever with two masses balanced on a fulcrum. In equation 14.15 the two mole terms are analogous to the masses and the  $\ell_\alpha$  and  $\ell_\beta$  terms are analogous to the lever arms.