### Molecular model for non-ideal solutions

We can express the potential energy of the solution in the form

 $\mathsf{U} = \mathsf{N}_{11}\mathsf{e}_{11} + \mathsf{N}_{12}\mathsf{e}_{12} + \mathsf{N}_{22}\mathsf{e}_{22}$ 

where N<sub>ii</sub> is the number of neighboring pairs of molecules of type i and j and where e<sub>ii</sub> is the interaction energy of a pair of molecules of type i and j when they are next to each other. We assume a coordination number z where z is between 6 and 10. There are N<sub>1</sub> component 1 molecules in solution so the number of 1-1 neighboring pairs is  $N_{11} = zN_1x_1/2$  where the factor of used to avoid counting each 1-1 pair twice. Similarly, for component 2 we have  $N_{22} = zN_2x_2/2$ . The same value of z is used because we assume that molecular sizes are about the same.

## Aspects of the microscopic model



self interaction

cross term



**e**<sub>11</sub>

**e**<sub>22</sub>

e<sub>12</sub>

z is the solvation number (here it is 6)

## Molecular model for non-ideal solutions

The number of 1-2 neighboring pairs is given by

 $N_{12} = zN_1x_2 = zN_2x_1$ . The total interaction energy in the solution is  $U = zN_1x_1e_{11}/2 + zN_2x_2e_{22}/2 + zN_1x_2e_{12}$ Using the definitions  $x_1 = N_1/(N_1+N_2)$  and  $x_2 = N_2/(N_1+N_2)$ we can reexpress the interaction energy as  $U = (N_1^2e_{11}/2 + N_2^2e_{22}/2 + N_1N_2e_{12})z/(N_1+N_2)$ We can focus on the non-ideality of the solution by introducing the quantity

 $w = U = e_{11} + e_{22} - 2e_{12}$ 

## Comparing ideal and real energies

For an ideal solution  $e_{11} = e_{22} = e_{12}$  and so w = 0. However, for a non-ideal solution  $e_{11} \neq e_{22} \neq e_{12}$ . Substituting  $e_{12} = (e_{11} + e_{22} - w)/2$  we have  $U = (N_1^2 e_{11}/2 + N_2^2 e_{22}/2 + N_1 N_2 (e_{11} + e_{22} - w)/2)z/(N_1 + N_2)$  $U = zN_1 e_{11}/2 + zN_2 e_{22}/2 - zwN_1 N_2/2(N_1 + N_2)$ 

The last term represents the non-ideality in the solution.

Therefore, we can express the Gibbs energy of the solution as

$$G_{soln} = G_{ideal} - zwN_1N_2/2(N_1+N_2)$$
  
or units of moles

$$G_{soln} = G_{ideal} - zwN_A n_1 n_2 / 2(n_1 + n_2)$$

The chemical potential of component 1 is given by

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right) = \left(\frac{\partial G^{id}}{\partial n_1}\right) - \frac{zwN_A}{2} \left(\frac{\partial n_1 n_2 / (n_1 + n_2)}{\partial n_1}\right)$$

Note that the chemical potential of an ideal solution is given by  $\mu_1 = \mu_1^* + \text{RT Inx}_1$ 

The derivative is

$$\left(\frac{\partial n_1 n_2 / (n_1 + n_2)}{\partial n_1}\right) = \frac{n_2}{n_1 + n_2} - \frac{n_1 n_2}{\left(n_1 + n_2\right)^2} = x_2 - x_1 x_2 = x_2(1 - x_1) = x_2^2$$

This leads to the expression

$$\mu_{1} = \mu_{1}^{*} + \text{RT Inx}_{1} - zwN_{A}x_{2}^{2}/2$$
$$\mu_{1} = \mu_{1}^{*} + \text{RT In}(x_{1}e^{-zwx_{2}^{2}/2kT})$$

where we have used the fact that  $k = R/N_{\Delta}$ .

Our simple model of a solution has led directly to an expression for the activity in terms of the interaction strength w, coordination number z, mole fraction x<sub>2</sub>, and thermal energy kT.

### Definition of a critical point

The activity is  $a_1 = P_1/P_1^* = x_1 exp(-zwx_2^2/2kT)$ 

The activity coefficient is  $\gamma_1 = \exp(-zwx_2^2/2kT)$ 

The expression derived is exactly analogous to the expressions used above for deviations from Raoult's law provided  $\alpha = -zw/2kT$ .

This simple model not only allows us to calculate activities from molecular properties, but it also includes the possibility of phase separation. A critical point in a two component phase diagram indicates that there is a region of temperature or pressure beyond which the solution separates into two phases.

#### Phase separation

In the case of the model liquid discussed here phase separation will occur if zw/2kT > 2 or in other words if the parameter  $\alpha < -2$ . We first show the relationship between the activities of two species in a non-ideal binary solution and then use all of the information to discuss the free energy of mixing. This leads naturally to the idea of limited solubility even with this very simple model.

# Application of the Gibbs-Duhem equation

At this point, you might well ask whether the activity coefficient for component 1 has any bearing on the magnitude of the activity coefficient for component 2. In fact, they are related as we now prove using the Gibbs-Duhem relation. The Gibbs-Duhem equation states that

 $n_1 d\mu_1 + n_2 d\mu_2 = 0.$ 

Dividing through by n the Gibbs-Duhem equation is

 $x_1 d\mu_1 + x_2 d\mu_2 = 0.$   $d\mu_2 = -x_1 d\mu_1 / x_2$ with  $\mu_1 = {\mu_1}^* + \text{RT} \ln(x_1 e^{\alpha x 2^2})$  where  $\alpha = -zw/2kT$ ,

# Application of the Gibbs-Duhem equation

 $d\mu_1 = -RTdx_1/x_1 + 2\alpha(1 - x_1)dx_1$  and  $d\mu_2 = -RTdx_1/x_2 + 2\alpha x_1dx_1$ Change variables from  $dx_1$  to  $-dx_2$ .

 $d\mu_2 = RTdx_2/x_2 + 2\alpha(1-x_2)dx_2$ 

Now we integrate,

 $\mu_2 - \mu_2^* = \text{RTInx}_2 + \alpha(1-x_2)^2$ and finally

$$\mu_2 = {\mu_2}^* + \text{RT} \ln(x_2 e^{\alpha x_1^2})$$

which shows that the activity of coefficient of component 1 implies the magnitude of the activity coefficient for component 2.

$$\gamma_1 = \exp(-zwx_2^2/2kT)$$
 implies  $\gamma_2 = \exp(-zwx_1^2/2kT)$ 

### Parameter for non-ideal solutions

As a result of our model for the interaction energy of particles in a non-ideal solution we can calculate  $\Delta_{mix}$ G.

For a two component solution

$$\begin{split} &\Delta_{mix}G = n_1RTln \ x_1 + n_2RTln \ x_2 - zwN_A/2(n_2x_1^2 + n_1x_2^2) \\ &\Delta_{mix}G = n_1RTln \ x_1 + n_2RTln \ x_2 - zwN_A(n_1 + n_2)x_1x_2/2 \\ &Our \ final \ expression \ for \ \Delta_{mix}G \ is \\ &\Delta_{mix}G = nRT(x_1ln \ x_1 + x_2ln \ x_2 - zwx_1x_2/2kT) \\ &which \ is \ clearly \ separable \ into \ an \ ideal \ part \ and \ the \ excess \ free \\ &energy \ discussed \ previously. \ We \ can \ plot \ \Delta_{mix}G/nRT \ for \ various \\ &values \ of \ zw/2kT \ as \ shown \ below. \end{split}$$

#### Parameter for non-ideal solutions



## Phase separation and critical point

Note that for  $\alpha < -2$  the curvature is negative in the central region (around a mole fraction of  $x_1 = 0.5$ ). This corresponds to a region where mixing is not spontaneous. In other words, there will be a phase separation in this region.

By assumption, the entropy of mixing is still equal to the entropy of mixing of an ideal solution. Thus,

 $\Delta_{\text{mix}} S = -nR(x_1 \ln x_1 + x_2 \ln x_2)$ 

and therefore the non-ideality appears in the enthalpy

 $\Delta_{\rm mix} H = - z w N_A x_1 x_2 / 2.$