

Thermodynamics of Ideal Solutions

In class we derived a relationship for the chemical potential of a component in an ideal solution:

$$\mu_i^\ell(T, P, X_{i,s}^\ell) = \mu_i^{\bullet\ell}(T, P) + RT \ln X_i^\ell$$

where $\mu_i^{\bullet\ell}(T, P)$ is the chemical potential of the pure liquid i at T and P .

The handout shows some thermodynamic consequences of this relationship. These are consistent with the 'picture' of an ideal solution where the interactions among the constituent molecules are the same (very similar) to those between the molecules in their individual pure (not solution) liquid phases.

0. Some useful relationships:

$$G(T, P, n_{i,s}) \quad (\text{extensive})$$

$$dG = -SdT + VdP + \sum_{k=1}^r \mu_k dn_k$$

$$\mu_i(T, P, X_{i,s}) \quad (\text{intensive})$$

$$d\mu_i = -\bar{S}_i dT + \bar{V}_i dP + \sum_{k=1}^{r-1} \left(\frac{\partial \mu_i}{\partial X_k} \right) dX_k$$

$$\mu_i = \bar{H}_i - T\bar{S}_i \quad (0.1)$$

where $\bar{S}_i = \left(\frac{\partial S}{\partial n_i} \right)_{T, P, n_j}$ i.e. partial molar entropy

$\bar{V}_i = \left(\frac{\partial V}{\partial n_i} \right)_{T, P, n_j}$ i.e. partial molar volume

$\bar{H}_i = \left(\frac{\partial H}{\partial n_i} \right)_{T, P, n_j}$ i.e. partial molar enthalpy

I. The partial molar volume of each component in solution is the same as its molar volume in pure liquid and thus the volume of the solution is the additive volume of the pure components:

from (0.1) $\left(\frac{\partial \mu_i}{\partial P} \right)_{T, n} = \bar{V}_i$ (1.1)

obtaining this derivative from:

$$\mu_i^\ell(T, P, X_{i,s}^\ell) = \mu_i^{\bullet\ell}(T, P) + RT \ln X_i^\ell \quad (1.2)$$

$$\left(\frac{\partial \mu_i^\ell}{\partial P} \right)_{T, n} = \left(\frac{\partial \mu_i^{\bullet\ell}}{\partial P} \right)_{T, n} + \left(\frac{\partial (RT \ln X_i^\ell)}{\partial P} \right)_{T, n}$$

the second term is 0, so

$$\left(\frac{\partial \mu_i^\ell}{\partial P} \right)_{T, n} = \left(\frac{\partial \mu_i^{\bullet\ell}}{\partial P} \right)_{T, n} = \bar{V}_i^{\bullet\ell} \quad \text{i.e. the molar volume of pure liquid } i \quad (1.3)$$

thus

$$\bar{V}_i = \bar{V}_i^{\bullet\ell} \quad (1.4)$$

i.e. the partial molar volume of i in solution is identical to the molar volume of pure liquid i

This relationship insures that the volume of the solution will be the sum of the volumes of the individual pure components that are mixed or

$$\Delta V_{mix} = V_{soln} - V_{pure\ components} = \sum_k n_k \bar{V}_k - \sum_k n_k \bar{V}_k^{\bullet\ell} = 0 \quad (1.5)$$

II. The enthalpy of mixing is zero

$$\mu_i = \bar{H}_i - T\bar{S}_i \quad (2.1)$$

one obtains

$$\left(\frac{\partial(\mu_i/T)}{\partial T} \right)_{P,n} = -\frac{\bar{H}_i}{T^2} \quad (\text{proof just like } \left(\frac{\partial(G/T)}{\partial T} \right)_P = -\frac{H}{T^2}) \quad (2.2)$$

with $\mu_i(T, P, X_{i,s}^\ell) = \mu_i^{\bullet\ell}(T, P) + RT \ln X_i^\ell$

$$\left(\frac{\partial(\mu_i^\ell/T)}{\partial T} \right)_{P,n} = \left(\frac{\partial(\mu_i^{\bullet\ell}/T)}{\partial T} \right)_{P,n} + R \left(\frac{\partial \ln X_i^\ell}{\partial T} \right)_{P,n} \quad (2.3)$$

the last term is zero so (again)

$$\left(\frac{\partial(\mu_i^\ell/T)}{\partial T} \right)_{P,n} = -\frac{\bar{H}_i^{\bullet\ell}}{T^2} = -\frac{\bar{H}_i^\ell}{T^2} \quad \text{thus } \bar{H}_i^{\bullet\ell} = \bar{H}_i^\ell \quad (2.4)$$

the partial molar enthalpy of i in solution is the same as the molar enthalpy of i in pure liquid!!!

$$\Delta H_{mix} = H_{soln} - H_{pure\ components} = \sum_k n_k \bar{H}_k^\ell - \sum_k n_k \bar{H}_k^{\bullet\ell} = 0 \quad (2.5)$$

III. The free energy of mixing

$$\Delta G_{mix} = G_{soln} - G_{pure\ components} = \sum_k n_k \mu_k - \sum_k n_k \mu_k^{\bullet\ell} \quad (3.1)$$

$$\text{with } \mu_k^\ell(T, P, X_{j,s}^\ell) = \mu_k^{\bullet\ell}(T, P) + RT \ln X_k^\ell \quad (3.2)$$

$$\Delta G_{mix} = \sum_k n_k (\mu_k^{\bullet\ell}(T, P) + RT \ln X_k^\ell) - \sum_k n_k \mu_k^{\bullet\ell} \quad (3.3)$$

$$\Delta G_{mix} = \sum_k n_k RT \ln X_k^\ell \quad (3.4)$$

IV. The entropy of mixing

$$\Delta S_{mix} = \frac{\Delta H_{mix} - \Delta G_{mix}}{T} = -\sum_k n_k R \ln X_k^\ell \quad (4.1)$$

look familiar !!

$$\Delta \bar{S}_{mix} = \frac{1}{n_{total}} \Delta S_{mix} = -\sum_k X_k^\ell R \ln X_k^\ell \quad (4.2)$$