Statistical Molecular Thermodynamics

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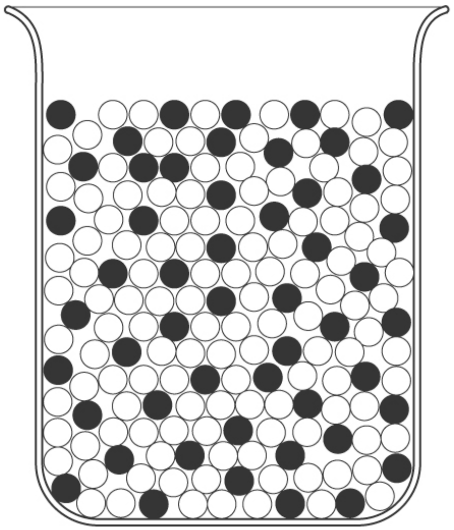
Video 10.4

Ideal Solutions I

Ideal Solutions



- Two (or more) types of molecules are randomly distributed
- Typically, molecules are similar in size and shape
- Intermolecular forces in pure liquids & mixture are similar
- Examples: benzene & toluene, hexane and heptane

In ideal solutions, the partial vapor pressure of component j is given by *Raoult's Law*:

$$P_j = x_j P_j^*$$

mole fraction of j in solution

vapor pressure of pure j

Total Vapor Pressure of Ideal Sol'n

$$\mu_j^{sol} = \mu_j^*(l) + RT\ln\frac{P_j}{P_j^*}$$

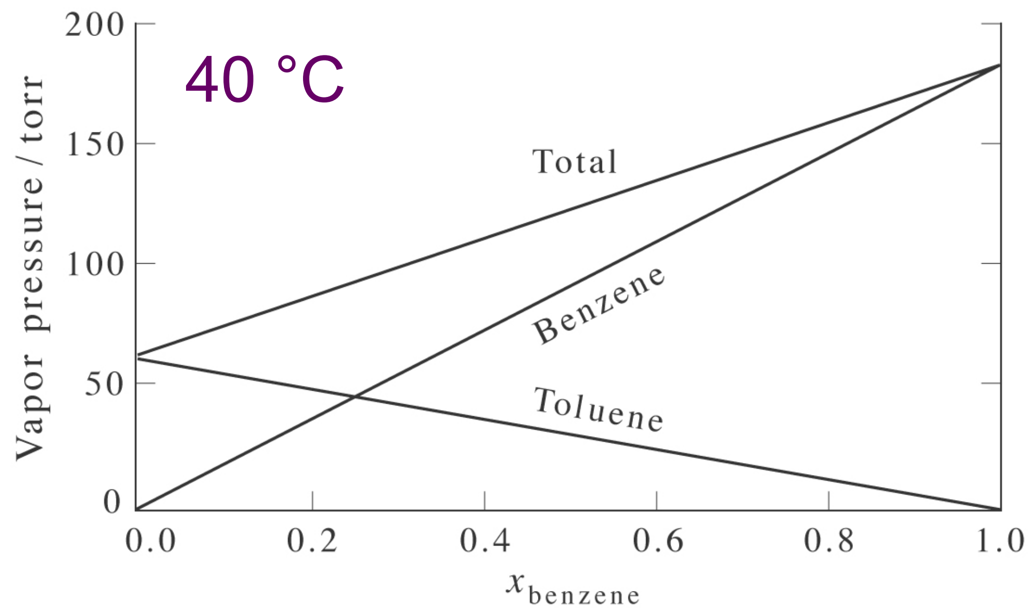
$$P_j = x_j P_j^*$$

$$\mu_j^{sol} = \mu_j^*(l) + RT\ln x_j$$

Thermodynamic <u>definition</u> of an ideal solution if true for all values of x_j

Total vapor pressure of ideal solution:

$$P_{total} = x_1 P_1^* + x_2 P_2^*$$
$$= (1 - x_2)P_1^* + x_2 P_2^*$$
$$= P_1^* + x_2\left(P_2^* - P_1^*\right)$$



Self-assessment

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$$

In an ideal solution, what are the maximum and minimum values of the chemical potential of component j?

Self-assessment Explained

$$\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$$

The maximum value occurs for $x_j = 1$, in which case the chemical potential is that of the pure liquid. The minimum potential goes to negative infinity (!) as the mole fraction goes to zero. In other words, there is an infinite driving force to eliminate the purity of everything...

ΔG of Forming An Ideal Solution

$$\Delta_{mix} G = G^{sol} - G_1^* - G_2^*$$

$$\Delta_{mix} G^{id} = n_1 \mu_1^{sol} + n_2 \mu_2^{sol} - n_1 \mu_1^* - n_2 \mu_2^*$$

Exploiting: $\mu_j^{sol} = \mu_j^*(l) + RT \ln x_j$ we may write

$$\boxed{\Delta_{mix} G = RT\left(n_1 \ln x_1 + n_2 \ln x_2\right)}$$

Since mole fraction is bounded by zero and one, mixing is *always* favorable for an ideal solution (as long as second component is present)

Other Quantities: Ideal Solutions

$$\boxed{\Delta_{mix} G = RT\left(n_1 \ln x_1 + n_2 \ln x_2\right)}$$

$$\Delta_{mix} S^{id} = -\left(\frac{\partial \Delta_{mix} G^{id}}{\partial T}\right)_{P,n_1,n_2} = -R\left(n_1 \ln x_1 + n_2 \ln x_2\right)$$

$$\Delta_{mix} V^{id} = \left(\frac{\partial \Delta_{mix} G^{id}}{\partial P}\right)_{T,n_1,n_2} = 0$$

$$\Delta_{mix} H^{id} = \Delta_{mix} G^{id} + T\Delta_{mix} S^{id} = 0$$

so, ideal solution mixing driven *totally* by entropy — zero heat of mixing, no variations in volume

Next: Ideal Solutions II