Raoult’s law standard state

Strictly speaking, we should use the words solute and solvent to describe a binary solution only when one component is sparingly soluble in the other. In this case that standard state may be based on Henry's law rather than Raoult's law. Assuming that component j is the sparingly soluble component we can write

$$\mu_1 = \mu_1^* + RT\ln(P_1/P_1^*)$$

We calso think of this as the standard state for an ideal solution.

Henry’s law standard state

For the solute j we use Henry's law $P_j \to x_j k_{H,j}$ as $x_j \to 0$ where $k_{H,j}$ is the Henry's law constant for component j. Thus we have.

$\mu_j = \mu_j^* + RT\ln(x_j k_{H,j}/P_j^*) = \mu_j^* + RT\ln(k_{H,j}/P_j^*) + RT\ln(x_j)$ $(x_j \to 0)$

We define the activity of component j by

$\mu_j = \mu_j^* + RT\ln(k_{H,j}/P_j^*) + RT\ln a_j$.

Just as above for the Raoult's law standard state $a_j \to x_j$ as $x_j \to 0$.

Thus, we define $a_j = P_j/k_{H,j}$. The standard state then implies that $k_{H,j} = P_j^*$. This is a formal definition since the Henry’s law constant may not be equal to the vapor pressure of the pure solvent.

Standard state for activity

The numerical value of the activity depends on the standard state. This is best demonstrated using an example. We consider a solution of CS_2 and $CH_3OCH_2OCH_3$. The Henry's law constants for this solution are $k_{H,CS2}$ = 1130 torr and $k_{H,dimeth}$ = 1500 torr. We are also given the information that P_{CS2}^* = 514.5 and P_{dimeth}^* = 587.7 torr.

Based on vapor pressure data we can calculate the activity and the activity coefficient based on each standard state (Raoult's Law and Henry's Law).

For x_{CS2} = 0.5393 we observe:

P_{CS2} = 357.2 and P_{dimeth} = 342.2 torr.

Calculate the activity for both Raoult’s and Henry’s law standard states.

Two definitions of standard state

Raoult's Law

$a_{CS2} = P_{CS2}/ P_{CS2}^{*} = 357.2/514.5 = 0.694$

$a_{dimeth} = P_{dimeth}/ P_{dimeth}^{*} = 342.2/587.7 = 0.582$

$\gamma_{CS2} = a_{CS2}/x_{CS2} = 0.694/0.539 = 1.287$

$\gamma_{dimeth} = a_{dumeth}/x_{dimeth} = 0.582/(1\text{-}0.539) = 1.262$

Henry's Law

$a_{CS2} = P_{CS2}/ k_{H,CS2} = 357.2/1130 = 0.316$

$a_{dimeth} = P_{dimeth}/ k_{H,dimeth} = 342.2/1500 = 0.228$

$\gamma_{CS2} = a_{CS2}/x_{CS2} = 0.316/0.539 = 0.586$

$\gamma_{dimeth} = a_{dumeth}/x_{dimeth} = 0.228/(1\text{-}0.539) = 0.494$