Ch. 24 : liquid-liquid solutions

For a binary solution we write \( \text{d}G = -SdT + VdP + \mu_1dn_1 + \mu_2dn_2 \)

where \( \frac{\partial G}{\partial T}_{P,n_1,n_2} = -S(P,T,n_1,n_2) \)

\( \frac{\partial G}{\partial P}_{T,n_1,n_2} = V(P,T,n_1,n_2) \)

Intensive/extensive relationships:

\( V(T,P,n_1,n_2) = \overline{V}_1n_1 + \overline{V}_2n_2 \)

\( S(T,P,n_1,n_2) = \overline{S}_1n_1 + \overline{S}_2n_2 \)

\( G(T,P,n_1,n_2) = \overline{G}_1n_1 + \overline{G}_2n_2 \)

"Partial molar" quantities:

\( \overline{V}_1 = \frac{\partial \overline{V}}{\partial n_1}_{T,P,n_2} \quad ; \quad \overline{S}_1 = \frac{\partial \overline{S}}{\partial n_1}_{T,P,n_2} \)

\( \overline{G}_1 = \frac{\partial \overline{G}}{\partial n_1}_{T,P,n_2} = \mu_1 \quad \text{(we give this one a new symbol)} \)

Physical interpretation of partial molar volumes:

When 1-propanol and water are mixed, the final volume of the solution is not equal to the sum of the volumes of pure 1-propanol and water. This reflects the intermolecular interactions and the structure of the solution.

Fig 24.1
From $dG = -SdT + VdP + \mu_1dn_1 + \mu_2dn_2$
we have at constant $T, P : dG = \mu_1dn_1 + \mu_2dn_2$

But from $G = G_1n_1 + G_2n_2 = \mu_1n_1 + \mu_2n_2$
we have $dG = \mu_1dn_1 + n_1d\mu_1 + \mu_2dn_2 + n_2d\mu_2$

$\Rightarrow n_1d\mu_1 + n_2d\mu_2 = 0$ \[\text{Gibbs-Duhem equation}\]
$\Rightarrow \chi_1d\mu_1 + \chi_2d\mu_2 = 0$

with $\chi_i = \frac{n_i}{n_1+n_2}$

These equations relate the chemical potential of one component to the other.

We can derive a Gibbs-Duhem volume relation:
from $V = V(T, P, n_1, n_2)$ we have, at constant $T, P,$ :
\[dV = V_1dn_1 + V_2dn_2\]

But from $V = V_1n_1 + V_2n_2$ we have
\[dV = V_1dn_1 + n_1dV_1 + V_2dn_2 + n_2dV_2\]

$\Rightarrow n_1dV_1 + n_2dV_2 = 0$

This equation relates the change in partial molar volume of one component to the other.
Consider two liquids in equilibrium with their vapors. We have \( G = G^\text{sol} + G^\text{vap} \). Let \( n_{j}^{\text{sol}}, n_{j}^{\text{vap}}, n_{2}^{\text{sol}}, n_{2}^{\text{vap}} \) be the mole numbers of each component in each phase.

Example: 1-propanol and water; benzene and toluene

Suppose \( d\bar{n}_{j} \) moles of component \( j \) are transferred from the solution to the vapor at constant T, P.

Then \( dG = dG^\text{sol} + dG^\text{vap} \)

\[
\begin{align*}
\frac{dG}{dn_{j}^{\text{sol}}} \cdot dn_{j}^{\text{sol}} + \frac{dG}{dn_{j}^{\text{vap}}} \cdot dn_{j}^{\text{vap}} &= \mu_{j}^{\text{vap}} \cdot dn_{j}^{\text{vap}} - \mu_{j}^{\text{sol}} \cdot dn_{j}^{\text{sol}} \\
\end{align*}
\]

Since \( dn_{j}^{\text{vap}} = dn_{j} \) and \( dn_{j}^{\text{sol}} = -dn_{j} \)

If the transfer is spontaneous, \( dG < 0 \Rightarrow \mu_{j}^{\text{vap}} < \mu_{j}^{\text{sol}} \).

Thus, molecules of component \( j \) move spontaneously from the phase of higher chemical potential to the phase of lower chemical potential.

At equilibrium, \( dG = 0 \Rightarrow \mu_{j}^{\text{vap}} = \mu_{j}^{\text{sol}} \).

If we take the vapor to be an ideal gas then

\( \mu_{j}^{\text{sol}} = \mu_{j}^{\text{vap}} = \mu_{j}^{\circ}(T) + RT \ln P_{j} \)

At standard conditions, \( P_{j}^{\circ} = 1 \text{ bar} \)

For pure component \( j \), we write \( \mu_{j}^{\ast}(T) = \mu_{j}^{\ast}(\text{vap}) = \mu_{j}^{\circ}(T) + RT \ln P_{j}^{\ast} \).

Where \( \ast = \text{pure} \). Combine: \( \mu_{j}^{\text{sol}} = \mu_{j}^{\ast}(T) + RT \ln \frac{P_{j}}{P_{j}^{\ast}} \).
Sometimes \( P_j = x_j P_j^* \) \( x_j \) = mole fraction

This is Raoult's Law.

\[ \Rightarrow \mu_j^* = \mu_j^*(0) + RT \ln x_j \]

A solution with this property is called an ideal solution.

In practice this requires components of similar size, shape, and intermolecular interactions.

Fig 24. 2: number of molecules at the surface is \( x_j \)
(fraction of \( j \) molecules at surface)

The total vapor pressure over an ideal solution is

\[ P_{TOT} = p_1 + p_2 = x_1 P_1^* + x_2 P_2^* = (1 - x_2) P_1^* + x_2 P_2^* \]
\[ = P_1^* + x_2 (P_2^* - P_1^*) \]

Thus \( P_{TOT} \) vs \( x_2 \) yields a straight line plot, Fig 24. 3

The vapor is enriched by the more volatile component.

Say \( x_1 = x_2 = 0.5 \) and \( P_1^* = 50 \) torr; \( P_2^* = 100 \) torr.

Then \( P_1 = 25 \) torr, \( P_2 = 50 \) torr \( \Rightarrow P_{TOT} = 75 \) torr.

Let \( y_1, y_2 \) be the mole fraction in the vapor phase

\[ y_1 = \frac{P_1}{P_{TOT}} = \frac{25}{75} = \frac{1}{3} \quad ; \quad y_2 = \frac{P_2}{P_{TOT}} = \frac{50}{75} = \frac{2}{3} \]
This lets us draw a pressure-composition diagram as shown in Fig 24.4.

The liquid-vapor coexistence region is in the middle. Consider point "C" in Fig 24.4. It lies on a horizontal line called a tie line connecting the composition of the liquid, \( x_2 \), with the vapor composition \( y_2 \).

At point C the overall (liquid-vapor) composition is \( x_\alpha \). What are the relative amounts of liquid and vapor?

\[
\begin{align*}
    x_2 &= \frac{n_2}{n_{sd}} \quad \text{and} \quad y_2 = \frac{n_{vap}}{n_{vap}} \quad \text{and} \quad x_\alpha = \frac{n_2}{n_{sd}} + \frac{n_{vap}}{n_{vap}} \\
    \Rightarrow x_\alpha (n_{sd} + n_{vap}) &= x_2 n_{sd} + y_2 n_{vap} \\
    \Rightarrow \frac{n_{sd}}{n_{vap}} &= \frac{y_2 - x_\alpha}{x_\alpha - x_2}
\end{align*}
\]

\( n_{vap} (y_2 - x_\alpha) = n_{sd} (x_\alpha - x_2) \) called the lever rule.

Can also construct a temperature-composition diagram as shown in Fig 24.5 which lets us understand fractional distillation.

\( A: \text{liquid composition} = x_\alpha, \text{no vapor} \)
\( B: \text{liquid} = x_\alpha, \text{vapor comp} = y_\alpha \)
\( C: \text{liquid} = x_2, \text{vapor} = y_2 \)
\( D: \text{liquid} = x_\alpha, \text{vapor} = x_\alpha \)
\( E: \text{no liquid} \)

\( n_{vap} \text{ and } n_{vap} = n_{sd} \text{ and } n_{vap} \) is the lever rule.

Proportion of \( sd \) and \( vap \) is:

\[
\frac{n_{vap}}{n_{sd} + n_{vap}} \quad \text{and} \quad \frac{n_{sd}}{n_{sd} + n_{vap}}
\]
Consider the change in thermodynamic properties upon forming an ideal solution from its pure components:

\[ \Delta G_{\text{mix}}^{\text{ideal}} = n_1 \mu_1^{\text{sd}} + n_2 \mu_2^{\text{sd}} - n_1 \mu_1^{*} - n_2 \mu_2^{*} \]
\[ = RT \left( n_1 \ln x_1 + n_2 \ln x_2 \right) \quad \text{using} \quad \mu_j^{\text{sd}} = \mu_j^{*}(0) + RT \ln x_j \]
\[ < 0 \quad \text{since} \quad x_1, x_2 < 1. \]

So always favorable to form an ideal solution:

\[ \Delta S_{\text{mix}}^{\text{ideal}} = -T \left( \frac{\Delta G_{\text{mix}}^{\text{ideal}}}{\partial T} \right)_{P, n_1, n_2} = -RT \left( n_1 \ln x_1 + n_2 \ln x_2 \right) \]

Same as for mixing ideal gases together!

\[ \Delta V_{\text{mix}}^{\text{ideal}} = \frac{\partial \Delta G_{\text{mix}}^{\text{ideal}}}{\partial P} \Bigg|_{T, n_1, n_2} = 0 \]

\[ \Delta H_{\text{mix}}^{\text{ideal}} = \Delta G_{\text{mix}}^{\text{ideal}} + T \Delta S_{\text{mix}}^{\text{ideal}} = 0 \]

Molecules are similar in size and intermolecular interactions.

Most solutions are non-ideal.

De can have positive or negative deviations from Raoult's Law; see Figs. 24.7 and 24.8.
As $X_1 \to 1$, component 1 molecules are completely surrounded by other component 1 molecules so that we expect to find the pure liquid 1 behavior, expressed as $P_i \to X_1 P'_1^* \text{ as } X_1 \to 1$.

This is Raoult's Law behavior (in a non-ideal solution in the limit $X_1 \to 1$).

As $X_1 \to 0$, component -1 molecules are completely surrounded by component -2 molecules, and the intermolecular interaction between the two components is what matters.

We capture this with the Henry's Law constant $K_{H,1}$, expressed as $P_i \to K_{H,1} X_1 \text{ as } X_1 \to 0$.

$K_{H,1} = P'_1^*$ for an ideal solution but usually $K_{H,1} \neq P'_1^*$.

The Henry's Law and Raoult's Law behaviors are coupled, because when $X_1 \to 1$, $X_2 \to 0$.

This can be rigorously shown using the Gibbs-Duhem equation (pg. 981).
Activities for Raoult's Law and Henry's Law:

Raoult's Law behavior is
\[ \mu^d_A = \mu^* A + RT \ln \frac{P_A}{P^*_A} = \mu^* A + RT \ln x_A \]

Deviations: let \( \alpha_A = \frac{P_A}{P^*_A} \) but don't assume \( \alpha_A = x_A \) except when \( x_A \to 1 \).

We simply measure \( P_A \) and \( P^*_A \), then \( \alpha_A = f(x_A) = \frac{P_A}{P^*_A} \).

Write \( \alpha_A = \gamma_A x_A \) \( \rightarrow \) Raoult's Law standard state

\[ \rightarrow \text{activity coefficient} \quad \text{See Fig 24.17} \]

Henry's Law behavior is \( P_B = x_B k_B \) as \( k x_B \to 0 \).

Thus, \[ \mu^d_B = \mu^*_B + RT \ln \frac{x_B k_B}{P^*_B} \]

\[ = \mu^*_B + RT \ln \frac{k_B}{P^*_B} + RT \ln x_B \]

Call this \( \mu^\pm_B \)

\[ = \mu^\pm_B + RT \ln \alpha_B \quad \text{for deviations} \]

Then define the activity coefficient by \( \alpha_B = \gamma_B x_B \)

\( \rightarrow \) Henry's Law standard state.