Ch. 24 : liquid-liquid solutions

For a binary solution we write $dG = -SdT + VdP + \mu_1 dn_1 + \mu_2 dn_2$

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

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

Intensive / extensive relationships :

$$V(T,P,n_1,n_2) = \bar{V}_1 n_1 + \bar{V}_2 n_2$$
$$S(T,P,n_1,n_2) = \bar{S}_1 n_1 + \bar{S}_2 n_2$$
$$G(T,P,n_1,n_2) = \bar{G}_1 n_1 + \bar{G}_2 n_2$$

"partial molar" quantities

$$\bar{V}_1 = \left.\frac{\partial V}{\partial n_1}\right)_{T,P,n_2} \quad ; \quad \bar{S}_1 = \left.\frac{\partial S}{\partial n_1}\right)_{T,P,n_2}$$

$$\bar{G}_1 = \left.\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} \equiv \mu_1$$

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 <u>not</u> equal to the sum of the volumes of <u>pure</u> 1-propanol and water.

This reflects the intermolecular interactions and the structure of the solution.

Fig 24.1

From $dG = -S\,dT + V\,dP + \mu_1\,dn_1 + \mu_2\,dn_2$

we have at constant T, P : $dG = \mu_1\,dn_1 + \mu_2\,dn_2$

But from $G = \bar{G}_1 n_1 + \bar{G}_2 n_2 = \mu_1 n_1 + \mu_2 n_2$

we have $dG = \mu_1\,dn_1 + n_1\,d\mu_1 + \mu_2\,dn_2 + n_2\,d\mu_2$

$$\left.\begin{aligned} &\Rightarrow n_1\,d\mu_1 + n_2\,d\mu_2 = 0 \\ &\Rightarrow x_1\,d\mu_1 + x_2\,d\mu_2 = 0 \end{aligned}\right\} \text{Gibbs-Duhem equation}$$

with $x_1 = \dfrac{n_1}{n_1 + n_2}$

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, :

$$dV = \bar{V}_1\,dn_1 + \bar{V}_2\,dn_2$$

But from $V = \bar{V}_1 n_1 + \bar{V}_2 n_2$ we have

$$dV = \bar{V}_1\,dn_1 + n_1\,d\bar{V}_1 + \bar{V}_2\,dn_2 + n_2\,d\bar{V}_2$$

$$\Rightarrow n_1\,d\bar{V}_1 + n_2\,d\bar{V}_2 = 0$$

This equation relates the change in partial molar volume of one component to the other.

Consider two liquids in equil. with their vapors.

We have $G = G^{sol} + G^{vap}$. Let $n_1^{sol}, n_2^{sol}, n_1^{vap}, n_2^{vap}$ be the mole number of each component in each phase.

ex: 1-propanol and water ; benzene and toluene

Suppose dn_j moles of component j are transferred from the solution to the vapor at constant T, P.

Then $dG = dG^{sol} + dG^{vap}$

$$= \left.\frac{\partial G^{sol}}{\partial n_j^{sol}}\right)_{T,P,n_{i\neq j}} dn_j^{sol} + \left.\frac{\partial G^{vap}}{\partial n_j^{vap}}\right)_{T,P,n_{i\neq j}} dn_j^{vap}$$

$$= \mu_j^{sol} dn_j^{sol} + \mu_j^{vap} dn_j^{vap} = (\mu_j^{vap} - \mu_j^{sol})\, dn_j^{vap}$$

Since $dn_j^{vap} = dn_j$ and $dn_j^{sol} = -dn_j$

If the transfer is spontaneous, $dG < 0 \Rightarrow \mu_j^{vap} < \mu_j^{sol}$.

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

At equil., $dG = 0 \Longrightarrow \mu_j^{vap} = \mu_j^{sol}$

If we take the vapor to be an ideal gas then

$$\Longrightarrow \mu_j^{sol} = \mu_j^{vap} = \mu_j^{\circ}(T) + RT \ln P_j \qquad {}^{\circ} = 1 \text{ bar}$$

For pure component j we write $\mu_j^*(l) = \mu_j^*(vap) = \mu_j^{\circ}(T) + RT \ln P_j^*$

where $* =$ pure. Combine: $\mu_j^{sol} = \mu_j^*(l) + RT \ln P_j / P_j^*$

Sometimes $P_j = x_j P_j^*$ $\quad x_j$ = mole fraction

This is Raoult's Law.

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

A solution with this property is called an <u>ideal solution</u>.

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} <u>vs</u> 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_a. What are the relative amounts of liquid and vapor?

$$x_2 = \frac{n_2^{sol}}{n^{sol}} \; ; \; y_2 = \frac{n_2^{vap}}{n^{vap}} \; ; \; x_a = \frac{n_2^{sol} + n_2^{vap}}{n^{sol} + n^{vap}}$$

$$\Rightarrow x_a(n^{sol} + n^{vap}) = x_2 n^{sol} + y_2 n^{vap}$$

$$\Rightarrow \frac{n^{sol}}{n^{vap}} = \frac{y_2 - x_a}{x_a - x_2} \quad \text{or} \quad n^{vap}\overbrace{(y_2 - x_a)}^{L^{vap}} = n^{sol}\overbrace{(x_a - x_2)}^{L^{sol}}$$

called the lever rule

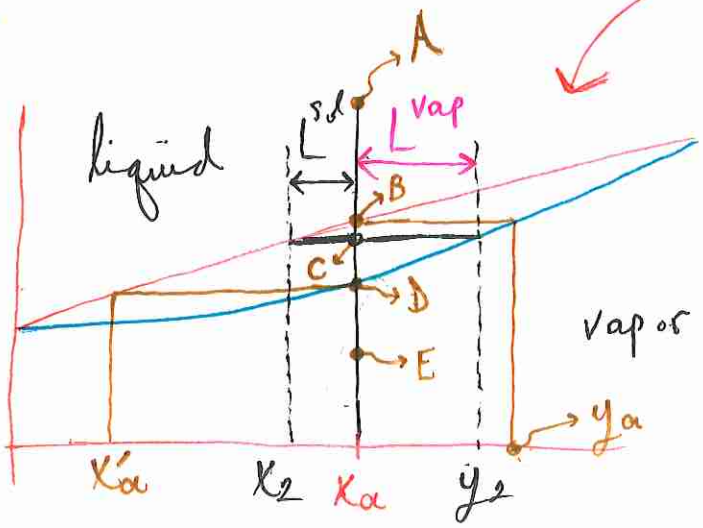
Can also construct a temperature-composition diagram as shown in Fig 24.5 which lets us understand fractional distillation.

A: liquid composition $= x_a$, no vapor
B: liquid $= x_a$, vapor comp $= y_a$
C: liquid $= x_2$, vapor $= y_2$
D: liquid $= x_a'$, vapor $= x_a$
E: no liquid, vapor $= x_a$.

$n^{vap} L^{vap} = n^{sol} L^{sol}$ is the lever rule:

proportion of sol and vap is:

$$\frac{L^{vap}}{L^{sol} + L^{vap}} \text{ and } \frac{L^{sol}}{L^{sol} + L^{vap}}$$



Consider the change in thermodynamic properties upon forming an ideal solution from its pure components:

$$\Delta G_{mix}^{ideal} = n_1\mu_1^{sol} + n_2\mu_2^{sol} - n_1\mu_1^* - n_2\mu_2^*$$

$$= RT\left(n_1 \ln x_1 + n_2 \ln x_2\right) \quad \text{using } \mu_j^{sol} = \mu_j^*(l) + RT\ln x_j$$

$$< 0 \text{ since } x_1, x_2 < 1.$$

So always favorable to form an ideal solution.

$$\Delta S_{mix}^{ideal} = -\left.\frac{\partial \Delta G_{mix}^{ideal}}{\partial T}\right)_{P, n_1, n_2} = -R\left(n_1 \ln x_1 + n_2 \ln x_2\right)$$

same as for mixing ideal gases together!

$$\Delta V_{mix}^{ideal} = \left.\frac{\partial \Delta G_{mix}^{ideal}}{\partial P}\right)_{T, n_1, n_2} = 0$$

$$\Delta H_{mix}^{ideal} = \Delta G_{mix}^{ideal} + T\Delta S_{mix}^{ideal} = 0$$

molecules are similar in size and intermolecular interactions.

Most solutions are non-ideal.

We 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 $P_1 \longrightarrow x_1 P_1^*$ 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 $P_1 \longrightarrow k_{H,1} x_1$ 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

$$\mu_A^{sd} = \mu_A^*(l) + RT \ln P_A/p_A^* = \mu_A^*(l) + RT \ln x_A$$

Deviations: let $a_A = P_A/p_A^*$ but don't assume

$a_A = x_A$ except when $x_A \to 1$.

We simply measure P_A and P_A^*, then $a_A = f(x_A) = P_A/p_A^*$.

Write $a_A = \gamma_A x_A \longrightarrow$ Raoult's Law standard state

$\hookrightarrow$ activity coefficient See Fig 24.17

Henry's Law behavior is $P_B = x_B k_B$ as $x_B \to 0$.

Thus $\mu_B^{sd} = \mu_B^* + RT \ln \dfrac{x_B k_B}{p_B^*}$

$$= \underbrace{\mu_B^* + RT \ln k_B/p_B^*}_{\text{call this } \mu_B^{\neq}} + RT \ln x_B$$

$= \mu_B^{\neq} + RT \ln a_B$ for deviations

Then define the activity coefficient by $a_B = \gamma_B x_B$

$\longrightarrow$ Henry's Law standard state.