P. Chem | Class Ch 24 3/24/23 Friday

- consider 2 liquids in equillibrium with their vapors, that are miscible in all proportions. assume both components are volatile

ex: 1-propanol and water ; benzene and toluene

missing surface tension, ignoring now

- write $G = G^{sol} + G^{vap}$ and let $n_1^{sol}, n_2^{sol}, n_1^{vap}, n_2^{vap}$ be the number of moles of each component of each phase

- move dn_2 moles from Sol → vap

$$dG = \frac{\partial G_{sol}}{\partial n_2^{sol}} dn_2^{sol} + \frac{\partial G^{vap}}{\partial n_2^{vap}} dn_2^{vap}$$

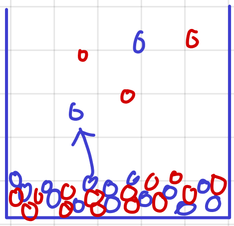
shorthand notation is μ

so,

$$= \mu_2^{sol} dn_2^{sol} + \mu_2^{sol} + \mu_2^{vap} dn_2^{vap}$$

$$= (-\mu_2^{sol} + \mu_2^{vap}) dn_2^{vap}$$

$$= (\mu_2^{vap} - \mu_2^{sol}) dn_2^{vap}$$



$dn_2 = 0$ not losing molecules

$n_2 = n_2^{vap} + n_2^{sol}$

$0 = dn_2^{vap} + dn_2^{sol}$

so this is spontaneous

$\Rightarrow dG < 0$

$\Rightarrow \mu_2^{sol} > \mu_2^{vap}$

molecules move to lower chemical potential

Equillibrium means: $dG = 0$

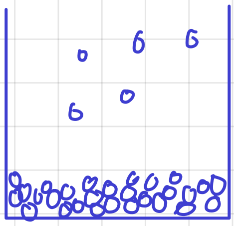
$\Rightarrow \mu_2^{sol} = \mu_2^{vap}$

*like a ball rolling downhill to change gravitational potential

Fix T

↓ ideal gas

$$\mu_j^{vap} = \mu_j^{\circ}(T) + RT \ln P_j$$



For pure component j, $\mu_j(\ell) = \mu_j^*(vap)$

$$= \mu_j^{\circ} + RT \ln P_j^*$$

$$\mu_j^{vap} = \mu_j^{\circ}(T) + RT \ln P_j^* - RT \ln P_j^* + RT \ln P_j$$

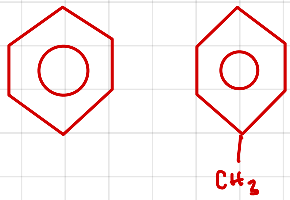
$$= \mu_j^*(\ell) + RT \ln P_j / P_j^*$$

sometimes $P_j = x_j P_j^*$ → ideal solution

In this case, $\mu_j^{vap} = \mu_j^*(\ell) + RT \ln x_j$ → Raoult's Law

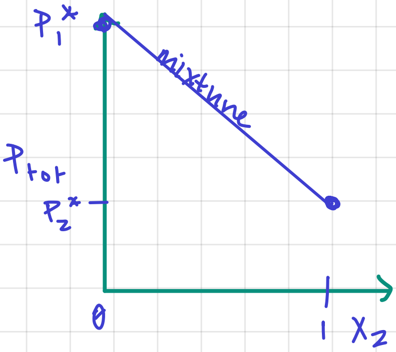
Raoult's : $P_{tot} = P_1 + P_2 = x_1 P_1^* + x_2 P_2^*$

benzene/toluene



$x_1 + x_2 = 1$ $P_{tot} = (1-x_2)P_1^* + x_2 P_2^*$

$= P_1^* + x_2(P_2^* - P_1^*)$



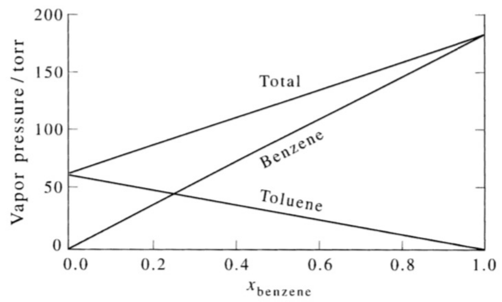


FIGURE 24.3
A plot of P_{total} against $x_{benzene}$ for a solution of benzene and toluene at 40°C. This plot shows that a benzene/toluene solution is essentially ideal.

$P_1^* = 100$ torr $P_2^* = 50$ torr

$x_1 = x_2 = 0.5 = 1/2$

$P_1 = x_1 P_1^* = \frac{1}{2} \cdot 100 = 50$ torr
$P_2 = x_2 P_2^* = \frac{1}{2} \cdot 50 = 25$ torr
} $P_{tot} = 75$ torr

Let y denote vapor composition

$y_1 = \frac{50}{75} = \frac{2}{3}$ $y_2 = \frac{25}{75} = \frac{1}{3}$

*Theory behind distilation