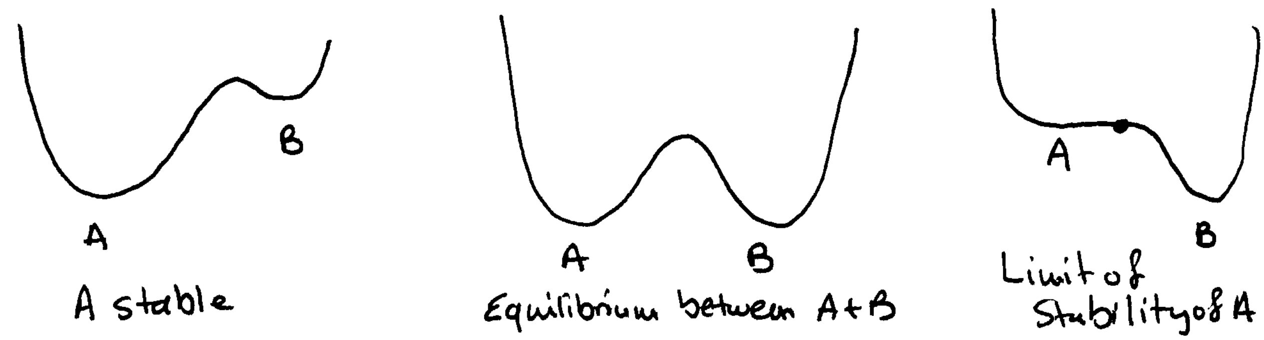
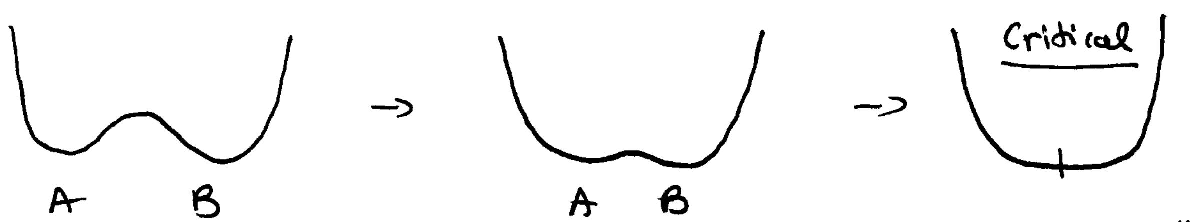
Critical Points

What happens if $y^{(n)}_{n+1,n+1} = \phi$ for our n-component system? Normally, this is an unstable point (limit of stability):



There is, however, another possibility: If A and B start approaching each other, one gets a "critical" state



e.g. $f(x) = x^4$

At the critical state, one has

$$\frac{df}{dx} = \phi \qquad \frac{d^2f}{dx^2} = 0 \qquad \frac{d^3f}{dx^3} = 0 \qquad \frac{d^4f}{dx^4} > \phi$$

Generalization for many-variable functions leads to the critical state condition:

$$y^{(n)}_{n+1,n+1} = 0 \quad \underline{\text{and}} \quad y^{(n)}_{n+1,n+1,n+1} = \phi$$

E.g. for $n=1$, $y^{(1)}_{22} = 0 \Rightarrow \left(\frac{\partial P}{\partial V}\right)_T = 0$ $\quad y^{(1)}_{222} = 0 \Rightarrow \left(\frac{\partial^2 P}{\partial V^2}\right)_T = \phi$

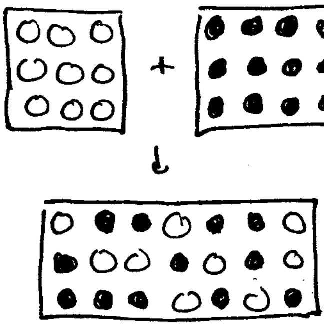
Ideal Solutions

- no preferential interactions
- similar-size components

  -or-

- very dilute solutions

N_A N_B



$N_A + N_B$

$$\Omega_{mix}(N_A, N_B) = \frac{(N_A+N_B)!}{N_A!\, N_B!} \quad \left[\begin{array}{c}\text{Note}\\ N_A+N_B=N\end{array}\right]$$

$$\Delta S_{mix} = k_B \ln \Omega_{mix} =$$

$$= k_B \left[(N_A+N_B)\ln(N_A+N_B) - N_A \ln N_A - N_B \ln N_B \right] \quad [1]$$

$$= -k_B \left[N_A \ln \frac{N_A}{N_A+N_B} + N_B \ln \frac{N_B}{N_A+N_B} \right] = -N k_B \left[x_A \ln x_A + x_B \ln x_B \right] \quad [2]$$

Generalizing for multicomponent: $\Delta S_{mix} = -N k_B \sum_i^c x_i \ln x_i$

Gibbs free energy: $G(T,P,N_1,\ldots N_c) = \sum_i^c N_i \mu_i(T,P,\text{pure}\, i) - T\Delta S_{mix}$

Chemical potential (for binary, $c=2$) $\mu_A = \left.\frac{\partial G}{\partial N_A}\right)_{T,P,N_B} \overset{=}{\text{(from [1])}}$

$$\mu_i\left(T,P,\text{pure}\, i\right) - k_B T \frac{\partial}{\partial N_A}\left[(N_A+N_B)\ln(N_A+N_B) - N_A \ln N_A - N_B \ln N_B \right] =$$

$$\mu_i\left(T,P,\text{pure}\, i\right) - k_B T \left[\ln(N_A+N_B) + 1 - 1 - \ln N_A \right] = \mu_i(T,P,\text{pure}) + k_B T \ln x_i$$

For dilute solutions a similar expression is obtained:

$$\mu_i(T,P,\{N_i\}) = \mu_i^*(T,P) + k_B T \ln x_i$$

But here μ_i^* is the limit of $\left[\mu_i(T,P,\{N_i\}) - k_B T \ln x_i\right]$ as $x_i \rightarrow 0$

Activities

$$k_B T \ln \gamma_i x_i = -\mu_i(T,P,\text{pure}\, i\}+ \mu_i(T,P,\{N_i\})$$

$$k_B T \ln \gamma_i^* x_i = -\mu_i^*(T,P) + \mu_i(T,P,\{x_i\})$$

Ideal VLE

$$\mu_i^G = \mu_i^L \Rightarrow \mu_i^{(0)}(T) + k_BT\ln P_i = \mu_i(T,P,\text{pure}) + k_BT\ln x_i$$

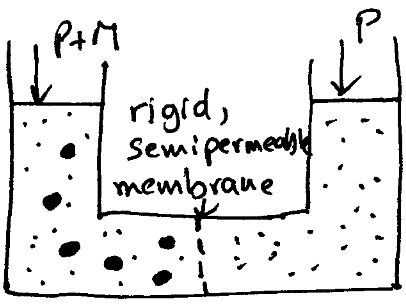
at the limit of pure i, $\mu_i^{(0)}(T) + k_BT\ln P_i^{vap} = \mu_i(T,P_i^{vap},\text{pure})$

$$\therefore\ k_BT\ln\frac{y_iP}{P_i^{vap}} = k_BT\ln x_i$$

[ignore difference between $\mu_i(T,P_i^{vap},\text{pure})$ and $\mu_i(T,P,\text{pure})$]

$$\Rightarrow \boxed{y_iP = x_iP_i^{vap}}$$

Osmotic Pressure



- solute-cannot cross membrane
- solvent, mole fraction x on left

$$\mu(T,P+\Pi,x) = \mu(T,P,\text{pure}) \quad ①$$

Assume ideal solutions,

$$\mu(T,P+\Pi,x) = \mu(T,P+\Pi,\text{pure}) + k_BT\ln x \quad ②$$

$$\left.\frac{\partial\mu}{\partial P}\right)_T = v \Rightarrow \mu(T,P+\Pi,\text{pure}) = \mu(T,P,\text{pure}) + v\Pi \quad ③$$

$$①,②,③ \Rightarrow \cancel{\mu(T,P,\text{pure})} + v\Pi + k_BT\ln x = \cancel{\mu(T,P,\text{pure})}$$

$$\Rightarrow \Pi = -\frac{k_BT}{v}\ln x = -\frac{k_BT}{v}\ln(1-x_\bullet) \underset{x_\bullet \ll 1}{\simeq} \frac{k_BTx_\bullet}{v}$$

$$x_\bullet = \frac{N_\bullet}{N};\ Nv = V \Rightarrow \Pi = \frac{k_BTN_\bullet}{V}$$

(very similar to ideal-gas equation)

E.g. Seawater 3.5 w/w NaCl $\quad X_{NaCl} = \dfrac{3.5\,g/58.4\frac{g}{mol}}{3.5/58.4 + 96.5/18.02}$

$\Rightarrow X_{NaCl} = 0.011 \quad X_{H_2O} = 1 - 2\cdot X_{NaCl} \quad \Pi = \dfrac{-RT}{v}\ln x_{H_2O} = 32$ bar