

Gibbs phase rule for multi-components

(1)

ex 2 component

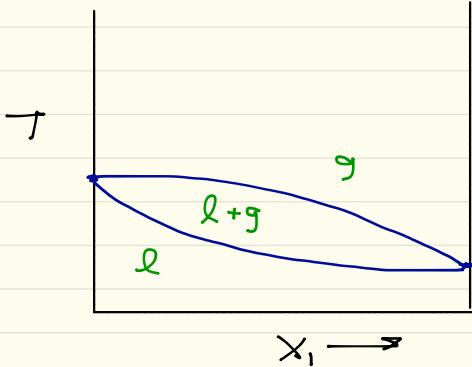
1 phase	3 dof	
2 phase	2 dof	plane
3 phase	1 dof	line
4 phase	0 dof	pt

Recall each equilibrated rxn provides another constraint on chemical potentials w/i each phase, so in total

$$dof = c - \pi - r + 2$$

Defines topology of phase diagrams.

2 components, 2 phases

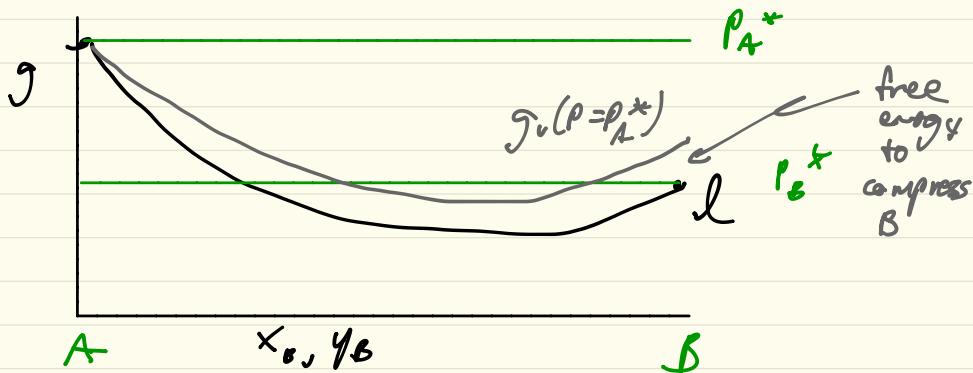


Requires us to say something about the thermo of mixtures

$$\begin{aligned} x, T &\rightarrow \rho \quad \text{or} \\ x, \rho &\rightarrow T \end{aligned}$$

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Ideal liquid + vapor ... Fix T, vary P



$$g_L = x_B \mu_B^* + (1-x_B) \mu_A^* + kT \sum x_i \ln x_i$$

$$g_v = y_B \mu_B(p) + (1-y_B) \mu_A(p) + kT \sum y_i \ln y_i$$

$$= y_B (\mu_B^* + kT \ln \frac{p}{p_B^*}) + (1-y_B) (\mu_A^* + kT \ln \frac{p}{p_A^*}) + kT \sum y_i \ln y_i$$

$$\mu_A^* > \mu_B^* \rightarrow p_A^* > p_B^*$$

$$p > p_A^* \quad g_v > g_L$$

$$p = p_A^*$$

$$y_B (\mu_B^* + kT \ln \frac{p}{p_B^*}) + (1-y_B) (\mu_A^* + kT \ln \frac{p}{p_A^*}) + kT \sum y_i \ln y_i$$

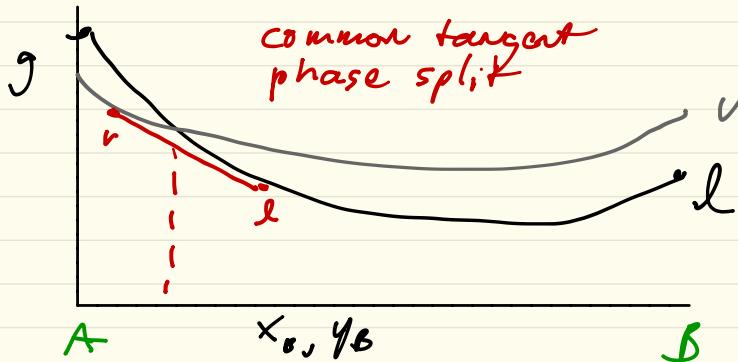
$$g_v \geq g_L$$

(3)

$$P_A^+ > P > P_B^+$$

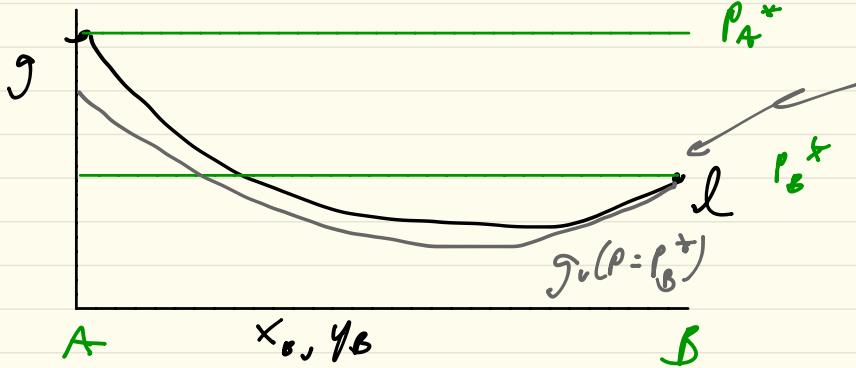
$$g_v = y_B \left(\mu_B^* + kT \ln \frac{P}{P_B^*} \right) + (1-y_B) \left(\mu_A^* + kT \ln \frac{P}{P_A^*} \right) \approx kT \bar{\varepsilon}_B y_B$$

> 1 < 1



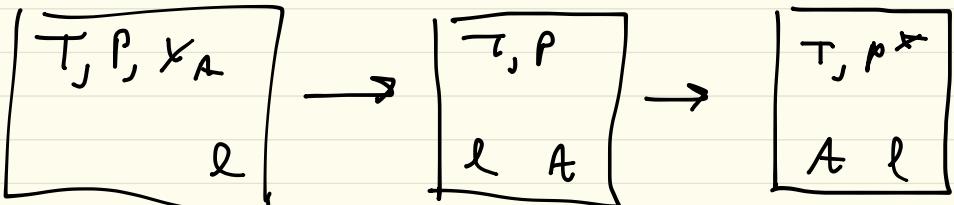
vapor enriched in A
liquid " " B

$$P = P_B^+$$



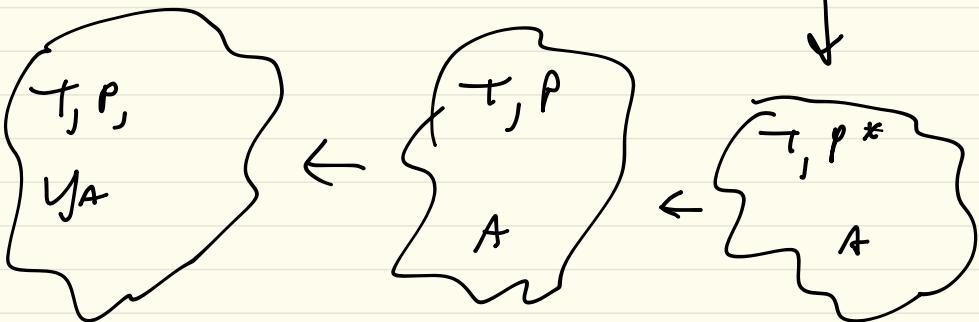
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Ideal liquid + vapor . . .



$$\Delta \mu = -kT \ln x_A \quad \Delta \mu \approx 0$$

$\downarrow \Delta \mu = 0 \qquad \qquad \downarrow \Delta \mu = 0$



$$\Delta \mu = kT \ln y_A \quad \Delta \mu = kT \ln \frac{P}{P^*}$$

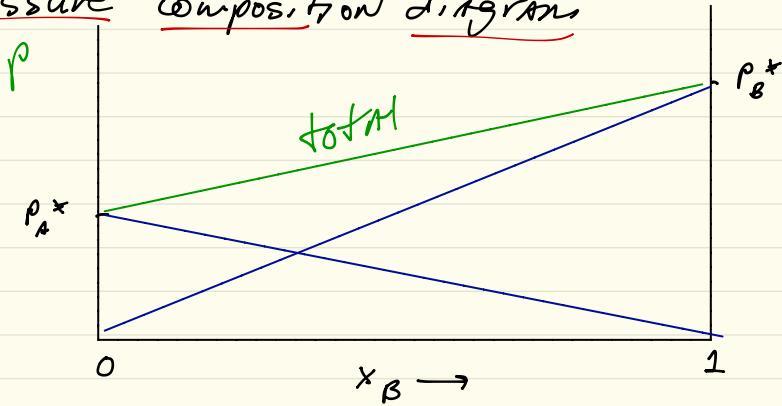
$$kT(-\ln x_A + \ln \frac{P}{P^*} + \ln y_A) = 0$$

$$P y_A = x_A P_A^*$$

$$P y_B = x_B P_B^*$$

@ given T

Ideal

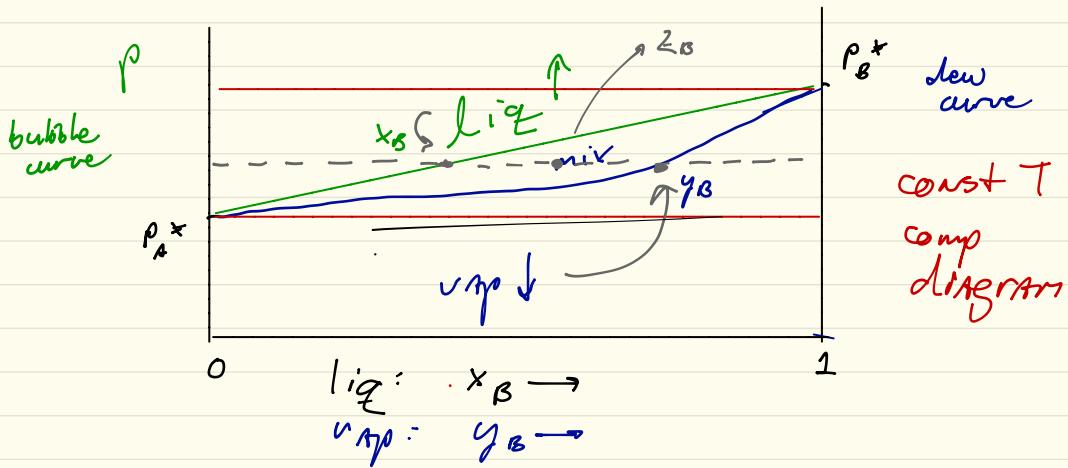
Pressure - composition diagramRaoult's law behavior

$$\rho = x_B P_B^* + (1-x_B) P_A^* \quad \rho = \frac{P_A^* P_B^*}{y_A P_B^* + y_B P_A^*}$$

For given x_B , $y_B = x_B P_B^* / \rho = \frac{x_B P_B^*}{x_B P_B^* + (1-x_B) P_A^*}$

Composition of vapor
≠ " of liquid

$$\rho = \frac{x_B}{y_B} P_B^*$$



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Above P_B^* all liquid minimizes $g = g_L + g_V$

Below P_A^* all vapor " " $g = g_L + g_V$

In between mixture minimizes g
liquid comp on liquid

vapor " " vapor "

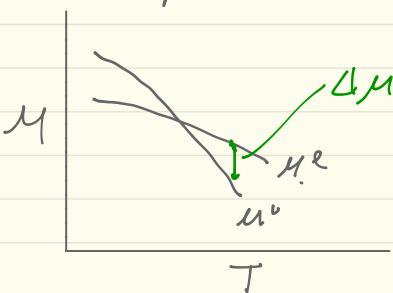
liquid rich in low P^* stuff

vapor " " high ^ "

Given total composition, use lever rule to find fraction of each phase

$$\frac{n_e}{N_{\text{vap}}} = \frac{Y_B - Z_B}{Z_B - X_B} \quad Z_B = \frac{N_B^L + N_B^{\text{vap}}}{N^L + N^{\text{vap}}}$$

Temperature - composition



Temperature-composition diagrams

$$A(l) \rightarrow A(g) \quad \left\{ \begin{array}{l} \mu_A^l > \mu_A^g, \quad T > T_{b,A} \\ \mu_A^l = \mu_A^g, \quad T = T_{b,A} \\ \mu_A^l < \mu_A^g, \quad T < T_{b,A} \end{array} \right. \quad \text{Ditto B}$$

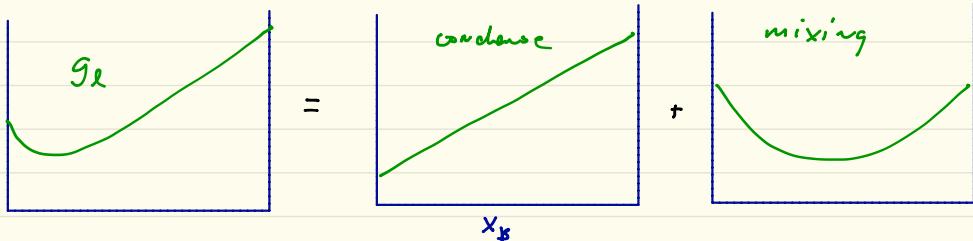
Suppose $T_A > T_B$, $\chi_{AB} = 0$

Above T_B everything is a gas, below T_B everything liquid. What happens in between if behave like ideal mixtures?

Liquid at x_B - above B's BP, have to condense

$$g_e(x_B) = x_B(\mu_B^l - \mu_B^g) + kT(x_B \ln x_B + (1-x_B) \ln(1-x_B))$$

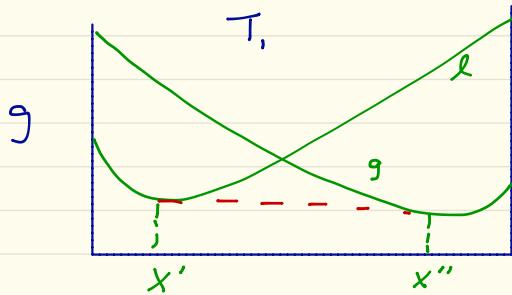
condense B mix A + B



Gas at x_B - below A's BP, have to vaporize

$$g_g(x_B) = (1-x_B)(\mu_A^g - \mu_A^l) + kT(x_B \ln x_B + (1-x_B) \ln(1-x_B))$$





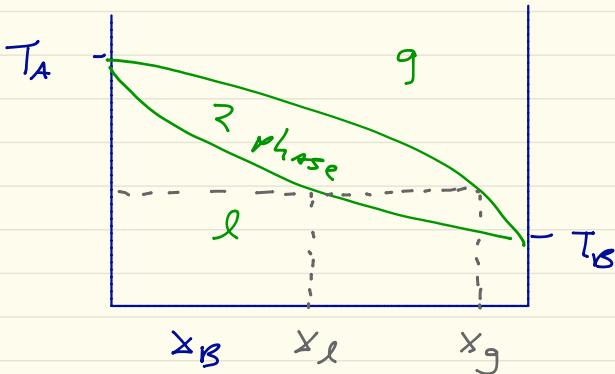
Common tangent

At this particular T , everything between x' + x'' phase separates into liquid of composition x' and gas of x'' .

As $T \uparrow$, liquid line goes up relative to gas (takes more free energy to condense B).

As $T \downarrow$, gas line goes up relative to liquid (takes more free energy to vaporize A).

Plot x', x'' vs T :



Very common phase behavior arising from pure phase character + ideal mixing.

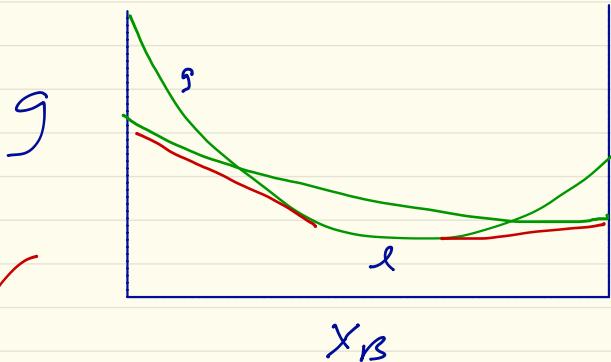
Basis of fractional distillation, zone refining
Raoult's Law for both components

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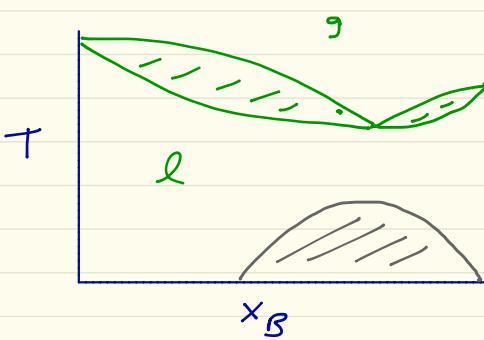
Non-ideal liquid mixture

Suppose we add in $K_{AB} > 0$ — molecules don't like each other.

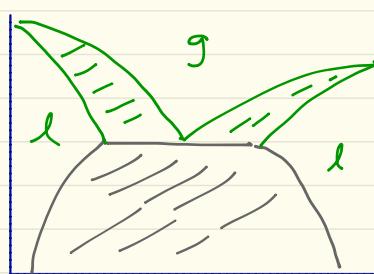
Pushes up liquid line by $\chi_{AB} x_B (1-x_B)$



Two
coexistence
regions!



$\beta \rightarrow$
 χ_{AB}



Coexistence regions
collide.

eutectic - 3 phase
coexistence

$l-l$ and $l-g$
coexistence regions
+
eutectic - $g + l$ comps
the same
entropy + energy balance

Vapor - liquid isotherms

Suppose mixture has one volatile component A/B in liquid phase, B as a gas.

$$\text{At equilibrium } \mu_B^{\text{gas}} = \mu_B^{\text{liq}}, \quad T^{\text{gas}} = T^{\text{liq}}$$

Suppose gas is ideal, so we can write

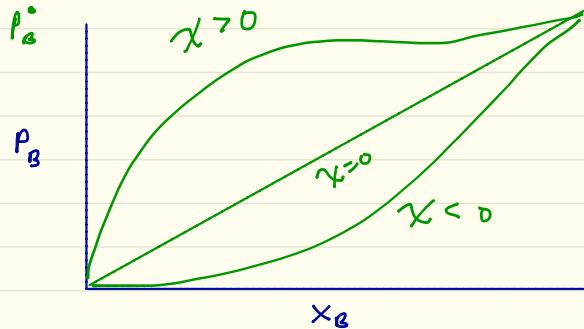
$$\mu_B^{\text{gas}}(T, P) = \mu_B^*(T) + k_B T \ln \frac{P}{P_B^*} \quad P_B^* : \text{sat } P \text{ at } T$$

$$\mu_B^L(T, P, x_B) = \mu_B^*(T) + \chi_{AB}(1-x_B)^2 kT + kT \ln x_B$$

equate $kT \ln \frac{P}{P_B^*} = \chi_{AB}(1-x_B)^2 kT + kT \ln x_B$

$\hookrightarrow P = P_B^* x_B \exp[\chi_{AB}(1-x_B)^2]$

$$P_B^* = P_B^\circ \exp\left[\frac{z u_{BB}}{2kT}\right] \quad \begin{matrix} \text{vapor pressure of} \\ \text{pure B liquid} \end{matrix}$$



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$\chi=0$ Raoult's Law no differential intersections

Vapor pressure of B suppressed for purely entropic reasons. B stays in condensed phase to enhance entropy.

$\chi > 0$ $u_{AB} > \frac{u_{AA} + u_{BB}}{2}$ Entropy counterbalanced by net repulsive interactions. B less favorable in condensed phase

$\chi < 0$ $u_{AB} < \frac{u_{AA} + u_{BB}}{2}$ Vapor pressure suppressed more

In the limit of $x_B \rightarrow 0$, get

$$P_B = P_B^{\circ} x_B \exp[\chi_{AB}(1-x_B)^2] \approx \underbrace{P_B^{\circ} e^{\chi_{AB}}} \underbrace{x_B}_{\text{Henry's Law H}}$$

$$P_B = K_H X_B$$

Related to vapor pres of B scaled by A-B vs AA/BB interactions.

Commonly observed behavior of dilute solutes in solvents.

In general A must be volatile as well

Cobb-Douglas tells us $N_A d\mu_A + N_B d\mu_B = 0$

vapor

$$\rightarrow x_A d\mu_A + x_B d\mu_B = 0$$

$$\mu_i = \mu_i^{\circ} + RT \ln \frac{P_i}{P_0} \rightarrow \left(\frac{\partial \mu_i}{\partial x_i} \right) = RT \left(\frac{\partial \ln P_i}{\partial x_i} \right)$$

$$x_A \left(\frac{\partial \ln P_A}{\partial x_A} \right) dx_A + x_B \left(\frac{\partial \ln P_B}{\partial x_B} \right) dx_B = 0 \quad -dx_A$$

$$x_A \left(\frac{\partial \ln P_A}{\partial x_A} \right) = x_B \left(\frac{\partial \ln P_B}{\partial x_B} \right)$$

Gibbs-Douglas

Raoult's Law for B $x_{AB} = 0 \quad P_B = x_B P_B^{\circ}$

$$x_B \left(\frac{\partial \ln P_B}{\partial x_B} \right) = x_B \cdot \frac{1}{x_B} = 1 = x_A \left(\frac{\partial \ln P_A}{\partial x_A} \right)$$

$$\int_{P_A^{\circ}}^{P_A} d \ln P_A = \int_1^{x_A} \frac{dx_A}{x_A}$$

$$\ln \frac{P_A}{P_A^{\circ}} = \ln x_A \rightarrow P_A = P_A^{\circ} x_A$$

Raoult's Law for 1 component implies the same for the other.

$$P_B = P_B^* x_B e^{X_{AB} (1-x_B)^2}$$

$$\ln P_B = \ln P_B^* - \ln x_B + X_{AB} (1-x_B)^2$$

$$\frac{\partial \ln P_B}{\partial x_B} = \frac{1}{x_B} - 2 X_{AB} (1-x_B)$$

$$x_B \cdot () = 1 - 2 X_{AB} x_B (1-x_B)$$

$$= 1 - 2 X_{AB} (1-x_A) \cdot x_A = v_A \left(\frac{\partial \ln P_A}{\partial x_A} \right)$$

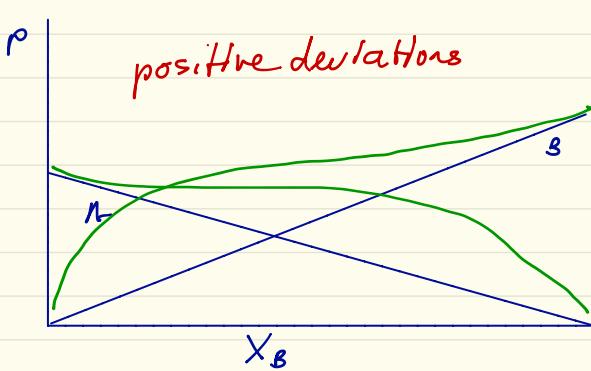
$$\Rightarrow P_A = P_A^* x_A e^{X_{AB} (1-x_A)^2}$$

$$\text{As } v_B \rightarrow 1 \quad P_B \rightarrow P_B^* x_B$$

$$x_A \rightarrow 0 \quad P_A \rightarrow P_A^* e^{X_{AB}} x_A$$

Raoult

Henry

eg $\text{CS}_2 / \text{MeOCH}_2\text{OMe}$

$e^{X_{AB} x_A^2}$: Margules factor for regular soln
 $\Rightarrow e^{\alpha x_A^2 + \beta x_A^3 + \dots}$ more generally

Activity models

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$$\text{Can rewrite } \mu_B = \frac{z u_{BB}}{2} + \chi_{AB} (1-x_B)^2 k_B T + k_B T \ln x_B$$

Suppose we are in the limit of a large amount of B. Makes sense to make our chemical pot'/ reference pure B

$$\mu_B^*(T) = \frac{1}{2} z u_{BB}$$
energy of pure B relative
to IG of B

$$\mu_B(x, T) = \mu_B^*(T) + k_B T \ln \gamma(x, T) \cdot x$$

$$\gamma(x, T) = e^{\chi_{AB}(1-x)} \quad \begin{matrix} \text{Activity} \\ \text{coefficient} \end{matrix}$$

$$\lim_{x \rightarrow 1} \gamma(x, T) = 1$$
in "solvent" convention

Alternatively, could be in the limit of very dilute B. Chemical potential reference should then be infinitely dilute B, energy to create a "cavity" in pure A and "insert" A B

$$\mu_B^* = -\frac{z}{2} w_{AA} + z w_{AB} = \frac{z}{2} w_{BB} + \chi_{AB}$$

$$\mu_B(x, T) = \mu_B^*(T) + k_B T \ln \gamma(x, T) \cdot x$$

$$\gamma(x, T) = e^{\chi_{AB} x_B (x_B - 1)} \quad \begin{matrix} \text{Activity} \\ \text{coefficient in} \\ \text{"solute" convention} \end{matrix}$$

$$\lim_{x \rightarrow 0} \gamma(x, T) = 1$$

In general, convenient to define "activity" a_i by

$$a_i(T, x) = \gamma_i(T, x) x_i = e^{(u_i - u_i^{\text{ref}})/k_B T} \\ = \bar{f}_i / f_i^{\text{ref}}$$

Lots of activity coefficient models. Key points:

- unlike fugacity, activity is only defined wrt some reference state
- ultimately determined by underlying molecular interactions

Activity coefficient measures deviation from ideal mixing behavior of components from their ref states.

$$G_i^{\text{ex}} = k_B T \ln \gamma_i$$

Boiling point suppression