Thermodynamics II Midterm Review

By James

Contents

Why Fugacity

$$\begin{cases} T^\alpha = T^\beta & \textit{Thermal equilibrium} \\ P^\alpha = P^\beta & \textit{Mechanical equilibrium} \\ g^\alpha = g^\beta & \textit{Energetic equilibrium} \end{cases} \longrightarrow \mu_i^\alpha = \mu_i^\beta$$

The true criteria for chemical equilibrium is the *chemical potential*

$$\mu_i - \mu_i^o = RT \ln\left[\frac{y_i P}{y_i P^o}\right] = RT \ln\left[\frac{p_i}{p_i^o}\right]$$

As y_i approaches 0 (or infinite dilution), pressure goes to zero and the solution becomes undefined or negative infinity

Chemical potential is mathematically inconvenient, so a new criterion, *Fugacity,* was introduced, making studying equilibrium easier

$$\mu_i - \mu_i^o \equiv RT \ln\left[\frac{\hat{f}_i}{\hat{f}_i^o}\right]$$

The drawback: Reference states are needed to calculate fugacity

At equilibrium, this new criterion is convenient:

$$\hat{f}_i^\alpha = \hat{f}_i^\beta$$

$$\hat{f}_i^v = \hat{f}_i^l$$

How do I calculate fugacity for vapor and liquid?

Fugacity for gasses

Fugacity: It is equal to the pressure of an ideal gas that has the chemical potential of a real gas. A mathematical "shortcut" to model behavior of real gasses by using ideal gas thermodynamics

The reference state is the **ideal gas** under low pressures

Fugacity: fudge factor that corrects for non-ideality of real gasses

$$\hat{\varphi}_i \equiv \frac{\hat{f}_i}{p_{i,sys}} = \frac{\hat{f}_i}{y_i P_{sys}}$$

Fugacity coefficient: the ratio of fugacity to the real gas pressure is a measure of how closely this substance behaves like an ideal gas. For ideal gasses, this is 1.

$\varphi_i^v > 1$ *repulsive forces dominating*
$\varphi_i^v < 1$ *attractive forces dominating*
$\varphi_i^v = 1$ *no interactions, ideal gas*

3 ways to calculate fugacity for vapors

$\hat{f}^v = \varphi_i^v y_i P$ Full rigor: all mixing rules apply, accounts for all interactions in mixture (a-a, a-b, a-c etc)

$\hat{f}^v = \varphi_i^v y_i P$ Lewis Fugacity Rule: all interaction approximately the same, no mixing rules needed

$\hat{f}^v = y_i P$ Ideal Gas Behavior: $\varphi_i^v = 1$, no interactions. Fugacity equal to partial pressure (Reasonable at low pressures)

Full Rigor Fugacity Calculation use EOS

$$a = \frac{27}{64}\frac{(RT_c)^2}{P_c}$$

$$a_{\text{mix}} = y_a^2 a_a + 2y_a y_b \sqrt{a_a a_b} + y_b^2 a_b$$

$$\hat{f}^v = \varphi_i^v y_i P$$

$$b = \frac{(RT_c)}{8P_c}$$

$$b_{\text{mix}} = y_a b_a + y_b b_b$$

Intermolecular interactions between species "a" and "b"

Equation of state	Expression for $\hat{\varphi}_1$
van der Waals	$\ln \hat{\varphi}_i = \frac{b_i}{v-b} - \ln\left(\frac{(v-b)P}{RT}\right) - \frac{2\sum_{k=1}^{m} y_k a_{ik}}{RTv}$
Redlich-Kwong	$\ln \hat{\varphi}_i = \frac{b_1}{b}(z-1) - \ln\left(\frac{(v-b)P}{RT}\right) + \frac{1}{bRT^{1.5}}\left[\frac{ab_i}{b} - 2\sum_{k=1}^{m} y_k a_{ik}\right]\ln\left(1+\frac{b}{v}\right)$
Peng-Robinson	$\ln \hat{\varphi}_i = \frac{b_i}{b}(z-1) - \ln\left(\frac{(v-b)P}{RT}\right) + \frac{a\alpha}{2\sqrt{2}bRT}\left[\frac{b_i}{b} - \frac{2}{a\alpha}\sum_{k=1}^{m} y_k (\alpha a)_{ik}\right]\ln\left[\frac{v+(1+\sqrt{2})b}{v+(1-\sqrt{2})b}\right]$

Lewis Fugacity Rule (mixtures)

$\hat{f}^v = \varphi_i^v y_i P$

Ideal interactions (all a-a) therefore $\Delta h_{mix} = \Delta v_{mix} = 0$

Valid when the following conditions are true:
1) Low pressure or high temperature (similar to Ideal Gas)
2) Component a is present in large excess (y_b is small)
3) Chemical nature is similar to other species ($a_a = a_b$)

$$\log \varphi_i = \log \varphi^{(0)} + \omega \log \varphi^{(1)}$$

Can use Generalized correlations (need reduced temperature and pressure and Lee-Kesler Tables)

$T_r = T/T_c$
$P_r = P/P_c$

Fugacity in the Liquid Phase

Unlike in the vapor phase which simply can use the ideal gas reference state, liquid phase fugacity must idealize a system. This is the **Ideal Solution**. At ideal solution, the activity coefficient γ = 1

All mixing rules same for ideal gas, $\Delta h_{mix} = \Delta v_{mix} = 0$, however contrary to ideal gasses, references states are required.
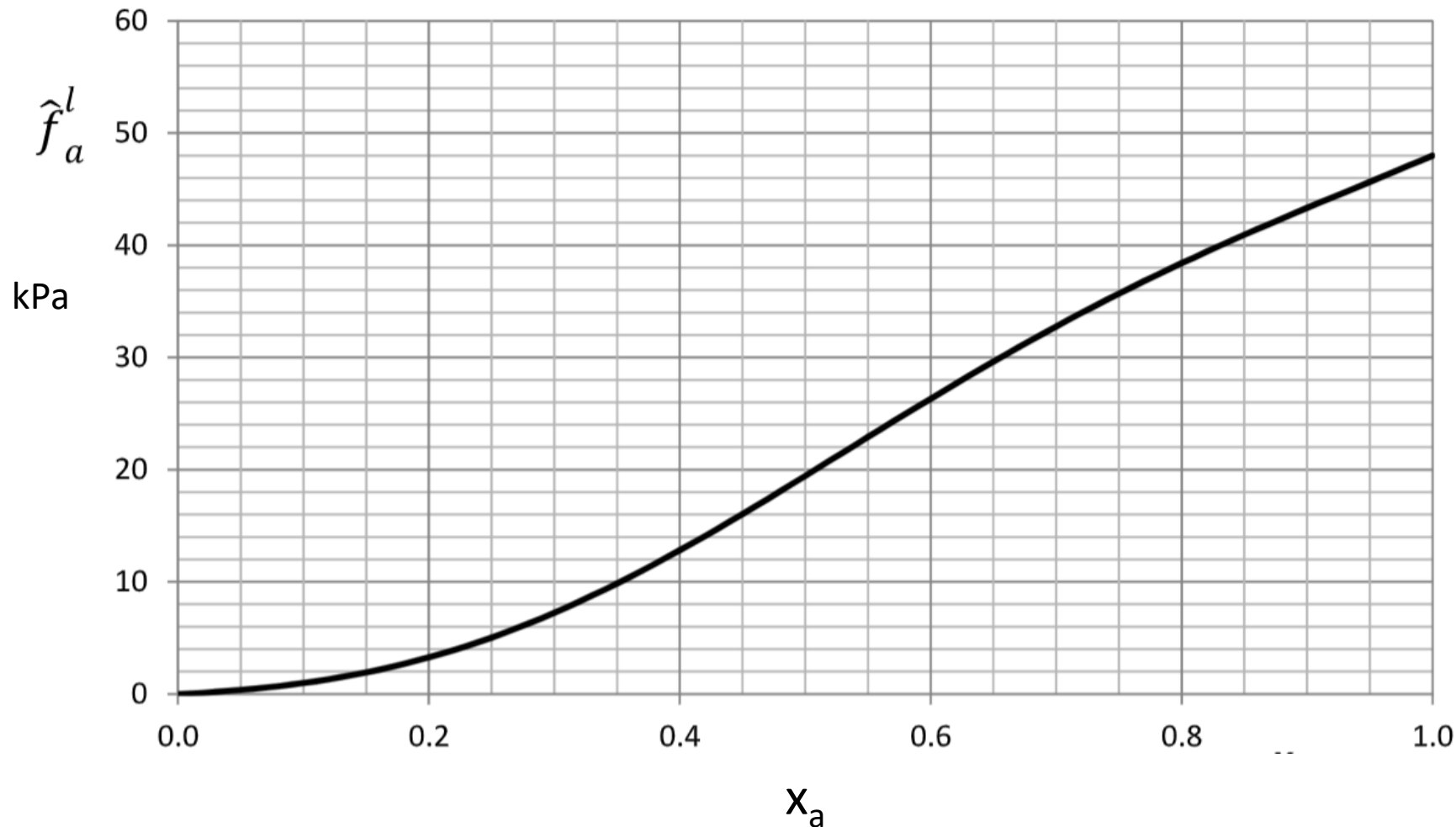
$$\hat{f}_i^{id} = x_i f_i^o$$

Two reference states:
The **Lewis Randall rule** (all interactions approximated by a-a) and
The **Henry's Law reference** (intermolecular interactions approximated by a-b)

Lewis Randall/Henry's Law

Take the tangent at $x_a = 1$ going through $f_a = 0$ this is your ideal Lewis Randall fugacity Line

Take the tangent at $x_a = 0$, this is your ideal Henry's Law fugacity line

Lewis Randall/Henry's Law

Take the tangent at $x_a = 1$ going through $f_a = 0$ this is your ideal Lewis Randall fugacity Line. This reference line represents like interactions for your real line (a – a)

Take the tangent at $x_a = 0$, this is your ideal Henry's Law fugacity line. This reference line represent unlike interactions for your real line (a – b)

Case A

Case B
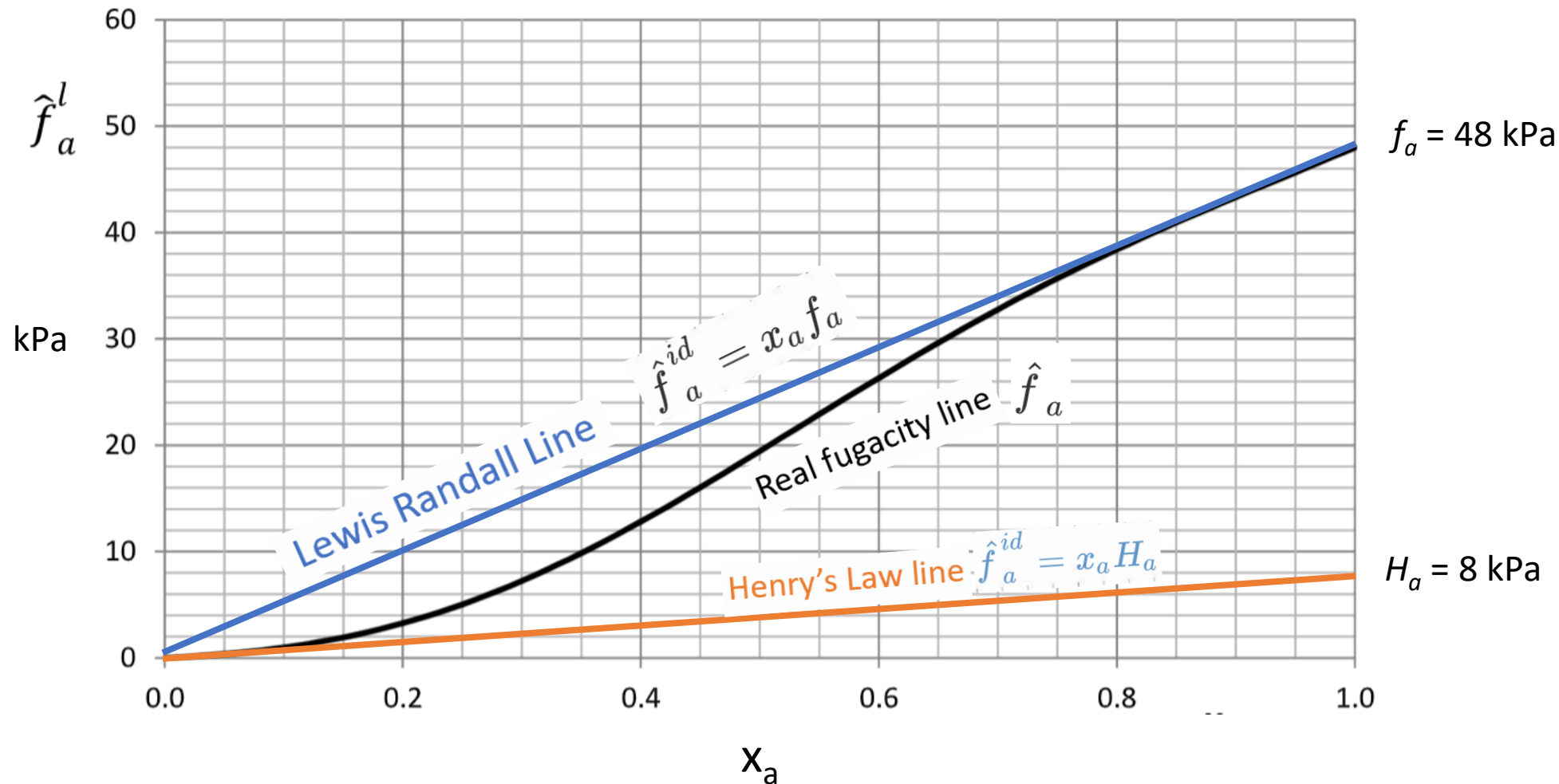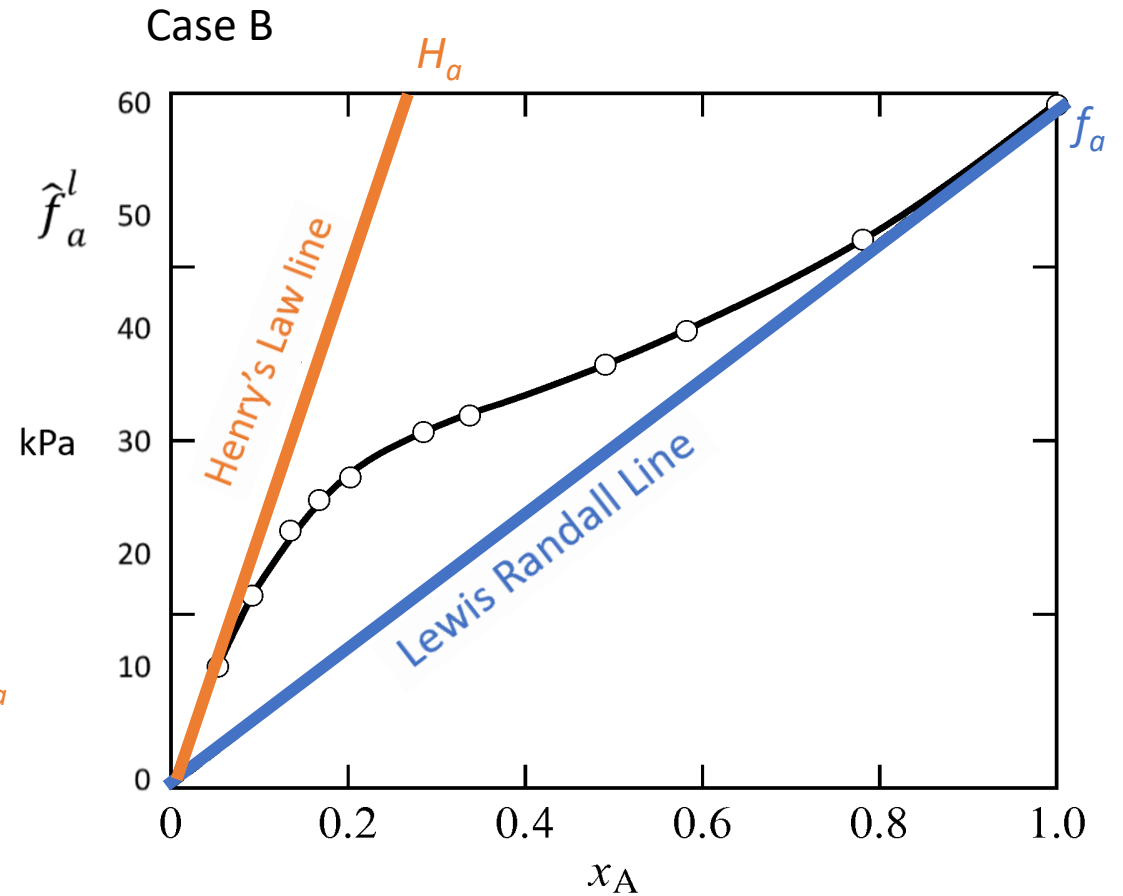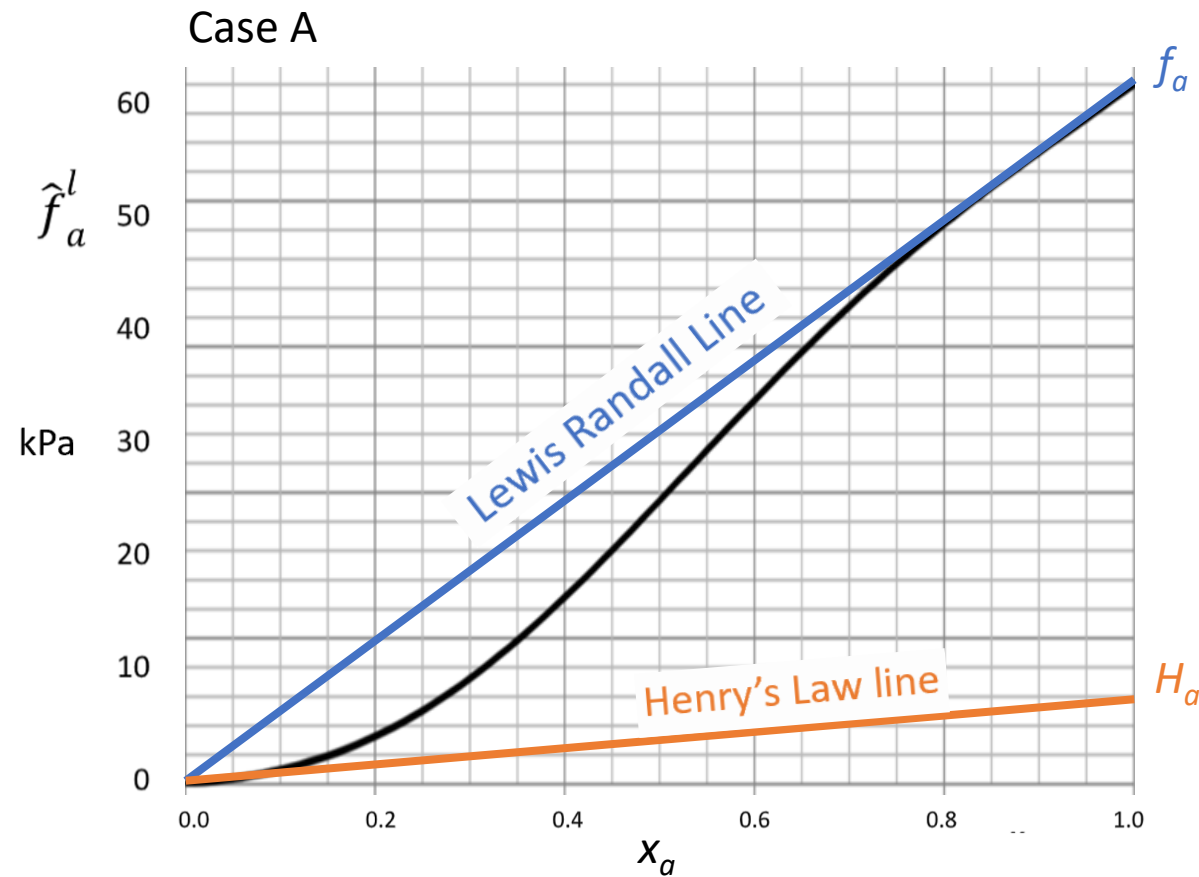
Fugacity: tendency for interactions to escape.   Which interactions are stronger for each?

Case A: The pure species Lewis Randal Fugacity, f_a, ("like" interactions, a – a,) has a higher fugacity than the pure species Henry's Law fugacity value, H_a (unlike, a – b). Therefore, there is a higher tendency for the "like" interactions of the real fugacity to escape, thus the "unlike" interactions must be stronger.

Case B: The pure species Henry's Law fugacity value, H_a ("unlike" interactions, a – b) has a higher fugacity than the pure species Lewis Randal Fugacity, f_a, (like interactions, a – a,) Therefore, there is a higher tendency for the "unlike" interactions of the real fugacity to escape, thus the "like" interactions must be stronger.

Activity Coefficient

Ratio of the fugacity of the "real" line and the ideal line. Quantifies how much fugacity of given species deviates from the value it would have in an ideal solution

$$\gamma_i = \frac{\hat{f}_i^{l\ real}}{\hat{f}_i^{l\ ideal}} = \frac{\hat{f}_i^l}{x_i f_i^o}$$

The ideal fugacity can be of either the Lewis-Randal or Henry's Law reference state

$$\hat{f}_a^{\ l} = x_a \gamma_a F_a^o \qquad \text{Based on Lewis}$$
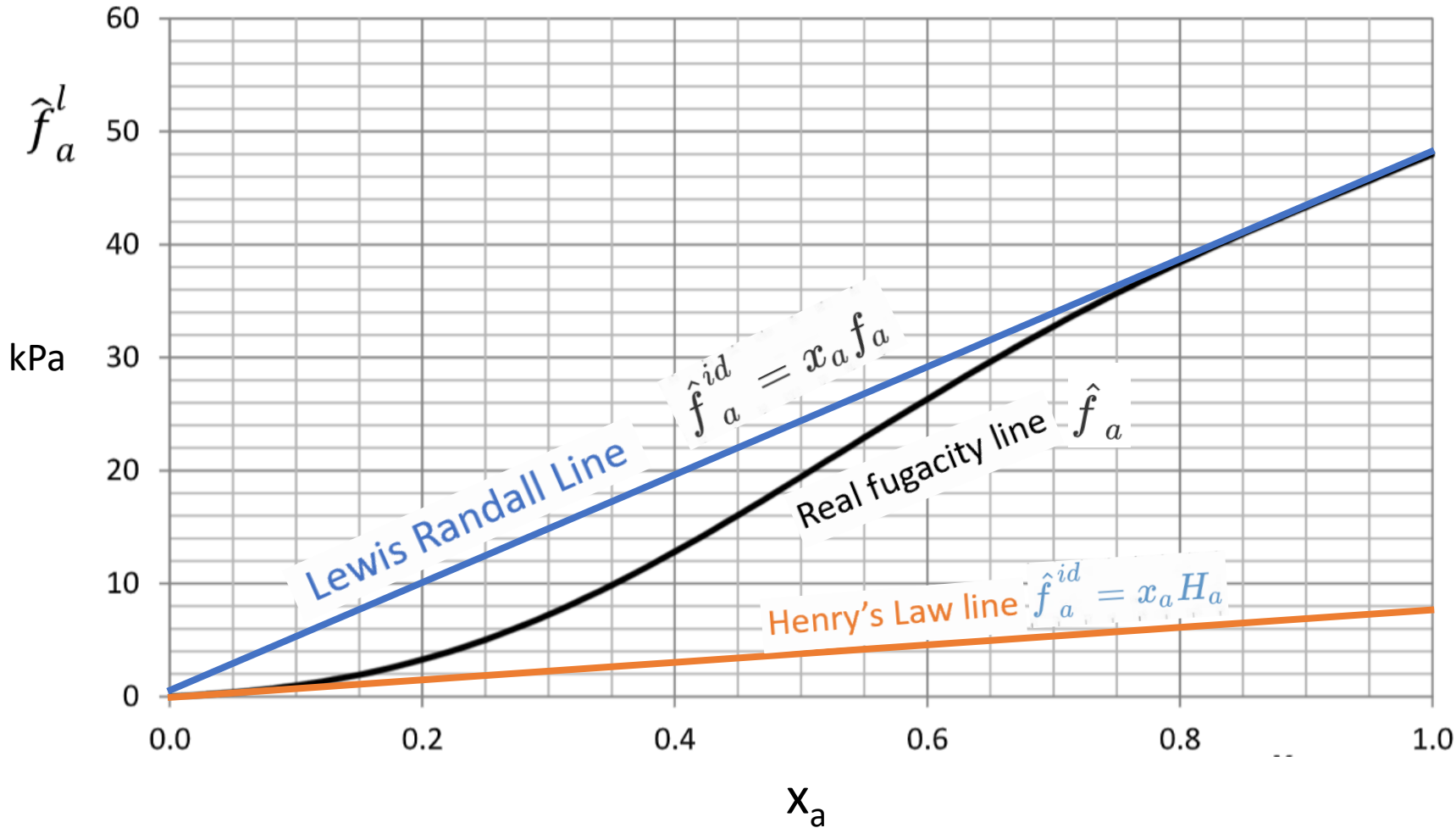
$$\hat{f}_a^{\ l} = x_a \gamma_a^{\text{Henry's}} H_a^o \qquad \text{Based on Henry's Law}$$

Activity

$$a_i \equiv \frac{\hat{f}_i^l}{f_i^o} = x_i \gamma_i$$
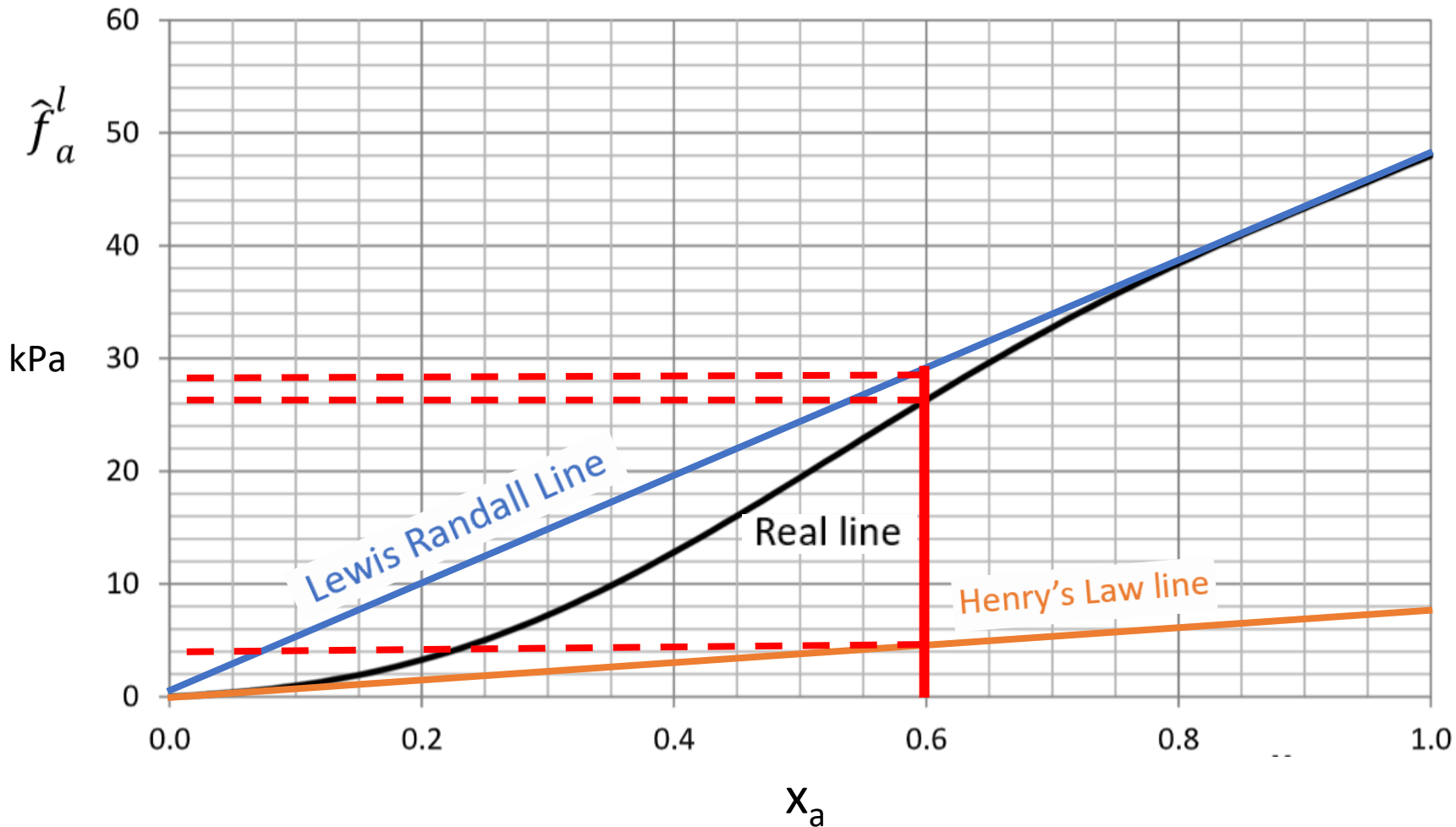
Activity Coefficient

Ratio of the fugacity of the "real" line and the ideal line. Quantifies how much fugacity of given species deviates from the value it would have in an ideal solution

$$\gamma_i = \frac{\hat{f}_i^{l}{}_{real}}{\hat{f}_i^{ideal}}$$

The ideal fugacity can be of either the Lewis-Randal or Henry's Law reference state

Activity Coefficient

Example: What are the Lewis-Randall and Henry's Law Activity Coefficients for a binary mixture of 3 mols of "a" and 2 mols of "b"?

$$\gamma_i = \frac{\hat{f}_i^{l}\,_{real}}{\hat{f}_i^{ideal}}$$

$X_a = 3/5 = 0.6$

Lewis Randal: $\gamma = 26/28 = 0.93$

Henry's Law: $\gamma^{Henry's} = 26/4 = 6.5$

$\gamma^{Henry's} > 1$, unlike interactions greater

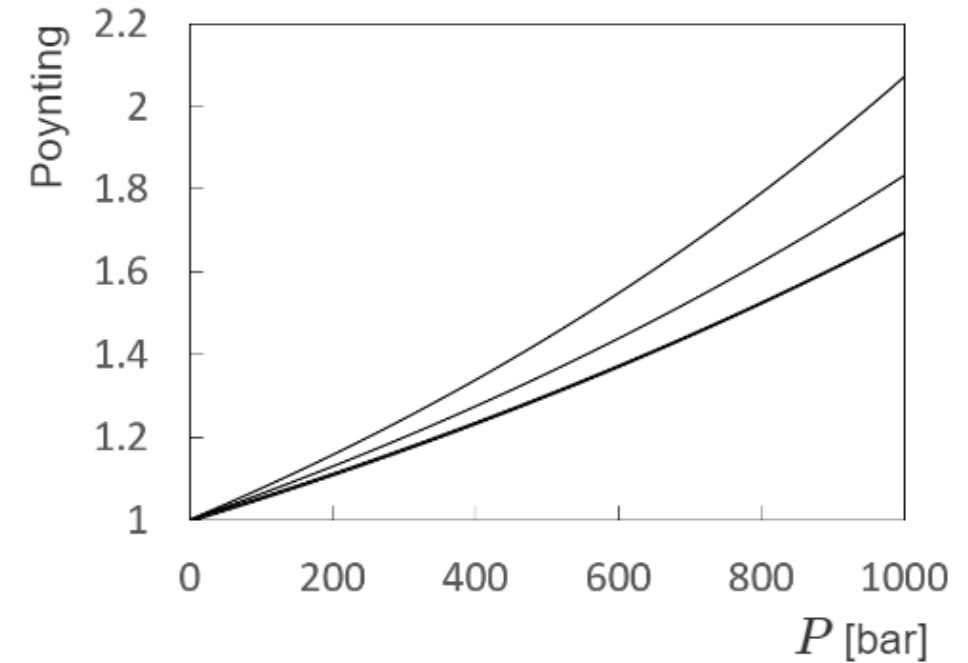$\gamma^{Henry's} < 1$, like interactions greater

Calculating pure liquid fugacity

If you are not given a graph

$$f_i^o = \varphi_i^{sat} P_i^{sat} \left(\exp\left[\frac{v_i^l}{RT}(P - P_i^{sat}) \right] \right)$$

Use Kesler-Tables if the saturation pressure is not less than around 3 bars. If it is, assume to be 1

The Poynting Correction, considers the pressure dependence of pure liquid species fugacity. (usually negligible at pressures below 100 bar)

$f_i^o = \varphi_i^{sat} P_i^{sat}$

At low pressures

Antoine's Equation

$$\ln P_i^{sat} = A_i - \frac{B_i}{C_i + T}$$

$f_i^o = P_i^{sat}$

At low pressures **and** saturation pressures

g^E and the Suffix-Margules Equations

g^E (excess gibb's energy): describes the activity coefficient, γ, for all species in a mixture.
Difference between real gibb's energy and ideal gibb's energy

$$g^E = g(T, P, x_i) - g^{\text{ideal}}(T, P, x_i)$$

$$g^E = A x_a x_b$$

Two-suffix Margules: symmetric models where "a" and "b" behave similarly under same proportions. (molecules that only have LD interactions or are approximately same size)

$$g^E = x_a x_b [A + B(x_a - x_b)]$$

Three-suffix Margules: asymmetric models

$$\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{\text{ideal}} = \mu_i - \mu_i^{\text{ideal}} = RT \ln \left(\frac{\hat{f}_i^l}{\hat{f}_i^{\text{ideal}}} \right)$$

$$\gamma_i = \frac{\hat{f}_i^l}{\hat{f}_i^{\text{ideal}}}$$

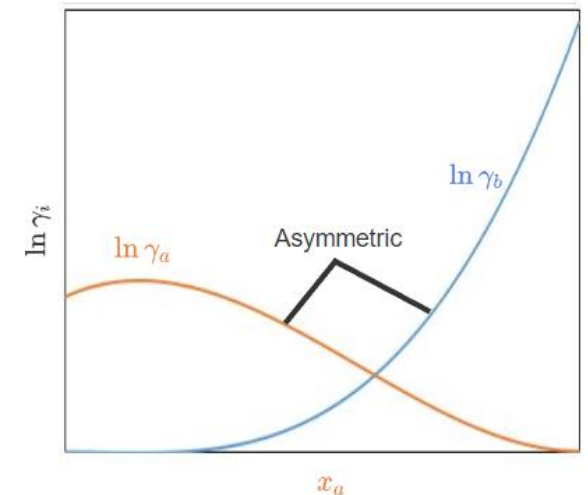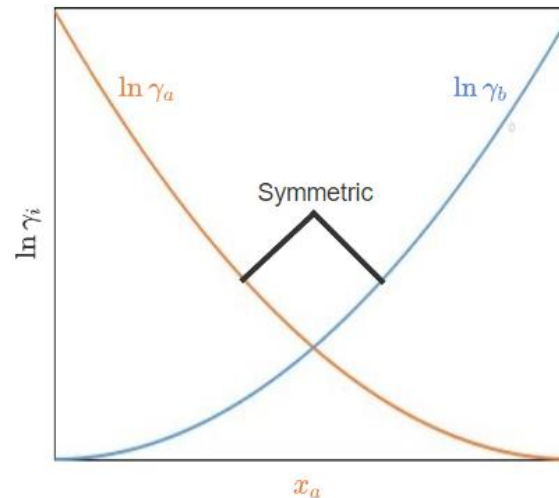$$\overline{G}_i^E = RT \ln \gamma_i$$

Table 7.6.1: Common binary activity coefficient models.

Model	g^E	$RT \ln \gamma_a$	$RT \ln \gamma_b$
Two-suffix Margules	$Ax_a x_b$	Ax_b^2	Ax_a^2
Three-suffix Margules	$x_a x_b [A + B(x_a - x_b)]$	$(A + 3B)x_b^2 - 4Bx_b^3$	$(A - 3B)x_a^2 + 4Bx_a^3$
(or) Three-suffix Margules	$x_a x_b [A_{ba}x_a + A_{ab}x_b]$	$x_b^2 [A_{ab} + 2(A_{ba} - A_{ab})x_a]$	$x_a^2 [A_{ba} + 2(A_{ab} - A_{ba})x_b]$
Van Laar	$x_a x_b \left(\dfrac{AB}{Ax_a + Bx_b} \right)$	$A \left(\dfrac{Bx_b}{Ax_a + Bx_b} \right)^2$	$B \left(\dfrac{Ax_a}{Ax_a + Bx_b} \right)^2$
Wilson	$-RT \begin{bmatrix} x_a \ln(x_a + \Lambda_{ab}x_b) + \\ x_b \ln(x_b + \Lambda_{ba}x_a) \end{bmatrix}$	$-RT \begin{bmatrix} \ln(x_a + \Lambda_{ab}x_b) + \\ x_b \left(\dfrac{\Lambda_{ba}}{x_b + \Lambda_{ba}x_a} - \dfrac{\Lambda_{ab}}{x_a + \Lambda_{ab}x_b} \right) \end{bmatrix}$	$-RT \begin{bmatrix} \ln(x_b + \Lambda_{ba}x_a) + \\ x_a \left(\dfrac{\Lambda_{ab}}{x_a + \Lambda_{ab}x_b} - \dfrac{\Lambda_{ba}}{x_b + \Lambda_{ba}x_a} \right) \end{bmatrix}$
NRTL[*]	$RT x_a x_b \left[\dfrac{\tau_{ba} \mathbf{G}_{ba}}{x_a + x_b \mathbf{G}_{ba}} + \dfrac{\tau_{ab} \mathbf{G}_{ab}}{x_b + x_a \mathbf{G}_{ab}} \right]$	$RT x_b^2 \left[\dfrac{\tau_{ba} \mathbf{G}_{ba}^2}{(x_a + x_b \mathbf{G}_{ba})^2} + \dfrac{\tau_{ab} \mathbf{G}_{ab}}{(x_b + x_a \mathbf{G}_{ab})^2} \right]$	$RT x_a^2 \left[\dfrac{\tau_{ba} \mathbf{G}_{ba}}{(x_a + x_b \mathbf{G}_{ba})^2} + \dfrac{\tau_{ab} \mathbf{G}_{ab}^2}{(x_a + x_b \mathbf{G}_{ab})^2} \right]$

Symmetric Model

Asymmetric Model

To solve for A or B parameter for complex models, typically need to set up 2 equations and 2 unknowns
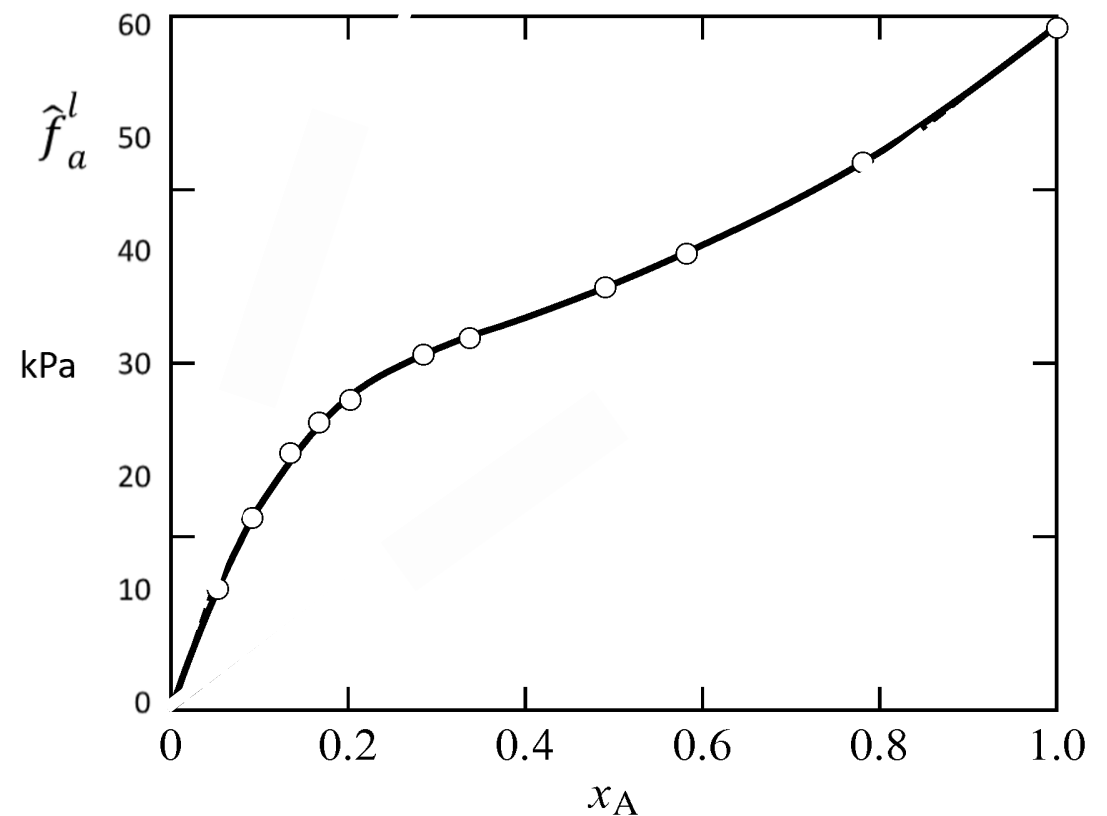
g^E and the Suffix-Margules Equation

$$g^E = Ax_ax_b$$

Positive A means g^E is positive. This means that unlike interactions for binary mixture (a – b) are unfavorable. Like interactions stronger

Negative A mean g^E is negative, and the unlike interactions are favorable. Unlike are stronger

Refer back to previous slides about what their real line fugacity will look like relative to the ideal Henry's Law line

Is g^E favorable or unfavorable for the real fugacity line on the right?

g^E and the Suffix-Margules

$$g^E = Ax_a x_b$$

Positive A means g^E is positive. This means that unlike interactions for binary mixture (a – b) are unfavorable. Like interactions stronger

Negative A mean g^E is negative, and the unlike interactions are favorable. Unlike are stronger

Refer back to previous slides about what their real line fugacity will look like relative to the ideal Henry's Law line

Is g^E favorable or <mark>unfavorable</mark> for the real fugacity line on the right? Ha (a – b interactions) are above the ideal Lewis-Randal line, so they have more fugacity and are weaker (unfavorable). This means g^E and A must be positive values
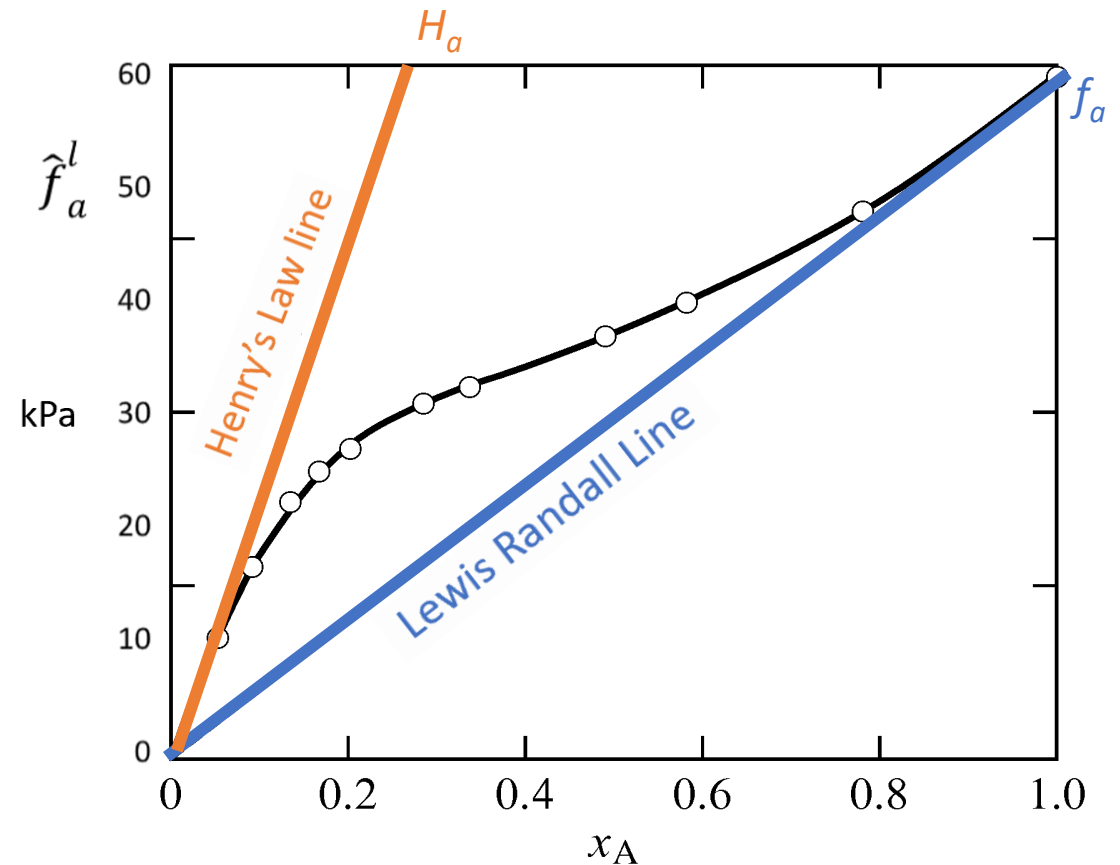
Infinite Dilution

$$\gamma_a^\infty = \exp\left[\frac{A}{RT}\right] = 0.46$$

For activity of species a, take the limit as $x_b \rightarrow 1$

$$\gamma_b^\infty = \exp\left[\frac{A}{RT}\right] = 0.50$$

Two-suffix:

What is the value of A/RT? Use infinite dilutio

$$\exp\left[\frac{A}{RT}\right] = \frac{\gamma_a^\infty + \gamma_b^\infty}{2} = 0.48$$

$$\lim_{x_b \rightarrow 1} RT ln \Upsilon_a^\infty = A x_b^2 \rightarrow ln \Upsilon_a^\infty = \frac{A}{RT}$$

$$\left[\frac{A}{RT}\right] = -0.73$$

$$\lim_{x_a \rightarrow 1} RT ln \Upsilon_b^\infty = A x_a^2 \rightarrow ln \Upsilon_b^\infty = \frac{A}{RT}$$

Υ_i

acetone/chloroform

$x_{acetone}$

Three-suffix:

$$RT \ln \gamma_a^\infty = A - B$$

$$RT \ln \gamma_b^\infty = A + B$$
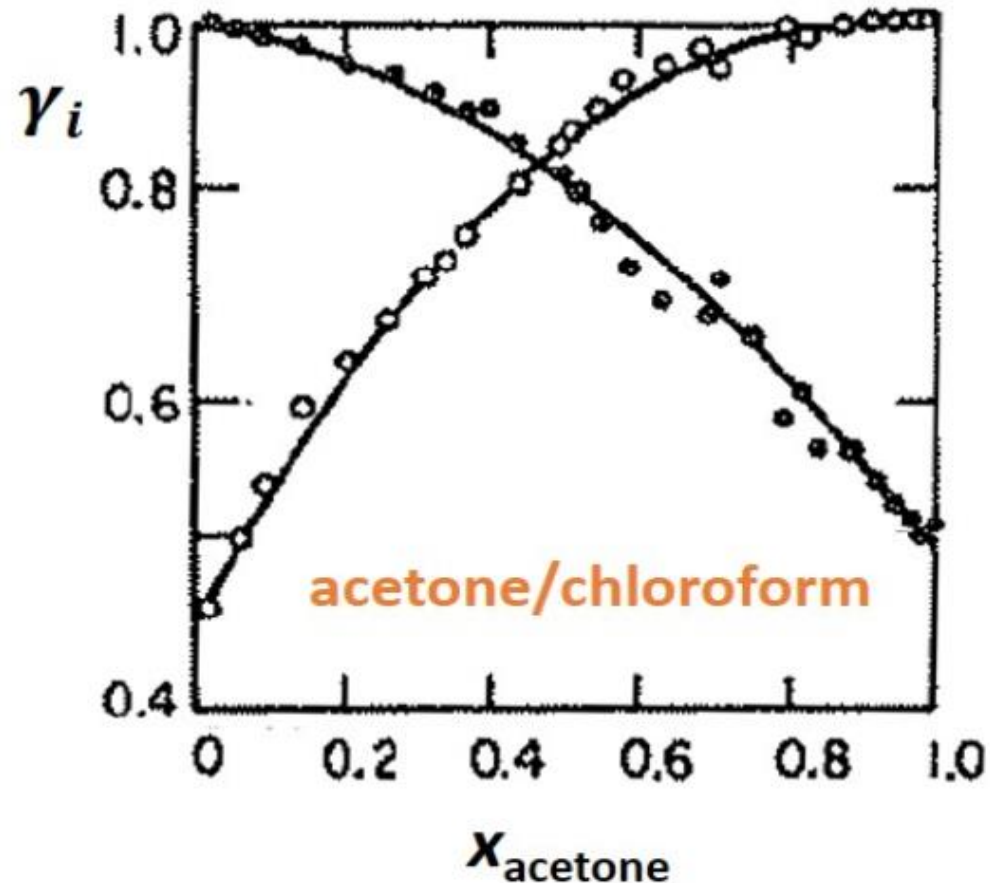
If $\gamma_i < 1$, unlike interactions are favored

If $\gamma_i > 1$, like interactions are favored

Conceptual Question
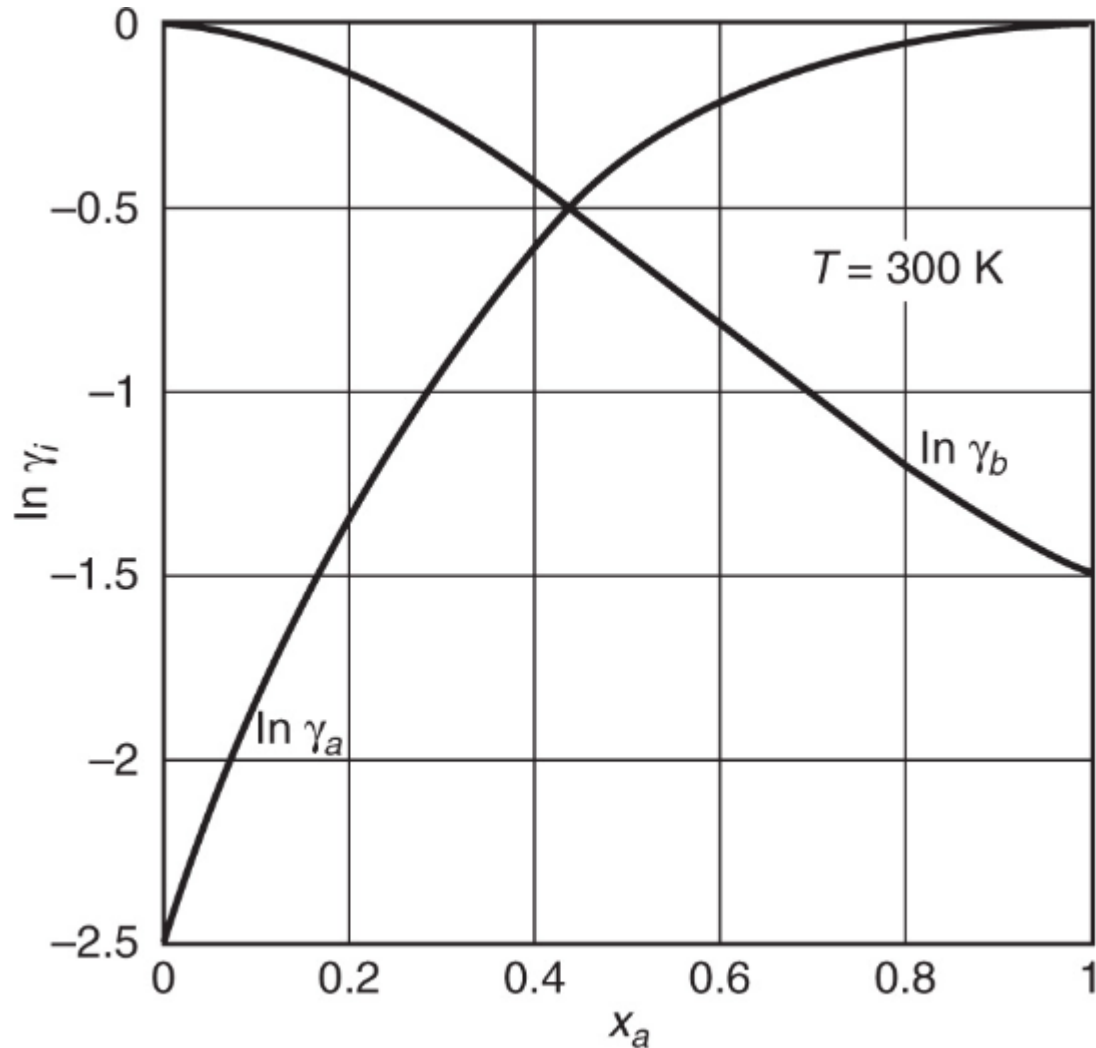
Is g^E better modeled by two-suffix or three suffix? Three-suffix, because asymmetrical

What is the reference state for each species (Lewis-Randall or Henry's)
As $x_a \rightarrow 1$, $\ln\gamma_a \rightarrow 0$
As $x_b \rightarrow 1$, $\ln\gamma_b \rightarrow 0$

$$g^E = g\left(T, P, x_i\right) - g^{\text{ideal}}\left(T, P, x_i\right)$$

Therefore, $g^E \rightarrow 0$ at infinite dilution
Both species approaches ideal Lewis Randal as $x_i \rightarrow 1$
They are both Lewis Randall

What are the values of the $\ln\gamma_a$ and $\ln\gamma_b$ at infinite dilution?
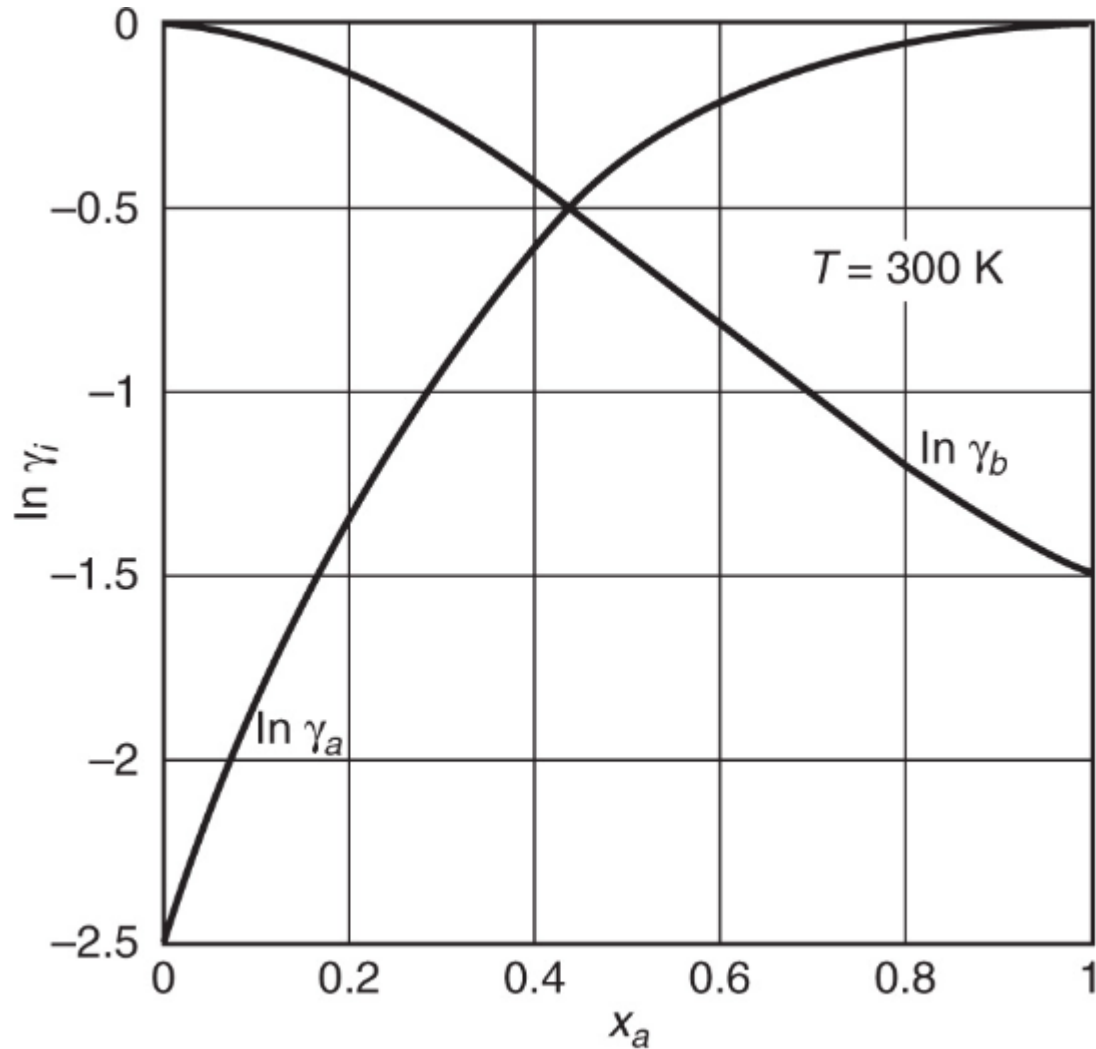$\ln\gamma_a^{\text{infinity}}$ when $x_b = 1 \rightarrow$ -2.5
$\ln\gamma_b^{\text{infinity}}$ when $x_a = 1 \rightarrow$ -1.5

Will this mixture separate into two separate liquid phases? Assume the g^E is given by

$$g^E = x_a x_b - 4988.4 + 1247.1 \left(x_a - x_b\right) \text{ J} \cdot \text{mol}^{-1}$$

No. (A + B) is negative, so g^E is also negative, thus unlike interactions are favored in this mixture

Conceptual Question

Is g^E better modeled by two-suffix or three suffix?

What is the reference state for each species (Lewis-Randall or Henry's)

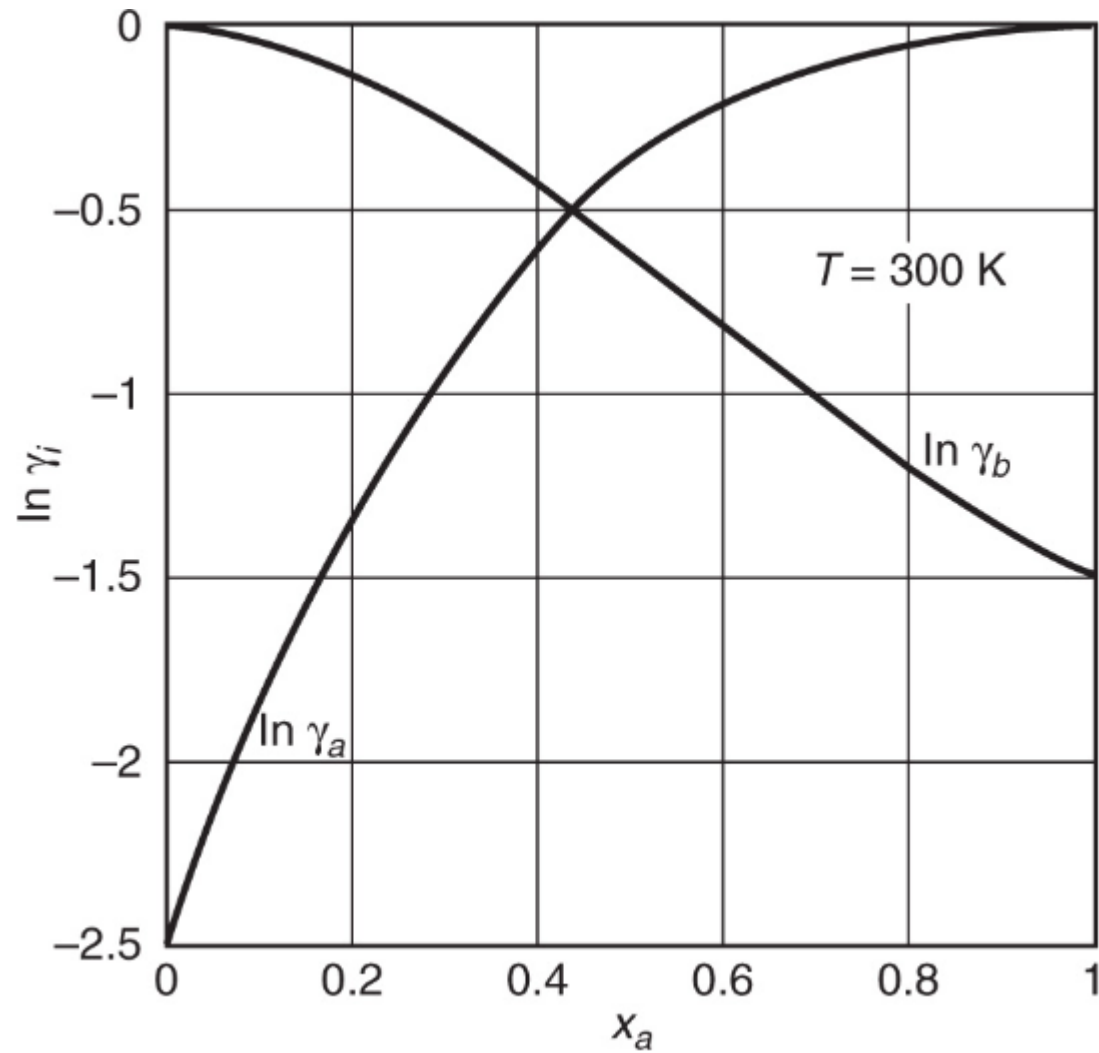As $x_a \to 1$, $\ln\gamma_a \to 0$

As $x_b \to 1$, $\ln\gamma_b \to 0$

$$g^E = g(T, P, x_i) - g^{\text{ideal}}(T, P, x_i)$$

What are the values of the $\ln\gamma_a$ and $\ln\gamma_b$ at infinite dilution?
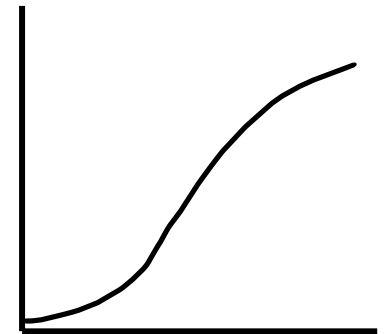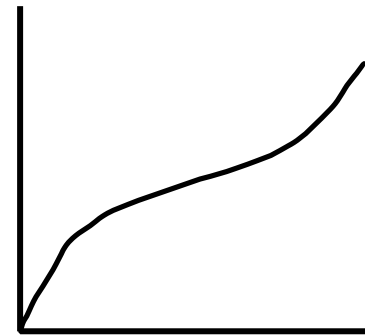
Will this mixture separate into two separate liquid phases? Assume the g^E is given by

$$g^E = x_a x_b - 4988.4 + 1247.1\,(x_a - x_b)\ \text{J}\cdot\text{mol}^{-1}$$

$T = 300$ K

$\ln \gamma_b$

$\ln \gamma_a$

Conceptual Question
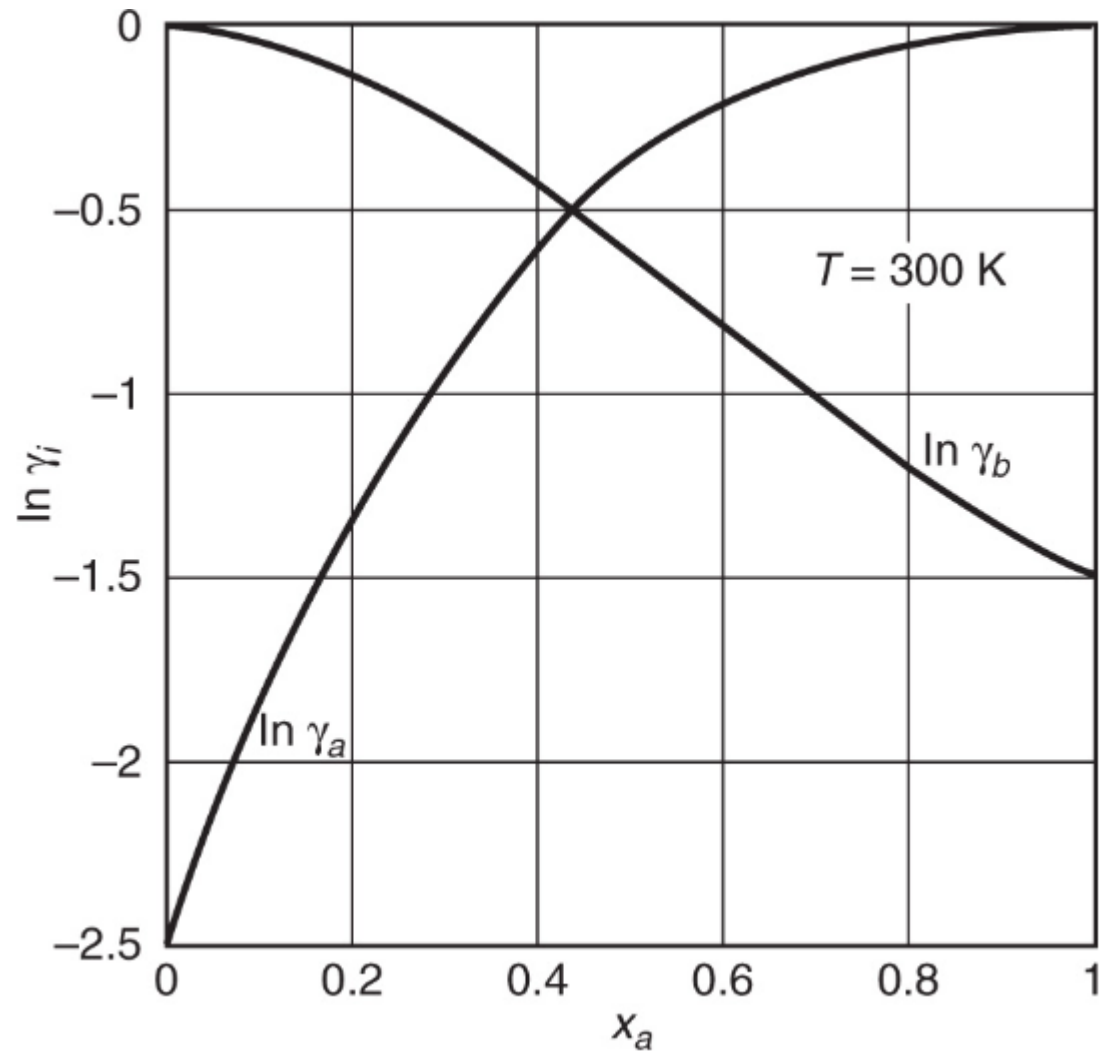

What would the fugacity vs x_a line look like?

Conceptual Question

What would the fugacity vs x_a line look like?
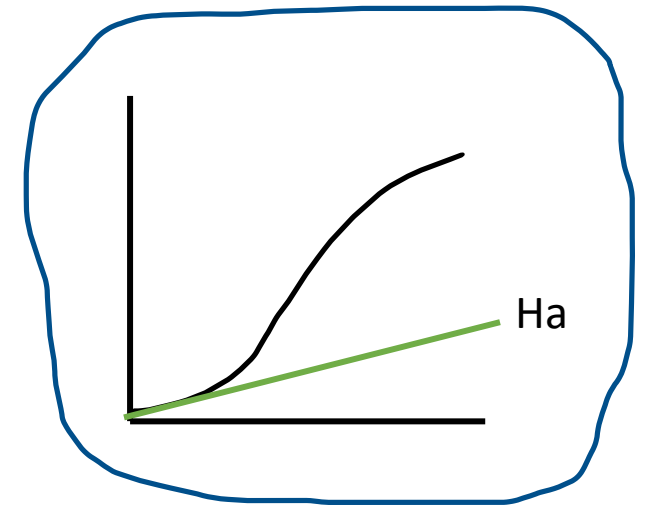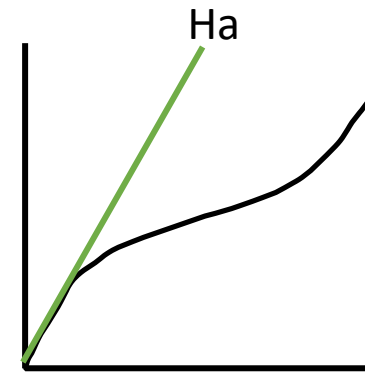
g^E was negative, so the unlike interactions for the ideal mixture are greater than unlike interactions of the real mixture. This is represented with the ideal fugacity line (Ha) being below the real fugacity line. The unlike interactions are therefore, greater.

Are the like interactions stronger or weaker than the unlike interactions? Explain.
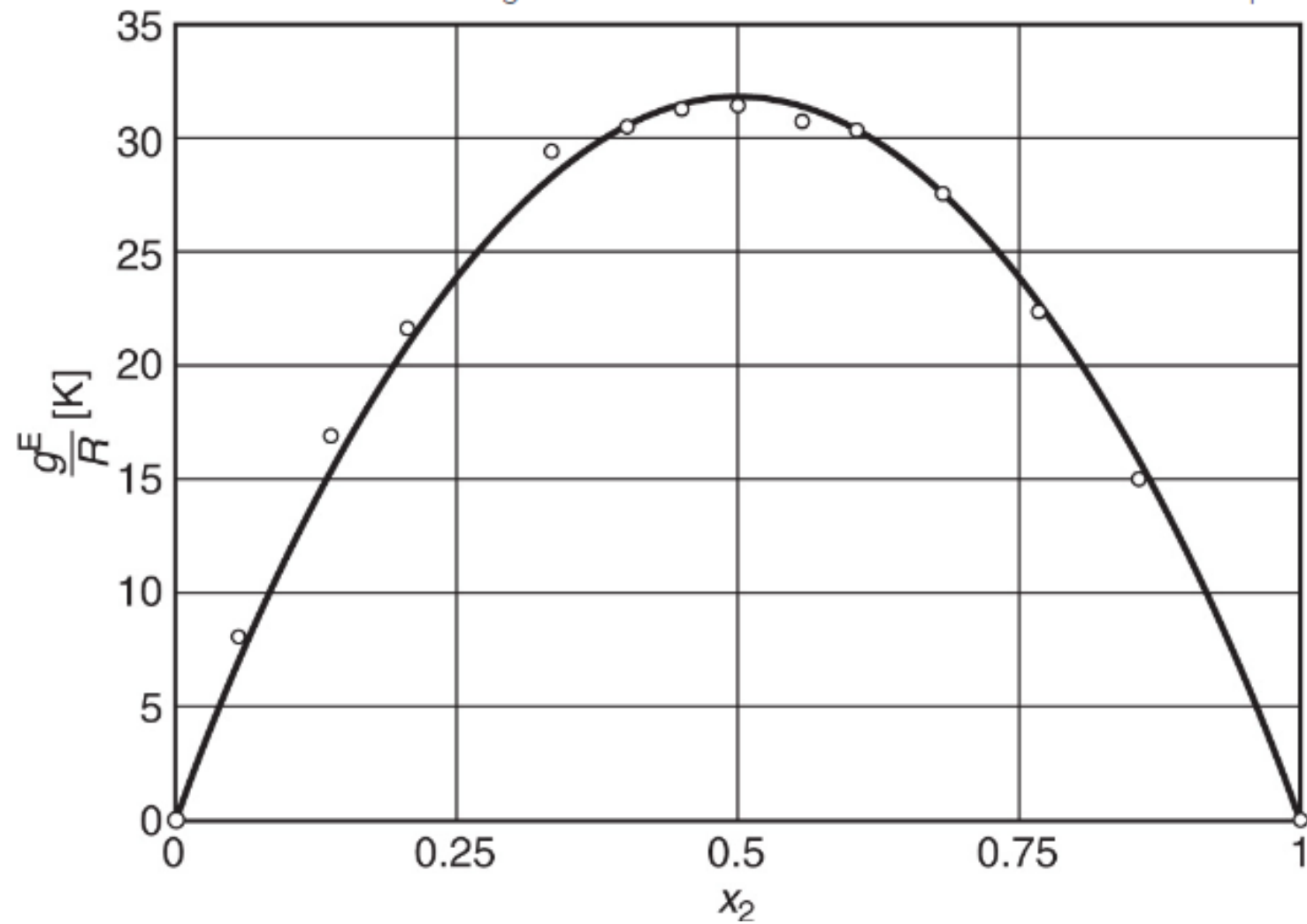
Are the like interactions stronger or weaker than the unlike interactions? Explain.
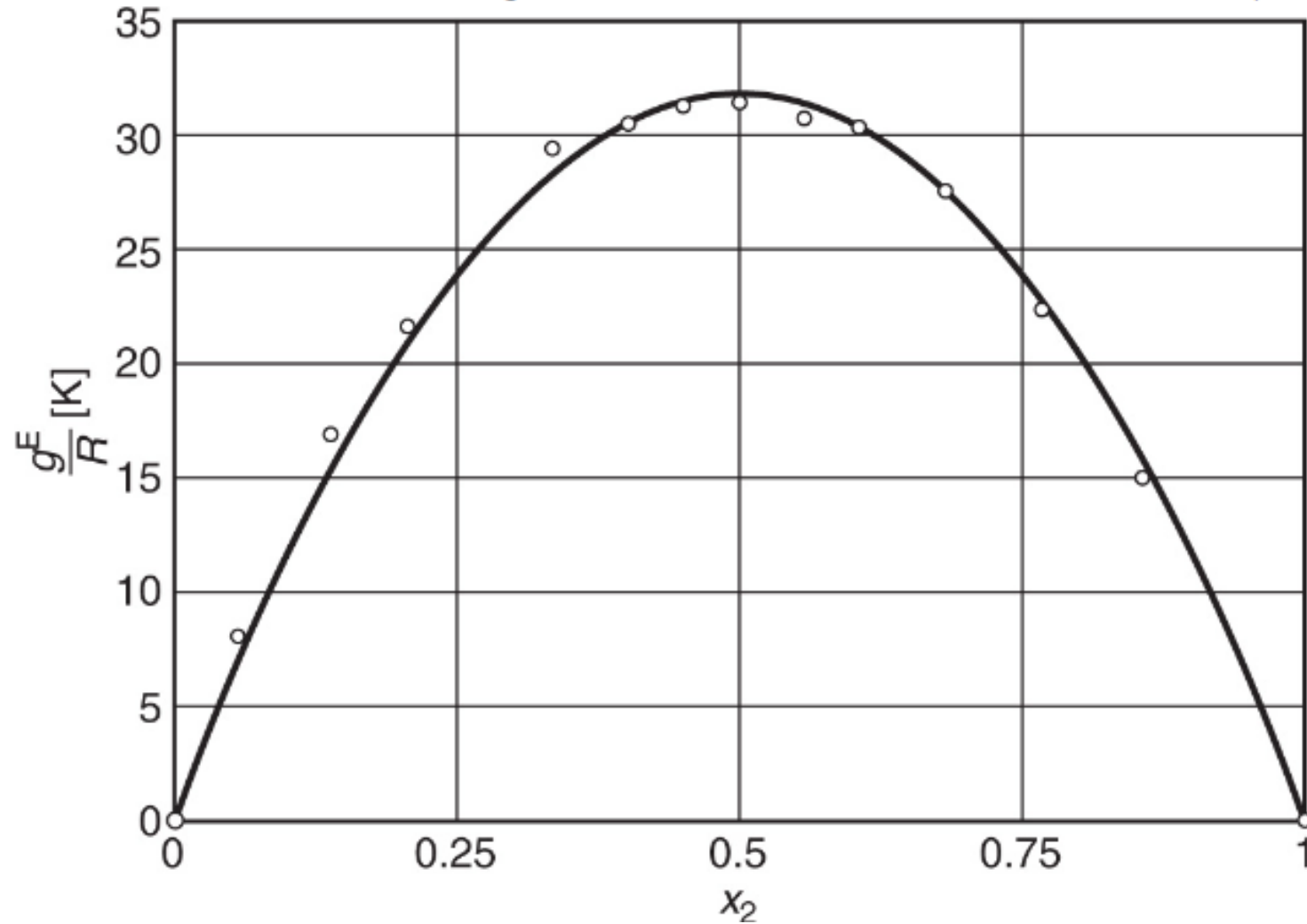
g^E is always positive, so the unlike interactions are always unfavored. Like interactions are greater

Applications of Fugacity: equilibrium

VLE (Vapor liquid equilibrium)

Recall that

For vapors: $\hat{f}_a{}^v = \varphi_a y_a P$ assuming Lewis-Randall Rule

For liquid : $\hat{f}^l_a = x_a \gamma_a f^o_a$ assuming low pressures and saturation pressure $f^o_i = P^{sat}_i$

then

$\hat{f}_a{}^l = \gamma_a x_a P^{sat}$

At equilibrium:

$\hat{f}_a{}^v = \hat{f}_a{}^l$

$\varphi_a y_a P = \gamma_a x_a P^{sat}$

Assume ideal?

Suffix Margules or graphically

Antoine Equation

$$\hat{f}^v_i = \hat{f}^l_i$$

$$y_i \hat{\varphi}^v_i P = x_i \gamma^l_i f^o_i$$

$$y_i P = x_i \gamma_i P^{sat}_i \quad \text{Non-ideal}$$

If assume ideal solution, $\gamma_i = 0$

$$y_i P = x_i P^{sat}_i$$

(Raoult's Law)

Using Raoult's Law for Bubble Point/Dew Point Calculations

In a bubble-point calculation, the liquid-phase mole fractions of the system are specified and the vapor mole fractions are solved for. Solve for y_i

Antoine Equation

$$y_i P = x_i P_i^{\text{sat}}$$

Total pressure:

$$P = \sum y_i P = \sum x_i P_i^{\text{sat}} = x_1 P_1^{\text{sat}} + x_2 P_2^{\text{sat}} + x_3 P_3^{\text{sat}} + x_4 P_4^{\text{sat}}$$

in a dew-point calculation, the liquid mole fractions are determined given the vapor mole fractions. Solve for x_i

$$x_i = \frac{y_i P}{P_i^{\text{sat}}}$$

$$1 = \sum \frac{y_i P}{P_i^{\text{sat}}} = \frac{y_1 P}{P_1^{\text{sat}}} + \frac{y_2 P}{P_2^{\text{sat}}} + \frac{y_3 P}{P_3^{\text{sat}}} + \frac{y_4 P}{P_4^{\text{sat}}}$$

	Bubble point x_i known	Dew point y_i known
T known	Find y_i, P P_i^{sat} set	Find x_i, P P_i^{sat} set
P known	Find y_i, T P_i^{sat} unknown	Find x_i, T P_i^{sat} unknown

Pxy Material Balance
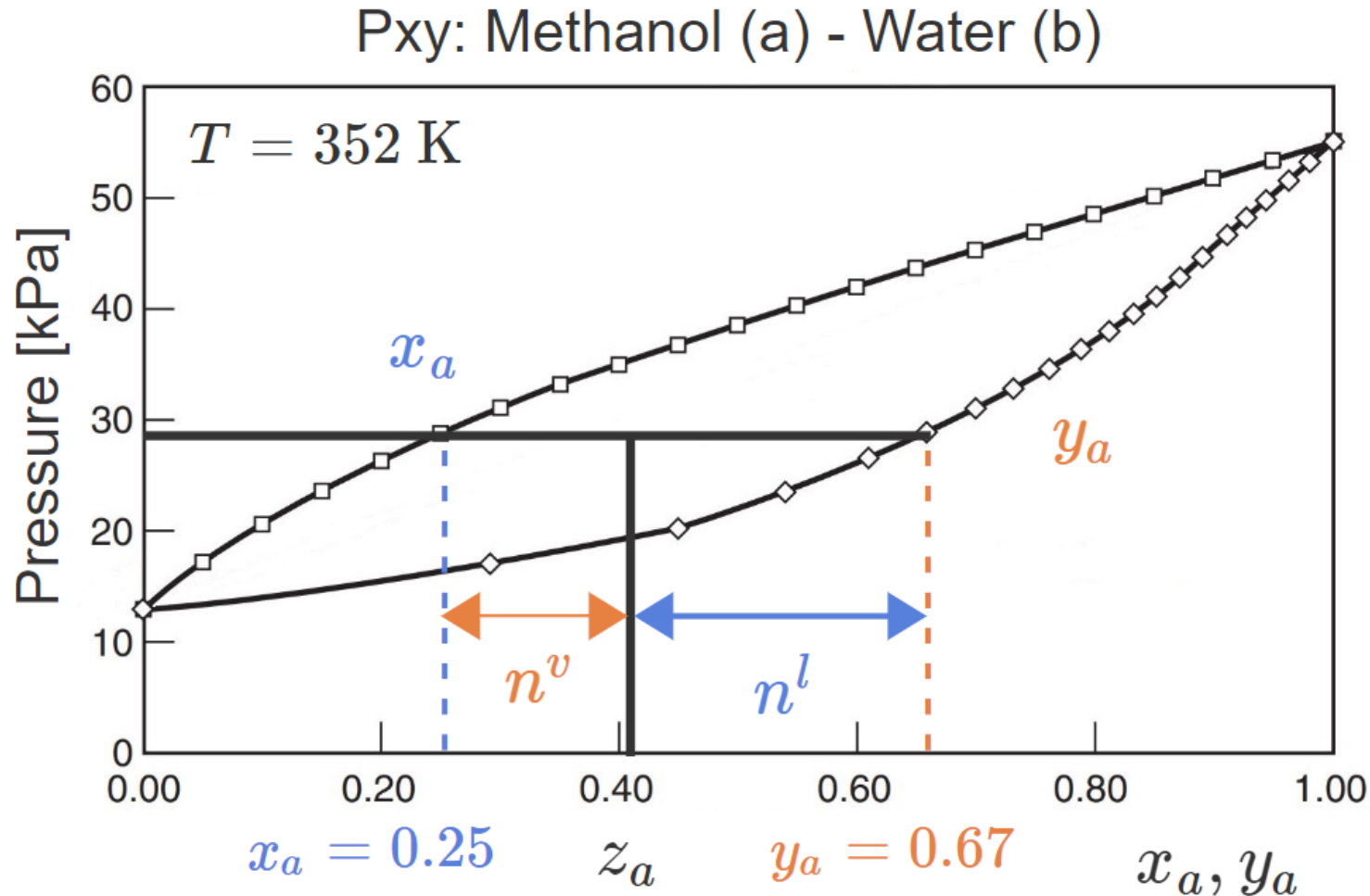
At 28 kPa and 352K and overall mole fraction for species a = 0.43, how many moles of gas and vapor?

Pxy: Methanol (a) - Water (b)

$T = 352$ K

x_a

y_a

n^v

n^l

$x_a = 0.25$ z_a $y_a = 0.67$ x_a, y_a

Total balance:

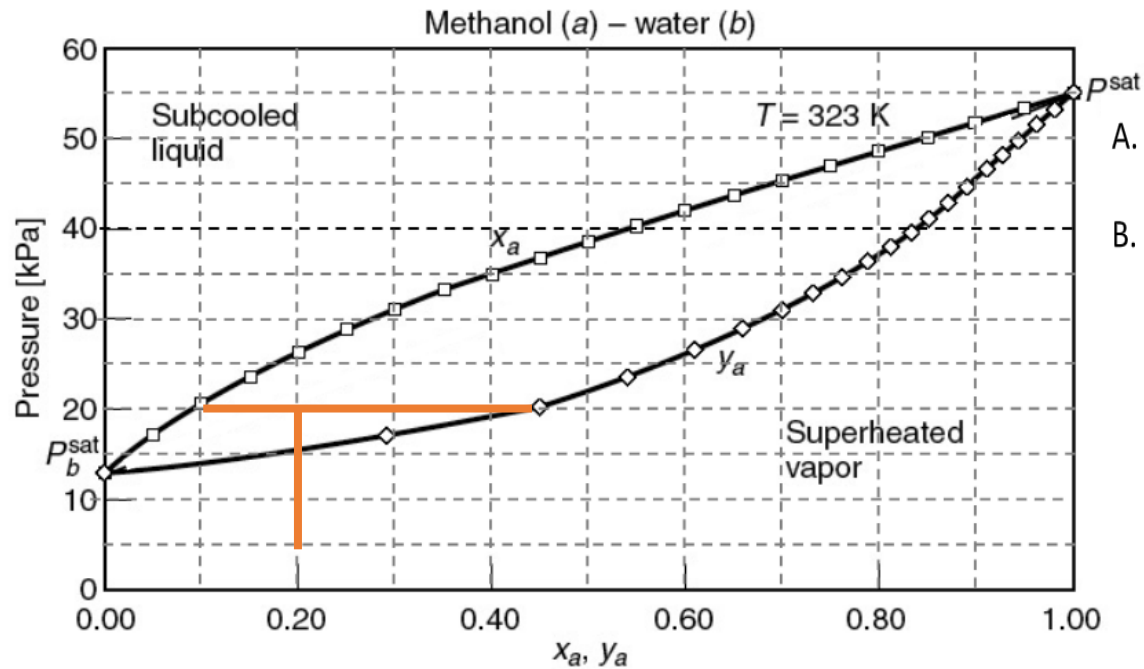$$n = n^v + n^l$$

Species a balance:

$$y_a n^v + x_a n^l = z_a n$$

Systems of equation

Methanol (a) – water (b)

Figure: Pressure–composition (x_a, y_a) diagram for the Methanol (a) – water (b) system at $T = 323\text{ K}$, showing subcooled liquid, superheated vapor regions, bubble curve (x_a) and dew curve (y_a), with P_a^{sat} and P_b^{sat} marked.

A. What is the pure species liquid fugacity of methanol? $f_a^l =$ ___55kPa___

B. What is the pure species liquid fugacity of water? $f_b^l =$ ___13kPa___

Question: 2 mol methanol, 8 mol water initially at 5 Kpa is compressed isothermally to 20 kPa

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What are the moles of vapor and liquid at this state?

At equilibrium with $z_a = 0.2$, $x_a = 0.1$ and $y_a = 0.45$

Overall balance:
$n_{total} = n^l + n^v \rightarrow$ $10 = n^l + n^v$

At composition:
$n_{total} = n^l + n^v \rightarrow z_a n_{total} = x_a n^l + y_a n^v \rightarrow$ $(0.2)(10) = 0.1(n^l) + 0.45(n^v)$

Solve:
n^v 2.86 and $n^l = 7.14$

How would I solve γ_a at this state?

$\hat{f}_a^v = \hat{f}_a^l$

$\varphi_a y_a P = \gamma_a x_a P^{sat}$

$\gamma_a = y_a P / x_a P^{sat} = (0.45 * 20)/(0.10 * 55) = 1.63$

Liquid-Liquid Equilibrium (LLE)

$$\hat{f}_a^\alpha = \hat{f}_a^\beta$$

$$x_a^\alpha \gamma_a^\alpha f_a = x_a^\beta \gamma_a^\beta f_a$$

$$x_a^\alpha \gamma_a^\alpha = x_a^\beta \gamma_a^\beta \qquad x_b^\alpha \gamma_b^\alpha = x_b^\beta \gamma_b^\beta$$

Difficult problem to solve!

If you know the equilibrium mole compositions but don't know A and B

$$\ln\left(\frac{x_a^\alpha}{x_a^\beta}\right) = \frac{1}{RT}(A + 3B)\left((x_b^\beta)^2 - (x_b^\alpha)^2\right) - 4B\left((x_b^\beta)^3 - (x_b^\alpha)^3\right)$$

$$\ln\left(\frac{x_b^\alpha}{x_b^\beta}\right) = \frac{1}{RT}(A - 3B)\left((x_a^\beta)^2 - (x_a^\alpha)^2\right) + 4B\left((x_a^\beta)^3 - (x_a^\alpha)^3\right)$$

If you know A and B for the activity coefficients but don't know the equilibrium mole fractions in each phase:

$$x_a^\alpha \exp\left[\frac{(A+3B)}{RT}(1 - x_a^\alpha)^2 - \frac{4B}{RT}(1 - x_a^\alpha)^3\right] = x_a^\beta \exp\left[\frac{(A+3B)}{RT}(1 - x_a^\beta)^2 - \frac{4B}{RT}(1 - x_a^\beta)^3\right]$$

and

$$(1 - x_a^\alpha)\exp\left[\frac{(A-3B)}{RT}(x_a^\alpha)^2 + \frac{4B}{RT}(x_a^\alpha)^3\right] = (1 - x_a^\beta)\exp\left[\frac{(A-3B)}{RT}(x_a^\beta)^2 + \frac{4B}{RT}(x_a^\beta)^3\right]$$

Concept Review

- *Fugacity* is a thermodynamic property used to meet the criterion for chemical equilibrium where chemical potential would otherwise have been too complex to describe real systems. Fugacity uses ideal references states and is equal to the pressure of an ideal state that would have the chemical potential of the real state.
- The vapor phase fugacity ideal reference is the ideal gas. There are many models that describe real gasses. It is a fudge factor that corrects for non-ideality of real gasses. This is shown by the *fugacity coefficient* which is the real gasses' deviation from an ideal gas. This coefficient is 1 for an ideal gas.
- The *Lewis-Fugacity Rule* is an approximation for fugacity in the vapor phase that suggests that all interactions are characterized by "like" interactions. There are 3 stipulations for this assumption.
- The liquid phase ideal fugacity references are the *Lewis-Randall* and *Henry's Law line*. These represent the ideal "like" and "unlike" interactions at $x_a \rightarrow 1$ and $x_a \rightarrow 0$. Fugacity can be thought of the tendency to escape the mixture or the "unhappiness" of the mixture, where a greater ideal Lewis-Randall or Henry's fugacity relative to the real fugacity is an overall *weaker* interaction.
- *Excess Gibb's energy* is a measure of the favorability of a mixture by describing the activity of all species in that mixture. The overall or relative activity coefficient for any species in the mixture can be described by the *Suffix-Margules* equations or graphically. An overall negative g^E means unlike interactions are greater in a mixture.
- Vapor-liquid equilibrium under ideal solution conditions gives *Raoult's Law,* which can be used to calculate either gas fraction or liquid fractions if the other is known or solve for total pressure

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