ChE 312 Final Exam Review

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Come to the front for practice exam ☺

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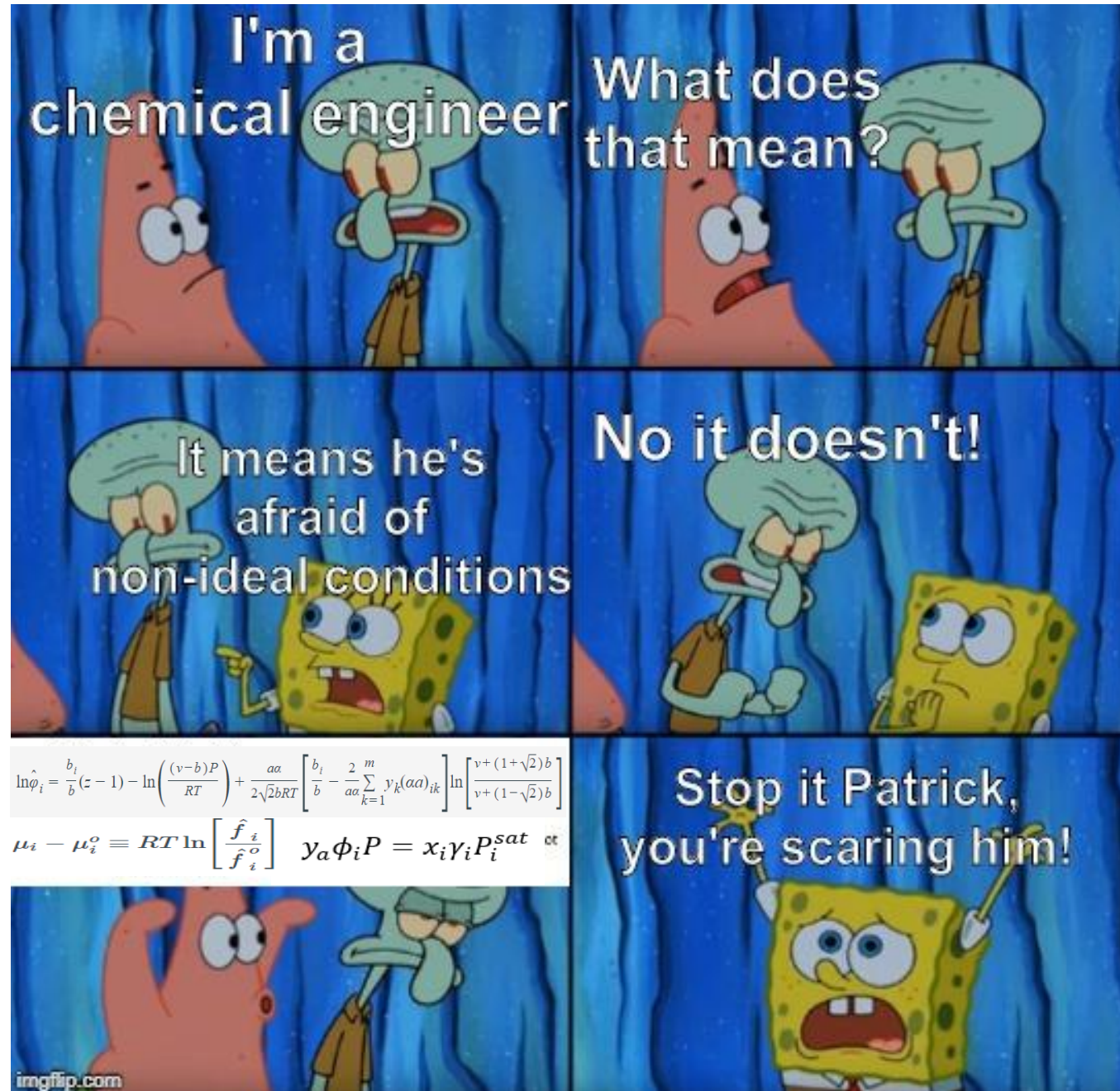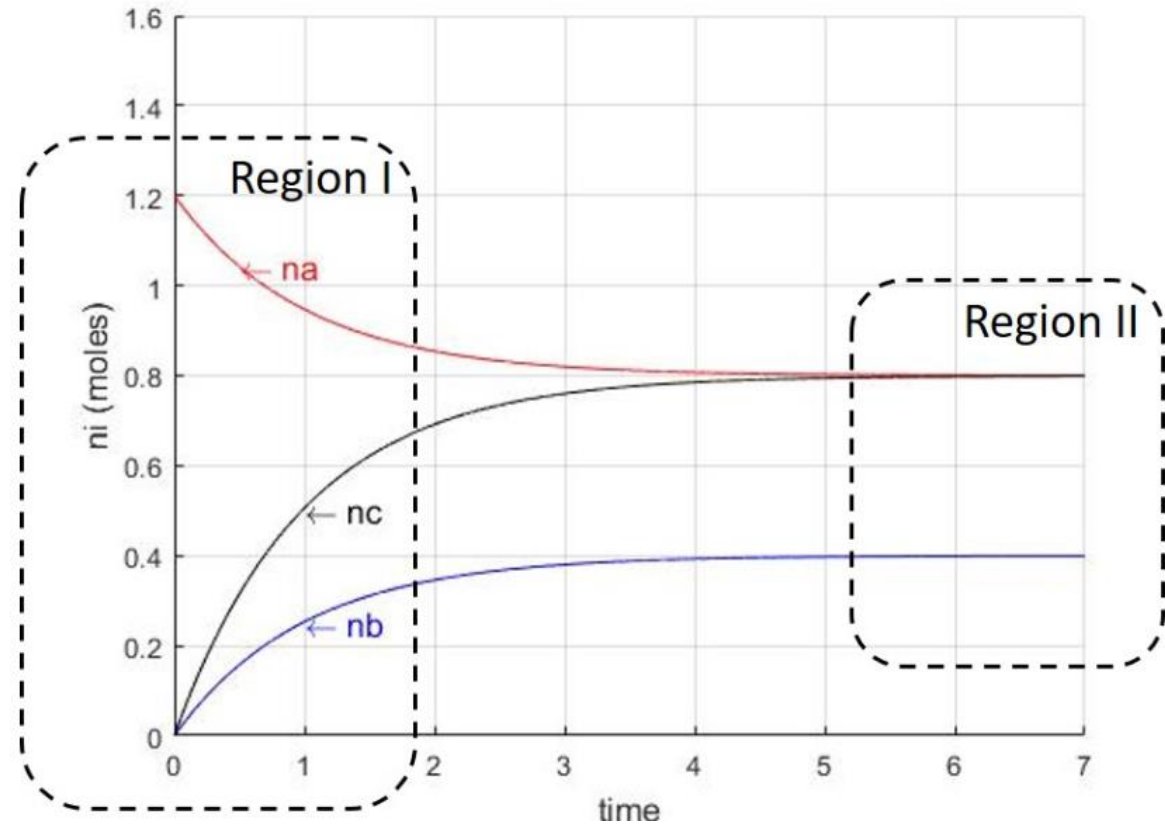
Chemical Reaction Equilibrium

The condition for equilibrium is the minimization of Gibb's energy

$$\frac{dG}{d\xi} = 0 = \sum \nu_i \mu_i$$

$$\mu_i = g_i^o + RT \ln \frac{\hat{f}_i}{f_i^o}$$

$$0 = \sum \nu_i \left[g_i^o + RT \ln \frac{\hat{f}_i}{f_i^o} \right]$$

$$\ln \prod \left(\frac{\hat{f}_i}{f_i^o} \right)^{\nu_i} = -\frac{\sum \nu_i g_i^o}{RT} \equiv -\frac{\Delta g_{rxn}^o}{RT}$$

Controlled by chemical kinetics, rate order, Arrhenius parameters, catalyst etc.

Thermodynamically controlled (most energetically and entropically favored state)

Chemical reaction equilibrium

$$K = \prod \left(\frac{\hat{f}_i}{f_i^o} \right)^{v_i} = \prod (y_i P)^{vi}$$

For gasses only

In general, K is the product multiple of each component partial pressures with respect to the power of their stoichiometric ratio. (products over reactants). Pure liquids and solids do not have this

$$K = \exp \left(-\frac{\Delta g_{rxn}^o}{RT} \right)$$

Function of only temperature. K equilibrium here is given at a constant temperature

$$\Delta g_{rxn}^o = \sum \nu_i g_i^o = \Delta h_{rxn}^o - T\Delta s_{rxn}^o$$

v_i is the stoichiometric coefficient. This is positive or negative depending if it is being produced or consumed

$$\ln \frac{K_2}{K_1} = -\frac{\Delta h_{rxn}^o}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta h_{rxn}^o = \sum v_i h_i^o$$

Temperature dependence of K. A reference K and temperature is needed (usually 298K). Assumes the enthalpy of reaction is independent of temperature and that heat capacity does not change. Δh_{rxn}^o = mcpdT

Equilibrium short cut methods

Multiplying the reaction coefficients by a factor raises the equilibrium constant by the same factor	$(vA + vB \rightarrow vC + vD)n$ $\qquad$ $K = K^n$ ½ A + ½ B → ½ C + ½ D $\qquad$ $K = K^{1/2}$ 3A + 3B → 3C + 3D $\qquad$ $K = K^3$
Reversing the reaction is simply taking the inverse of the equilibrium constant	A + B → C + D $\qquad$ $K = K$ C + D → A + B $\qquad$ $K = 1/K$
In a series of reactions, the overall equilibrium constant is the product of each reactant equilibrium constant	Rxn 1: A + B → C + D $\qquad$ $K = K_1$ Rxn 2: C + D → E $\qquad$ $K = K_2$ Overall rxn: A + B → E $\qquad$ $K_{overall} = K_1 \times K_2$
If solving for extent of a reaction in a case such as to the left, simply take the square root of both sides to simplify algebra	$$K = \frac{(x)^2}{(1-x)^2} \rightarrow K^{\frac{1}{2}} = \frac{x}{1-x}$$
If faced with complex equilibrium expression that has a very large K, it is assumed that the reaction proceeds to completion, so the extent of reaction is approximated to the limiting number of initial moles in reactants	Example $$\lim_{K \to +\infty} K = \text{large number} = \frac{(100 + \xi)^2}{(200 - \xi)^2(300 - \xi)}$$ $\xi \approx 199.999 \approx 200$

Determining K with gibb's

Given the following chemical reaction and thermodynamic data at 298 K

$$C_5H_{12} + 10H_2O \rightleftarrows 5CO_2 + 16H_2$$

A) <mark>Determine K at 298K</mark>

	Δh_f	Δg_f
C_5H_{12}	-146.54	-8.37
H_2O	-241.82	-228.57
CO_2	-393.51	-394.36
H_2O	0	0

Determining K with gibb's

Given the following chemical reaction and thermodynamic data at 298 K

$$C_5H_{12} + 10H_2O \rightleftharpoons 5CO_2 + 16H_2$$

A) Determine K at 298K

$$\Delta g_{rxn}^o = \sum \nu_i g_i^o$$

Δg_{rxn}^o = (-1)(-8.37)+(-10)(-228.57) + (5)(-394.36)+16(0)
= 322.26 kJ/mol = 3.2*10^5 J/mol

	Δh_f	Δg_f
C_5H_{12}	-146.54	-8.37
H_2O	-241.82	-228.57
CO_2	-393.51	-394.36
H_2O	0	0

$$K_{298} = \exp\left(-\frac{\Delta g_{rxn}^o}{RT}\right) = 3.23 \cdot 10^{-57}$$

Determining K at a new temperature

Given the following chemical reaction and thermodynamic data at 298 K

$$C_5H_{12} + 10H_2O \rightleftharpoons 5CO_2 + 16H_2$$

B) Determine K at 600K

	Δh_f	Δg_f
C_5H_{12}	-146.54	-8.37
H_2O	-241.82	-228.57
CO_2	-393.51	-394.36
H_2O	0	0

$K_{298} = 3.23 * 10^{-57}$

Determining K at a new temperature

Given the following chemical reaction and thermodynamic data at 298 K

$$C_5H_{12} + 10H_2O \rightleftharpoons 5CO_2 + 16H_2$$

	Δh_f	Δg_f
C_5H_{12}	-146.54	-8.37
H_2O	-241.82	-228.57
CO_2	-393.51	-394.36
H_2O	0	0

B) Determine K at 600K

$$\Delta h_{rxn}^o = \sum v_i h_i^o$$

Δh_{rxn}^o = (-1)(-146.54)+(-10)(-241.82) + (5)(-393.51)+16(0) =
597.19kJ/mol = 5.97*10⁵ J/mol

$$\ln \frac{K_2}{K_1} = -\frac{\Delta h_{rxn}^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_{600}}{K_{298}}\right) = -\frac{\Delta h_{rxn}^o}{R}\left(\frac{1}{600K} - \frac{1}{298K}\right)$$

K₂₉₈ = 3.23 * 10⁻⁵⁷

$$K_{600} = 1.58 \cdot 10^{-4}$$

Setting up K equilibrium expressions

$$C_5H_{12} + 10H_2O \rightleftharpoons 5CO_2 + 16H_2$$

C) Set up the equilibrium expression in terms of extent of reaction

$$K = \prod \left(\frac{\hat{f}_i}{f_i^\circ}\right)^{v_i} = \prod (y_iP)^{vi} = (y_aP)^{-1}(y_bP)^{-10}(y_cP)^5 (y_dP)^{16} = \frac{(y_cP)^5(y_dP)^{16}}{(y_aP)(y_bP)^{10}} = \frac{y_c^5 y_d^{16} P^{21}}{y_a y_b^{10} P^{11}} = \frac{y_c^5 y_d^{16}}{y_a y_b^{10}} P^{10} \qquad y_i = \frac{n_i}{n_{total}}$$

	A (C_5H_{12})	B (H_2O)	C (CO_2)	D (H_2)
Initial moles (n_o)				
Change (+vξ)				
Equilibrium Mole Balance ($n_i = n_o + v\xi$)				
Mole fraction $y_i = \dfrac{n_i}{n_{total}}$				

Setting up K equilibrium expressions

$$C_5H_{12} + 10H_2O \rightleftharpoons 5CO_2 + 16H_2$$

C) <mark>Set up the equilibrium expression in terms of extent of reaction</mark>

$$K = \prod \left(\frac{\hat{f}_i}{f_i^o}\right)^{v_i} = \prod (y_iP)^{v_i} = (y_aP)^{-1}(y_bP)^{-10}(y_cP)^5 (y_dP)^{16} = \frac{(y_cP)^5(y_dP)^{16}}{(y_aP)(y_bP)^{10}} = \frac{y_c^5 y_d^{16} P^{21}}{y_a y_b^{10} P^{11}} = \frac{y_c^5 y_d^{16}}{y_a y_b^{10}} P^{10} \qquad y_i = \frac{n_i}{n_{total}}$$

	A (C_5H_{12})	B (H_2O)	C (CO_2)	D (H_2)
Initial moles (n_o)	1	1	0	0
Change ($+v\xi$)	$-\xi$	-10ξ	$+5\xi$	$+16\xi$
Equilibrium Mole Balance ($n_i = n_o + v\xi$)	$n_a = 1 - \xi$	$n_b = 1 - 10\xi$	$n_c = 5\xi$	$n_d = 16\xi$
Mole fraction $y_i = \frac{n_i}{n_{total}}$	$\frac{1-\xi}{2+10\xi}$	$\frac{1-10\xi}{2+10\xi}$	$\frac{5\xi}{2+10\xi}$	$\frac{16\xi}{2+10\xi}$

$$K = \frac{\left(\dfrac{5\xi}{2+10\xi}\right)^5 \left(\dfrac{16\xi}{2+10\xi}\right)^{16}}{\left(\dfrac{1-\xi}{2+10\xi}\right)\left(\dfrac{1-10\xi}{2+10\xi}\right)^{10}} P^{10}$$

$$n_{total} = \sum n_i = 2 + 10\xi$$

Equilibrium expressions with series of reactions

Equation 1 : $C_5H_{12} + 10H_2O \Leftrightarrow 5CO_2 + 16H_2$

$$K_1 = \frac{y_c^5 y_d^{16}}{y_a y_b^{10}} P^{10}$$

Equation 2 : $CO_2 + H_2 \Leftrightarrow CO + H_2O$

D) <mark>Set up the equilibrium expression in terms of extent of reaction for both reactions</mark>

	A (C_5H_{12})	B (H_2O)	C (CO_2)	D (H_2)	E (CO)	
Initial moles (n_o)	1	1	0	0	0	
Change $(+\nu\xi)$	$-\xi_1$	$-10\xi_1$	$+5\xi_1$	$+16\xi_1$	$+\xi_2$	
Equilibrium Mole Balance ($n_i = n_o + \nu\xi$)	$n_a = 1 - \xi_1$	$n_b = 1 - 10\xi_1$	$n_c = 5\xi_1$	$n_d = 16\xi_1$	$n_e = \xi_2$	$n_{total} = \sum n_i = 2 + 10\xi$
Mole fraction $y_i = \dfrac{n_i}{n_{total}}$	$\dfrac{1-\xi_1}{2+10\xi_1}$	$\dfrac{1-10\xi_1}{2+10\xi_1}$	$\dfrac{5\xi_1}{2+10\xi_1}$	$\dfrac{16\xi_1}{2+10\xi_1}$	$\dfrac{\xi_2}{2+10\xi_1}$	

Equilibrium expressions with series of reactions

Equation 1 : $C_5H_{12} + 10H_2O \Leftrightarrow 5CO_2 + 16H_2$

$$K_1 = \frac{y_c^5 y_d^{16}}{y_a y_b^{10}} P^{10} = \frac{\left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi_1}\right)^5 \left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi_1}\right)^{16}}{\left(\dfrac{1 - \xi_1}{2 + 10\xi_1}\right)\left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi_1}\right)^{10}} P^{10}$$

Equation 2 : $CO_2 + H_2 \Leftrightarrow CO + H_2O$

$$K_2 = \frac{y_e y_b}{y_c y_d} = \frac{\left(\dfrac{\xi_2}{2 + 10\xi_1}\right)\left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi_1}\right)}{\left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi_1}\right)\left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi_1}\right)}$$

D) <mark>Set up the equilibrium expression in terms of extent of reaction for both reactions</mark>

	A (C_5H_{12})	B (H_2O)	C (CO_2)	D (H_2)	E (CO)	
Initial moles (n_o)	1	1	0	0	0	
Change ($+\nu\xi$)	$-\xi_1$	$-10\xi_1 + \xi_2$	$+5\xi_1 - \xi_2$	$+16\xi_1 - \xi_2$	$+\xi_2$	
Equilibrium Mole Balance ($n_i = n_o + \nu\xi$)	$n_a = 1 - \xi_1$	$n_b = 1 - 10\xi_1 + \xi_2$	$n_c = 5\xi_1 - \xi_2$	$n_d = 16\xi_1 - \xi_2$	$n_e = \xi_2$	$n_{total} = \sum n_i = 2 + 10\xi$
Mole fraction $y_i = \dfrac{n_i}{n_{total}}$	$\dfrac{1 - \xi_1}{2 + 10\xi_1}$	$\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi_1}$	$\dfrac{5\xi_1 - \xi_2}{2 + 10\xi_1}$	$\dfrac{16\xi_1 - \xi_2}{2 + 10\xi_1}$	$\dfrac{\xi_2}{2 + 10\xi_1}$	

Equilibrium expressions with series of reactions

Equation 1 : $C_5H_{12} + 10H_2O \Leftrightarrow 5CO_2 + 16H_2$

$$K_1 = \frac{y_c^5 y_d^{16}}{y_a y_b^{10}} P^{10} = \frac{\left(\frac{5\xi_1 - \xi_2}{2 + 10\xi}\right)^5 \left(\frac{16\xi_1 - \xi_2}{2 + 10\xi}\right)^{16}}{\left(\frac{1 - \xi}{2 + 10\xi}\right) \left(\frac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)^{10}} P^{10}$$

Equation 2 : $CO_2 + H_2 \Leftrightarrow CO + H_2O$

$$K_2 = \frac{y_e y_b}{y_c y_d} = \frac{\left(\frac{\xi_2}{2 + 10\xi}\right) \left(\frac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)}{\left(\frac{5\xi_1 - \xi_2}{2 + 10\xi}\right) \left(\frac{16\xi_1 - \xi_2}{2 + 10\xi}\right)}$$

E) What is the overall K expression for this series of reaction?

$K_{overall} = K_1 \times K_2 =$

$$K_{overall} =$$

Equilibrium expressions with series of reactions

Equation 1 : $C_5H_{12} + 10H_2O \Leftrightarrow 5CO_2 + 16H_2$

$$K_1 = \frac{y_c^5 y_d^{16}}{y_a y_b^{10}} P^{10} = \frac{\left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi}\right)^5 \left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi}\right)^{16}}{\left(\dfrac{1 - \xi}{2 + 10\xi}\right) \left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)^{10}} P^{10}$$

Equation 2 : $CO_2 + H_2 \Leftrightarrow CO + H_2O$

$$K_2 = \frac{y_e y_b}{y_c y_d} = \frac{\left(\dfrac{\xi_2}{2 + 10\xi}\right) \left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)}{\left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi}\right) \left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi}\right)}$$

E) What is the overall K expression for this series of reaction?

$$K_{overall} = K_1 \times K_2 = \frac{\left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi}\right)^{\cancel{5}} \left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi}\right)^{\cancel{16}}}{\left(\dfrac{1 - \xi}{2 + 10\xi}\right) \left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)^{\cancel{10}}} P^{10} \frac{\left(\dfrac{\xi_2}{2 + 10\xi}\right) \left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)}{\left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi}\right) \left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi}\right)}$$

$$K_{overall} = \frac{\left(\dfrac{\xi_2}{2 + 10\xi}\right) \left(\dfrac{5\xi_1 - \xi_2}{2 + 10\xi}\right)^4 \left(\dfrac{16\xi_1 - \xi_2}{2 + 10\xi}\right)^{15}}{\left(\dfrac{1 - \xi}{2 + 10\xi}\right) \left(\dfrac{1 - 10\xi_1 + \xi_2}{2 + 10\xi}\right)^9} P^{10}$$

Multiphase reactions

Recall the criterion for chemical equilibria:

$$K = \prod \left(\frac{\hat{f}_i}{f_i^o} \right)^{\nu_i}$$

Recall that the fugacity of the species $\left(\frac{f_i}{f_i^o} \right)$ is dependent on its phase
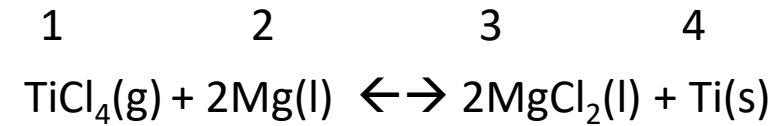
$$\left(\frac{f_i}{f_i^o} \right)^{\nu}_{vapor} = (y_i P)^{\nu}$$

$$\left(\frac{f_i}{f_i^o} \right)^{\nu}_{liquid} = (x_i \gamma_i)^{\nu}$$

$$\left(\frac{f_i}{f_i^o} \right)^{\nu}_{solid} = (X_i \Gamma_i)^{\nu}$$

Solid phase mole fraction

Solid phase activity coefficient

$$\begin{array}{cccc} 1 & 2 & 3 & 4 \end{array}$$

$$TiCl_4(g) + 2Mg(l) \longleftrightarrow 2MgCl_2(l) + Ti(s)$$

$$K = \left(\frac{f_1}{f_1^o} \right)^{-1} \left(\frac{f_2}{f_2^o} \right)^{-2} \left(\frac{f_3}{f_3^o} \right)^{2} \left(\frac{f_4}{f_4^o} \right)^{1}$$

Ideal vapor   liquid   liquid   solid

$$K = (y_1 P)^{-1} (x_2 \gamma_2)^{-2} (x_3 \gamma_3)^{2} (X_4 \Gamma_4)^{1}$$

Multiphase reactions

1   2   3   4

$TiCl_4(g) + 2Mg(l) \longleftrightarrow 2MgCl_2(l) + Ti(s)$
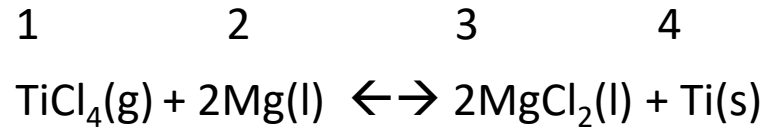
$$K = \left(\frac{f_1}{f_1^o}\right)^{-1} \left(\frac{f_2}{f_2^o}\right)^{-2} \left(\frac{f_3}{f_3^o}\right)^{2} \left(\frac{f_4}{f_4^o}\right)^{1}$$

Ideal vapor | liquid | liquid | solid

$$K = (y_1 P)^{-1}(x_2\gamma_2)^{-2}(x_3\gamma_3)^2 (X_4\Gamma_4)^1$$

$$K = \frac{(x_3\gamma_3)^2 X_4\Gamma_4}{(y_1 P)(x_2\gamma_2)^2}$$

-There is only one vapor component, so $y_1 = 1$
-There is only one solid component so $X_4 = 1$. if $X_4 = 1$, then the solid solution is pure solid, and the activity coefficient Γ_4 is ideal = 1

$$K = \frac{(x_3\gamma_3)^2}{(x_2\gamma_2)^2 P}$$

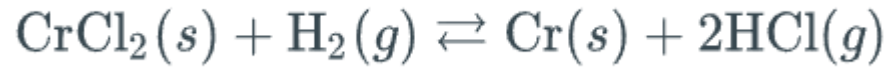Assuming non-ideal liquid, would need activity coefficients

$$K = \frac{(x_3)^2}{(x_2)^2 P}$$

Assuming ideal liquid

	$TiCl_4$	Mg	$MgCl_2$	Ti
Initial moles (n_o)	n_i	n_i	0	0
Change $(+\nu\xi)$	$-\xi$	-2ξ	$+2\xi$	$+\xi$
Equilibrium Mole Balance ($n_i = n_o + \nu\xi$)	$n_i - \xi$	$n_i - 2\xi$	2ξ	ξ
Liquid mole fraction $x_i = \frac{n_i}{n_{total}}$	$\frac{n_i - \xi}{n_i - \xi}$	$\frac{n_i - \xi}{n_i}$	$\frac{2\xi}{n_i}$	$\frac{\xi}{\xi}$

The equilibrium total moles belongs to its respective phase. The mole fractions are then calculated with respect to its phase, x_i, y_i, or X_i. This equilibrium only depends on liquid mole fraction. n_{tot} = liquid moles

Example

$$CrCl_2(s) + H_2(g) \rightleftharpoons Cr(s) + 2HCl(g)$$

	CrCl$_2$	H$_2$	Cr	HCl
Initial moles (n$_o$)	1	1	0	0
Change (+νξ)	-ξ	-ξ	+ξ	+2ξ
Equilibrium Mole Balance (n$_i$ = n$_o$ + νξ)	n$_a$= 1 - ξ	n$_b$= 1 - ξ	n$_c$= ξ	n$_d$= 2ξ
Mole fraction $y_i = \dfrac{n_i}{n_{total}}$	$\dfrac{1-\xi}{1+\xi}$	$\dfrac{1-\xi}{1+\xi}$	$\dfrac{\xi}{1+\xi}$	$\dfrac{2\xi}{1+\xi}$

$$n_{total} = \sum n_i = 1 + \xi$$

Only gasses considered in total moles

$$K = \frac{(X_{Cr}\Gamma_{Cr})y_{HCL}^2}{(X_{CrCl_2}\Gamma_{CrCl_2})y_{H2}}P = \frac{y_{HCL}^2}{y_{H2}}P = \frac{4\xi^2}{(1+\xi)(1-\xi)}P$$

Only gasses affect the equilibrium

Assuming Cr and CrCl$_2$ separate and form pure solid solutions

Another multiphase example

$$K = \frac{(y_D P)^2 (x_E \gamma_E)^4 X_F \Gamma_F}{(y_A P)(x_B \gamma_B)^2 (X_C \Gamma_C)^2}$$

$A_{(gas)} + 2B_{(liquid)} + 2C_{(solid)} \longleftrightarrow 2D_{(gas)} + 4E_{(liquid)} + F_{(solid)}$
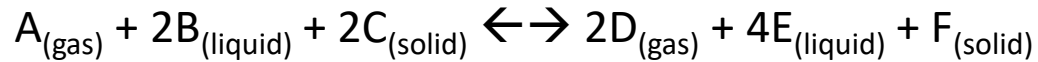
	A	B	C	D	E	F
Initial moles (n_o)	1	1	1	0	0	0
Change $(+\nu\xi)$	$-\xi$	-2ξ	-2ξ	$+2\xi$	$+3\xi$	$+\xi$
Equilibrium Mole Balance $(n_i = n_o + \nu\xi)$	$1-\xi$	$1-2\xi$	$1-2\xi$	2ξ	4ξ	ξ
Mole fraction (x_i, y_i, X_i) $= \dfrac{n_i}{n_{total}}$	$\dfrac{1-\xi}{1+\xi}$	$\dfrac{1-2\xi}{1+2\xi}$	$\dfrac{1-2\xi}{1-2\xi}$	$\dfrac{2\xi}{1+\xi}$	$\dfrac{4\xi}{1+2\xi}$	$\dfrac{\xi}{\xi}$

$$K = \frac{\left(\frac{2\xi}{1+\xi}P\right)^2 \left(\frac{4\xi}{1+2\xi}\gamma_E\right)^4 \cancel{\frac{\xi}{\xi}\Gamma_F}}{\left(\frac{1-\xi}{1+\xi}P\right)\left(\frac{1-2\xi}{1+2\xi}\gamma_B\right)^2 \left(\cancel{\frac{1-2\xi}{1-2\xi}\Gamma_C}\right)^2}$$

$$K = \frac{\left(\frac{2\xi}{1+\xi}P\right)^2 \left(\frac{4\xi}{1+2\xi}\gamma_E\right)^4}{\left(\frac{1-\xi}{1+\xi}P\right)\left(\frac{1-2\xi}{1+2\xi}\gamma_B\right)^2}$$

This equilibrium depends on liquid **and** gas mole fractions

$n_{\text{total gas}} = 1+\xi$
$n_{\text{total liquid}} = 1 + 2\xi$
$n_{\text{total solid C}} = 1 - 2\xi$
$n_{\text{total solid F}} = \xi$

Solids C and F do not mix and are in separate solid states. Pure solids are ideal "solutions"

LeChatelier's Principle

$$K = \frac{y_{HCL}^2}{y_{H_2}}P = \frac{4\xi^2}{(1+\xi)(1-\xi)}P$$

$$\mathrm{CrCl_2}(s) + \mathrm{H_2}(g) \rightleftarrows \mathrm{Cr}(s) + 2\mathrm{HCl}(g)$$

$\Delta h_{rxn}^o = +$

Disturbance	Response	Conceptual interpretation	Mathematical interpretation
Adding more H$_2$	Shift right	Adding more reactant, shift towards product to re-establish equilibrium. Temporarily decreased K, will need to create more product to re-stablish K (Le Chatelier's principle)	$y_{H_2}K = y_{HCL}^2P$ Adding y$_{H2}$ increases y$_{HCL}$
Adding more HCl	Shift left	Adding more product, shift towards reactant to re-establish equilibrium (Le Chatelier's principle	$\frac{K}{y_{HCL}^2} = \frac{1}{y_{H_2}}P$ Adding y$_{HCL}$ increases y$_{H2}$
Add Cr	Nothing	Solids do not affect partial pressure, thus not included in equilibrium expression	$K = \frac{y_{HCL}^2}{y_{H_2}}P = \frac{y_{HCL}^2}{y_{H_2}}P$ no change
Remove H$_2$	Shift left	Removed reactant, produces more reactant to re-establish equilibrium	$y_{H_2}K = y_{HCL}^2P$ decreasing y$_{H2}$ increase K, so the reaction must create more H$_2$ to reverse this
Increase Pressure	Shift left	This system prefers to have more moles of gas as products, but increasing the pressure will make it "too crowded" so it will favor reactants	$\frac{K}{P} = \frac{y_{HCL}^2}{y_{H_2}}$ Increase in pressure will decrease y$_{HCL}$
Increase Temperature	Shift right	Bonds breaking (reactants) favored over bonds forming (products) because endothermic. Thus, shift reaction towards product when heat is added	Endothe... T, K$_1$ < K$_2$ $\ln\frac{K_2}{K_1} = -\frac{\Delta h_{rxn}^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$

LeChatelier's Principle

A + B → C + D $$K = \frac{[C][D]}{[A][B]} \qquad Q = \frac{(C)(D)}{(A)(B)}$$
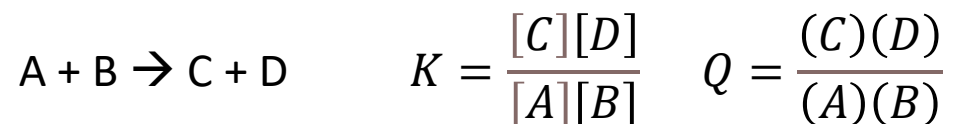
Reaction quotient Q, is the current state of the reaction outside of equilibrium ( ). Only has significance to inform the position of the equilibrium relative to K [ ]. Q = K at equilibrium

How to increase conversion/increase extent of reaction/favor the forward reaction	Action	Implication
A + B → C + D	Add more reactants	Adding more reactants will leave Q < K temporarily, so more products will form to reach equilibrium Q = K
A + B → C + D	Take out products as they form	Taking products will leave Q < K temporarily, so more products will form to reach equilibrium Q = K
If endothermic Heat+ A + B → C + D Δh^o_{rxn} = +	Increase the temperature	Increasing temperature will need to increase K which is possible only by increasing product formation
If exothermic A + B → C + D + Heat Δh^o_{rxn} = -	Decrease the temperature	Decreasing temperature will need to increase K which is possible only by increasing product formation
If more moles gas in products $A_{(g)}$ + $B_{(g)}$ → $2C_{(g)}$ + $D_{(g)}$	Decrease the pressure	See previous slide
If more moles gas in reactants $A_{(g)}$ + $2B_{(g)}$ → $C_{(g)}$ + $D_{(g)}$	Increase the pressure	See previous slide

Review of Earlier Term

Gas mixtures

Non-ideal gasses

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

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

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

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.

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
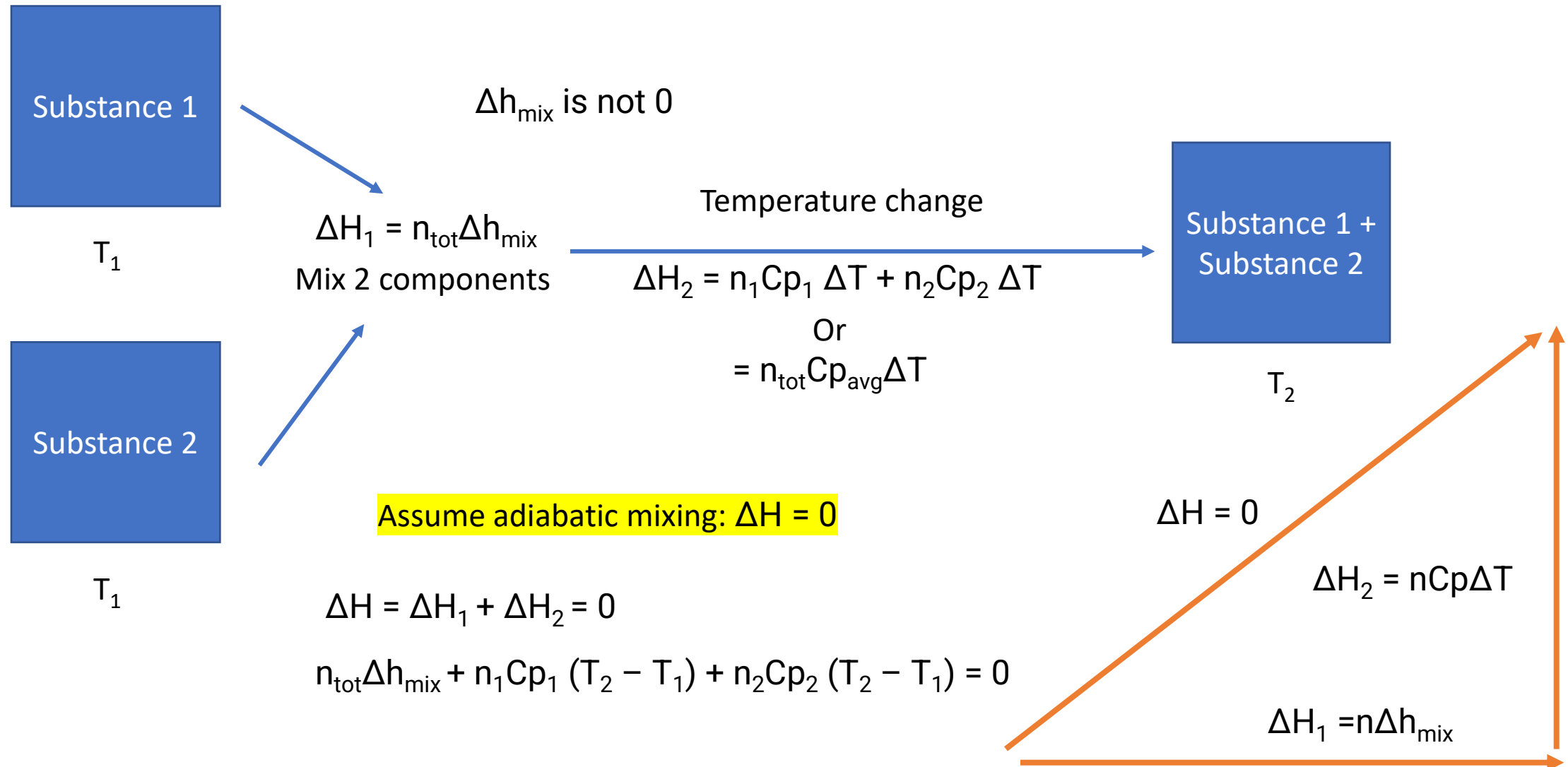temperature and pressure and Lee-Kesler Tables)

Non-ideal liquid mixtures

Activity Coefficient is *not* 1

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

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	$x_a x_b \left[A + B \left(x_a - x_b \right) \right]$	$(A + 3B)x_b^2 - 4Bx_b^3$	$(A - 3B)x_a^2 + 4Bx_a^3$
(or) Three-suffix Margules	$x_a x_b \left[A_{ba} x_a + A_{ab} x_b \right]$	$x_b^2 \left[A_{ab} + 2 \left(A_{ba} - A_{ab} \right) x_a \right]$	$x_a^2 \left[A_{ba} + 2 \left(A_{ab} - A_{ba} \right) x_b \right]$
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	$-RT \begin{bmatrix} x_a \ln \left(x_a + \Lambda_{ab} x_b \right) + \\ x_b \ln \left(x_b + \Lambda_{ba} x_a \right) \end{bmatrix}$	$-RT \begin{bmatrix} \ln \left(x_a + \Lambda_{ab} x_b \right) + \\ x_b \left(\dfrac{\Lambda_{ba}}{x_b + \Lambda_{ba} x_a} - \dfrac{\Lambda_{ab}}{x_a + \Lambda_{ab} x_b} \right) \end{bmatrix}$	$-RT \begin{bmatrix} \ln \left(x_b + \Lambda_{ba} x_a \right) + \\ x_a \left(\dfrac{\Lambda_{ab}}{x_a + \Lambda_{ab} x_b} - \dfrac{\Lambda_{ba}}{x_b + \Lambda_{ba} x_a} \right) \end{bmatrix}$
NRTL[*]	$RT x_a x_b \left[\dfrac{\tau_{ba} G_{ba}}{x_a + x_b G_{ba}} + \dfrac{\tau_{ab} G_{ab}}{x_b + x_a G_{ab}} \right]$	$RT x_b^2 \left[\dfrac{\tau_{ba} G_{ba}^2}{\left(x_a + x_b G_{ba} \right)^2} + \dfrac{\tau_{ab} G_{ab}}{\left(x_b + x_a G_{ab} \right)^2} \right]$	$RT x_a^2 \left[\dfrac{\tau_{ba} G_{ba}}{\left(x_a + x_b G_{ba} \right)^2} + \dfrac{\tau_{ab} G_{ab}^2}{\left(x_a + x_b G_{ab} \right)^2} \right]$

Non-ideal liquid mixtures

Substance 1

T_1

Substance 2

T_1

Δh_{mix} is not 0

$\Delta H_1 = n_{tot}\Delta h_{mix}$

Mix 2 components

Temperature change

$\Delta H_2 = n_1 Cp_1 \, \Delta T + n_2 Cp_2 \, \Delta T$

Or

$= n_{tot} Cp_{avg} \Delta T$

Substance 1 + Substance 2

T_2

Assume adiabatic mixing: ΔH = 0

$\Delta H = \Delta H_1 + \Delta H_2 = 0$

$n_{tot}\Delta h_{mix} + n_1 Cp_1 \, (T_2 - T_1) + n_2 Cp_2 \, (T_2 - T_1) = 0$

$\Delta H = 0$

$\Delta H_2 = nCp\Delta T$

$\Delta H_1 = n\Delta h_{mix}$

Temperature and Phase Changes

*For mixtures, assume average heat capacity and enthalpy of vaporization
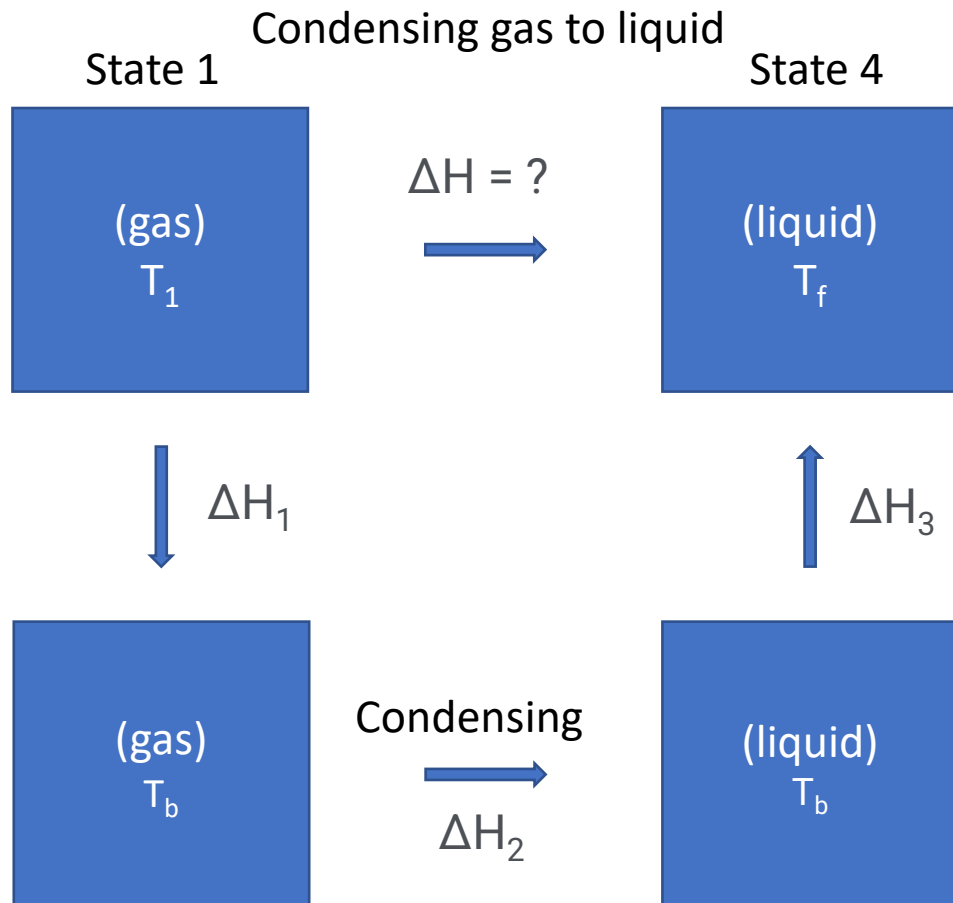
$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

$\Delta H = nCp_{gas}\Delta T + n\Delta h_{cond} + nCp_{liq}\Delta T$

$\Delta H = n(Cp_{gas}(T_b - T_2) + \Delta h_{cond} + Cp_{liq}(T_f - T_b))$

Condensing gas to liquid

State 1

State 4

(gas)
T_1

$\Delta H = ?$

(liquid)
T_f

ΔH_1

ΔH_3

(gas)
T_b

Condensing

(liquid)
T_b

ΔH_2

T_1

T_b

T_f

State 1

$\Delta H_1 = nCp_{gas}\Delta T$

$\Delta H_2 = n\Delta h_{cond}$

$\Delta H_3 = nCp_{liq}\Delta T$

State 2
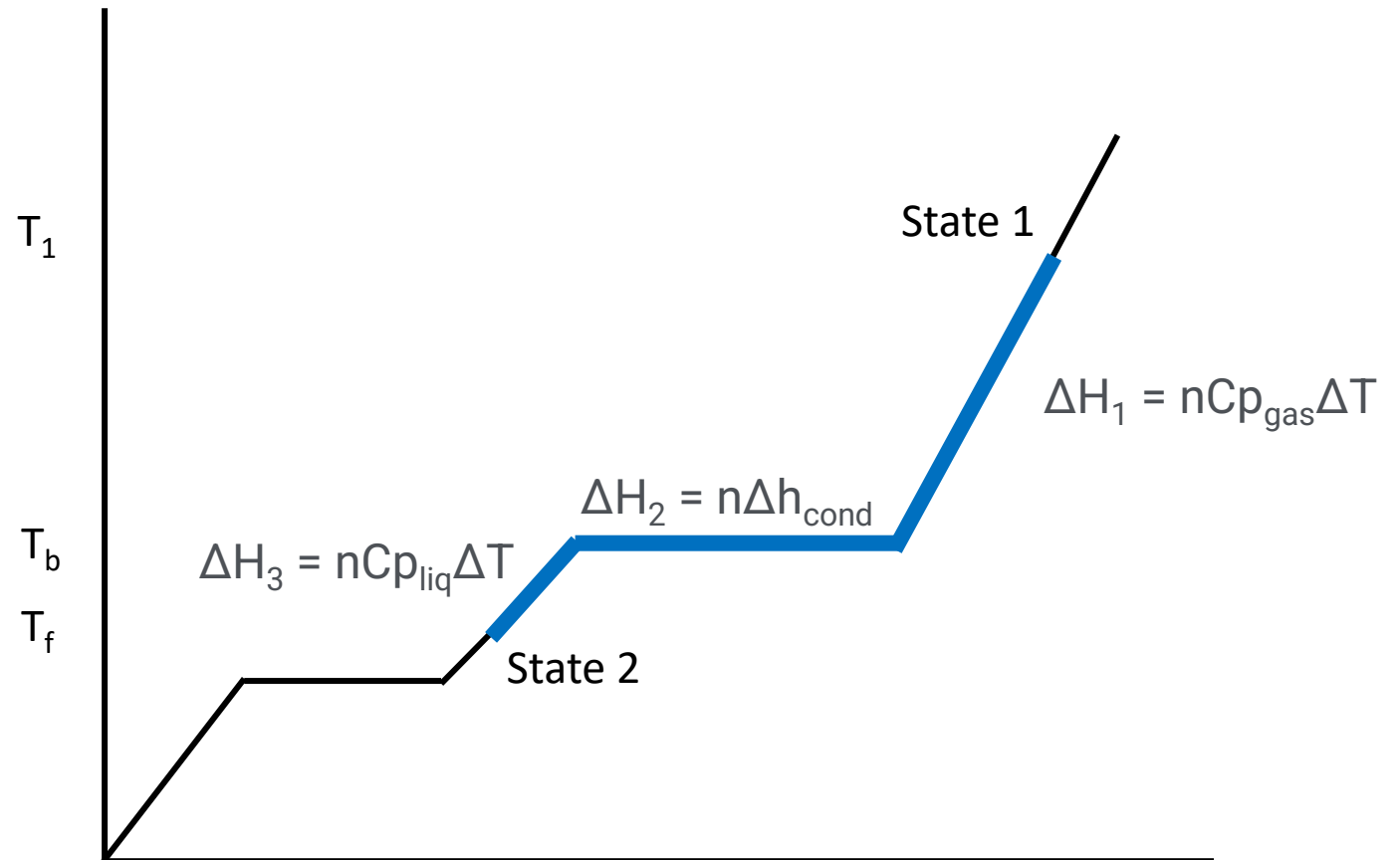
Ideal Solution/Mixture

No molecular interactions between molecules (similar to ideal gasses), thus $\Delta h_{mix} = \Delta v_{mix} = 0$

More importantly, $\gamma_i = 1$

$\Delta s_{mix}^{ideal} = -R \sum_{i=1}^{m} y_i \ln y_i$ Overall molar entropy of mixing

$\Delta S_{mix,1}^{ideal} = -R\ln(y)$ Partial molar entropy of mixing

Entropy of mixing will always be positive for an ideal mixture as there are more molecular configurations in a mixture compared to a pure species

$\Delta H = \Delta U + \Delta PV$
$\Delta H_{mix} = 0$

$\Delta \bar{G}_{mix,1} = \Delta \overline{H}_{mix,1} - T\Delta \bar{S}_{mix,1}$
$\Delta \bar{G}_{mix,1} = -T\Delta \bar{S}_{mix,1}$

$\Delta \bar{G}_{mix,1}^{ideal} = RT\ln(y_1)$ Partial molar Gibbs of mixing

$\Delta g_{mix}^{ideal} = RT \sum x_i \ln(x_i)$ Overall molar Gibbs of mixing

Notice resemblance between partial molar and molar properties for ideal solution

Partial Molar properties

Example) how do I go to some mixing property to partial molar property?

Given $\Delta k_{mix,}$ for a mixture, find $\overline{K}_i$

$$\Delta k_{mix,} \rightarrow \Delta K_{mix,} \rightarrow \overline{\Delta K}_{mix,i} \rightarrow \overline{K}_i$$

$$n_{tot}\Delta k_{mix} = \Delta K_{mix} \qquad \left(\frac{\partial \Delta K_{mix}}{\partial n_i}\right)_{T,P,n_i} = \overline{\Delta K}_{mix,i} \qquad \overline{\Delta K}_{mix,i} = \overline{K}_i - k_i$$

$$\left(\frac{\partial \Delta K_{mix}}{\partial n_i}\right)_{T,P,n_i} = \overline{\Delta K}_{mix,i}$$

$$\left(\frac{\partial \Delta H_{mix}}{\partial n_i}\right)_{T,P,n_i} = \overline{\Delta H}_{mix,l}$$

$$\begin{cases} K(H,V,G,S,\dots) & Extensive\ probertie s \\ k(h,v,g,s,\dots) & Molar\ properties \\ \overline{K}_i = \dfrac{dK}{dn_i} & Partial\ molar\ property \end{cases}$$

Example

Exam 1 question 10:
Determine the partial molar enthalpy of mixing of water in a mixture of water
and butanol, given that $\Delta h_{mix} = -2239 x_B x_W$

$\Delta h_{mix} = -2239 x_B x_W$

$$\Delta h_{mix} n_T = \Delta H_{mix}$$

$$\Delta H_{mix} = -2239 \, x_b x_w \, \boxed{n_T} \rightarrow \Delta h_{mix} = -2239 \left(\frac{n_w}{n_T}\right)\left(\frac{n_B}{n_T}\right) n_T =$$

$$\Delta H_{mix} = -2239 \, n_w n_B \left(\frac{1}{n_B + n_w}\right)$$

$$\Delta \overline{H}_{mix,w} = \left(\frac{\partial \Delta H_{mix}}{\partial n_w}\right)_{T,P,n_B}$$

$$\Delta \overline{H}_{mix_w} = \frac{\partial}{\partial n_w}\left(-2239 \, n_w \frac{n_B}{n_B + n_w}\right) = -2239 \, n_B \frac{\partial}{\partial n_w}\left(\frac{n_w}{n_B + n_w}\right)_{P,T,n_B}$$

$$= -2239 \, n_B \frac{(n_B + n_w) - n_w}{(n_B + n_w)^2} = -2239 \, n_B^2 \frac{1}{n_T^2} = \boxed{-2239 \, x_B^2 = \Delta \overline{H}_{mix_w}}$$

K^E Excess properties

Excess property is any thermodynamic property which is the difference of the real value and the hypothetical value it would have in an ideal solution

$$k^E \equiv k(T, P, x_i) - k^{ideal}(T, P, x_i)$$

$$g^E = \Delta g_{mix} - \Delta g_{mix}^{ideal}$$

$$s^E = \Delta s_{mix} - \Delta s_{mix}^{ideal}$$

$$v^E = \Delta v_{mix} - \Delta v_{mix}^{ideal}$$

$$h^E = \Delta h_{mix} - \Delta h_{mix}^{ideal}$$

$$v^E = \Delta v_{mix}$$

$$h^E = \Delta h_{mix}$$

$$g^E = Ax_a x_b$$

A negative g^E means the unlike interactions are stronger and the mixture is favorable!

Ideal mix, $\Delta h_{mix} = \Delta v_{mix} = 0$

$$\Delta g_{mix}^{ideal} = RT\, \Sigma x_i \ln(x_i)$$

$$\Delta s_{mix}^{ideal} = -R \sum_{i=1}^{m} y_i \ln y_i$$

We know that

$$\Delta s_{mix}^{ideal} = -R \sum_{i=1}^{m} y_i \ln y_i$$

Difficult to solve Δs_{mix} for a real mixture because Δv_{mix} changes. If you know h$_{mix}$ and g^E, can estimate the **molar excess entropy s^E** by assuming an ideal mixture

$$g^E = h^E - Ts^E$$

$$g^E = \Delta h_{mix} - Ts^E \qquad \text{True for an ideal mixture}$$

K^E Excess properties relationships

$$k^E \equiv k(T, P, x_i) - k^{ideal}(T, P, x_i)$$

$$v^E = v(T, P, x_i) - v^{ideal}(T, P, x_i)$$

$$h^E = h(T, P, x_i) - h^{ideal}(T, P, x_i)$$

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

$$\overline{K}_i^E \equiv \left(\frac{\partial (nk^E)}{\partial n_i} \right)_{T,P,n_{j\neq i}} = \left(\frac{\partial (K - K^{ideal})}{\partial n_i} \right)_{T,P,n_{j\neq i}} = \overline{K}_i - \overline{K}_i^{ideal}$$

$$\overline{V}_i^E = \overline{V}_i - \overline{V}_i^{ideal}$$

$$\overline{H}_i^E = \overline{H}_i - \overline{H}_i^{ideal}$$

$$\overline{G}_i^E = \overline{G}_i - \overline{G}_i^{ideal}$$

How to relate excess molar properties to other properties.

Example: how are excess partial molar entropy related to other partial molar properties?

finding $\bar{S}_A$ (partial molar entropy of "a") from g^E and h_{mix}

assume: $g^E = A x_a x_b$ and $\Delta h_{mix} = B x_a x_b$

$$g^E = h^E - T s^E \longrightarrow g^E = \Delta h_{mix} - T s^E$$

$$s^E = \frac{\Delta h_{mix}}{T} - \frac{g^E}{T} \longrightarrow s^E = \frac{B x_a x_b}{T} - \frac{A x_a x_b}{T}$$

$$s^E = \frac{(B-A)}{T} x_a x_b$$

intensive total excess molar entropy $(J/_{K-mol})$

$$\bar{S}_a^E = \left(\frac{S^{E}}{\partial n_a}\right)_{T,P,n_b}$$

extensive (J/K)

Solving partial molar excess entropy of "a"

$$S^E = \frac{(B-A)}{T} x_a x_B n_T = \frac{(B-A)}{T} \frac{n_a}{n_T} \frac{n_B}{n_T} n_T$$

$$\bar{S}_a^E = \frac{(B-A)}{T} n_B \, \partial \left(\frac{n_a}{n_a + n_B}\right)$$

$$= \frac{(B-A)}{T} n_B \left(\frac{(n_a + n_B) - n_a}{(n_a + n_B)^2}\right)$$

$$\bar{S}_a^E = \frac{(B-A)}{T} x_B^2$$

recall any property $K_i^E = K_i - K_i^{ideal}$

so similarly $\bar{K}_i^E = \bar{K}_i - \bar{K}_i^{ideal}$

so $\bar{S}_a^E = \bar{S}_a - \bar{S}_a^{ideal}$

↑ $\frac{(B-A)}{T} x_B^2$

↑ $-R \ln x_a$

↖ same as $\Delta \bar{S}_{mix_i}$
$= -R \ln x_i$

$$\bar{S}_a = \frac{(B-A)}{T} x_B^2 + \left(-R \ln x_a\right) \quad (J/K)$$

Vapor Liquid Equilibrium (VLE)

Clausius-Clapeyron Equation

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = -\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2[K]} - \frac{1}{T_1[K]}\right)$$
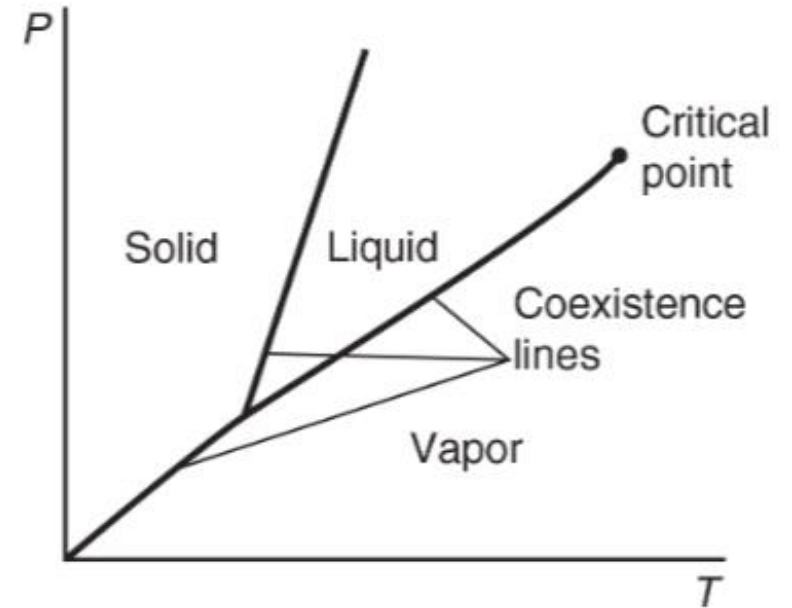
Assumes:
1) L-V equilibrium
2) ΔH_{vap} constant
3) $v^v \gg v^l$
4) Ideal gas (low pressure) $v^v = RT/P$

Used for single component equilibrium, need reference temperature and pressure on the coexistence line (such as triple point) or can be used to solve for triple point temperature. Can sometimes use for S-V equilibrium if assume $v^v \gg v^s$

Antoine Equation

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

Vapor Liquid Equilibrium (VLE)

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

$$y_i \hat{\varphi}_i^v P = x_i \gamma_i^l f_i^o$$

$$y_a \phi_i P = x_i \gamma_i P_i^{sat}$$

Is assuming ideal vapor (fugacity coefficient =1)

$$y_i P = x_i \gamma_i P_i^{\text{sat}}$$ Non-ideal solution

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

bubble-point calculation

$$P = \sum x_i \gamma_i P_i^{sat}$$

Total system pressure calculation

$$y_i P = x_i P_i^{\text{sat}}$$ Ideal (Raoult's Law)

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

$$P = \sum x_i P_i^{sat}$$

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

VLE Pxy and Txy diagrams

Azeotrope: $x_i = y_i$

$$x_a \gamma_a P_a^{sat} = y_a P$$
$$\gamma_a P_a^{sat} = P$$
$$\gamma_b P_b^{sat} = P$$

Chloroform (a) – n-Hexane (b)

$T = 318$ K

Azeotrope

Ideal Raoult's Law Line

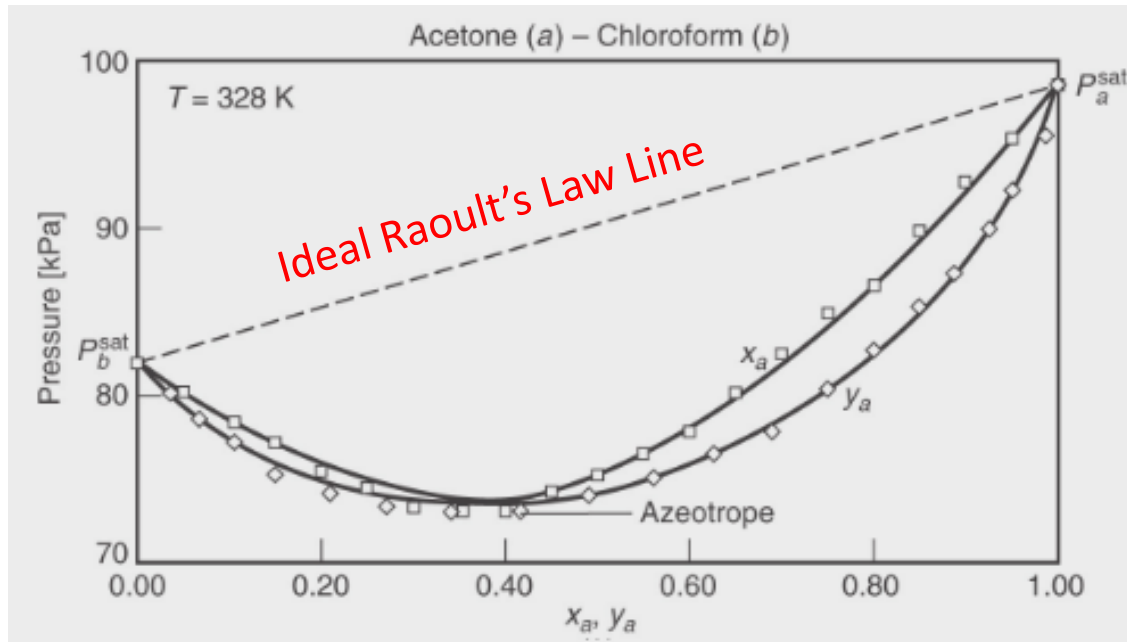Chloroform (a) – n-Hexane (b)

$P = 1$ atm

Azeotrope
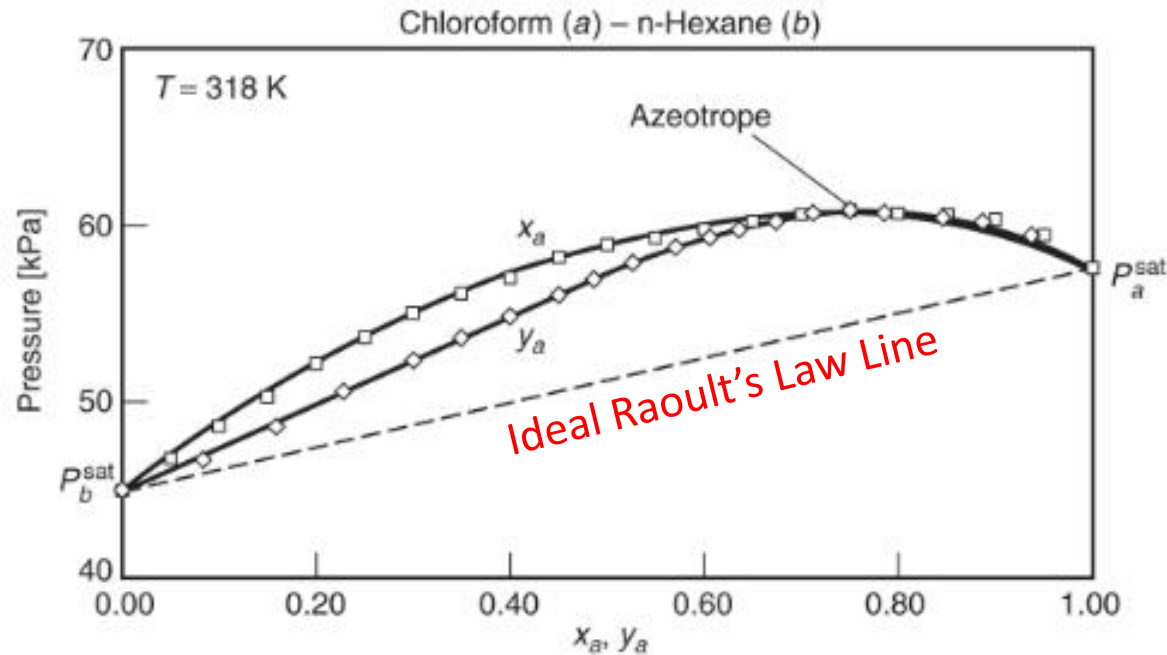
Real pressure of mixture P_{mix} is greater than ideal $P_{raoults}$ and exhibits positive deviation from Raoult's Law. Thus $\gamma_i > 1$ and like interactions are greater (from g^E determination)
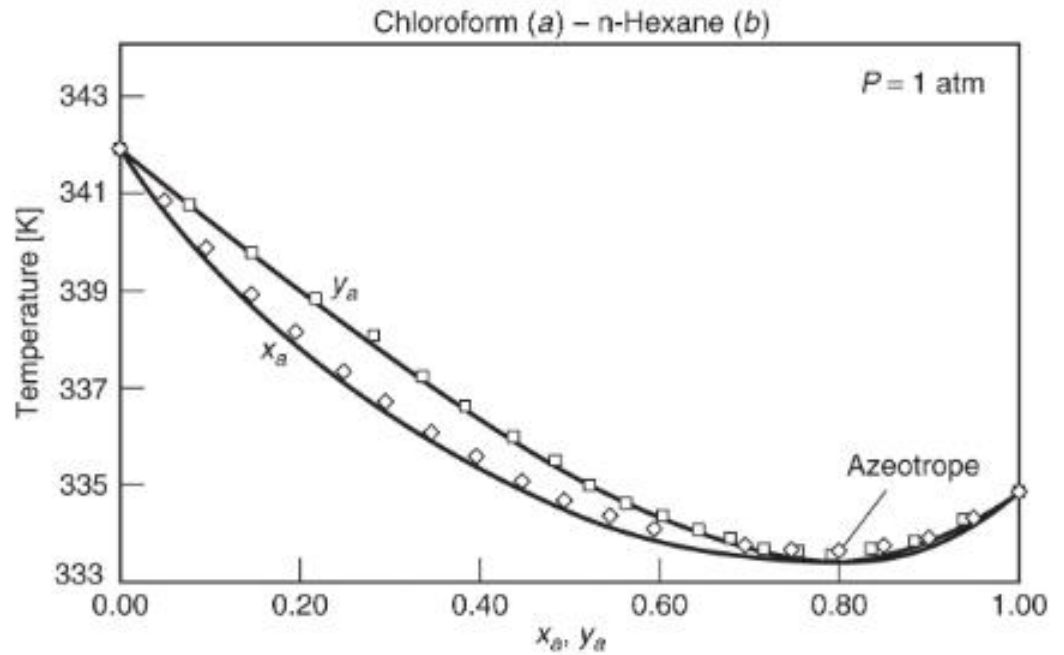
Like interactions greater, means mixture is unfavored, take less energy to vaporize the mixture and will boil easier. The minimum in temperature is at the azeotrope.

VLE Pxy and Txy diagrams
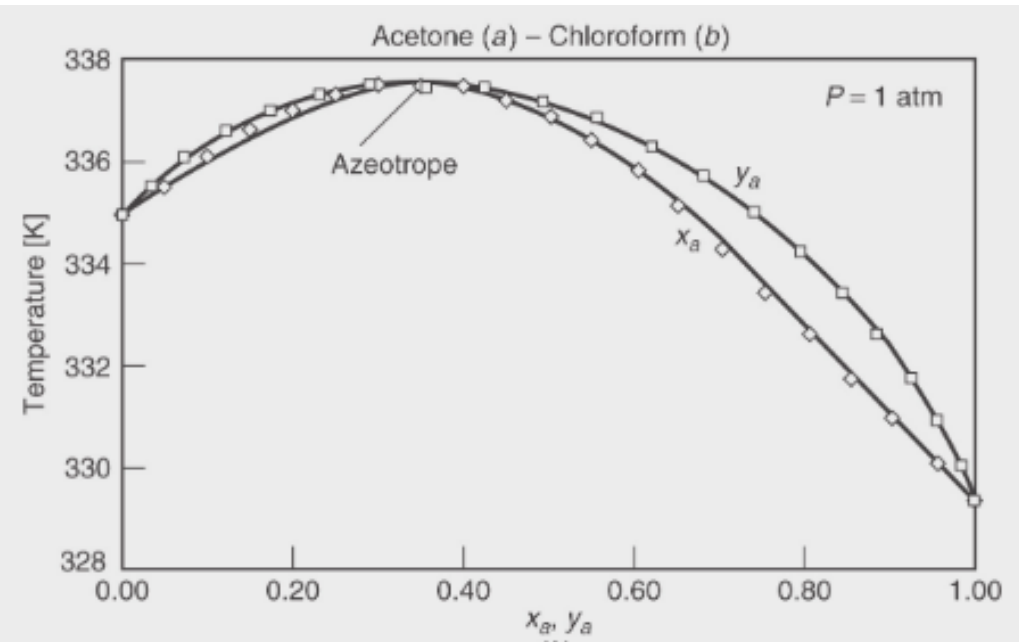
Real pressure of mixture P_{mix} is less than ideal $P_{raoults}$ and exhibits negative deviation from Raoult's Law. Thus $\gamma_i < 1$ and unlike interactions are greater (from g^E determination)
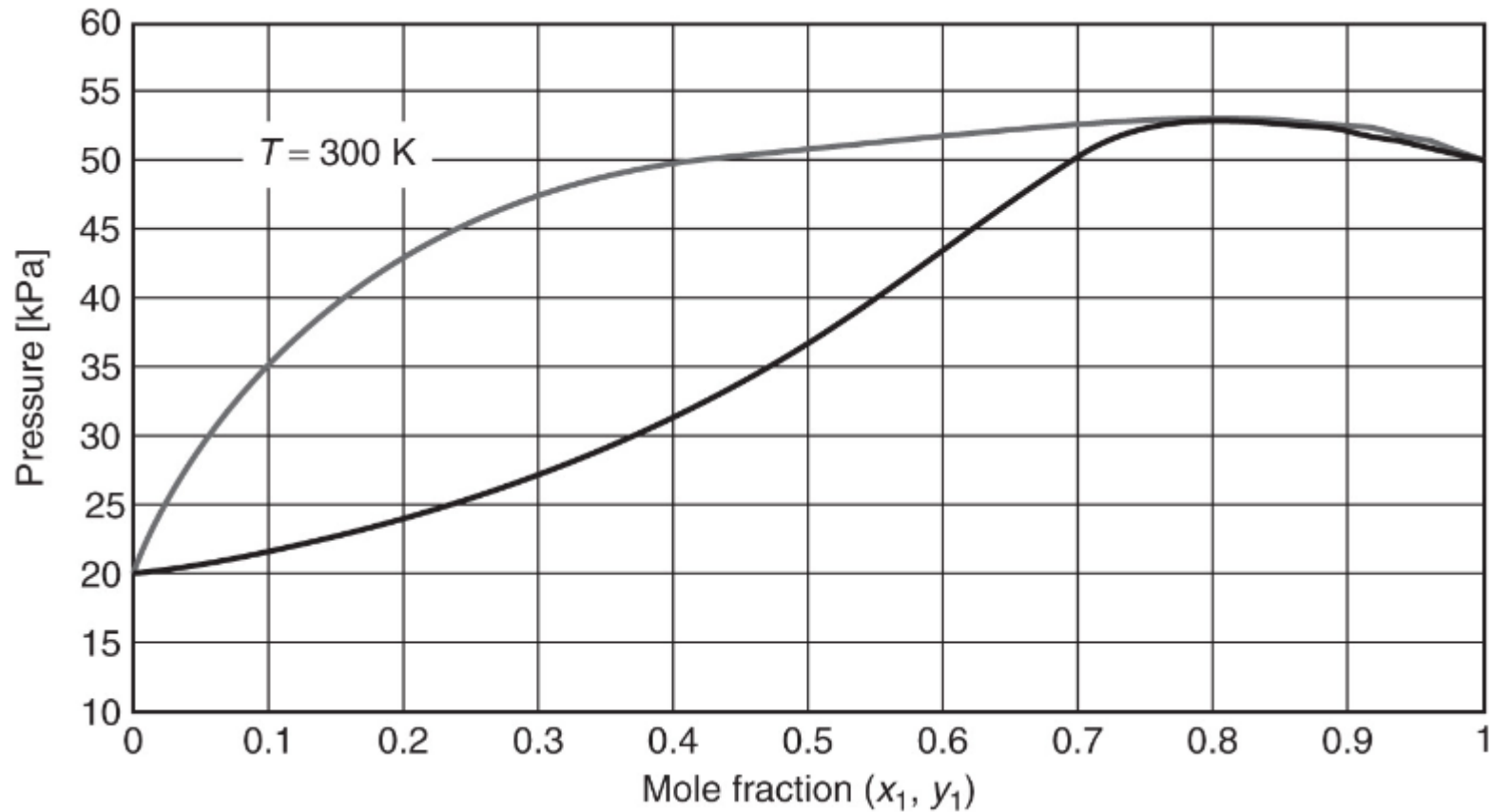
unlike interactions greater, means mixture is favored, take more energy to vaporize the mixture and will not boil as easily. The maximum in temperature is at the azeotrope.

Example
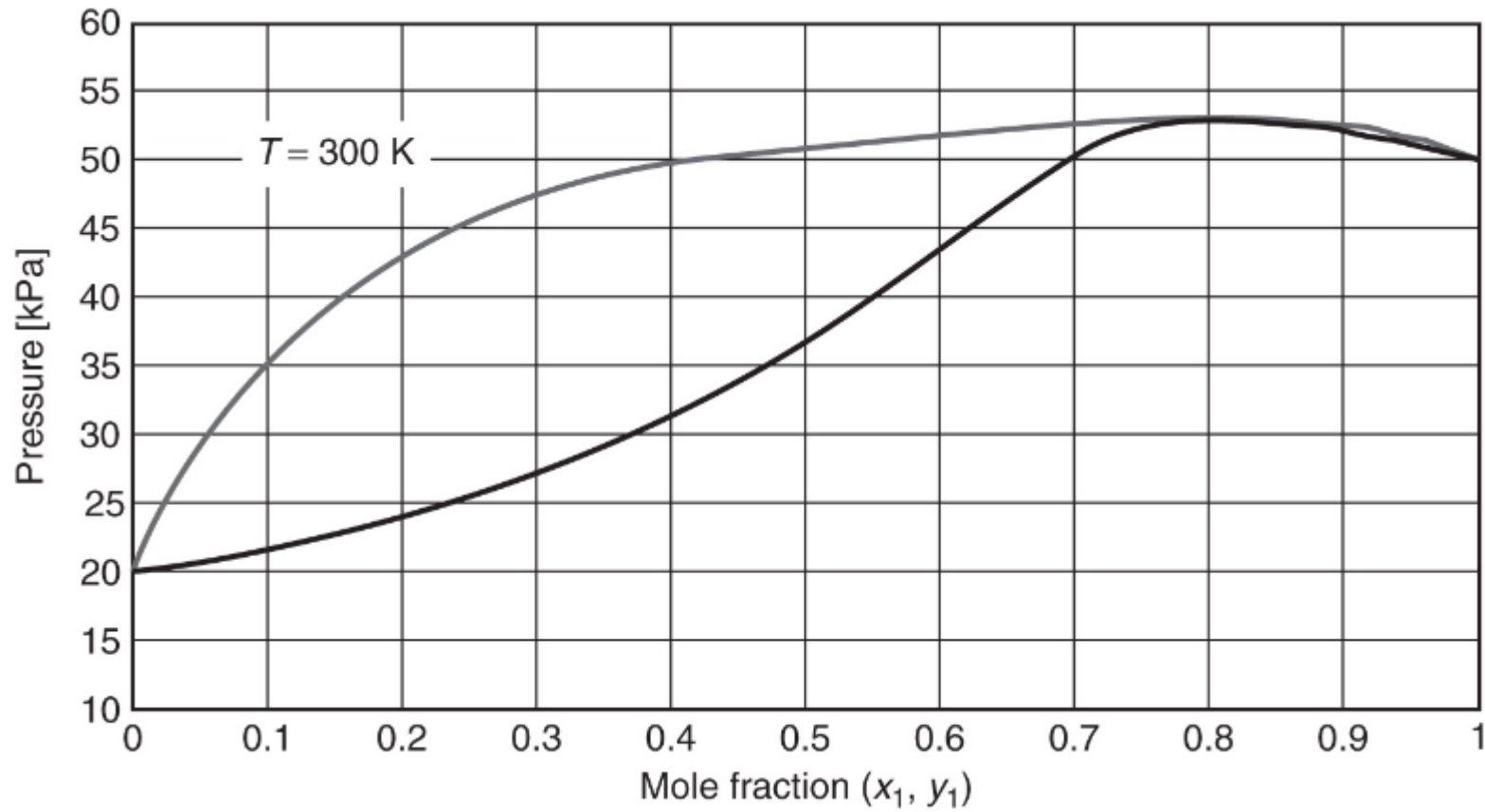
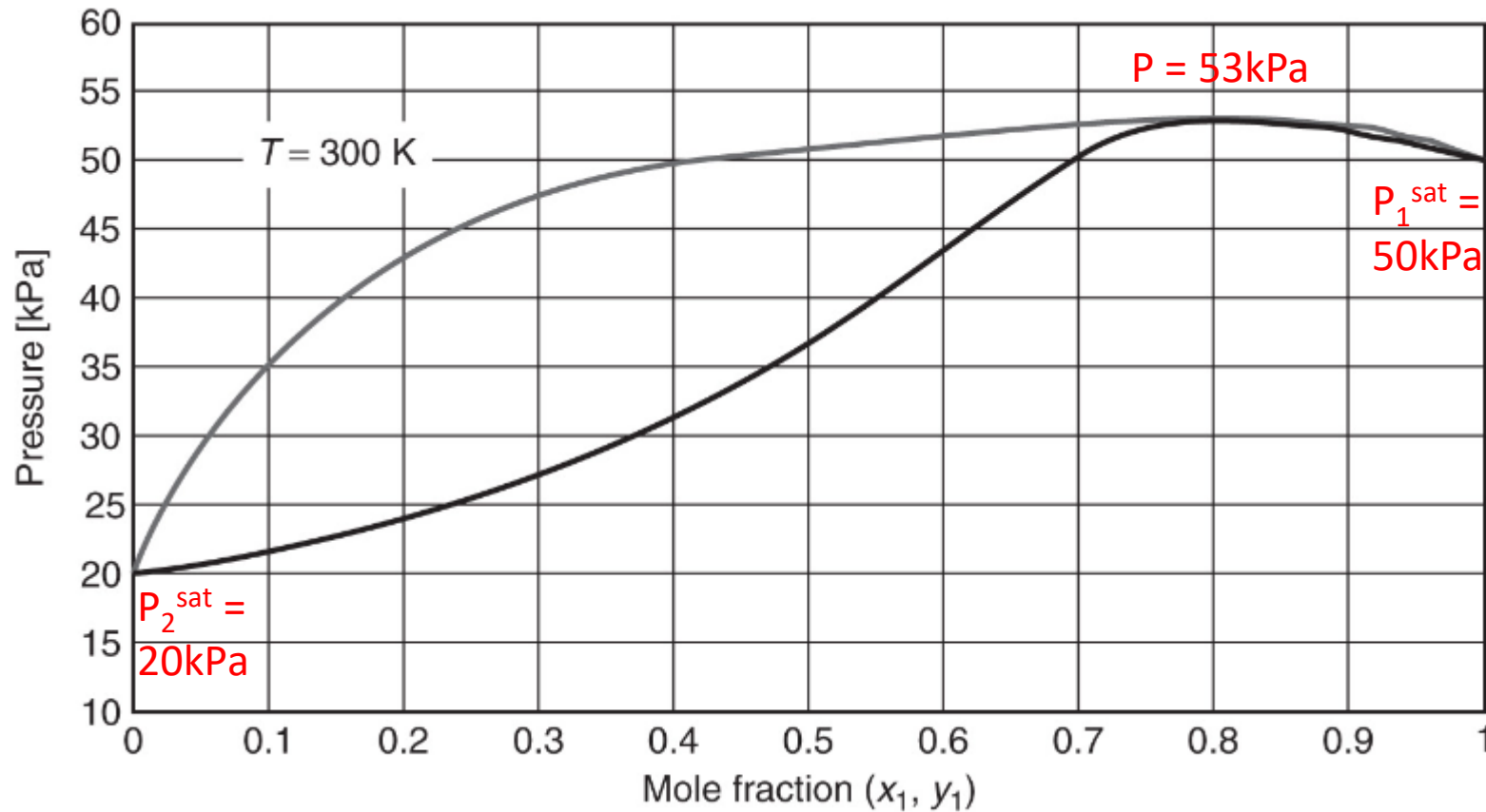Are the like or unlike interactions greater?

Example

Are the like or unlike interactions greater?

Like interactions: This has a maximum azeotrope in pressure, therefore its Txy diagram will show an azeotrope that is at a minimum in boiling. Thus, the mixture vaporizes easier because the unlike interactions are weaker.

Example

Estimate the value of the two-suffix Margules parameter, A
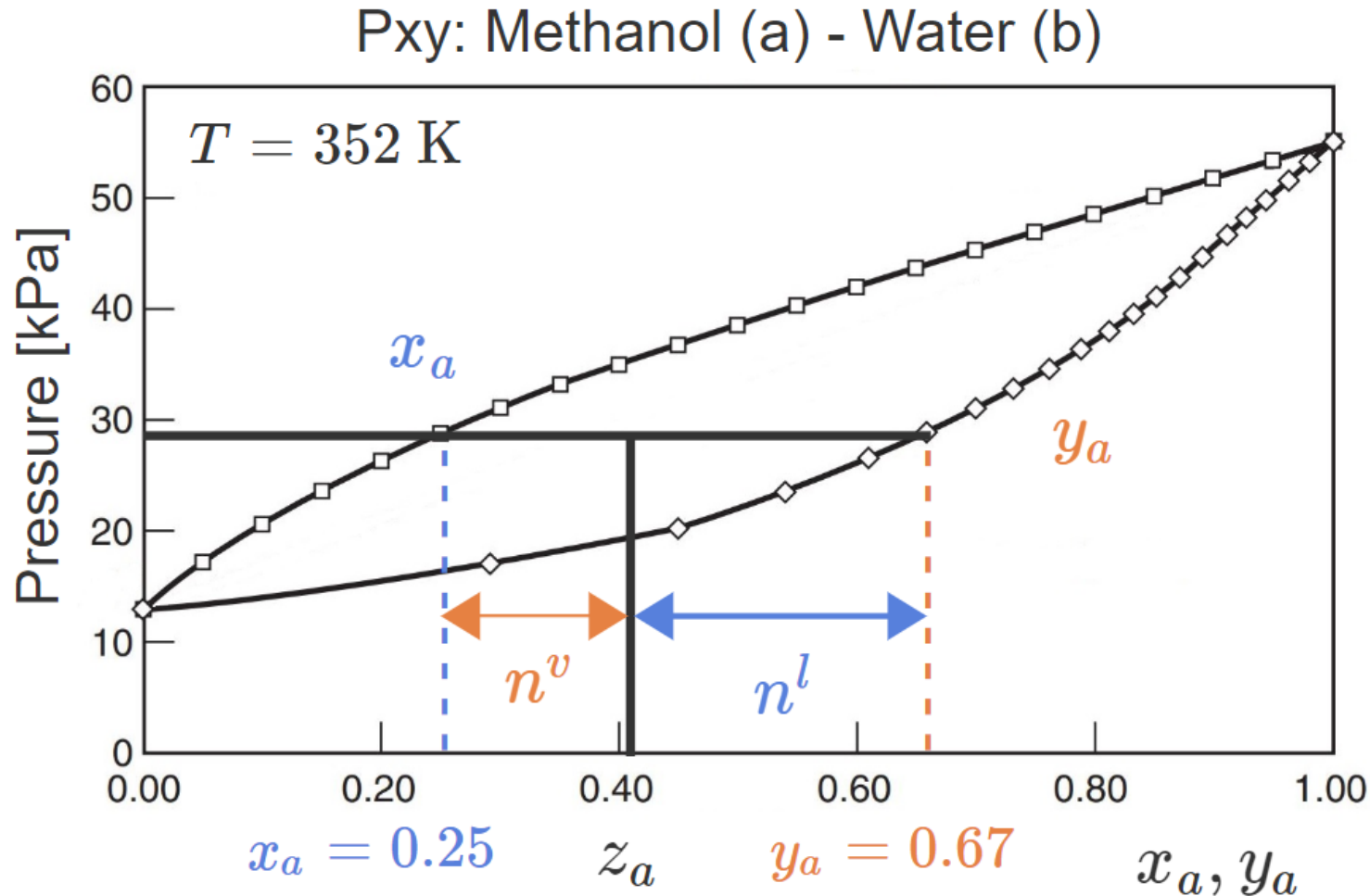
At the azeotrope, $x_1 = y_1$

At VLE: $x_i \gamma_i P_a^{sat} = y_i P$

$$\gamma_1 P_1^{sat} = P$$

$$\gamma_2 P_2^{sat} = P$$

-Solve for γ_i,
-Solve for A using 2-suffix at the azeotrope composition x_1 and x_2
-Take the average the A

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)

$T = 352 \text{ K}$

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

Liquid-Liquid Equilibrium (LLE) 2-Suffix

Like interactions >> unlike, can split into two different partially miscible phases to lower total gibb's energy

If you know the equilibrium mole compositions but don't know A. Assuming 2-suffix Margules

$$\hat{f}^{\alpha}_{\ a} = \hat{f}^{\beta}_{\ a}$$

$$x^{\alpha}_a \gamma^{\alpha}_a f_a = x^{\beta}_a \gamma^{\beta}_a f_a \qquad \text{Substituting...}$$

$$RT ln\gamma^{\alpha}_a = A(x^{\alpha}_b)^2$$

$$RT ln\gamma^{\beta}_a = A\left(x^{\beta}_b\right)^2$$

$$x^{\alpha}_a \gamma^{\alpha}_a = x^{\beta}_a \gamma^{\beta}_a \qquad \text{For component a}$$

$$x^{\alpha}_a \exp\left[\frac{A}{RT}(x^{\alpha}_b)^2\right] = x^{\beta}_a \exp\left[\frac{A}{RT}\left(x^{\beta}_b\right)^2\right]$$

$$\ln\left(\frac{x^{\alpha}_a}{x^{\beta}_a}\right) = \frac{A}{RT}\left(\left(x^{\beta}_b\right)^2 - (x^{\alpha}_b)^2\right)$$

$$\ln\left(\frac{x^{\alpha}_a}{x^{\beta}_a}\right) = \frac{A}{RT}\left(\left(1 - x^{\beta}_a\right)^2 - (1 - x^{\alpha}_a)^2\right)$$

In terms of a

$$x^{\alpha}_b \gamma^{\alpha}_b = x^{\beta}_b \gamma^{\beta}_b \qquad \text{For component b}$$

$$x^{\alpha}_b \exp\left[\frac{A}{RT}(x^{\alpha}_a)^2\right] = x^{\beta}_b \exp\left[\frac{A}{RT}\left(x^{\beta}_a\right)^2\right]$$

$$\ln\left(\frac{x^{\alpha}_b}{x^{\beta}_b}\right) = \frac{A}{RT}\left(\left(x^{\beta}_a\right)^2 - (x^{\alpha}_a)^2\right)$$

$$\ln\left(\frac{1 - x^{\alpha}_a}{1 - x^{\beta}_a}\right) = \frac{A}{RT}(\left(x^{\beta}_a\right)^2 - (x^{\alpha}_a)^2))$$

In terms of a

$\alpha - phase$

Oil + Ethanol

Water + Ethanol

$\beta - phase$

Liquid-Liquid Equilibrium (LLE) 3-suffix

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

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

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

Difficult problem to solve!

If you know the equilibrium mole compositions but don't know A and B. Assuming 3-suffix

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

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

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

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

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