Chapter 15
Excel/PrMix.xlsx
Excel/PrFug.xlsx - explore fugacity cal
Excel/Virial.xlsx - explore fugacity cal
Objectives: See Objective Handout

Two EOSs

Virial - can do vapor phase for VLE

vdW, PR - can do vapor &/or liquid phase for VLE

15.1 Random mixing rules

EOS used to represent *PVT*, and thus *H, U, G, A*. From composition dependence of props, find component props. EOS keeps same overall form/parameters as for pure fluids, but parameters depend on composition using 'mixing rules' for

parameters.

<u>van der Waals</u>

$$Z = \frac{1}{1-b\rho} - \frac{a\rho}{RT}$$

$$\frac{U-U^{ig}}{RT} = -\frac{a\rho}{RT}$$

<u>Virial</u>

$$Z = 1 + \frac{BP}{RT}$$

$$\frac{G-G^{ig}}{RT} = \frac{BP}{RT}$$

- The probability of finding a (1) molecule is the fraction of (1) atoms, x_1
- The probability of a (1)-(1) interaction is a *conditional probability.* -- probability of finding a second interacting molecule of a certain type given the first is a certain type -- the product of the individual probabilities.

  The probability of a (1)-(1) interaction is x_1^2.

  The probability of a (2)-(2) interaction is x_2^2.

The probability of a (1)-(2) interaction is x_1x_2 and the probability of a (2)-(1) interaction is also x_1x_2.

If the attractive interactions are characterized by a_{11}, a_{22}, and a_{12}, the mixing rule for a is given by:

0.1

$$U - U^{ig} = -a\rho = -\rho(x_1^2 a_{11} + 2x_1x_2a_{12} + x_2^2 a_{22})$$

mixing rule is called a *quadratic mixing rule*

For Cubic EOS:

$\boxed{a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij}}$ and $\boxed{b = \sum_{i=1}^{n} x_i b_i}$ $\boxed{a_{ij} = (a_i a_j)^{1/2}(1-k_{ij})}$;

k_{ij} is *binary interaction coefficient*

For Virial EOS:

$$\boxed{B = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j B_{ij}}$$

B_{12} is *cross coefficient*

$$V = \frac{RT}{P} + B$$

Ex 15.1

Fugacity and Phase Equilibria

	Chap 9 pure	Chap 10 ideal	Chap 15 EOS
vapor	$f_i = P$	$\hat{f}_i^{ig} = y_i P$	$\hat{f}_i = y_i \hat{\varphi}_i^V P$
liquid	$f_i \approx P_i^{sat}$	$\hat{f}_i^{is} \approx x_i P_i^{sat}$	$\hat{f}_i = x_i \hat{\varphi}_i^L P$

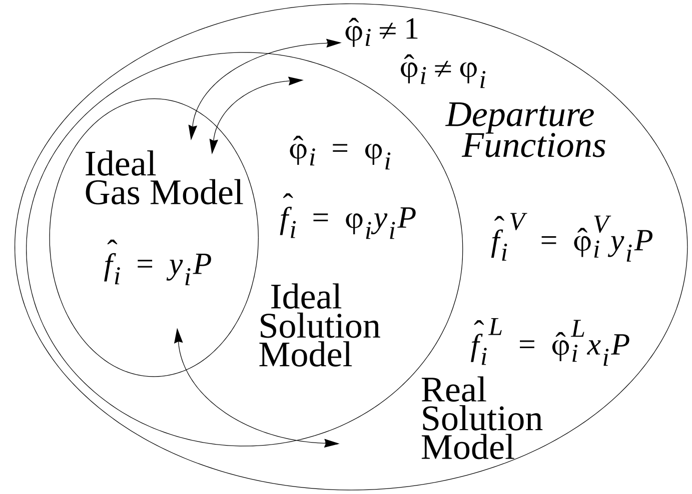
For EOS calculation, use $\hat{f}_i^V = \hat{f}_i^L$, without simplification

$\hat{\varphi}_i \equiv \dfrac{\hat{f}_i}{y_i P}$, fugacity coefficient for component in mixture

So, if we can characterize

Then

get   from departure function:



$$\boxed{\ln\left(\frac{\hat{f}_i}{y_i P}\right) = \frac{(\mu_i - \mu_i^{ig})}{RT} = \left(\frac{\partial(\underline{G} - \underline{G}^{ig})/(RT)}{\partial n_i}\right)_{T,P,n_{j\neq i}}}$$

example, $\dfrac{G - G^{ig}}{RT} = \dfrac{BP}{RT}$

binary: $\ln\hat{\varphi}_1 = ([2y_1 B_{11} + 2y_2 B_{12} - B]P)/(RT)$ 15.14

$\hat{f}_i^V = \hat{\varphi}_i^V y_i P$

OR

$$\ln\left(\frac{\hat{f}_i}{y_i P}\right) = (\mu_i - \mu_i^{ig})/RT = \left(\frac{\partial(\underline{A} - \underline{A}^{ig})_{TV}/RT}{\partial n_i}\right)_{T,\underline{V},n_{j\neq i}} - \ln Z$$

example (see Example 15.5 and 15.5)

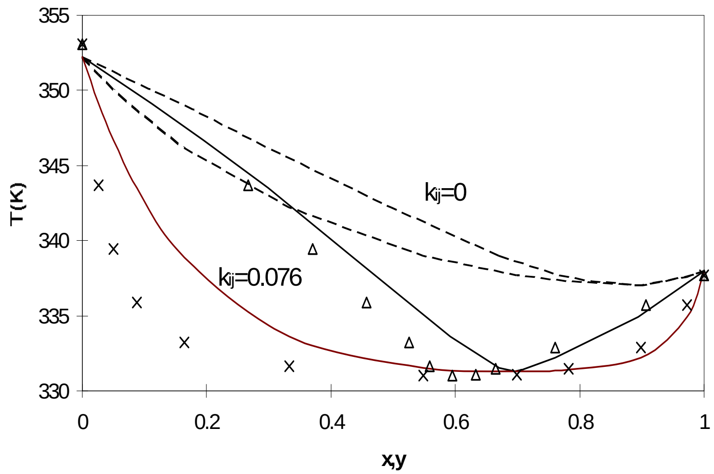
$$\frac{(A - A^{ig})_{TV}}{RT} = -\ln(1 - b\rho) - \frac{a}{bRT\sqrt{8}}\ln\left(\frac{1 + (1+\sqrt{2})b\rho}{1 + (1-\sqrt{2})b\rho}\right)$$

becomes:

$$\ln(\hat{\varphi}_k) = -\ln(1 - b\rho) - \ln Z + \frac{b_k\rho}{1 - b\rho} - \frac{ab_k\rho}{bRT\sqrt{8}}\left\{\frac{(1+\sqrt{2})}{1 + (1+\sqrt{2})b\rho} - \frac{(1-\sqrt{2})}{1 + (1-\sqrt{2})b\rho}\right\}$$
$$- \frac{a}{bRT\sqrt{8}}\left[\frac{2\sum_j x_j a_{jk}}{a} - \frac{b_k}{b}\right]\ln\left[\frac{1 + (1+\sqrt{2})b\rho}{1 + (1-\sqrt{2})b\rho}\right]$$

or Eqn. 15.34

$$\ln(\hat{\varphi}_k) = -\ln(Z - B) + \frac{B_k}{B}\{Z - 1\} - \frac{A}{B\sqrt{8}}\left[\frac{2\sum_j x_j A_{jk}}{A} - \frac{B_k}{B}\right]\ln\left[\frac{Z + (1+\sqrt{2})B}{Z + (1-\sqrt{2})B}\right]$$



methanol + benzene

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Iteration Procedure:

$$x_i \hat{\varphi}_i^L P = y_i \hat{\varphi}_i^V P$$

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Component	z_i	Tc (K)	Pc (MPa)		kij nitrogen	kij methane	kij n-heptane
nitrogen	0.5	126.1	3.394	0.040	-	-	-
methane	0.5	190.6	4.604	0.011	0	-	-
n-heptane	0	540.3	2.736	0.349	0	0	-

Current State		Roots Z	V cm³/gmol	fugacity MPa	component fugacity coeff nitrogen	methane	n-heptane	component fugacity(MPa) nitrogen	methane	n-heptane
T (K)	100									
P (MPa)	0.4119									
answers for three		0.861016	1737.919	0.36145609	0.92073498	0.83635927	0.21245832	0.189625	0.172248	0
root region		0.109979	221.9863							
		0.01642	33.14242	0.16875299	1.79139529	0.09369748	6.5075E-16	0.368938	0.019297	0
& for 1 root region		#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!	#NUM!

mixture	
A	0.1362835
B	0.0125858
R(cm³MPa/molK)	
8.314	

	Tr	Pr			ac	a	b	A	B	A nitrogen	A methane	A n-heptane
nitrogen	0.793021	0.121361	0.435899	1.09772403	148073.842	162544.215	24.031	0.09686	0.011906	0.0968597	0.132926	0.662394
methane	0.524659	0.089466	0.391572	1.22753847	249385.092	306129.793	26.777	0.182422	0.013266	0.1329261	0.182422	0.909041
n-heptane	0.185082	0.150548	0.880011	2.25426114	3372204.1	7601828.66	127.728	4.529913	0.06328	0.6623942	0.909041	4.529913

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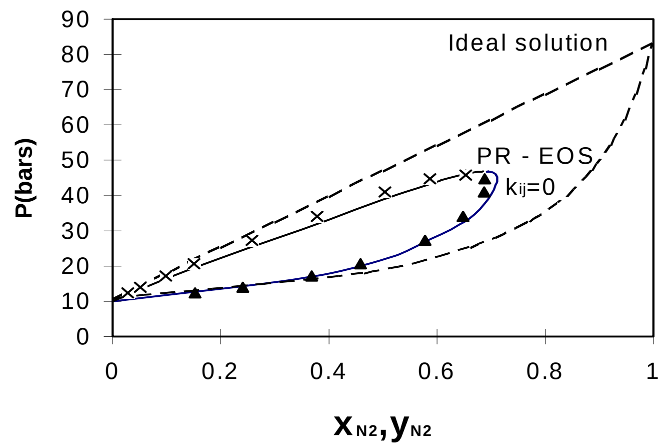

nitrogen + methane

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