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ABSTRACT

Title of Thesis: A New Density-Dependent Mixing Rule
for Equations of State

Theodore John Shatynski, Master of Science in Chemical Engineering, 1986

Thesis directed by: Dr. Dana E. Knox, Professor of Chemical Engineering

A general procedure for the development of density-dependent mixing rules is demonstrated. This method is used to obtain a density-dependent local-composition mixing rule based on an extension of the work of Knox et al (1984). The resulting expression is tested with the Soave-Redlich-Kwong equation of state. Results for normal and cryogenic vapor-liquid systems for both one-parameter and three-parameter versions of the mixing rule are compared with results using the classical mixing rules.

A NEW DENSITY-DEPENDENT MIXING RULE
FOR
EQUATIONS OF STATE

by
Theodore John Shatynski

Thesis submitted to the Faculty of the Graduate School of
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DEDICATION

In this the centennial year of the Statue of Liberty, and in view of what she stands for, I wish to dedicate this thesis to my immigrant grandparents. This dedication is made in memory of my grandparents who have passed away (Theodore Shatynski, Julia (Lewycky) Shatynski and my mother's father Kasian Dobriansky and stepfather Hnat Marchak) and to my one surviving grandparent Rose Dobriansky Marchak. I thank and honor them for coming to this country from their native Ukraine so that their children and their children's descendants could enjoy the freedoms and privileges that we often take for granted.

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CHAPTER I: INTRODUCTION

Equations of state (EOS) are a popular way of predicting and correlating fluid phase equilibria. EOS can adequately describe both liquid and vapor phase behavior using the classical mixing rules when dealing with nonpolar or slightly polar mixtures. However, when polar mixtures are encountered, the EOS with the classical mixing rules can no longer accurately predict the liquid phase. The inadequacy of these mixing rules with EOS to model liquid phase nonideality gave rise to the liquid phase activity coefficient concept. Some of the most successful of these activity coefficient expressions are local-composition equations such as the Wilson (1964), the NRTL of Renon and Prausnitz (1968), and the UNIQUAC of Abrams and Prausnitz (1975).

The use of local-composition activity coefficient models to describe liquid-phase molecular behavior coupled with an EOS using the classical mixing rules to predict vapor-phase molecular behavior has been successful in correlating vapor liquid equilibria (VLE) for many polar mixtures where large degrees of nonideality are present in the liquid phase. However, this approach to VLE (known as the γ/ϕ approach) has a critical shortcoming in that the activity coefficient frequently loses its physical significance. This is due to the definition given to the standard-state fugacity which is given as the fugacity of pure liquid at system temperature and pressure. Quite often a particular component cannot physically exist as a pure liquid at the system's temperature and pressure, and extrapolation into the hypothetical region

leads to uncertainties. In addition, this approach to VLE lacks continuity between the mixing rules for the liquid and vapor phases.

These shortcomings of the γ/ϕ approach can be bridged by the use of density-dependent mixing rules in EOS. The concept is to make a local-composition model a function of density and develop it into a EOS mixing rule applicable to both phases. At the high density limit (liquid-like behavior), the fugacity coefficient behaves as if it is an activity coefficient. At the low density limit (vapor-like behavior), the mixing rule reduces to the standard classical or quadratic mixing rule. Typically, the use of the classical mixing rules in EOS to describe molecular behavior of mixtures in the vapor phase, even for strongly polar compounds, is adequate due to the random arrangement of molecules which results in minimal molecular interaction.

Work in the area of density-dependent mixing rules stemmed from the contributions of Vidal (1978), Huron and Vidal (1979), Heyen (1981) and Won (1981). These contributors showed that non-quadratic mixing rules could be successfully used in EOS to correlate complex polar-polar and polar-nonpolar systems. One shortcoming of these mixing rules was that they were density-independent and could not reproduce the required (by statistical mechanics) quadratic composition dependence of the second virial coefficient in the vapor phase (low densities). Thus, these models gave better results at liquid-like densities, but poorer results at lower densities. Table I of Appendix I summarizes typical results obtained by Huron and Vidal (1979). Overall, the systems containing

gaseous components gave poorer results than the liquid systems.

To get these mixing rules to reduce to the classical mixing rules at the low density limit, Whiting and Prausnitz (1982), Mollerup (1981) and Won (1983) proposed density-dependent local-composition mixing rules for EOS. These rules use conventional mixing rules for the repulsive term, b , and local-composition mixing rules with some type of density dependence for the attractive term, a , of the EOS. However, the theoretical basis of some of these two-fluid mixing rules has been criticized by a number of authors. McDermott and Ashton (1977) and Flemr (1976) have noted that two-fluid models have shortcomings because they do not contain a material balance constraint. Thus, the number of ij pair interactions do not equal the number of ji pair interactions. Use of one-fluid models, which contain the material balance constraint, would overcome this shortcoming.

The purpose of the thesis is to show how a local-composition model may be developed into a density-dependent mixing rule for EOS. In this thesis, the local-composition expression of Knox et al (1984), a one-fluid model, is used to demonstrate this procedure with the Soave-Redlich-Kwong (SRK) EOS. Correlative results using the new mixing rule are then compared with results using the classical mixing rule for a variety of normal and cryogenic systems.

CHAPTER II: BASIC MOLECULAR MODEL

This thesis will develop a mixing rule that is based on a statistical thermodynamic model developed by Knox et al (1984). This local-composition model is an alternative to those of the Wilson equation (1964), the NRTL equation of Renon and Prausnitz (1968), and the UNIQUAC equation of Abrams and Prausnitz (1975).

The Knox local-composition model is a one-fluid model which has its physical concepts firmly based on molecular theory. The previously mentioned local-composition models are two-fluid models which lack physical significance since mixture properties are derived from postulated properties of hypothetical fluids. Specifically, each fluid has its own interchange energy and local composition which is independent of those of the other fluid(s). A one-fluid model, on the other hand, is based on one interchange energy for each binary and a local composition that is dependent on the mixture's constituents.

The basic assumptions of the Knox one-fluid model are as follows:

1. The translational partition function is given as a free translation in a volume equal to the actual volume less the excluded volume; the excluded volume is taken as a linear composition average over all components. Note that this assumption produces the repulsive contribution to the pressure normally found in cubic equations of

state. A different assumption may be used if another form is desired for this contribution.

2. The rotational, vibrational and electronic contributions to the molecular partition functions are all independent of both density and composition.
3. Each molecule engages in a characteristic average number of interactions, z_i , of pair interactions with other molecules. Since only pair interactions are considered, the number of interactions attributable to the presence of a single molecule i is $z_i/2$, and the total number of such interactions is:

$$I = \sum_i z_i N_i / 2 \quad (\text{II.1})$$

The above assumptions are introduced into the canonical partition function of statistical mechanics. The details of this development are given in Appendix II. The resulting expression follows:

$$Q = w^{\text{ath}} \frac{[\prod_i (z_i N_i / 2)!]^2}{I! \prod_i \prod_j N_{ij}!} \left[\exp - \sum_i \sum_j \frac{N_{ij} u_{ij}}{kT} \right] \prod_i q_i^{N_i} \quad (\text{II.2})$$

where the numbers of interactions by type (N_{ij}) are given by solution of the set of equations:

$$N_{ij} = N_{ji} \quad (\text{II.3})$$

$$\frac{z_i N_i}{2} = \sum_j N_{ij} \quad (\text{II.4})$$

$$\frac{N_{ii}N_{jj}}{N_{ii}N_{jj}} = \exp \frac{-(2u_{ii} - u_{ii} - u_{jj})}{kT} \quad (\text{II.5})$$

The molecular partition functions are given as:

$$q_i = q_i^{\text{trn}} q_i^{\text{rot}} q_i^{\text{vib}} q_i^{\text{elc}} = q_i^{\text{int}} (V^t - b^t) \quad (\text{II.6})$$

where b^t represents the excluded volume, and q_i^{int} contains those portions of the molecular partition function which depend only on temperature (and not on density or composition). The excluded volume is assumed to be given by the usual expression:

$$b^t = nb = \sum_i n_i b_i = \sum_i N_i \sigma_i = n \sum_i x_i b_i \quad (\text{II.7})$$

CHAPTER III: EXTENSION TO EQUATIONS OF STATE

The last section gave the molecular theory that formed the basis of this mixing rule. This section shows how the density-dependent mixing rule is developed from the canonical partition function.

The density dependence is introduced into the canonical partition function by assuming that the average interaction energy for a given type of molecular pair is given to within a multiplicative constant by a universal function, f , of density and composition:

$$u_{ij} = \varepsilon_{ij} f \quad (\text{III.1})$$

Thus the canonical partition function becomes:

$$Q = W^{\text{ath}} \frac{[\prod_i (z_i N_i / 2)!]^2}{I! \prod_i \prod_j N_{ij}!} \left[\exp - \sum_i \sum_j \frac{N_{ij} \varepsilon_{ij} f}{kT} \right] \prod_i q_i^{N_i} \quad (\text{III.2})$$

The following thermodynamic expression relates the canonical partition function to the Helmholtz energy:

$$A^t = -kT \ln Q$$

Applying this relationship, we obtain the Helmholtz energy:

$$\begin{aligned} \frac{A^t}{kT} = & - \ln W^{\text{ath}} - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + \sum_i \sum_j N_{ij} \ln \frac{N_{ij}}{z_i N_i / 2} \\ & + \sum_i \sum_j N_{ij} \frac{\varepsilon_{ij}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) - \sum_i N_i \ln \left[(V^t - b^t) q_i^{\text{int}} \right] \end{aligned} \quad (\text{III.3})$$

We have chosen the density-dependent function f so as to obtain a Redlich-Kwong equation of state:

$$f = \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) \quad (\text{III.4})$$

Thermodynamics gives us the relationships between the Helmholtz energy (expressed as a function of T , V^t , and N_i), the pressure, and the component fugacity coefficient as:

$$P = - \left(\frac{\partial A^t}{\partial V^t} \right)_{T, N_i} \quad (\text{III.5})$$

$$\ln \hat{\phi}_i = - \left\{ \left[\frac{\partial (A^t/kT)}{\partial N_i} \right]_{T, V^t, N_j} + \ln V^t \right\} \Big|_{V^t} - \ln Z \quad (\text{III.6})$$

From these equations, we find (after considerable algebra which is covered in Appendices III and IV) that:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (\text{III.7})$$

$$\begin{aligned} \ln \hat{\phi}_i &= \frac{z_i}{2} \ln \frac{x_{ii}}{\theta_i} + \frac{z_i}{2} \frac{\epsilon_{ii}}{kT} \frac{\ln(1+b/V)}{b} + \frac{b_i}{V-b} - \ln \left[\frac{P(V-b)}{RT} \right] \\ &- \frac{a}{RT} \left(\frac{b_i/b}{V+b} \right) + \frac{a}{RT} \frac{\ln(1+b/V)}{b} \left[\frac{b_i}{b} - 1 \right] \end{aligned} \quad (\text{III.8})$$

where we have noted that the quantity a is given by:

$$a = - \sum_i \sum_j \frac{z_i x_i}{2} x_{ij} \epsilon_{ij} L = \sum_i \sum_j x_i x_{ij} a_{ij} \quad (\text{III.9})$$

and L is Avogadro's number. We thus arrive at the conclusion that the Redlich-Kwong parameter a is given by $z_i/2$ times the negative of the

characteristic energy of the interaction. The local compositions x_{ij} are evaluated by the following equations, which follow directly from the earlier equations for the N_{ij} .

$$\theta_i x_{ij} = \theta_j x_{ji} \quad (\text{III.10})$$

$$1 = \sum_j x_{ij} \quad (\text{III.11})$$

$$\frac{x_{ij}x_{ji}}{x_{ii}x_{jj}} = \exp \left[\left\{ \frac{-(2\varepsilon_{ij} - \varepsilon_{ii} - \varepsilon_{jj})}{kT} \right\} f \right] \quad (\text{III.12})$$

The θ_i represent the interaction fraction of component i , and are calculated as:

$$\theta_i = \frac{z_i x_i / 2}{\sum_j z_j x_j / 2} \quad (\text{III.13})$$

From the above equations, as the density tends towards zero, the predicted local compositions (x_{ij}) will approach the interaction fractions θ_i . If all the z_i values are equal, then the local compositions will approach the overall compositions (x_i), and the given mixing rule will reduce to the classical mixing rule. At higher densities, this will not be true; the difference will represent the nonideality of the dense mixture.

The model is completed by specifying that the pure component energy parameters are evaluated by the Soave (1972) expression:

$$a = a_c \left[1.0 + (0.480 + 1.574\omega - 0.176\omega^2)(1 - T_r^{0.5}) \right]^2 \quad (\text{III.14})$$

CHAPTER IV: RESULTS AND DISCUSSION

Vapor/liquid equilibrium data for a variety of binary systems have been fitted using the new density-dependent mixing rule. Bubble point calculations were performed using the Michelsen (1980) algorithm. A Marquardt regression program was used to determine the optimal values for the parameter(s). The objective function used was the sum of the squared residual pressures:

$$OBJ = \sum (P - P_{exp})^2$$

where the summation is over all the data points in a given set. An objective function including the sum of the squared residual vapor-phase compositions may also have been selected. However, the above objective function was chosen since most of the experimental data only reported equilibrium pressures and contained no vapor-phase compositions.

The model has one energy parameter, ϵ_{ij} , for each interaction and one 'size' parameter, z_i , for each molecule. The pure-component energy parameters are related to the pure-component values of the Soave-Redlich-Kwong parameter a (eqn III.14). Rather than regress for ϵ_{ij} directly, we choose the more traditional approach and define ϵ_{ij} in terms of the pure component values:

$$\epsilon_{ij} = - (\epsilon_{ii} \epsilon_{jj})^{0.5} (1 - k_{ij})$$

The minus sign is necessary since all energy parameters are less than zero. Thus, the three adjustable parameters associated with a binary

system are z_1 , z_2 and k_{12} . In order for the proposed mixing rule to reduce to precisely the classical mixing rule at zero density, all the z_i values should be equal to 2. If instead we treat the z_i values as adjustable parameters then the local compositions will approach the interaction fractions θ_i rather than the overall compositions. This behavior is in agreement with the observations of Sandler and Lee (1986), who have noted that local compositions do not generally equal overall compositions in the limit of zero density.

The experimental data have been fitted using both options. In addition, for comparison purposes, the data were fitted with the same SRK equation-of-state using the classical mixing rule. In Tables II and III a summary of the results for the correlation of vapor/liquid equilibria data are presented for five normal and four cryogenic binary systems using a) the SRK equation with the classical mixing rule, b) the SRK equation with the 1-parameter density-dependent mixing rule, and c) the SRK equation with the 3-parameter density-dependent mixing rule. The tables list, for each model, the standard error of the correlation in (kPa), the average absolute per cent deviation of the calculated pressures from the experimental pressures, and the parameter values used to obtain the listed results.

As can be seen from Tables II and III of Appendix I, use of the one-parameter density-dependent mixing rule results in a slight improvement over the classical mixing rule for the systems studied. However, a more noticeable improvement is obtained with the three-

parameter mixing rule, particularly for the polar mixtures chloroform/acetone, ethanol/toluene, ethanol/water, and acetonitrile/ethanol. This is to be expected, of course, due to the additional adjustable parameters.

The mixing rule's flexibility for modeling both polar and nonpolar systems is also shown in the results of Tables II and III. For the relatively ideal systems of benzene/cyclohexane, argon/methane, and nitrogen/argon there is little deviation (less than 0.5%) between the calculated and experimental pressures for all three mixing rule comparisons. The deviation of results between the mixing rule comparisons are much more pronounced for the polar mixtures of chloroform/acetone, ethanol/toluene, ethanol/water, and acetonitrile/ethanol. In these cases, the 3-parameter version of the density-dependent mixing rule drops the deviation in calculated and experimental pressures between 2.1 - 7.6% below the classical mixing rule. The 1-parameter version of the mixing rule reduces the calculated/experimental pressure deviation between 0.04 - 3.5% below the classical mixing rule with the exception of the ethanol/water system where it is 0.07% higher.

A study of the z_i parameter values of Table II indicate that they are all nearly equal to 2 for these organic systems, while the z_i values for the cryogenic systems in Table III deviate much further from 2. Although the z_i parameters are related to the size of the molecule and to its orientation around other molecules, there is no obvious

relationship between these z parameters and the relative sizes of a mixture's components. The large value of z_2 (10.00) in the nitrogen/carbon monoxide system tends to indicate that molecular interaction may influence the value of the z parameter when dealing with polar gases. The results may also indicate that the z_i values need to be a function of density.

Regression statistics show that the z_i parameters are not at all correlated with the k_{12} parameter, but that the z_1 and z_2 parameters are highly correlated with each other. This is supported by the observation that the precise values of z_1 and z_2 are less important than their relative values.

For the systems that did report vapor-phase compositions, Table IV reports percent deviations between calculated and experimental values. It should be noted that the deviation between calculated and experimental vapor-phase compositions may appear larger than one is accustomed to but this is due to the objective function only minimizing the squared residual sums of pressures and not vapor compositions. In turn, the reported deviation between calculated and experimental bubble point pressures are smaller than what they would be if both pressure and vapor composition were contained in the objective function. The selected objective function should not have any bearing on the new mixing rule's improvement in correlating vapor/liquid equilibrium since it is compared to results using the classical mixing rule which has been regressed with the same objective function.

CHAPTER V: CONCLUSIONS AND RECOMMENDATIONS

We have described a straightforward approach for the development of both equations of state and mixing rules for equations of state. The method is based on the construction of the canonical partition function, with particular attention paid to the density- and composition-dependent portions. These are the portions of greatest practical importance to obtaining expressions for the pressure, fugacity coefficients and mixing rules. The temperature dependence of the molecular partition function tends to be much more complicated and is better handled by empirical means, as with the Soave modification to the Redlich-Kwong equation.

Significant improvement over the classical mixing rules is obtained only with the three-parameter density-dependent mixing rules. However, it may well be possible to rework the model so that only one parameter (reflecting the relative sizes of the molecules) is required in addition to the k_{12} parameter.

However, it is unlikely that truly significant advances will be made without abandoning the cubic equation of state. In terms of the model presented here, one likely improvement would be to include an athermal combinatorial factor which is density-dependent. Such a factor would be a theoretical improvement, but would necessarily lead to a non-cubic equation of state. Also, the simple free-volume correction may also be replaced by a more rigorous expression, again leading to a non-cubic equation of state. In all cases, however, the current method of

development would still be applicable.

The model has by no means been fully tested. Regressed binary interaction parameters should be used to predict ternary systems using both the classical mixing rule and the density-dependent mixing rules. This will be a stronger test of the model's theory rather than just a comparison of correlated results.

NOMENCLATURE

a	Equation-of-state attractive parameter
b	Equation-of-state volume parameter
f	Density dependence function for energy parameter
k	Boltzmann constant
n	Number of moles
q	Molecular partition function
u	Interaction energy
x	(one subscript) Mole fraction
x	(two subscripts) Local composition - molecular model
z	Average number of interactions for a molecule or group
A	Helmholtz energy
I	Total number of interactions in mixture
N	(one subscript) Number of molecules in mixture
N	(two subscripts) Number of molecule-molecule interactions in mixture
P	Pressure
Q	Canonical partition function for mixture
R	Gas constant
T	Temperature
V	Volume
W	Combinatorial factor for mixture
ϵ	Interaction energy parameter
θ	Interaction fraction
ϕ	Fugacity coefficient

Superscripts

ath	Athermal
elc	Electronic
int	Internal
t	Total
trn	Translational
vib	Vibrational

Subscripts

i, j	Refer to molecules
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APPENDICES

APPENDIX I: TABLES

Table I : Typical Correlation Results of Huron and Vidal (1979)
Using Density-Independent Local-Composition Mixing Rules

<u>TEMP (°C)</u>	<u>NUMBER OF PARAMETERS</u>	<u>EQUIL. PRESS. ΔP (ATM)</u>	<u>VAPOR PHASE Δy</u>
Methanol/1,2 Dichloroethane			
50	1	0.049	0.07
50	2	0.140	0.02
50	3	0.005	0.01
Acetone/Cyclohexane			
25	1	0.016	0.049
25	2	0.004	0.012
25	3	0.001	0.004
Acetone/Water			
100	1	0.360	0.08
100	2	0.060	0.01
100	3	0.050	0.01
Carbon Dioxide/Ethane			
10	1	0.340	0.005
10	2	0.160	0.006
10	3	0.150	0.005
Ethane/Acetone			
25	1	1.020	0.001
25	2	0.660	0.002
25	3	0.520	0.001
Propane/Ethanol			
51.85	1	0.650	0.01
51.85	2	0.480	0.01
51.85	3	0.140	0.02

TABLE II: Correlation of Normal Vapor/Liquid Equilibrium data

<u>T (K)</u>	<u>Mixing¹ Rule</u>	<u>k_{ij}</u>	<u>z₁</u>	<u>z₂</u>	<u>Stand. Error (kPa)</u>	<u>$\frac{\delta P}{P} \times 100$</u>
Benzene/Cyclohexane (Li and Lu, 1973)						
298.15	a	0.0283	-	-	0.1266	0.74
298.15	b	0.0305	-	-	0.1261	0.71
298.15	c	0.0337	2.005	1.999	0.0826	0.49
Chloroform/Acetone (Van Ness and Abbott, 1978)						
323.15	a	-0.0495	-	-	2.239	2.57
323.15	b	-0.0466	-	-	2.194	2.53
323.15	c	-0.0567	2.005	1.980	0.2865	0.39
Acetonitrile/Ethanol (Wilson et al, 1979)						
323.15	a	0.0783	-	-	1.317	2.71
323.15	b	0.1002	-	-	1.141	2.41
323.15	c	0.0929	1.976	2.022	0.0542	0.12
Ethanol/Toluene (Van Ness and Abbott, 1977)						
303.15	a	0.0805	-	-	1.225	9.84
303.15	b	0.1754	-	-	0.7299	6.34
303.15	c	0.1610	2.052	1.956	0.2707	2.28
Ethanol/Water (Wilson et al, 1979)						
323.15	a	-0.0863	-	-	1.842	7.10
323.15	b	-0.0859	-	-	1.861	7.17
323.15	c	-0.0969	1.983	1.933	0.9489	3.61

- ¹ Mixing Rule: a) Classical Mixing Rule
b) Density Dependent Mixing Rule (with $z_1 = z_2 = 2$)
c) Density Dependent Mixing Rule

Table III: Correlation of Cryogenic Vapor/Liquid Equilibrium Data

T (K)	Mixing ¹		z ₁	z ₂	Stand. Error (kPa)	$\frac{\delta P}{P} \times 100$
	Rule	k _{ij}				
Argon/Methane (Prausnitz et al, 1966)						
90.67	a	0.0352	-	-	2.016	1.50
90.67	b	0.0519	-	-	1.384	1.72
90.67	c	0.0886	1.261	1.556	0.904	1.09
Nitrogen/Argon (Prausnitz et al, 1966)						
83.82	a	0.0043	-	-	0.982	0.62
83.82	b	0.0044	-	-	0.980	0.62
83.82	c	-0.0679	1.832	4.03	0.887	0.57
Nitrogen/Carbon Monoxide (Prausnitz et al, 1966)						
83.82	a	0.0095	-	-	1.805	0.97
83.82	b	0.0097	-	-	1.802	0.97
83.82	c	-0.3718	1.656	10.000	0.798	0.36
Nitrogen/Methane (Prausnitz et al, 1966)						
90.67	a	0.0234	-	-	2.549	1.34
90.67	b	0.0360	-	-	2.706	1.36
90.67	c	0.0018	2.385	1.973	1.145	0.39

- ¹ Mixing Rule: a) Classical Mixing Rule
b) Density Dependent Mixing Rule (with $z_1 = z_2 = 2$)
c) Density Dependent Mixing Rule

Table IV: Average Percentage Error in Vapor-Phase Composition
for Cryogenic Vapor/Liquid Systems

Argon/Methane (Prausnitz et al, 1966)

Mixing rule a:	1.64 %
Mixing rule b:	1.4 %
Mixing rule c:	1.11 %

Nitrogen/Argon (Prausnitz et al, 1966)

Mixing rule a:	2.50 %
Mixing rule b:	2.50 %
Mixing rule c:	2.36 %

Nitrogen/Carbon Monoxide (Prausnitz et al, 1966)

Mixing rule a:	2.07 %
Mixing rule b:	2.07 %
Mixing rule c:	2.40 %

Nitrogen/Methane (Prausnitz et al, 1966)

Mixing rule a:	0.27 %
Mixing rule b:	0.24 %
Mixing rule c:	0.24 %

NOTES: Percent error was calculated as follows:

$$\frac{y_{cal} - y_{exp}}{y_{exp}} \times 100$$

a = Classical Mixing Rule

b = Density Dependent Mixing Rule (with $z_1 = z_2 = 2$)

c = Density Dependent Mixing Rule

APPENDIX II: DEVELOPMENT OF CANONICAL PARTITION FUNCTION

The canonical partition function of statistical mechanics may be written as:

$$Q = \left(\sum \exp \left\{ - \frac{E^t}{kT} \right\} \right) \left(\prod_i q_i^{N_i} \right) \quad (\text{AII.1})$$

where the summation is over all possible molecular arrangements of the mixture, E^t is the total intermolecular energy of arrangement, and q_i is the molecular partition function arising from the translational, rotational, and vibrational properties of molecule i . Since the Knox model assumes that q_i is independent of molecular arrangement, equation (AII.1) may be rewritten [Hill, 1960, eqn. (20-5)] :

$$Q = \left(\sum W \exp \left\{ - \frac{E^t}{kT} \right\} \right) \left(\prod_i q_i^{N_i} \right) \quad (\text{AII.2})$$

where the summation is now over all values of E^t , and the combinatorial factor W gives the number of molecular arrangements associated with the energy E^t .

The energy E^t is the sum of all individual pair-interaction energies, u_{ij} :

$$E^t = \sum_i \sum_j N_{ij} u_{ij} \quad (\text{AII.3})$$

W is assumed proportional to the number of distinguishable ways in which the total of I pair interactions can be distributed over the I interaction sites:

$$W = h \frac{I!}{\prod_i \prod_j N_{ij}!} \quad (\text{AII.4})$$

For the case of an athermal solution, for which all pair interactions have the same energy, eqn (AII.2) has but a single term and a single W which is the total number of molecular arrangements. Thus W^{ath} is obtained by summing eqn (AII.4) over all sets of N_{ij} :

$$W^{\text{ath}} = \sum W = h \sum \frac{I!}{\prod_i \prod_j N_{ij}!} \quad (\text{AII.5})$$

The sum in equation (AII.5) is evaluated (Knox, 1984, Appendix A) and solved for h:

$$h = W^{\text{ath}} \left[\frac{\prod_i (z_i N_i / 2)!}{I!} \right]^2 \quad (\text{AII.6})$$

Combining equations (AII.2), (AII.4), and (AII.6) gives:

$$Q = \prod_i q_i^{N_i} \sum W^{\text{ath}} \frac{\left[\frac{\prod_i (z_i N_i / 2)!}{I! \prod_i \prod_j N_{ij}!} \right]^2 \left[\exp \left\{ - \frac{E_t}{kT} \right\} \right]}{\prod_i \prod_j N_{ij}!} \quad (\text{AII.7})$$

Replacing the sum in eqn (AII.7) by its maximum term (Hill, 1960, Appendix II), we get the canonical partition function in its final form:

$$Q = W^{\text{ath}} \frac{\left[\prod_i (z_i N_i / 2)! \right]^2}{I! \prod_i \prod_j N_{ij}!} \left[\exp - \sum_i \sum_j \frac{N_{ij} u_{ij}}{kT} \right] \prod_i q_i^{N_i} \quad (\text{AII.8})$$

APPENDIX III: DEVELOPMENT OF EQUATION OF STATE

Thermodynamics gives us the following relationship between the Helmholtz energy (expressed as a function of T, V^t , and N_i) and the pressure:

$$P = - \left(\frac{\partial A^t}{\partial V^t} \right)_{T, N_i} \quad (\text{AIII.1})$$

The expression for A^t is given as:

$$\begin{aligned} \frac{A^t}{kT} = & - \ln W^{\text{ath}} - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + \sum_i \sum_j N_{ij} \ln \frac{N_{ij}}{z_i N_i / 2} \\ & + \sum_i \sum_j N_{ij} \frac{\epsilon_{ij}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) - \sum_i N_i \ln \left[(V^t - b^t) q_i^{\text{int}} \right] \quad (\text{AIII.2}) \end{aligned}$$

Differentiating with respect to V^t and dropping terms which are not density dependent:

$$\begin{aligned} \frac{P}{kT} = - \left(\frac{\partial A^t / kT}{\partial V^t} \right)_{T, N_i} = & + 0 + 0 - \frac{\partial}{\partial V^t} \left[\sum_i \sum_j N_{ij} \ln \left(\frac{N_{ij}}{z_i N_i / 2} \right) \right] \\ & - \frac{\partial}{\partial V^t} \left[\sum_i \sum_j N_{ij} \frac{\epsilon_{ij}}{kT} \frac{1}{b} \ln \left\{ 1 + \frac{b}{V} \right\} \right] \\ & + \frac{\partial}{\partial V^t} \left[\sum_i \ln \left\{ (V^t - b^t) q_i^{\text{int}} \right\} \right] \quad (\text{AIII.3}) \end{aligned}$$

Simplifying we get:

$$\begin{aligned} \frac{P}{kT} = & - \sum_i \sum_j \left[\frac{z_i N_i}{2} + \ln \frac{N_{ij}}{z_i N_i / 2} + \frac{\epsilon_{ij}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) \right] \frac{\partial N_{ij}}{\partial V^t} \\ & + \sum_i \sum_j \frac{N_{ij} \epsilon_{ij}}{kT} \frac{1}{V(V+b)} + \sum_i N_i \left(\frac{1}{V^t - b^t} \right) \end{aligned} \quad (\text{AIII.4})$$

Expanding the summation which contains the differential $\frac{\partial N_{ij}}{\partial V^t}$

for $j > i$, $j = i$, $j < i$, we get:

$$\begin{aligned} - \sum_i \sum_{j > i} & = - \sum_i \sum_{j > i} \left[\frac{z_i N_i}{2} + \ln \frac{N_{ij}}{z_i N_i / 2} + \frac{\epsilon_{ij}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) \right] \frac{\partial N_{ij}}{\partial V^t} \\ - \sum_i & \left[\frac{z_i N_i}{2} + \ln \frac{N_{ii}}{z_i N_i / 2} + \frac{\epsilon_{ii}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) \right] \frac{\partial N_{ii}}{\partial V^t} \\ - \sum_i \sum_{j < i} & \left[\frac{z_i N_i}{2} + \ln \frac{N_{ij}}{z_i N_i / 2} + \frac{\epsilon_{ij}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) \right] \frac{\partial N_{ij}}{\partial V^t} \end{aligned} \quad (\text{AIII.5})$$

Differentiating N_{ij} with respect to V^t we get:

$$\frac{\partial}{\partial V^t} \left(\sum_i N_{ij} \right) = 0 \quad (\text{AIII.6})$$

Expanding the differential for $j>i$, $j=i$, $j<i$, we find:

$$\frac{\partial}{\partial V^t} (N_{ii}) = - \frac{\partial}{\partial V^t} \left(\sum_{j>i} N_{ij} \right) - \frac{\partial}{\partial V^t} \left(\sum_{j<i} N_{ij} \right) \quad (\text{AIII.7})$$

Substituting this relationship into the expanded summation, eqn (AIII.5), we find that the entire series is equal to zero. Thus the remaining expression is as follows:

$$\frac{P}{kT} = \sum_i N_i \left(\frac{1}{V^t - b^t} \right) + \sum_i \sum_j \frac{N_{ij} \epsilon_{ij}}{kT} \frac{1}{V(V+b)} \quad (\text{AIII.8})$$

Moving kT to the other side of the eqn (AIII.8), multiplying by L/L , and noting the following relationships:

$$\frac{N_{ij}}{z_i N_i / 2} = x_{ij} \quad (\text{AIII.9})$$

$$\frac{N_i}{L} = n_i \quad (\text{AIII.10})$$

$$kL = R \quad (\text{AIII.11})$$

We arrive at the equation:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \quad (\text{AIII.12})$$

where we have noted that the quantity a is given by:

$$a = - \sum_i \sum_j \frac{z_i x_j}{2} x_{ij} \varepsilon_{ij} L = \sum_i \sum_j x_i x_j a_{ij} \quad (\text{AIII.13})$$

APPENDIX IV: DEVELOPMENT OF FUGACITY COEFFICIENT EXPRESSION

Thermodynamics gives us the relationship between the Helmholtz energy (expressed as a function of T , V^t , and N_i) and the component fugacity coefficient as:

$$\ln \hat{\phi}_k = - \left\{ \left[\frac{\partial (A^t/kT)}{\partial N_k} \right]_{T, V^t, N_j} + \ln V^t \right\} \Bigg|_{V^t}^{\infty} - \ln Z \quad (\text{AIV.1})$$

Thus, we choose to evaluate the expression A^t/kT at the limits $V^t = \infty$ and $V^t = V^t$ before we differentiate.

Noting that at $V^t = \infty$, we have:

$$x_{ij} = x_j \quad (\text{AIV.2})$$

$$N_{ij} = (z_i N_i / 2) (z_j N_j / 2) / I \quad (\text{AIV.3})$$

Therefore:

$$\begin{aligned} \frac{A^t(\infty)}{kT} &= - \ln W^{\text{ath}} - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + 'T' \\ &+ 0 - \sum_i N_i \ln (\infty) - \sum_i N_i \ln q^{\text{int}} \quad (\text{AIV.4}) \end{aligned}$$

Here we have defined 'T' as:

$$' T ' = \sum_i \sum_j N_{ij} \ln \frac{N_{ij}}{z_i N_i / 2} \quad (\text{AIV.5})$$

Noting that $I = \sum_i z_i N_i / 2$, ' T ' is simplified to the following:

$$' T ' = \sum_i \frac{z_i N_i}{2} \ln \left(\frac{z_i N_i / 2}{I} \right) \quad (\text{AIV.6})$$

Thus:

$$\begin{aligned} \frac{A^t(V^t) - A^t(\infty)}{kT} = & - \sum_i \frac{z_i N_i}{2} \ln \frac{z_i N_i / 2}{I} + \sum_i \sum_j N_{ij} \ln \frac{N_{ij}}{z_i N_i / 2} \\ & + \sum_i \sum_j N_{ij} \frac{\epsilon_{ij}}{kT} \frac{1}{b} \ln \left(1 + \frac{b}{V} \right) - \sum_i N_i \ln (V^t - b^t) - \sum_i N_i \ln (\infty) \end{aligned} \quad (\text{AIV.7})$$

Differentiating eqn (AIV.7) with respect to N_k , we obtain:

$$\begin{aligned}
\frac{\partial}{\partial N_k} \left[\frac{A^t(V^t) - A^t(\infty)}{kT} \right] &= - \sum_i \left\{ \left[\frac{z_i}{2} \left(\frac{\partial N_i}{\partial N_k} \right) - \frac{(z_i N_i/2) z_k}{I} \right] + \frac{(z_i \partial N_i)}{2 \partial N_k} \ln \left(\frac{z_i N_i/2}{I} \right) \right\} \\
&+ \sum_i \sum_j \left\{ \left(\frac{\partial N_{ij}}{\partial N_k} \right) - \left(\frac{N_{ij}}{z_i N_i/2} \right) \left(\frac{z_i}{2} \right) \left(\frac{\partial N_i}{\partial N_k} \right) + \left(\frac{\partial N_{ij}}{\partial N_k} \right) \ln \left(\frac{N_{ij}}{z_i N_i/2} \right) \right\} \\
&+ \sum_i \sum_j \left(\frac{\partial N_{ij}}{\partial N_k} \right) \left[\frac{\epsilon_{ij} \ln(1+b/V)}{kT} \right] - \sum_i \sum_j \frac{N_{ij} \epsilon_{ij}}{kT} \frac{\ln(1+b/V)}{b^2} \frac{\partial b}{\partial N_k} \\
&+ \sum_i \sum_j \frac{N_{ij} \epsilon_{ij}}{kT} \frac{1}{b(V^t+b^t)} \frac{\partial b^t}{\partial N_k} - \sum_i \left(\frac{\partial N_i}{\partial N_k} \right) \ln(V^t - b^t) + \sum_i \frac{N_i}{V^t - b^t} \frac{\partial b^t}{\partial N_k} + \sum_i \left(\frac{\partial N_i}{\partial N_k} \right) \ln \infty
\end{aligned} \tag{AIV.8}$$

For $i = k$, eqn (AIV.8) can be factored and simplified to:

$$\begin{aligned}
\frac{\partial}{\partial N_k} \left[\frac{A^t(V^t) - A^t(\infty)}{kT} \right] &= - \frac{z_k}{2} - \frac{z_k}{2} \ln \left(\frac{z_k N_k/2}{I} \right) \\
&+ 'R' - \sum_i \sum_j \frac{N_{ij} \epsilon_{ij}}{kT} \frac{\ln(1+b/V)}{b^2} \frac{\partial b}{\partial N_k} \\
&+ \sum_i \sum_j \frac{N_{ij} \epsilon_{ij}}{kT} \frac{1}{b(V^t+b^t)} \frac{\partial b^t}{\partial N_k} - \sum_i \left(\frac{\partial N_i}{\partial N_k} \right) \ln(V^t - b^t) + \sum_i \frac{N_i}{V^t - b^t} \frac{\partial b^t}{\partial N_k} + \sum_i \left(\frac{\partial N_i}{\partial N_k} \right) \ln \infty
\end{aligned} \tag{AIV.9}$$

where:

$$'R' = \sum_i \sum_j \left(\frac{\partial N_{ij}}{\partial N_k} \right) \left[1 + \ln \left(\frac{N_{ij}}{z_i N_i/2} \right) + \frac{\epsilon_{ij} \ln(1+b^t/V^t)}{kT} \right] \tag{AIV.10}$$

Equation (AIV.10) is now expanded and simplified:

$$\begin{aligned}
' R ' &= \frac{z_k}{2} \left[1 + \ln \frac{N_{kk}}{z_k N_k / 2} + \frac{\epsilon_{kk}}{kT} \frac{\ln(1 + b/V)}{b} \right] \\
&+ \sum_{j < i} \left(\frac{\partial N_{ij}}{\partial N_k} \right) \left[\ln \frac{N_{ij}}{N_{ii}} + \frac{\epsilon_{ij} - \epsilon_{ii}}{kT} \frac{\ln(1 + b/V)}{b} \right] \\
&+ \sum_{j > i} \left(\frac{\partial N_{ij}}{\partial N_k} \right) \left[\ln \frac{N_{ij}}{N_{ii}} + \frac{\epsilon_{ij} - \epsilon_{ii}}{kT} \frac{\ln(1 + b/V)}{b} \right]
\end{aligned} \tag{AIV.11}$$

Changing the indices in the last summation and noting that:

$$\frac{\partial N_{ij}}{\partial N_k} = \frac{\partial N_{ji}}{\partial N_k} \tag{AIV.12}$$

$$' R ' = \frac{z_k}{2} \left[1 + \ln \frac{N_{kk}}{z_k N_k / 2} + \frac{\epsilon_{kk}}{kT} \frac{\ln(1 + b/V)}{b} \right] \tag{AIV.13}$$

with the result:

$$\ln \frac{N_{ii} N_{jj}}{N_{ii} N_{jj}} + \frac{(2\epsilon_{ij} - \epsilon_{ii} - \epsilon_{jj}) \ln(1 + b/V)}{kT b} = 0 \tag{AIV.14}$$

OR

$$\frac{N_{ii} N_{jj}}{N_{ii} N_{jj}} = \exp \left\{ - \frac{(2\epsilon_{ij} - \epsilon_{ii} - \epsilon_{jj}) \ln(1 + b/V)}{kT b} \right\} \tag{AIV.15}$$

Substituting ' R ' back into eqn (AIV.9) and simplifying, we get:

$$\begin{aligned}
\frac{\partial}{\partial N_k} \left[\frac{A^t(V^t) - A^t(\infty)}{kT} \right] = & - \frac{z_k}{2} \ln(\theta_k) + \frac{z_k}{2} \ln x_{kk} + \frac{z_k}{2} \frac{s_{kk}}{kT} \frac{\ln(1+b/V)}{b} \\
& + \sum_i \sum_j \frac{N_{ij} e_{ij}}{kT} \frac{1}{b(V^t + b^t)} + \sum_i \frac{N_i}{(V^t - b^t)} \frac{\partial b^t}{\partial N_k} \\
& - \sum_i \sum_j \frac{N_{ij} e_{ij}}{kT} \frac{\ln(1+b/V)}{b^2} \frac{\partial b}{\partial N_k} - \sum_i \ln(V^t - b^t) + \ln \infty \quad (\text{AIV.16})
\end{aligned}$$

Here we have noted $\theta_k = (z_k N_k / 2) / I$ and $x_{kk} = N_{kk} / (z_k N_k / 2)$. Substituting the above expression into the fugacity coefficient expression, eqn (AIV.1), and combining similar terms we get:

$$\begin{aligned}
\ln \hat{\phi}_k = & \frac{z_k}{2} \ln \frac{x_{kk}}{\theta_k} + \frac{z_k}{2} \frac{s_{kk}}{kT} \frac{\ln(1+b/V)}{b} \\
& + \left[\sum_i \sum_j \frac{N_{ij} e_{ij}}{kT} \frac{1}{b(V^t + b^t)} + \sum_i \frac{N_i}{(V^t - b^t)} \right] \frac{\partial b^t}{\partial N_k} \quad (\text{AIV.17}) \\
& - \sum_i \sum_j \frac{N_{ij} e_{ij}}{kT} \frac{\ln(1+b/V)}{b^2} \frac{\partial b}{\partial N_k} - \ln \frac{P(V^t - b^t)}{nRT}
\end{aligned}$$

Noting that:

$$\frac{\partial b}{\partial N_k} = \frac{1}{L} b_k \quad (\text{AIV.18})$$

$$\frac{\partial b}{\partial N_k} = \frac{1}{N} (b_k - b) \quad (\text{AIV.19})$$

$$N_{ij} = \frac{z_i N_i}{2} x_{ij} \quad (\text{AIV.20})$$

$$N = nL \quad (\text{AIV.21})$$

$$N_k = n_k L \quad (\text{AIV.22})$$

The fugacity coefficient expression, eqn (AIV.17) is simplified to give:

$$\begin{aligned} \ln \hat{\theta}_k &= \frac{z_k}{2} \ln \frac{x_{kk}}{\theta_k} + \frac{z_k}{2} \frac{\epsilon_{kk}}{kT} \frac{\ln(1+b/V)}{b} + \frac{b_k}{V-b} - \ln \left[\frac{P(V-b)}{RT} \right] \\ &\quad - \frac{a}{RT} \left(\frac{b_k/b}{V+b} \right) + \frac{a}{RT} \frac{\ln(1+b/V)}{b} \left[\frac{b_k}{b} - 1 \right] \end{aligned} \quad (\text{AIV.23})$$

where a is given by the quantity:

$$a = - \sum_i \sum_j \frac{z_i x_i}{2} x_{ij} \epsilon_{ij} L_{ij} = \sum_i \sum_j x_i x_{ij} a_{ij} \quad (\text{AIV.24})$$