



VGTPR - AN IMPROVED GROUP CONTRIBUTION VOLUME TRANSLATED PENG-ROBINSON EQUATION OF STATE

Alan Foster

Thermodynamics Research Unit

University of KwaZulu-Natal, Durban, South Africa

OVERVIEW

- **Introduction**
- **Review**
- **The VGTPR model**
- **Future work**



- There are 2 traditional classes of thermodynamic models for phase equilibria calculations:
 - Activity Coefficient / g^E Models
 - Equations of State

- **g^E MODELS**

- In VLE calculations → used for description of non-ideality in liquid phase
- Mixtures of almost any complexity
- Full predictive capabilities (group contribution)
- Robust and simple
- Limited to liquids well away from critical point

- **EQUATIONS OF STATE**

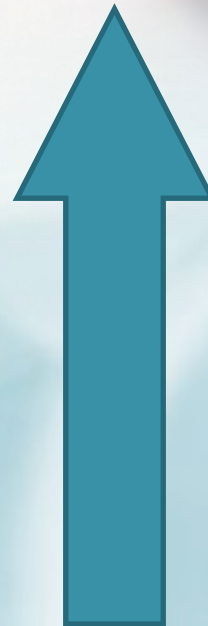
- Cubic EOS based on van der Waals equation = most popular
- In VLE calculations → used to describe non-ideality of both liquid and vapour phase
- Can handle supercritical components
- Calculation of a large number of thermodynamic properties
- Results for mixtures depend strongly on mixing rule used

- **LINKING THE TWO METHODS**

Disadvantages



Advantages



- **HOW TO LINK THE TWO METHODS?**
 - Apply the following assumption for calculation of the α_m parameter
 - Replace traditional mixing rules
 - Known as a g^E mixing rule

$$g_{EOS}^E = g_{\gamma\text{-model}}^E$$

$$\gamma_{i,EOS} = \gamma_{i,\gamma\text{-model}}$$

- Vidal
- Mollerup
- PSRK
- VTPR
- Additionally reviewed:
 - MHV1
 - MHV2
 - Wong-Sandler
 - LCVM
 -



- **Vidal**

- Vidal and later Huron and Vidal were the first to successfully link g^E
- Applied infinite pressure limit to simplify EOS g^E expression
- As $P \rightarrow \infty$:

$$v_m \rightarrow b_m$$

$$v_i \rightarrow b_i$$

- Assumed pressure dependence of g^E is negligible

- Vidal

$$g_{EOS}^E = -RT \left[\ln \left(\frac{P(v_m - b_m)}{RT} \right) - \sum_{i=1}^{nc} x_i \ln \left(\frac{P(v_i - b_i)}{RT} \right) \right] + Pv_m - \sum_{i=1}^{nc} x_i Pv_i - \frac{a_m}{b_m} \ln \left(\frac{v_m + b_m}{v_m} \right) + \sum_{i=1}^{nc} x_i \frac{a_i}{b_i} \ln \left(\frac{v_i + b_i}{v_i} \right)$$

$P \rightarrow \infty$

From Redlich-Kwong EOS

$$a_m = b_m \left(\sum_{i=1}^{nc} \frac{a_i}{b_i} x_i - \frac{g_{\infty}^E}{\ln 2} \right)$$

$g_{\gamma\text{-model}}^E$

- **PROBLEM:** g^E model parameters are fitted at low pressure and g^E is dependent on pressure, therefore:

$$g_{EOS}^E (P \rightarrow \infty) \neq g_{\gamma\text{-model}}^E (P = \text{low})$$

- g^E model parameters must be refitted for use in the Vidal mixing rule

- **Mollerup**

- Huge step forward
- Applied zero pressure limit to simplify EOS g^E expression
- g^E from EOS at zero pressure much closer to g^E from model than at infinite pressure
- No refitting of model parameters required
- **Assumed** constant reduced liquid volume, u :

$$u = \frac{v_i}{b_i} = \frac{v_m}{b_m} = \text{constant}$$

- **PSRK (Predictive Soave-Redlich-Kwong)**

- Very successful and widely used
- Combines SRK EOS and UNIFAC
- Uses MHV1 mixing rule at atmospheric reference pressure
- Different reference pressure = Different u-value

$$u = 1.1$$

- The PSRK mixing rule:

$$a_m = b_m \left(\sum_{i=1}^{nc} x_i \frac{a_i}{b_i} - \frac{1}{0.64663} \left(g_\gamma^E + RT \sum_{i=1}^{nc} x_i \ln \left(\frac{b_m}{b_i} \right) \right) \right)$$

=0.593 in MHV1

- **PSRK (Predictive Soave-Redlich-Kwong)**

- Advantages:

- Reliable results
- Supercritical — addition of gas groups to UNIFAC matrix
- No refitting of parameters required
- Large number of available UNIFAC parameters

- Disadvantages

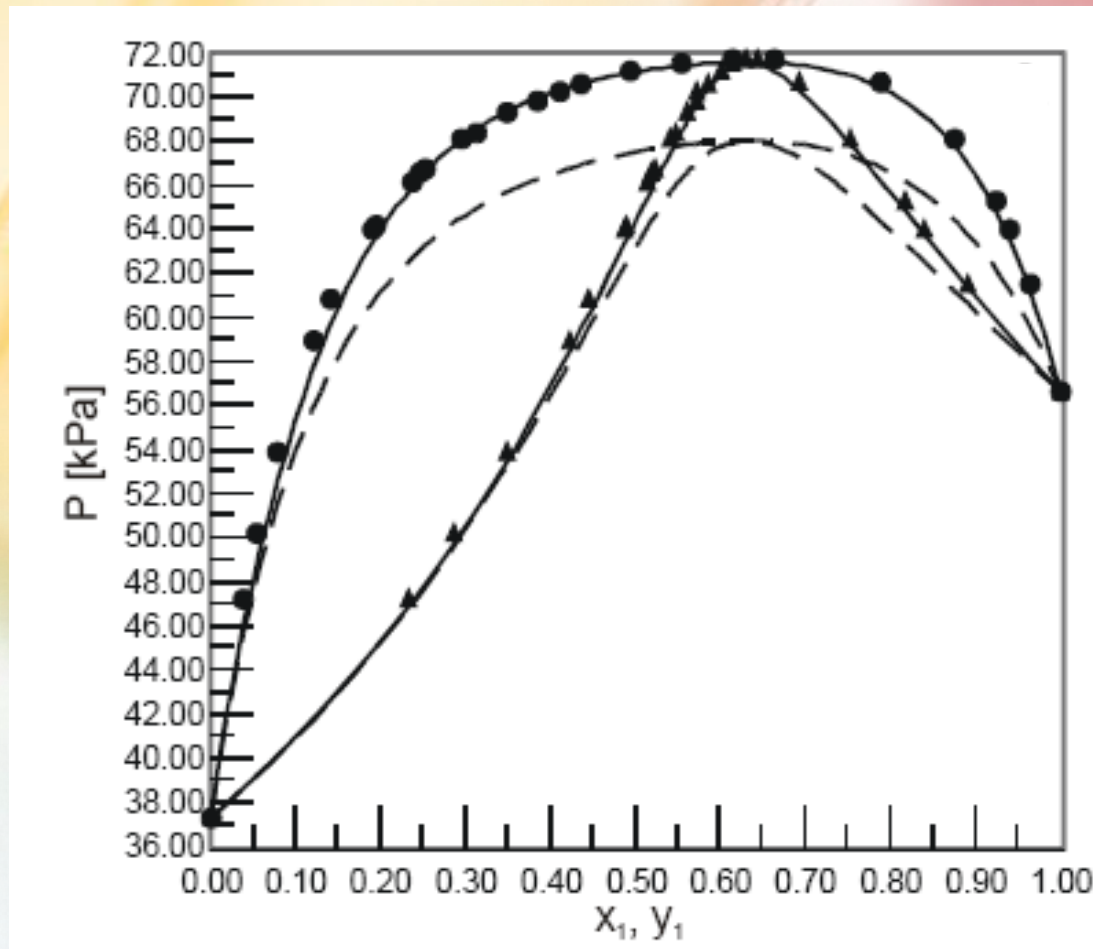
- Poor liquid density representation - general problem of cubic equations of state
- Mathias-Copeman α function
- Unsatisfactory predictions of asymmetric systems
- Unsatisfactory predictions of (a) h^E and (b) γ^∞ of asymmetric systems

- **VTPR (Volume Translated Peng-Robinson)**
 - **Changes made to PSRK:**

Model	PSRK	VTPR
Equation of State	Soave-Redlich-Kwong	Volume Translated Peng-Robinson
α - Function	Mathias - Copeman	Two
g^E mixing rule	$a_m = b_m \left(\sum_{i=1}^{nc} x_i \frac{a_i}{b_i} - \frac{1}{0.64663} \left(g_\gamma^E + RT \sum_{i=1}^{nc} x_i \ln \left(\frac{b_m}{b_i} \right) \right) \right)$	$a_m = b_m \left(\sum_{i=1}^{nc} x_i \frac{a_i}{b_i} - \frac{g_{res}^E}{0.53087} \right)$
b mixing rule	$b_m = \sum_{i=1}^{nc} x_i b_i$	$b_m = \sum_{i=1}^{nc} \sum_{j=1}^{nc} x_i x_j b_{ij} \quad b_{ij} = \left(\frac{b_i^{3/4} + b_j^{3/4}}{2} \right)^{4/3}$
g^E model	UNIFAC	mod. UNIFAC (Do)
g^E model parameters	Temperature independent original UNIFAC parameters	Temperature dependent VTPR specific parameters

- **VTPR**
 - Much improved model over PSRK
 - Wide range of applicability
 - Only downside when compared to PSRK = availability of parameters

- **VGTPR (Volume Gibbs Translated Peng-Robinson)**
 - The Problem:
 - VTPR = hugely advantageous
 - **BUT** limited by availability of parameters
 - Can not directly use mod. UNIFAC parameters in VTPR g^E mixing rule as real mixture behavior is predicted differently by the two methods

P-x-y for the system Acetone (1) + Hexane (2) at 313 K

(- - -) VTPR with mod. UNIFAC (Do)
(—) VTPR
(● ▲) Experimental Results

- **What does VGTPR do?**

- Greatly increases available parameters for VTPR by allowing the use of large number of existing mod. UNIFAC (Do) parameters
- While still maintaining the advantages of the very successful VTPR model

- **How?**

- Forces the real mixture behavior description by the EOS to match that of the g^E model (which is assumed correct)
- Introduces a g^E translation term to the VTPR g^E mixing rule:

VGTPR g^E mixing rule

$$a_m = b_m \left(\sum_{i=1}^{nc} x_i \frac{a_i}{b_i} - \frac{g_{res}^E + g_{trans}^E}{0.53087} \right)$$

- **g^E Translation Term**

- May be defined as:

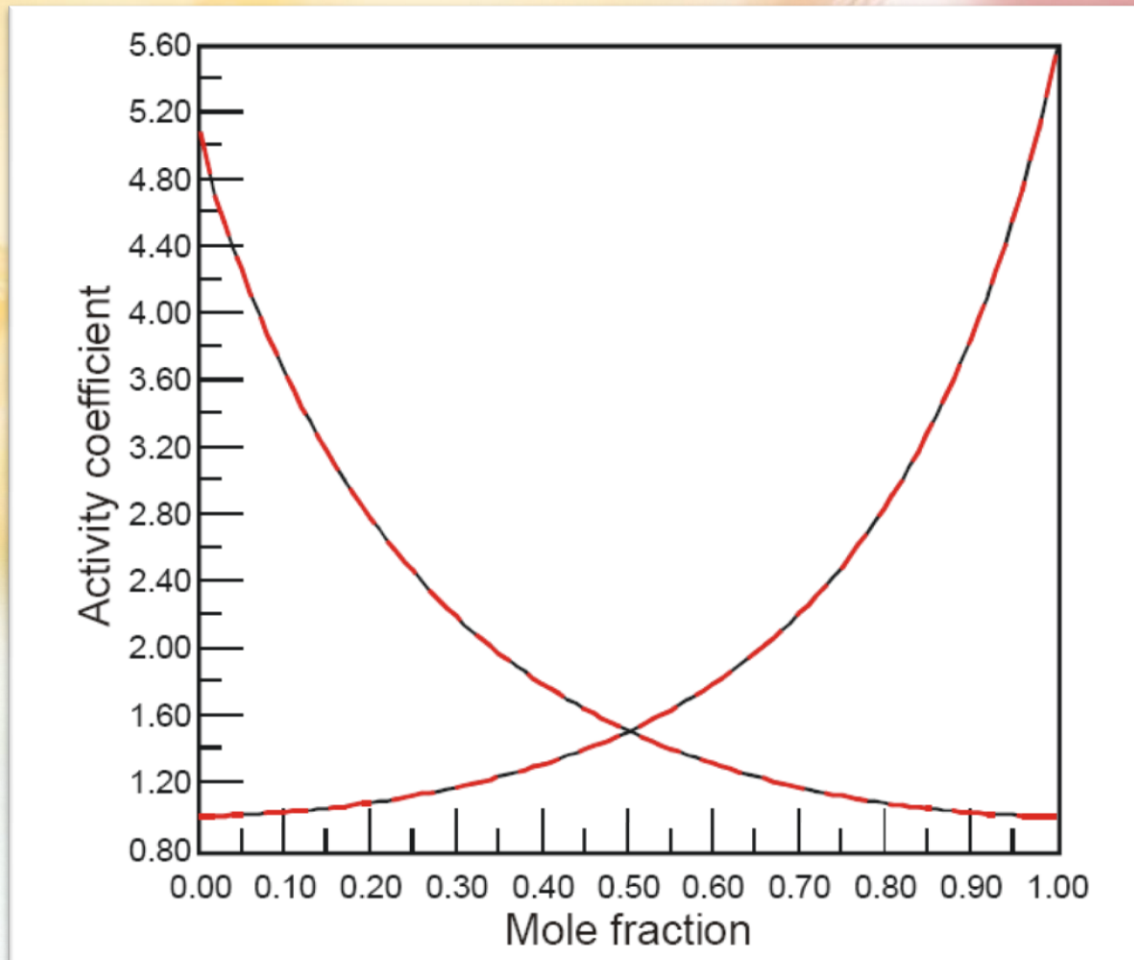
$$g_{trans}^E = RT \sum_i x_i \ln \gamma_i^{trans}$$

Translates the $\gamma_i^{\gamma\text{-model}}$ term found in the EOS fugacity coefficient calculation

- Found by iterative adjustments of γ_i^{trans} until the following equality is satisfied for all i :

$$\gamma_i^{EOS} = \gamma_i^{\gamma\text{-model}}$$

- **The Result**



Activity coefficients for
the system:
Acetone (1) + Hexane
(2) at 313 K

(- - -) mod. UNIFAC (Do)
(—) VGTPR

- **Supercritical Systems**

- VGTPR may be used in calculations of supercritical systems by introducing a constant reference volume:

Reference Volume

$$v = u \cdot b = 1.22489 \cdot b$$

- Sub and supercritical calculations are performed at this reference volume instead of following the saturation curve
- Subcritical → Difference between the saturation volume and reference volume is assumed to be very small
- Supercritical → Some mod. UNIFAC (Do) parameters may be used directly , however some may need to be refitted
- Concept needs further testing

- **Review of the VGTPR model**
 - Same advantages as very successful VTPR model
 - Able to use large amount of existing mod. UNIFAC parameters
 - Activity coefficients between EOS and g^E model matched **EXACTLY**
 - Fixed reference volume may allow supercritical calculations
 - Gas parameters need to be fitted — no gas parameters in mod. UNIFAC (Do)

- Promising results so far from the work of Eileen Collinet
- These results need to be confirmed and understood
- Further tests on the model need to be performed — especially regarding the fixed reference volume
- Fit mod. UNIFAC (Do) gas parameters to PSRK results to check capability of the VGTPR model for representation of gas systems

AKNOWLEDGMENTS

- **Supervisors**
 - Prof. Dr. J. Rarey
 - Prof. Dr. D. Ramjugernath
- **VTPR project**
 - Arbeitsgemeinschaft industrieller Forschungseinrichtungen (AiF)
- **National Research Foundation**