

H. Knapp
R. Döring
L. Oellrich
U. Plöcker
J. M. Prausnitz

VAPOR – LIQUID EQUILIBRIA FOR MIXTURES OF LOW BOILING SUBSTANCES



Chemistry Data Series

Vol. VI

**H. Knapp
R. Döring
L. Oellrich
U. Plöcker
J. M. Prausnitz**

VAPOR – LIQUID EQUILIBRIA FOR MIXTURES OF LOW BOILING SUBSTANCES



Chemistry Data Series

Vol. VI

**Published by DECHEMA
Deutsche Gesellschaft für Chemisches Apparatewesen
Editors: Dieter Behrens, Reiner Eckermann**

© 1982 DECHEMA Deutsche Gesellschaft für Chemisches Apparatewesen
6000 Frankfurt/Main, Federal Republic of Germany

ISBN 3-921 567-38-6

All rights reserved

No part of this work may be reproduced or used in any form or by any means — graphic, electronic, or mechanical, including photocopying, recording, or taping, or information storage and retrieval systems — without written permission of the publishers.

Printed by Schön & Wetzel GmbH, Frankfurt/Main, F. R. Germany

Vapor-Liquid Equilibria for Mixtures of Low Boiling Substances

H. Knapp, R. Döring, L. Oellrich, U. Plöcker, J. M. Prausnitz

Institute of Thermodynamics and Plant Design
Technical University Berlin (West)

PREFACE OF AUTHORS

Phase equilibrium data are basic information required in process design for the chemical, oil and gas industry. It is important to know where to find experimental data, how to correlate these data and when to rely on predicted data. This volume is intended to assist in answering these questions by presenting a literature review and a data bank, a summary of correlations with four generalized equations of state and a numerical and graphical comparison between measured and calculated data — for mixtures containing a limited number of substances, so-called normal fluids.

The work was done in the Institute of Thermodynamics and Plant Design at the Technical University of Berlin.

It could only be done with the assistance and with the contributions of various persons, groups and institutions. The authors highly appreciate the comments and the cooperation of the members of the Engineering Data Development Group. We are grateful for the financial aid received from the European Relief Program and from the Ministry of Research and Technology of the Federal Republic of Germany. We also acknowledge the assistance given by the library and the computer centre of the Technical University. We are indebted to Dechema for initiating and editing our work.

We feel that of all those persons who helped, some should be mentioned by name:

C. H. Jakob of LURGI, R. Eckermann and C. Hammer of DECHEMA, H. W. Kremer and H. Wendeler of the Institute of Thermodynamics and Plant Design. And finally, we thank Mrs. I. Skowronski and Mrs. I. B. Weise for their dedicated secretarial help.

We hope that this volume will help its users to save time and effort in their daily work. Any questions with respect to the Berlin Data Bank, the program modules and their further development should be directed to the Institute of Thermodynamics and Plant Design, Technical University, D-1000 Berlin (West).

The data bank is also integrated into the DSD (Dechema Data Service) in Frankfurt/Main.

Prof. Dr.rer.nat. Helmut Knapp is with the Institute of Thermodynamics and Plant Design at the Technical University of Berlin, Prof. Dr.Ing. Reinhold Döring is now with the Technical College Münster, Dr.Ing. Lothar Oellrich is now with Liquid Gas International, Bonn, Dr.Ing. Ulf Plöcker is now with Degussa, Hanau-Wolfgang, Prof. Dr. John M. Prausnitz is with the Department of Chemical Engineering at the University of California, Berkeley.

Berlin, 30th of November, 1981

H. Knapp R. Döring L. Oellrich U. Plöcker J. M. Prausnitz

PREFACE OF EDITORS

Subjects of the DECHEMA Chemistry Data Series are the physical and thermodynamic property data of chemical compounds and mixtures essentially for the fluid state covering PVT data, heat capacity, and entropy data, phase equilibrium data, transport and interfacial tension data.

Thermophysical property data are needed for the designing of process units. In designing process units, one cannot rely on the data found in the literature alone: for example, one can seldom find data for mixtures. What one needs in modern plant design is the exactest possible advance computation of physical property data.

For computer based calculations appropriate correlation methods and accurate data must be used. For that reason the publication of critically evaluated and recommended values is most urgent, which is the main purpose of the series.

Therefore, the DECHEMA gives the opportunity to authors especially from universities to publish not only their theoretical results, but also their measured, compiled and evaluated data resulting from the development of methods for the computation of thermophysical properties, most often a large amount that would otherwise never have been published.

For the prediction of low-temperature phase equilibria the work of H. Knapp, R. Döring, L. Oellrich, U. Plöcker, J. M. Prausnitz resulted in a comprehensive data collection and bibliography and led to an extension of the Lee-Kesler equation of state.

We present the evaluation of the data material and the results of the application of several equations of state to low-temperature vapor-liquid equilibria with this volume of the DECHEMA Chemistry Data Series.

We hope that this material will give the users an instrument that allow them to solve their problems considerably more easily and quickly than before.

Frankfurt/Main, November 1981

Dieter Behrens
Reiner Eckermann

LIST OF SYMBOLS

a, b	parameters in van der Waals equation of state
B, C	coefficients in virial equation of state
f_i	fugacity of component i
h	molal enthalpy
K_i	equilibrium constant of component i , $K_i = y_i/x_i$
k_{ij}	binary interaction parameter for BWRS, RKS and PR equation of state
k_{ij}^*	binary interaction parameter for LKP equation of state
M	molar mass
n	number of moles
p	pressure
R	gas constant
T	temperature
v	molar volume
V	total volume
x_i	liquid phase mole fraction of component i
y_i	vapor phase mole fraction of component i
γ_i	activity coefficient of component i
ϕ	fugacity coefficient
ϕ_i	fugacity coefficient of component i
μ_i	chemical potential of component i
ρ	molal density
ω	acentric factor

Superscripts

o	standard or reference state
L	Liquid phase
V	vapor phase
e	experimental
c	calculated

Subscripts

i, j	component i, j
o, i	pure substance i
M	mixture
c	critical
r	reduced

GENERAL REMARKS AND EXPLANATIONS

1. INTRODUCTION

One of the most important and most frequent operations carried out in the chemical, oil and gas industries is the separation of mixtures. Separation is necessary in order to recover pure substances or desired fractions, either from raw materials or from the products of chemical reactions. Whenever calculations for these separation processes are performed, information is required concerning thermodynamic properties such as enthalpies, entropies and phase equilibrium coefficients (K-values). The conditions in single separation stages and, to a higher degree, the conditions in multistage separation processes are found by applying iterative procedures — often multiple stacked iterations. It is therefore useful — especially when working with digital computers — to have the information available in the form of mathematical equations. It is also advantageous to have generalized equations, e.g. generalized equations of state where a few specific parameters characterize pure components and mixtures.

2. LISTING OF SUBSTANCES

The information presented in this book is restricted to a limited number of substances listed below and their mixtures:

Ar, CH₄, CO, CO₂, C₂H₂, C₂H₄, C₂H₆, C₃H₆, C₃H₈, 1C₄H₈, iC₄H₁₀, nC₄H₁₀, cC₅H₁₀, C₅H₁₂, iC₅H₁₂, nC₅H₁₂, C₆H₆, cC₆H₁₀, cC₆H₁₂, 1C₆H₁₂, nC₆H₁₄, C₇H₈, 1C₇H₁₄, nC₇H₁₆, iC₈H₁₈, nC₉H₂₀, nC₁₀H₂₂, Cl₂, D₂, D₂O, He, He₃, HCl, H₂, H₂O, H₂S, Kr, Ne, NH₃, NO, NO₂, N₂, N₂O, O₂, SO₂, Xe.

Mixtures of the above listed substances were considered in the first review that was completed 1973. The supplementary review for the period beginning 1973 was extended to include additional substances listed below:

CClF₃, CCl₂F₂, CCl₄, CF₄, CHClF₂, CHCl₂F, CHF₃, CH₂F₂, CH₂O, CH₃Cl, CH₃NO₂, CH₄O, COS, CS₂, C₂ClF₅, C₂Cl₂F₄, C₂Cl₃F₃, C₂H₂Cl₄, C₂H₃N, C₂H₄Cl₂, C₂H₄O, C₂H₅NO₂, C₂H₆O, C₃H₆O, C₃H₆O₂, C₃H₇NO, C₃H₈O, C₄H₆, C₄H₆O₂, C₄H₁₀O, C₅H₄O₂, C₅H₁₀O, C₅H₁₂O, C₆F₆, C₆H₅Cl, C₆H₇N, C₆H₁₀, C₆H₁₀O, C₆H₁₄, C₆H₁₄O, C₆H₁₄O₂, C₇H₈O, C₇H₉N, C₇H₁₄, C₈H₁₀, C₈H₁₆, C₈H₁₈O, C₉H₇N, C₉H₂₀, C₉H₂₀, C₁₀H₁₂, C₁₀H₁₄, C₁₀H₁₈, C₁₀H₂₂O, C₁₁H₁₀, nC₁₁H₂₄, C₁₂H₂₂, nC₁₂H₂₆, C₁₃H₁₂, C₁₃H₂₂, nC₁₆H₃₄, nC₁₈H₃₄, nC₁₉H₄₀, nC₂₀H₄₂, nC₂₂H₄₆, nC₂₃H₄₈, nC₂₄H₅₀, C₂₇H₄₆O, C₃₀H₆₂, SF₆, Cephalin, Lecithin.

The 1973—1980 survey is not complete with respect to the added substances. Acetone, alcohols and halogenated hydrocarbons are considered only in combination with hydrocarbons.

Most of these substances are components of technically important mixtures such as air, natural gas and synthetic gases produced by the gasification of coal and oil. As large quantities of such gas mixtures are treated in chemical process plants, there is continuous demand for reliable methods to calculate their thermodynamic properties.

3. THERMODYNAMIC FUNDAMENTALS

3.1. Methods for Calculation of Vapor-Liquid Phase Equilibria

In process design, the important variables in an equilibrium stage are temperature, pressure and the compositions of the liquid phase and the vapor phase (Fig. 1).

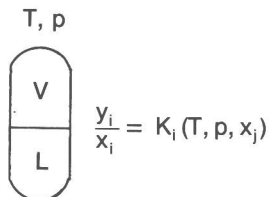


Fig. 1 Vapor-liquid phase equilibrium

In addition, the enthalpies and the molal volumes should be known.

The required information, in other words, is

$$\left. \begin{array}{l} \text{the molar volume} \\ \text{the enthalpy} \\ \text{the equilibrium coefficient} \end{array} \right\} \left\{ \begin{array}{l} \text{all as functions} \\ \text{of temperature, pressure} \\ \text{and composition} \end{array} \right.$$

This information can be produced only by experimental investigations and can then be presented in tables or diagrams. As the results of experiments are always fragmentary with respect to temperature, pressure and composition, it is often necessary to interpolate, to extrapolate and perhaps, to predict. For this purpose, experimental data must be evaluated, reduced and correlated. Hereby thermodynamic laws and functions as well as chemical and physical models provide a useful basis.

The state of equilibrium in a two-phase, multicomponent system is characterized by the condition that all intensive parameters — i.e. the temperature, the pressure and the chemical potential of each component — have constant values in the entire system. (Effects due to surface tension, gravitational, electric and magnetic fields, or any other special forces are neglected.)

Therefore $\mu_i^V = \mu_i^L$

and with $d\mu_i = RT d \ln f_i$

also $f_i^V = f_i^L$

As the chemical potential and the fugacity are functions of temperature, pressure and composition, these equilibrium conditions can be used to calculate the dependent variables after the allowable number of independent variables has been specified.

The major problem is to find the proper functions for the chemical potential or the fugacity.

It is helpful to introduce activity or fugacity coefficients and write

$$f_i^V = \phi_i^V(T, p, y_i) y_i p$$

and $f_i^L = \phi_i^L(T, p, x_i) x_i p$

or $f_i^L = \gamma_i(T, p, x_i) x_i f_i^{oL}$

The fugacity coefficient ϕ_i is an indication of the nonideal behavior of a substance, i.e. of the deviation from ideal-gas conditions. It is normalized by $\phi_i \rightarrow 1$ when $p \rightarrow 0$.

The activity coefficient is an indication of the nonideal behavior of a substance in a mixture. It is usually normalized by $\gamma_i \rightarrow 1$ when $x_i \rightarrow 1$.

Departure functions indicating the effect of temperature and pressure on the properties of a fluid, pure or multicomponent, can be calculated if the PVTX behavior of the fluid is known. Many equations of state are available for describing the compressibility factor of a fluid as a function of temperature, pressure or density and composition.

$$z = pv/(RT) \\ = z(T, p, x) \text{ or } z(T, v, x)$$

The coefficients in the equation of state can be determined e.g. from experimental PVTX data. The characteristic coefficients of a multicomponent fluid can also be determined by mixing rules. These mixing rules contain the coefficients of the pure components, the concentration of the components, sometimes the molal volumes and binary coefficients.

The departure functions are computed at constant temperature starting from the ideal-gas state as the reference or standard state. As most equations of state are functions of temperature and molal volume, it is convenient to integrate at constant temperature and composition with respect to volume.

The general thermodynamics formulas important in the calculation of phase equilibria are briefly represented:

The enthalpy departure of a pure or multicomponent fluid is calculated as follows

$$\begin{aligned} h - h^o &= \int_0^p (\partial h / \partial p)_{T,x} dp && \text{or} \\ h - h^o &= \int_0^p [v - T(\partial v / \partial T)_{p,x}] dp && \text{or} \\ h - h^o &= \int_{\infty}^v [T(\partial p / \partial T)_{v,x} - p] dv + pv - RT && \text{or} \\ (h - h^o)/RT &= \int_{\infty}^v [T(\partial z / \partial T)_{v,x} - 1] d \ln v + z - 1 \end{aligned}$$

The fugacity coefficient of a pure or multicomponent fluid is calculated as follows

$$\begin{aligned} RT \ln \phi &= \int_0^p (v - RT/p) dp && \text{or} \\ \ln \phi &= \int_0^p (z - 1) d \ln p && \text{or} \\ RT \ln \phi &= \int_{\infty}^v (RT/v - p) dv + pv - RT - RT \ln (pv/RT) && \text{or} \\ \ln \phi &= \int_{\infty}^v (1 - z) d \ln v + (z - 1) - \ln z \end{aligned}$$

The fugacity coefficient ϕ_i of component i in the mixture of r components is calculated as follows

$$RT \ln \phi_i = \int_0^p (v_i - RT/p) dp \quad \text{with } v_i = (\partial V / \partial n_i)_{T, p, n_{j \neq i}} \quad \text{or}$$

$$V = n \bar{v} \quad n = \sum_i n_i$$

$$RT \ln \phi_i = \int_0^p [RT/\bar{v} - n(\partial p / \partial n_i)_{T, p, n_{j \neq i}}] d\bar{v} - RT \ln(p\bar{v}/RT) \quad \text{or}$$

$$\ln \phi_i = [\partial(\ln \phi) / \partial n_i]_{T, p, n_{j \neq i}}$$

$$= \ln \phi - \sum_{j \neq i} x_j (\partial \ln \phi / \partial x_j)_{T, p, x_{k \neq i, j}}$$

If the same equation of state is valid for the vapor and for the liquid, the equilibrium coefficient can be calculated

$$K_i = y_i/x_i$$

$$= (\phi_i^L p) / (\phi_i^V p)$$

$$= \phi_i^L / \phi_i^V$$

As the usual equations of state describe corrections to the behavior of an ideal gas, it cannot be expected that the high density state can always be accurately described.

For liquid mixtures with strong complex interactions (e.g. polarity or chemical associations), the usual mixing rules are too simple to account for real conditions in the mixture.

Various models for excess properties can be used to develop useful correlations for activity coefficients. These, however, are not discussed here.

The correlations discussed in this volume are based on the application of equations of state. This method offers several advantages:

- The only information required for the calculation of the equilibrium coefficients is the equation of state.
- The principle of corresponding states allows the use of a generalized equation of state. Very few parameters characterize a pure substance and usually only one interaction parameter is necessary per mixture.
- Phase equilibria can be calculated at high pressure and for mixtures containing supercritical components.

The application of the method and its advantages are limited to mixtures consisting of so-called "normal" fluids such as noble gases, nitrogen, oxygen, carbon monoxide, hydrocarbons, certain hydrocarbon derivatives. Carbon dioxide, hydrogen sulfide, hydrogen and, with certain reservations, some polar substances can also be included.

Mixtures of strongly interacting substances, especially at low pressures can be better described with models for the excess functions. The equations of state fails mainly because the usual mixing rules are inadequate. For such mixtures more sophisticated mixing rules are necessary to extend the validity of the equation-of-state method.

3.2. Structure of Equations of State

The PVT behavior of an ideal gas can be described by the simple equation of

state

$$z = \frac{pv}{RT} = 1$$

There are two different techniques to correct for non ideality effects in real gases, one based on the equation proposed by van der Waals (1873) [1]

$$z = \frac{v}{v-b} - \frac{a}{RTv}$$

The two parameters a and b in the van der Waals equation account for the effect of intermolecular forces and for the volume occupied by the molecules. These physically meaningful corrections give a simple, qualitatively correct, but quantitatively less accurate analytical description of the behavior of a real gas. The other technique is based on the virial equation proposed e.g. by Kammerlingh Onnes (1901) [2]

$$z = 1 + \frac{B}{v} + \frac{C}{v^2} + \dots$$

The virial coefficients B , C , etc. depend only on temperature in the case of pure substances and can be calculated by the methods of statistical mechanics. The virial equation is theoretically important but fails at high densities.

Over the years innumerable modifications of these basic equations have been proposed in order to improve the accuracy and to extend the range of validity. Most of the new equations have been developed empirically. They are characterized by increasingly complicated structures especially since the advent of fast digital computers. The large number of coefficients contained in these extended equations is determined by fitting to experimental data i.e. by minimizing the deviations between calculated and measured data.

For the description of mixtures, mixing rules must be given for each coefficient.

When the principle of corresponding states is used, reduced temperatures, pressures and volumes are introduced into an equation with a set of universal coefficients. A mixture is characterized by "pseudo critical" parameters which can be calculated with a few mixing rules.

It should be pointed out that it is important to consider the purpose for which an equation of state is to be used.

Case I: A pure substance (e.g. H_2O , He , CH_4 , NH_3) has been thoroughly investigated i.e. vapor pressures, PVT data, Joule Thomson effects, specific heat capacities, velocities of sound have been measured. If it is desired to represent the properties of this substance in tables or diagrams with an accuracy comparable to the experimental accuracy, an equation of state or a fundamental equation with many adjustable coefficients (often more than 40) is required. If several sets of coefficients are used to represent various areas in the p - T field, possibly a smaller number of coefficients may suffice.

Case II: Only few experimental points (e.g. vapor pressures or liquid densities) are known. Sometimes nothing but the chemical structural

formula of the substance is known. If it is desired to estimate thermodynamic properties, a simple but "safe" equation of state, mostly of the van der Waals type, is required.

Case III: Process calculations have to be performed for a large variety of multicomponent mixtures. Here it is most practical to use generalized equations of state which include only a few parameters and therefore only a few mixing rules.

The specific purpose, therefore, decides which type of equation is most suitable. Here, in this volume, we are concerned only with **case III**.

3.3. Generalized Equations of State

Equations of state based on the principle of corresponding states for pure substances as well as for mixtures are advantageous when used in process design. Only a limited number of characteristic parameters has to be stored for each substance and each binary mixture.

For the user it is important to have an indication of the accuracy of the calculated data. Therefore, four frequently used and "proven" equations of state were selected and tested, two of the virial type and two of the van der Waals type.

All these equations have in common that they require three parameters to characterize a pure substance, the critical temperature, the critical pressure or the critical volume and the acentric factor. One binary parameter per binary is required to achieve better accuracy in the description of binary or multicomponent mixtures.

The four generalized equations of state considered here are the following:

- BWRS:** **Benedict-Webb-Rubin-Starling** [3], an extension proposed by Starling to the equation of Benedict, Webb, Rubin [4]
- LKP:** **Lee-Kesler-Plöcker** [5] an extension proposed for mixtures by Plöcker, Knapp and Prausnitz to the equation of Lee and Kesler [6]
- RKS:** **Redlich-Kwong-Soave** [7], a modification proposed by Soave to the equation of Redlich, Kwong [8]
- PR:** **Peng-Robinson** [9], a modification proposed by Peng and Robinson to the equation of van der Waals.

These four equations of state are now written in detail:

3.3.1 BWRS

This generalized equation of state is an extension of the BWR equation of state and is presented by Starling and by Starling and Han with the pressure given as a function of temperature and density

$$p = \rho RT + (B_o RT - A_o - C_o/T^2 + D_o/T^3 - E_o/T^4)\rho^2 \\ + (b RT - a - d/T)\rho^3 + \alpha(a + d/T)\rho^6 \\ + (c/T^2)\rho^3(1 + \gamma\rho^2) \exp(-\gamma\rho^2)$$

It can be rewritten for $z = pv/RT$ as a function of temperature and molal volume

$$z = 1 + B/v + C/v^2 + D/v^3 + (C'/v^2)(1 + \gamma/v^2) \exp(-\gamma/v^2) \\ \text{with } B = (1/RT)(B_o RT - A_o - C_o/T^2 + D_o/T^3 - E_o/T^4) \\ C = (1/RT)(b RT - a - d/T) \\ D = (1/RT)\alpha(a + d/T) \\ C' = (1/RT)(c/T^2)$$

The 11 pure component coefficients A_o , B_o , C_o , D_o , E_o , a , b , c , d , α and γ can be expressed as functions of T_c , ρ_c and ω .

$$\rho_c B_o = A_1 + B_1 \omega \\ \rho_c A_o/(RT_c) = A_2 + B_2 \omega \\ \rho_c C_o/(RT_c^3) = A_3 + B_3 \omega \\ \rho_c^2 \gamma = A_4 + B_4 \omega \\ \rho_c^2 b = A_5 + B_5 \omega \\ \rho_c^2 a/(RT_c) = A_6 + B_6 \omega \\ \rho_c^3 \alpha = A_7 + B_7 \omega \\ \rho_c^2 c/(RT_c^3) = A_8 + B_8 \omega \\ \rho_c D_o/(RT_c^4) = A_9 + B_9 \omega \\ \rho_c^2 d/(RT_c^2) = A_{10} + B_{10} \omega \\ \rho_c E_o/(RT_c^5) = A_{11} + B_{11} \omega \exp(-3.8 \omega).$$

The 2 sets of 11 constants A_j and B_j were determined by simultaneous fitting to PVT, enthalpy and vapor pressure data of normal paraffin hydrocarbons

	A_j	B_j
$j = 1$	0.443690	0.115449
2	1.28438	-0.920731
3	0.356306	1.70871
4	0.544979	-0.270896
5	0.528629	0.349261
6	0.484011	0.754130
7	0.0705233	-0.044448
8	0.504087	1.32245
9	0.0307452	0.179433
10	0.0732828	0.463492
11	0.006450	-0.022143

The coefficients for mixtures are found with 11 mixing rules

$$B_o = \sum_i x_i B_{oi} \\ A_o = \sum_i \sum_j x_i x_j A_{oi}^{1/2} A_{oj}^{1/2} (1 - k_{ij}) \\ C_o = \sum_i \sum_j x_i x_j C_{oi}^{1/2} C_{oj}^{1/2} (1 - k_{ij})^3 \\ \gamma = [\sum_i x_i \gamma_i^{1/2}]^2 \\ b = [\sum_i x_i b_i^{1/3}]^3$$

$$\begin{aligned}
 a &= [\sum_i x_i a_i^{1/3}]^3 \\
 \alpha &= [\sum_i x_i \alpha_i^{1/3}]^3 \\
 c &= [\sum_i x_i c_i^{1/3}]^3 \\
 D_o &= \sum_i \sum_j x_i x_j D_{oi}^{1/2} D_{oj}^{1/2} (1 - k_{ij})^4 \\
 d &= [\sum_i x_i d_i^{1/3}]^3 \\
 E_o &= \sum_i \sum_j x_i x_j E_{oi}^{1/2} E_{oj}^{1/2} (1 - k_{ij})^5
 \end{aligned}$$

The binary interaction parameters k_{ij} are zero when i equals j (pure fluid interaction); for unequal pairs $i \neq j$, the value of k_{ij} can be determined by fitting to available binary VLE data.

The isothermal departure functions showing the effect of pressure on the properties of a fluid, pure or multicomponent can be calculated starting from the ideal gas state as the reference or standard state:

$$\begin{aligned}
 h - h^o &= (B_o RT - 2 A_o - 4 C_o / T^2 + 5 D_o / T^3 - 6 E_o / T^4) \rho \\
 &\quad + (1/2) (2 b RT - 3 a - 4 d / T) \rho^2 + (1/5) \alpha (6 a + 7 d / T) \rho^5 \\
 &\quad + (c / \gamma T^2) [3 - (3 + (1/2) \gamma \rho^2 - \gamma^2 \rho^4) \exp(-\gamma \rho^2)] \\
 RT \ln f &= RT \ln(\rho RT) + 2 (B_o RT - A_o - C_o / T^2 + D_o / T^3 \\
 &\quad - E_o / T^4) \rho + (3/2) (b RT - a - d / T) \rho^2 \\
 &\quad + (6 \alpha / 5) (a + d / T) \rho^5 \\
 &\quad + [c / (\gamma T^2)] [1 - (1 - (1/2) \gamma \rho^2 - \gamma^2 \rho^4) \exp(-\gamma \rho^2)]
 \end{aligned}$$

The fugacity f_i of each component i in the mixture can be calculated as follows

$$\begin{aligned}
 RT \ln f_i &= RT \ln(\rho RT x_i) + \rho (B_o + B_{oi}) RT \\
 &\quad + 2 \rho \sum_{j=1}^n x_j [- (A_o A_{oi})^{1/2} (1 - k_{ij}) - (C_o C_{oi})^{1/2} (1 - k_{ij})^3 / T^2 \\
 &\quad + (D_o D_{oi})^{1/2} (1 - k_{ij})^4 / T^3 - (E_o E_{oi})^{1/2} (1 - k_{ij})^5 / T^4] \\
 &\quad + (\rho^2 / 2) [3 (b^2 b_i)^{1/3} RT - 3 (a^2 a_i)^{1/3} - 3 (d^2 d_i)^{1/3} / T] \\
 &\quad + (\alpha \rho^5 / 5) [3 (a^2 a_i)^{1/3} + 3 (d^2 d_i)^{1/3} / T] \\
 &\quad + (3 \rho^5 / 5) (a + d / T) (\alpha^2 \alpha_i)^{1/3} \\
 &\quad + 3 (c^2 c_i)^{1/3} \rho^2 / T^2 [(1 - \exp(-\gamma \rho^2)) / (\gamma \rho^2) \\
 &\quad - (1/2) \exp(-\gamma \rho^2)] \\
 &\quad - [2 c (\gamma_i / \gamma)^{1/2} / (\gamma T^2)] [(1 - \exp(-\gamma \rho^2)) (1 + \gamma \rho^2 + (1/2) \gamma^2 \rho^4)]
 \end{aligned}$$

3.3.2 LKP

The volumetric and thermodynamic functions correlated by Pitzer and co-workers in accordance with the 3-parameters corresponding states principle were analytically represented by Lee and Kesler with improved accuracy by a modified BWR equation of state.

$$Z = Z^{(o)} + (\omega / \omega^{(r)}) (Z^{(r)} - Z^{(o)})$$

The compressibility factors of both the simple fluid $z^{(s)}$ and the reference fluid $z^{(r)}$ are represented by a modified BWR equation of state as a function of reduced variables $T_r = T/T_c$, $p_r = p/p_c$ and $v_r = p_c v/(RT_c)$

$$\begin{aligned} z &= pv/(RT) \\ &= p_r v_r/T_r \\ &= 1 + B/v_r + C/v_r^2 + D/v_r^5 \\ &\quad + [C_4/(T_r^3 v_r^2)][(\beta + \gamma/v_r^2)\exp(-\gamma/v_r^2)] \end{aligned}$$

$$\text{where } B = b_1 - b_2/T_r - b_3/T_r^2 - b_4/T_r^3$$

$$C = c_1 - c_2/T_r + c_3/T_r^3$$

$$D = d_1 + d_2/T_r$$

Experimental data for argon, krypton and methane were used to determine the 12 constants for the simple fluid; experimental data for n-octane were used to determine the 12 constants for the reference fluid:

Constant	simple fluid	reference fluid
b_1	0.1181193	0.2026579
b_2	0.265728	0.331511
b_3	0.154790	0.027655
b_4	0.030323	0.203488
c_1	0.0236744	0.0313385
c_2	0.0186984	0.0503618
c_3	0.0	0.016901
c_4	0.042724	0.041577
$d_1 \times 10^4$	0.155488	0.48736
$d_2 \times 10^4$	0.623689	0.0740336
β	0.65392	1.226
γ	0.060167	0.03754
ω	0.0	0.3978

Mixtures are characterized by pseudocritical properties that are determined with a few mixing rules suggested by Plöcker, Knapp and Prausnitz [5].

$$T_{cm} = (1/v_{cm})^n \sum_i \sum_j x_i x_j (v_{cij})^n T_{cij}$$

$$T_{cij} = (T_{ci} \cdot T_{cj})^{1/2} k_{ij}^*$$

with

$$k_{ii}^* = k_{jj}^* = 1$$

k_{ij}^* = the binary parameter for $i \neq j$ can be found by fitting to binary experimental data. It can also be correlated for certain groups of substances.

$$v_{cm} = \sum_i \sum_j x_i x_j v_{cij}$$

$$v_{cij} = (1/8)(v_{ci}^{1/3} + v_{cj}^{1/3})^3$$

$$v_{ci} = z_{ci} RT_{ci}/p_{ci}$$

$$z_{ci} = 0.2905 - 0.085 \omega_i$$

$$p_{cm} = RT_{cm} z_{cm} / v_{cm}$$

$$z_{cm} = 0.2905 - 0.085 \omega_M$$

$$\omega_M = \sum_i x_i \omega_i$$

The optimal value of η was empirically found to be 0.25.

The isothermal departure functions showing the effect of pressure on the properties of a fluid, pure or multicomponent, can be calculated starting from the ideal gas as the reference or standard state.

$$\begin{aligned}(h-h_0)/(RT_c) &= T_r[z-1-(b_2 + 2b_3/T_r + 3b_4/T_r^2)/(T_r v_r) \\ &\quad -(c_2-3c_3/T_r^2)/(2T_r v_r^2) + d_2/(5T_r v_r^5) + 3E] \\ \ln \phi &= z-1-\ln z + B/v_r + C/(2v_r^2) + d_2/(5v_r^5) + E \\ \text{with } E &= c_4/(2T_r^3\gamma)[\beta+1-[\beta+1+(\gamma/v_r^2)] \exp(-\gamma/v_r^2)]\end{aligned}$$

For mixtures (index M) use T_{cM} , p_{cM} and ω_M instead of T_c , p_c , ω and calculate the departure functions of the mixture according to the general rule:

$$\begin{aligned}q_M &= q_M^{(0)} + (\omega_M/\omega^{(r)})(q_M^{(r)} - q_M^{(0)}) \\ \text{with e.g. } q_M &= (h_M - h_M^0)/(RT_{cM}) \text{ or } \ln \phi_M\end{aligned}$$

The fugacity coefficient ϕ_i of each component i in a mixture can be calculated as follows:

$$\begin{aligned}\ln \phi_i &= \ln \phi_M - [(h_M - h_M^0)/(RT_{cM})] \sum_{j \neq i} x_j (\partial T_{cM} / \partial x_j)_{x_K} \\ &\quad + [(z_M - 1)/p_{cM}] \sum_{j=i} x_j (\partial p_{cM} / \partial x_j)_{x_K} \\ &\quad - [(\partial \ln \phi_M / \partial \omega_M)_{T_r, p_r}] \sum_{j \neq i} x_j (\partial \omega_M / \partial x_j)_{x_K}\end{aligned}$$

with $(\partial \ln \phi_M / \partial \omega_M)_{T_r, p_r} = (1/\omega^{(r)}) [(\ln \phi_M)^{(r)} - (\ln \phi_M)^{(0)}]$, neglecting the indirect effect of a change of ω_M on p_{cM} and therefore on p_r .

$$\begin{aligned}(\partial T_{cM} / \partial x_j)_{x_K} &= [2 \sum_i x_i (v_{cli}^\eta T_{cli} - v_{cli}^\eta T_{cli}) \\ &\quad - \eta v_{cM}^{(\eta-1)} (\partial v_{cM} / \partial x_j)_{x_K} T_{cM}] / v_{cM}^\eta \\ (\partial v_{cM} / \partial x_j)_{x_K} &= 2 \sum_i x_i (v_{cli} - v_{cli}) \\ (\partial p_{cM} / \partial x_j)_{x_K} &= p_{cM} [(\partial z_{cM} / \partial x_j)_{x_K} / z_{cM} \\ &\quad + (\partial T_{cM} / \partial x_j)_{x_K} / T_{cM} \\ &\quad - (\partial v_{cM} / \partial x_j)_{x_K} / v_{cM}] \\ (\partial z_{cM} / \partial x_j)_{x_K} &= -0.085 (\partial \omega_M / \partial x_j)_{x_K} \\ (\partial \omega_M / \partial x_j)_{x_K} &= \omega_j - \omega_i\end{aligned}$$

In all derivatives with constant x_k , k means all components except i and j , i.e. $k \neq i, j$.

3.3.3 RKS

This equation is a modification and a generalization of the original Redlich-Kwong equation of state suggested by Soave.

$$z = v/(v-b) - a/RT(v+b)$$