



CHAPTER 2

LITERATURE REVIEW

2.1 Nonideal Gases

As a basis of comparison, the concept of the ideal gas is invaluable since all gases approach ideality at low pressures. Moreover, the methods of statistical mechanics are readily applicable to the calculation of properties of ideal gases, with results that are regarded as often superior to experimental data on nearly ideal gases.

2.1.1 Deviations from Ideality

Many properties of real substances can be expressed conveniently as deviations from ideality - for example, the residual volume, $\Delta V = V - RT/P$, whose difference from zero is a measure of nonideality, or the compressibility, $Z = PV/RT$. The marked deviation of the latter quantity from unity is shown for some substances in Figure 2.1 (a), (b). Other informative plots of the compressibility are shown in Figure 2.2. Ideal gas isotherms are rectangular hyperbolas, but those of isopentane in Figure 2.3 deviate sharply from that shape, particularly in the vicinity of the critical temperature.

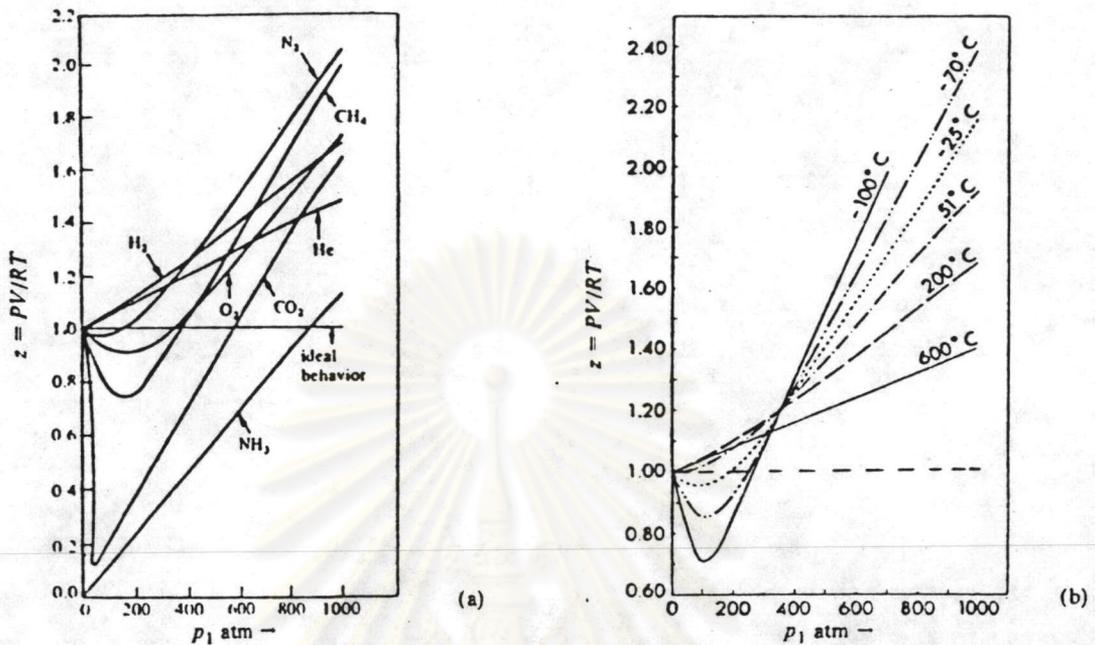


Figure 2.1 Effects of temperature and pressure on the compressibility $Z = PV/RT$, of some gases : (a) compressibilities of several gases at 0°C over a range of pressures:(b) compressibility of nitrogen at several temperatures over a range of pressures (Walas (9)).

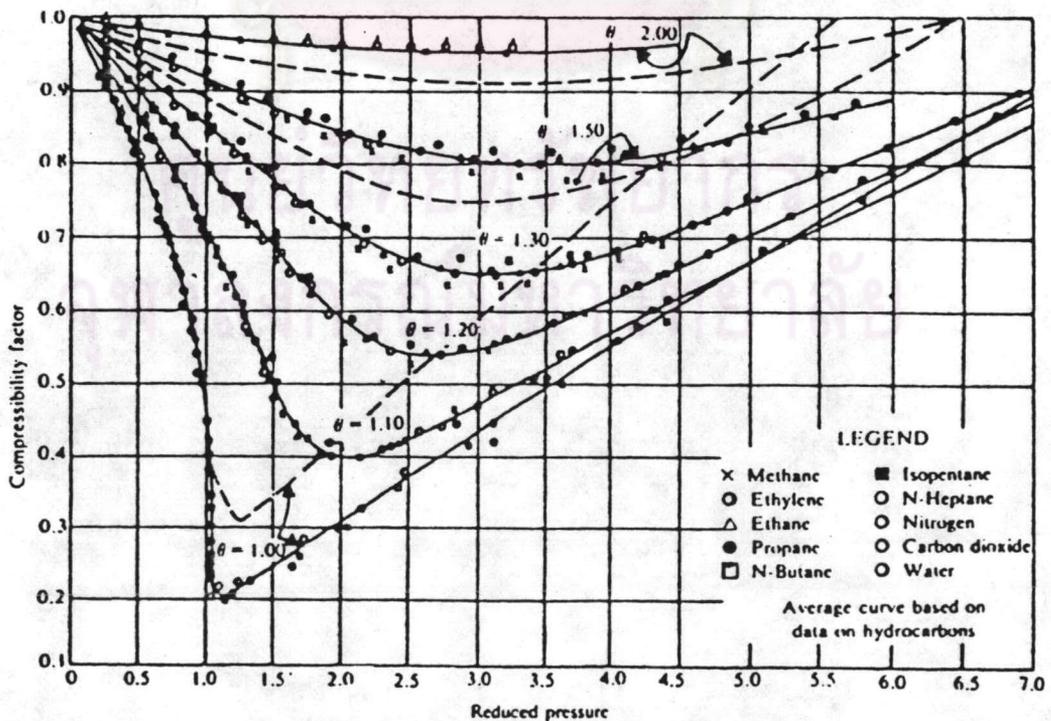


Figure 2.2 Correlation of compressibilities of common gases. The broken lines are based on van der Waals equation, $\theta = T/T_c$ (Walas(9))

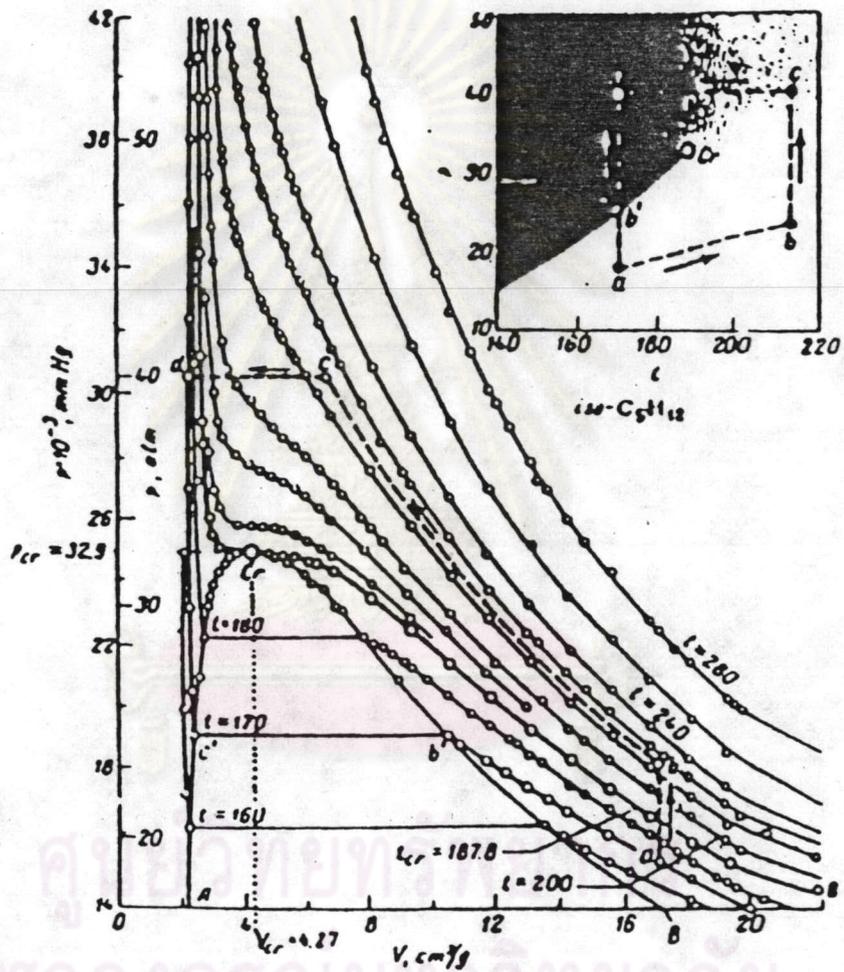


Figure 2.3 Phase diagram of isopentane in the two phase and homogeneous regions. Near the critical point, the transition from a vapor to a liquid phase may be a heterogeneous path (a-b'-c'-d), or a homogeneous path (a-b-c-d) (Walas (9)).

2.1.2 Intermolecular Forces

Sizes, shapes, and structures of molecules determine the forces between them and ultimately their P-V-T behavior. Attractive forces tend to keep molecules together, and repulsive forces prevent them from mutual annihilation. The former come into play at greater separations of the molecules; the latter are effective at close range. The effects of forces are describable in terms of potentials, quantities whose gradients are forces. Figure 2.4 shows how the potentials are visualized to depend on the distance of separation of molecules. Here it may be simply stated that attractive forces may be regarded as resulting in a pressure that is greater than that due to the kinetic energies of the molecules, whereas repulsive forces reduce the effective volume that is available to molecular movement.

In term of their electrical properties, molecules may be classified as

1. Electrically neutral and symmetrical, and usually nonpolar.
2. Electrically neutral but unsymmetrical--- that is, possessing dipole moments and called polar.
3. Those having residual valences that may result in association and hydrogen bonding.

Forces of repulsion and attraction are present in all molecules, but they appear in exaggerated forms in associating and polar molecules. The most success with P-V-T correlations has been achieved for nonpolar substances, which includes the important category

of hydrocarbons. Second virial coefficients even for polar substances, however, have been well correlated in terms of certain geometrical and electrical characteristics of the molecules. Several theoretical and empirical relations for the effects of molecular attraction and repulsion have been incorporated in equations of state. Historically, rather more attention has been paid to modifying the attraction term a/V^2 in the van der Waals equation, whereas the repulsion term has been largely accepted in the form proposed by him. Recently, however, there has been a revival of interest in the latter term; some useful developments are mentioned in Section 2.4.

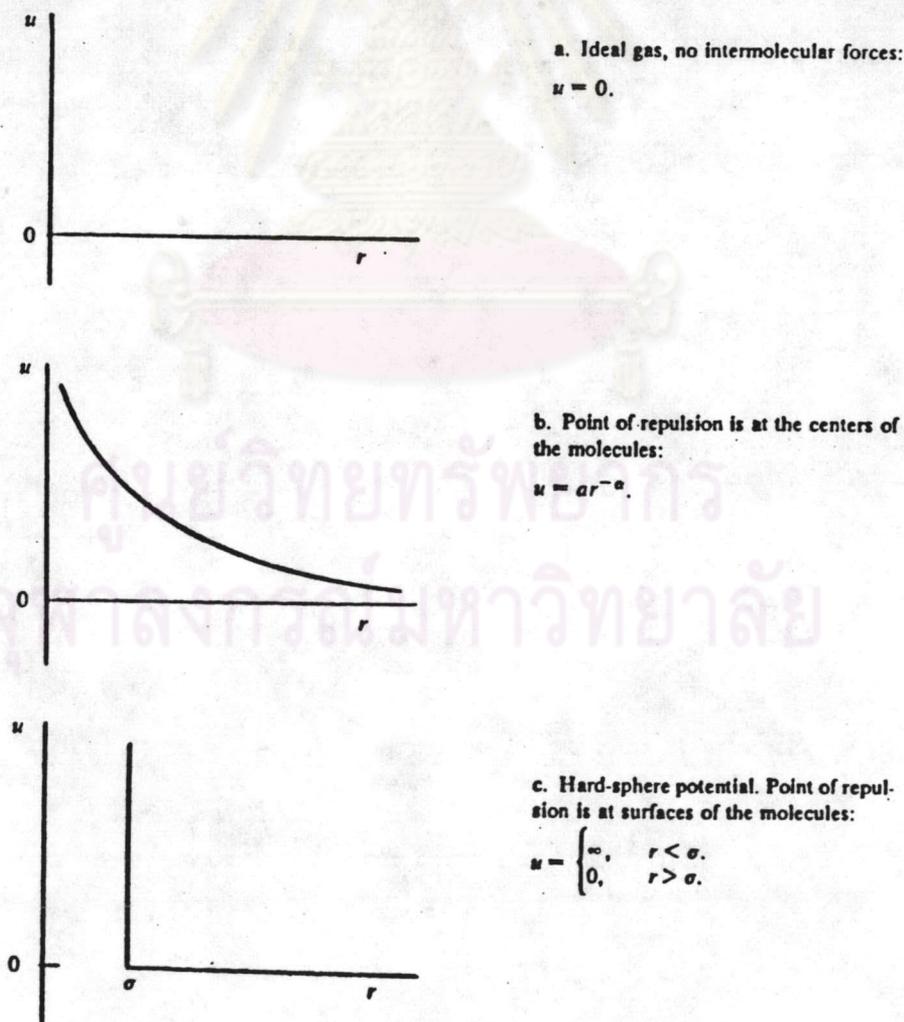


Figure 2.4 Some Commonly Used Potential Functions (Walas (9)).

2.2 Cubic Equations

2.2.1 The van der Waals Equation

Since the ideal equation was recognized early to be inadequate for the demands of science and technology, many other equations of varying merits were proposed over the years. Almost every one of these has been shown, or claimed, to be superior in some respects to earlier EOS—because of a sound theoretical basis, or in some particular range of temperature and pressure, or for some particular substances, or for the evaluation of some particular thermodynamic property, or for being easier to use, or because the inventor had become interested in the topic. Most of these equations have not been accepted, not always because they were inferior, but simply because they were not superior.

The most famous and one of the most fruitful equations of state is that of van der Waals, whose dissertation was "on the continuity of the gas and liquid states". In the van der Waals equation,

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2} \quad (2.1)$$

a is called the attraction parameter and b the repulsion parameter. The latter also is called the effective molecular volume, which van der Waals theorized to be four times the actual volume of the molecules. Related mathematical material is collected in Table 2.1.

Since the van der Waals equation is of the third degree in volume, and the subcritical isotherm has three real positive roots, whereas supercritical isotherms have only one real root. When there are three real roots, the smallest is interpreted as the specific volume of a liquid phase, the largest as that of the vapor phase, and the intermediate one as physically meaningless.

Table 2.1 The van der Waals Equation of State

Standard forms of the equation are:	Derivation of the formulas for a and b:
$(P + a/V^2)(V - b) = RT,$	(1) Method 1: At the critical condition, the first and second derivatives with respect to V at constant T are zero. Per-
$z = PV/RT = V/(V - b) - a/RTV.$	(2) forming these differentiations,
Polynomial forms are:	$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{RT_c}{(V_c - b)^2} + \frac{2a}{V_c^3} = 0, \quad (11)$
$V^3 - \left(b + \frac{RT}{P}\right)V^2 + \frac{a}{P}V - \frac{ab}{P} = 0,$	(3)
$z^3 - \left(\frac{bP}{RT} + 1\right)z^2 + \frac{aP}{(RT)^2}z - \frac{abP^2}{(RT)^3} = 0.$	(4) $\left(\frac{\partial^2 P}{\partial V^2}\right)_T = \frac{2RT_c}{(V_c - b)^3} - \frac{6a}{V_c^4} = 0. \quad (12)$
Virial form:	Also,
$z = 1 + \left(b - \frac{a}{RT}\right)\frac{1}{V} + \left(\frac{b}{V}\right)^2 + \left(\frac{b}{V}\right)^3 + \dots$	$\left(P_c + \frac{a}{V_c^2}\right)(V_c - b) = RT_c. \quad (13)$
Reduced form:	(5) Eqs. 11-13 are solved simultaneously to obtain the results of lines 7-9.
$\left(P_r + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r,$	(6) Method 2: At the critical point, the three roots of the polynomial, Eq. 3, are equal.
The parameters in terms of critical properties:	$(V - V_c)^3 = V^3 - 3V_cV^2 + 3V_c^2V - V_c^3 = 0. \quad (14)$
$a = 3P_cV_c^2 = 27R^2T_c^2/64P_c,$	(7) Comparison of coefficients of like powers of Eqs. 3 and 14 will lead to the same results for the parameters as by method 1.
$b = V_c/3 = RT_c/8P_c,$	(8) For mixtures, the parameters are expressed in terms of the pure component parameters by the combining rules:
$R = 8P_cV_c/3T_c,$	(9)
$z_c = 0.375.$	(10) $a = (\Sigma y_i \sqrt{a_i})^2 = \Sigma \Sigma y_i y_j \sqrt{a_i a_j} = \Sigma \Sigma y_i y_j a_{ij}; \quad (15)$
The value of R given by Eq. 9 is not the same as the true gas constant, 8.314 joules/gmol-K; the true value should be used for evaluation of the parameters a and b from Eqs. 7 & 8.	$b = \Sigma y_i b_i. \quad (16)$

2.2.2 The Redlich-Kwong Equation

Since van der Waals proposed his cubic equation of state, many modifications have been made to improve the agreement with experimental data. One of the most successful modifications was that made by Redlich and Kwong (1).

Otto Redlich always stressed that the Redlich-Kwong equation of state retained "three good properties" of the van der Waals EOS:

- I. As $P \rightarrow \infty, V \rightarrow b$ (it would be incorrect if $V \rightarrow 0$, as in the case of the virial EOS or the Benedict-Webb-Rubin EOS.)
- II. a and b have physical significance
- III. The EOS is of the third degree in volume

In addition to these three properties, however, the Redlich-Kwong has a significantly better volume and temperature dependence than the van der Waals EOS.

The Redlich-Kwong EOS:

$$P = \frac{RT}{(V-b)} - \frac{a T^{-1.5}}{V(V+b)} \quad (2.2)$$

Redlich and Kwong not only succeeded in demonstrating that a simple adjustment in the terms of Equation (2.1) could considerably improve the prediction of vapor phase properties, but also that the cubic EOS can be a reliable tool for engineering calculations. Comparisons of several such equations are made in Figure 2.5.

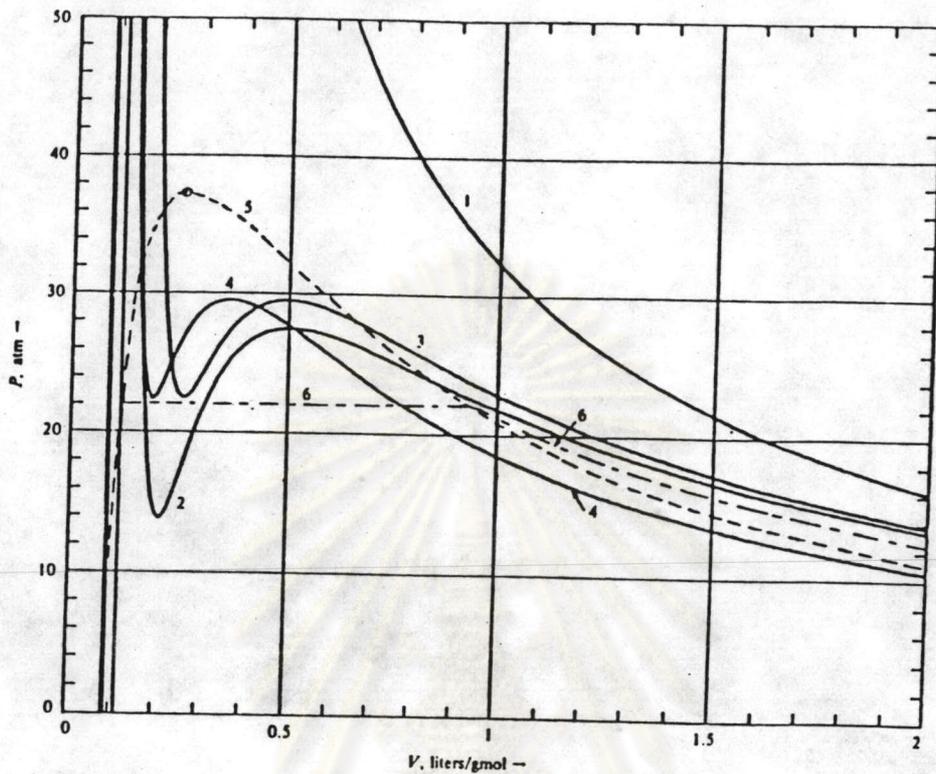


Figure 2.5 Saturation curve and 394.2 K isotherm of *n*-butane, and comparisons with predictions from the ideal, van der Waals and Redlich-Kwong equations of state.

Curve 1. Ideal gas: $P = 0.0825 T/V$.

Curve 2. Redlich-Kwong: $P = 0.08205 T/(V - 0.0806) - 286.1/[T^{0.5}V(V + 0.0806)]$.

Curve 3. van der Waals: $P = 0.08205 T/(V - 0.1163) - 13.693/V^2$.

Curve 4. van der Waals with $R = 8P_c V_c/3T_c = 0.060$, $a = 7.322$, $b = 0.0850$.

Curve 5. Saturation curve.

Curve 6. True isotherm.

Various forms of the equation and related quantities are summarized in Table 2.2. By application of the criticality conditions, the parameters a and b are found in terms of the critical properties.

Thus:

$$a = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \quad , \quad (2.3)$$

$$b = \frac{\Omega_b RT_c}{P_c} \quad , \quad (2.4)$$

Table 2.2 The Redlich-Kwong Equation of State

Standard form:

$$P = \frac{RT}{V-b} - \frac{a}{\sqrt{T}V(V+b)} \quad (1)$$

Parameters: (see Example 1.12):

$$a = \Omega_a R^2 T_c^{2.5} / P_c = 0.42748 R^2 T_c^{2.5} / P_c \quad (2)$$

$$b = \Omega_b R T_c / P_c = 0.08664 R T_c / P_c \quad (3)$$

$$A = aP/R^2 T^{2.5} = 0.42748 P_r / T_r^{2.5} \quad (4)$$

$$B = bP/RT = 0.08664 P_r / T_r \quad (5)$$

Polynomial forms:

$$V^3 - \frac{RT}{P} V^2 + \frac{1}{P} \left(\frac{a}{\sqrt{T}} - bRT - Pb^2 \right) V - \frac{ab}{P\sqrt{T}} = 0 \quad (6)$$

$$z^3 - z^2 + (A - B - B^2)z - AB = 0 \quad (7)$$

$$z^3 - z^2 + \frac{P_r}{T_r} \left[\frac{0.42748}{T_r^{1.5}} - 0.08664 - 0.007506 \frac{P_r}{T_r} \right] z - 0.03704 \frac{P_r^2}{T_r^{3.5}} = 0 \quad (8)$$

Reduced form:

$$P_r = \frac{3T_r}{V_r - 3\Omega_b} - \frac{9\Omega_a}{T_r^{0.5} V_r (V_r + 3\Omega_b)} \quad (9)$$

Compressibility relations:

$$h = \frac{b}{V} = \frac{bP}{zRT} = \frac{0.08664 R T_c}{V P_c} = \frac{0.08664 P_r}{z T_r} \quad (10)$$

$$z = \frac{1}{1-h} - \frac{a}{bRT^{1.5}} \left(\frac{h}{1+h} \right) = \frac{1}{1-h} - \frac{4.934}{T_r^{1.5}} \left(\frac{h}{1+h} \right) \quad (11)$$

$$z = \frac{V}{V-b} - \frac{a}{RT^{1.5}(V+b)} \quad (12)$$

Mixtures:

$$a = \sum \sum y_i y_j a_{ij} = y_1^2 a_{11} + y_2^2 a_{22} + \dots + 2(y_1 y_2 a_{12} + y_1 y_3 a_{13} + \dots + y_2 y_3 a_{23} + \dots) \quad (13)$$

$$b = \sum y_i b_i \quad (14)$$

$$A = \sum \sum y_i y_j A_{ij} \quad (15)$$

$$B = \sum y_i B_i \quad (16)$$

Cross-parameters:

$$a_{ij} = \sqrt{a_i a_j} \text{ (Redlich \& Kwong's original rule),} \quad (17)$$

$$a_{ij} = (1 - c_{ij}) \sqrt{a_i a_j} \text{ (Zudkevich \& Joffe 1970),} \quad (18)$$

$$a_{ij} = \frac{\Omega_a R (V_{ci}^{1/3} + V_{cj}^{1/3})^3 [(1 - k_{ij}) \sqrt{T_{ci} T_{cj}}]^{1.5}}{8[0.291 - 0.04(\omega_i + \omega_j)]} \text{ (Prausnitz \& Chueh 1968).} \quad (19)$$

$$\Omega_a = 0.427480 \quad , \quad (2.5)$$

$$\Omega_b = 0.086640 \quad . \quad (2.6)$$

Usually the fit of data to the equation of state is improved by allowing the coefficients Ω_a and Ω_b to vary from substance to substance. In recent times these coefficients have been correlated in terms of reduced temperature and acentric factor. Perhaps the most widely used correlations is that of Soave (2), which is discussed in the next section. The RK equation is not at all satisfactory for the liquid phase, and cannot be used by itself for calculating vapor-liquid equilibria.

2.2.3 The Soave Equation

The temperature-dependent term $a/T^{.5}$ of the RK equation was replaced by a function $a(T,\omega)$ involving the temperature and the acentric factor by Soave (2) (Table 2.3 and 2.4), so that the equation of state becomes

$$P = \frac{RT}{(V-b)} - \frac{a(T,\omega)}{V(V+b)} \quad (2.7)$$

The parameter $a(T,\omega)$ was formulated primarily to make the equation fit the vapor pressure data of hydrocarbons, with the result

$$a(T,\omega) = a \alpha = 0.42748 (R^2 T_c^2 / P_c) \alpha \quad . \quad (2.8)$$

Table 2.3 The Soave Equation of State

Standard form:	$z^3 - z^2 + (A - B - B^2)z - AB = 0.$	(9)	
$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)}$	(1)	Partly reduced form (see Example 1.16).	
Parameters:	$P_r = \frac{3T_r}{V_r - 0.2599} - \frac{3.8473\alpha}{V_r(V_r + 0.2599)}$	(10)	
$a = 0.42747R^2T_c^2/P_c$	(2)	Mixtures:	
$b = 0.08664RT_c/P_c$	(3)	$a\alpha = \sum y_i y_j (a\alpha)_{ij}$	(11)
$\alpha = [1 + (0.48508 + 1.55171\omega - 0.15613\omega^2)(1 - T_r^{0.5})]^2$	(4)	$b = \sum y_i b_i$	(12)
$\alpha = 1.202 \exp(-0.30288T_r)$ for hydrogen (Graboski & Daubert 1979).	(5)	$A = \sum y_i y_j A_{ij}$	(13)
$A = a\alpha P/R^2T^2 = 0.42747\alpha P_r/T_r^2$	(6)	$B = \sum y_i B_i$	(14)
$B = bP/RT = 0.08664P_r/T_r$	(7)	Cross-parameters:	
Polynomial forms:		$(a\alpha)_{ij} = (1 - k_{ij})\sqrt{(a\alpha)_i(a\alpha)_j}$	(15)
$V^3 - \frac{RT}{P}V^2 + \frac{1}{P}(a\alpha - bRT - Pb^2)V - \frac{a\alpha b}{P} = 0.$	(8)	k_{ij} in Table 1.12;	(16)
		$k_{ij} = 0$ for hydrocarbon pairs and hydrogen.	(17)

Table 2.4 Binary interaction Parameters for the Soave Equation

1. Correlations in terms of absolute differences between solubility parameters of the hydrocarbon, δ_{HC} , and of the inorganic gas.

Gas	k_{ij}
H ₂ S	$0.0178 + 0.0244 \delta_{HC} - 8.80 $
CO ₂	$0.1294 - 0.0292 \delta_{HC} - 7.12 - 0.0222 \delta_{HC} - 7.12 ^2$
N ₂	$-0.0836 + 0.1055 \delta_{HC} - 4.44 - 0.0100 \delta_{HC} - 4.44 ^2$

For CO₂ and hydrocarbons,

$$\log k_{ij} = -0.8849 - 0.2145\omega_{HC}|\delta_{HC} - 7.12|.$$

2. Direct values from vapor-liquid equilibrium measurements.

	H ₂ S	CO ₂	N ₂	CO
H ₂ S	—	0.102	0.140	—
CO ₂	0.102	—	-0.022	-0.064
N ₂	0.140	-0.022	—	-0.046
CO	—	-0.064	0.046	—
Methane	0.0850	0.0973	0.0319	0.03
Ethane	0.0829	0.1346	0.0388	0.00
n-Propane	0.0831	0.1018	0.0807	0.02
2-Methylpropane	0.0523	0.1358	0.1357	—
n-Butane	0.0609	0.1474	0.1007	—
2-Methylbutane	—	0.1262	—	—
n-Pentane	0.0697	0.1278	—	—
n-Hexane	—	—	0.1444	—
n-Heptane	0.0737	0.1136	—	—
n-Octane	—	—	—	0.10
n-Nonane	0.0542	—	—	—
n-Decane	0.0464	0.1377	0.1293	—
Propylene	—	0.0914	—	—
Cyclohexane	—	0.1087	—	—
Isopropylcyclohexane	0.0562	—	—	0.01
Benzene	—	0.0810	0.2131	—
1,3,5-Trimethylbenzene	0.0282	—	—	—

where

$$\alpha^{0.5} = 1 + (1 - T_r)^{0.5} (0.480 + 1.574 \omega - 0.176 \omega^2) \quad (2.9)$$

the coefficients of this term were modified by Graboski and Daubert (10) to

$$\alpha^{0.5} = 1 + (1 - T_r)^{0.5} (0.48508 + 1.55171 \omega - 0.15613 \omega^2) \quad (2.10)$$

For hydrogen, Graboski and Daubert (10) wrote

$$\alpha^{0.5} = 1.096 \exp(-0.15114 T_r) \quad (2.11)$$

The effect of the acentric factor on the shape of reduced isotherms and a comparison with the van der Waals equation are shown in Figure 2.6.

For some mixtures the mixing rules are the same as for the RK equation, with the cross-parameter

$$a_{1j} = (1 - k_{1j}) \sqrt{a_1 a_j} \quad (2.12)$$

For strongly polar substances such as water, alcohols, and others, further changes are proposed by Soave (11), making

$$\alpha = 1 + (1 - T_r)(m + nT_r) \quad (2.13)$$

where m and n are two adjustable parameters that must be derived from experimental vapor pressure data for each pure substance. Simplified methods for evaluating these parameters are described by Soave (12).

Application to mixtures requires two binary interaction parameters:

$$a_{1j} = 0.5(a_1 + a_j)(1 - C_{1j}) \quad (2.14)$$

$$b_{1j} = 0.5(b_1 + b_j)(1 - D_{1j}) \quad (2.15)$$

$$a = \sum \sum y_i y_j a_i a_j \quad (2.16)$$

$$b = \sum \sum y_i y_j b_i b_j \quad (2.17)$$

No generalizations are made for these interaction parameters in this study (12).

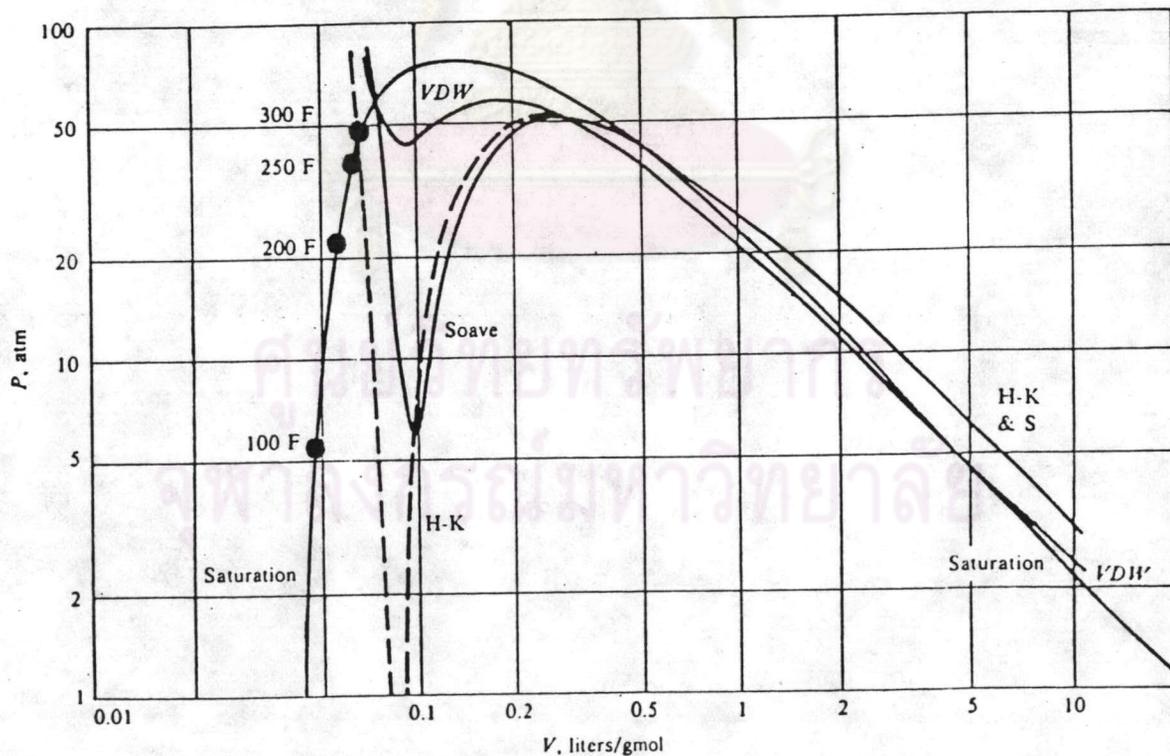


Figure 2.6 Plots of 250°F isotherms of sulfur dioxide with the Harmens-Knapp, Soave, and van der Waals equations, and comparison with the true saturation curve (Walas (9)).

2.2.4. The Peng-Robinson Equation

Several goals were set by Peng and Robinson (3) in developing a new two-parameter equation of state cubic in volume (see Table 2.5):

1. The parameters should be expressible in term of P_c , T_c and acentric factor.
2. The model should result in improved performance in the vicinity of the critical point, particularly for calculations of Z_c and liquid density.
3. The mixing rules should not employ more than one binary interaction parameter, and that should be independent of temperature, pressure, and composition.
4. The equation should be applicable to all calculations of all fluid properties in natural gas processes.

They proposed the equation :

$$\begin{aligned}
 P &= \frac{RT}{(V-b)} - \frac{a(T)}{V(V+b) + b(V-b)} \\
 &= \frac{RT}{(V-b)} - \frac{a(T)}{V^2 + 2bV - b^2} \quad (2.18)
 \end{aligned}$$

At the critical point,

$$a(T_c) = 0.45724 R^2 T_c^2 / P_c \quad (2.19)$$

$$b(T_c) = 0.07780 RT_c / P_c \quad (2.20)$$

$$Z_c = 0.307 \quad (2.21)$$

At other temperatures the parameter $a(T)$ is corrected to

$$a(T) = a(T_c) \alpha(T_r, \omega) \quad (2.22)$$

similarly to the Soave treatment. Correlating in terms of the vapor pressure curve up to the critical point results in

$$\alpha^{0.5} = 1 + (1 - T_r^{-0.5}) (0.37464 + 1.5422 \omega - 0.26992 \omega^2) \quad (2.23)$$

A range of applications of this equation of state is described by Robinson et al. (13). According to the PR equation the critical compressibility is $Z_c = 0.307$. This value is nearer the values of many substance, particularly nonpolar ones, than are the Z_c of some other two-parameter EOS. This is a partial explanation of the fact that the PR equation is able to predict liquid densities more accurately than does the Soave equation, which is otherwise quite similar in performance. Improved prediction of liquid densities, however, also has been achieved by Fuller (14), who expressed the parameters a and b of the Soave equation as functions of the temperature and used critical volumes and parachors in their evaluation. Even such polar molecules as water and ammonia are covered by this correlation. Liquid density predictions by the Soave and Fuller methods also they are discussed by Chung et al. (15).

Combining rules of the PR system for mixtures are the usual

ones of cubic equation, but binary interaction parameters for the cross-parameter are considered essential:

$$a_{1j} = (1 - k_{1j}) \sqrt{a_1 a_j} \quad (2.24)$$

They are found by optimizing bubble point pressures over an appropriate range of pressures and temperatures.

Table 2.5 The Peng-Robinson Equation of State

Standard form:

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \quad (1)$$

Parameters:

$$a = 0.45724R^2T_c^2/P_c \quad (2)$$

$$b = 0.07780RT_c/P_c \quad (3)$$

$$\alpha = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \quad (4)$$

$$A = a\alpha P/R^2T^2 = 0.45724\alpha P_r/T_r^2 \quad (5)$$

$$B = bP/RT = 0.07780P_r/T_r \quad (6)$$

Polynomial form:

$$z^3 - (1-B)z^2 + (A-3B^2-2B)z - (AB-B^2-B^3) = 0 \quad (7)$$

Mixtures:

$$a\alpha = \sum y_i y_j (a\alpha)_{ij} \quad (8)$$

$$b = \sum y_i b_i \quad (9)$$

$$(a\alpha)_{ij} = (1 - k_{ij}) \sqrt{(a\alpha)_i (a\alpha)_j} \quad (10)$$

$$A = \sum y_i y_j A_{ij} \quad (11)$$

$$B = \sum y_i B_i \quad (12)$$

$$A_{ij} = (1 - k_{ij})(A_i A_j)^{0.5} \quad (13)$$

$$k_{ii} = 0 \quad (14)$$

Data of Katz & Firoozabadi (16)

nitrogen + HC	$k_{ij} = 0.12$	
CO ₂ + HC	0.15	
ethane + HC	0.01	
propane + HC	0.01	
methane + {	ethane	0
	propane	0
	nC4	0.02
	nC5	0.02
	nC6	0.025
	nC7	0.025
	nC8	0.035
	nC9	0.035
	nC10	0.035
	nC20	0.054
	benzene	0.06
cyclohexane	0.03	

2.3 Other Modifications of Redlich-Kwong Equation

Since that time, numerous modified Redlich-Kwong equations have been proposed. Some have introduced deviation functions to fit pure substance PVT data while others have improved the equation's capability for vapor-liquid equilibrium (VLE) predictions. Depending on the form selected to express the relationship between EOS variables, EOS may be arbitrary classified in the following types :

1. modifications with one temperature-dependent parameter
2. modifications with two temperature-dependent parameters
3. modifications of the attractive term
4. modifications of the repulsive term

2.3.1 Modifications with One Temperature-Dependent Parameter

The key recommendation for making the Redlich-Kwong, or any other, EOS a good VLE predictor was made by Wilson (17). He suggested that the a parameter in Equation (2.2) be made a function of temperature to improve the prediction of the pure-compound vapor pressure.

Equation (2.2) in the form popularized by Soave (2):

$$P = \frac{RT}{(V-b)} - \frac{a\alpha}{V(V+b)} \quad (2.7)$$

then Wilson's recommendation makes α a linear function of T_r :

$$\alpha = Tr[1 + m (Tr^{-1} - 1)] \quad (2.24)$$

$$m = 1.57 + 1.62 \omega \quad (2.25)$$

Wilson's recommendation was largely ignored, even though he applied it successfully to many systems. It was not until Soave's modification that this approach gained popularity.

Soave recommended the following generalized relationship for α .

$$\alpha = [1 + m (1 - Tr^{0.5})]^2 \quad (2.26)$$

$$m = 0.48508 + 1.55171 \omega - 0.15613 \omega^2 \quad (2.27)$$

Soave's modification gained quick and wide acceptance, and became the most popular method for high-pressure VLE calculations.

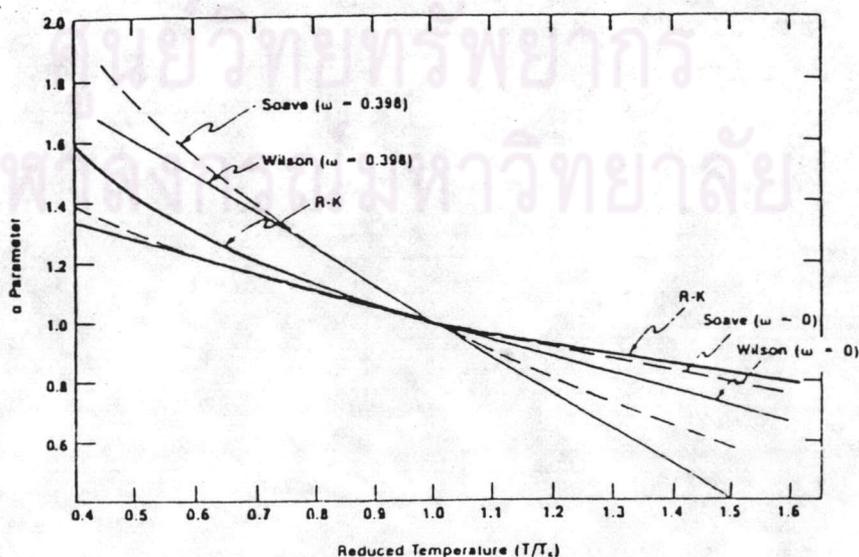


Figure 2.7 Temperature-dependence of α parameter (Tsonopoulos et al.(62)).

The temperature-dependence of the a parameter, that is, the parameter, is illustrated in Figure 2.7 for the original equation and the modifications of Wilson and Soave. The Wilson and Soave α 's are very similar for $\omega=0$, but are farther apart for $\omega = 0.398$ (the value for n-octane). This is because Wilson emphasized light hydrocarbons, and therefore his modification is at its best for low values of ω (≤ 0.2).

Figure 2.7 also demonstrates, however, that the Wilson and Soave modifications are poor predictors of second virial coefficients. The RK α for $T_r < 1.0$ is significantly larger than the Wilson and Soave α 's for $\omega=0$, and therefore these two modifications would predict too positive a B . Thus, the Wilson and Soave α 's are good for VLE, but are inferior to the original RK EOS for B . This deficiency has been ignored by most investigators, although little can be done to remove it with EOS that have only two parameters (that is, a and b). A choice between VLE and B needs to be made.

2.3.2 Modifications with Two Temperature-Dependent parameters

Most investigators since Soave have made only a temperature dependent, but, even before Soave, Joffe and Zudkevitch (18) recommended that both a and b in Equation (2.2) be functions of temperature. Joffe et al. suggested that the temperature dependence of a and b be determined by simultaneously matching liquid density and forcing the vapor and liquid fugacities to be equal at the pure component's vapor pressure.

These constraints on a and b , along with the additional constraint that $Z_c = 0.333$, lead to unusual temperature dependence for $T_r < 1.0$. This is illustrated in Figure 2.8 for argon and n-octane. As T_c is approached, both Ω_a and Ω_b increase very rapidly. It would be unwise to extrapolate above T_c with these limiting slopes. Accordingly, Joffe and Zudkevitch recommended that, at supercritical temperatures, Ω_a and Ω_b be temperature-independent and equal to their values at T_c . Thus, a discontinuity exists at T_c , and therefore the Joffe-Zudkevitch modification cannot be used for enthalpy calculations, although it is a powerful VLE method.

Two recent modifications of the RK EOS also use two temperature-dependent parameters, but have a total of three parameters. One is Heyen's (19), which fits the vapor pressure and liquid density. The Henyen equation :

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2 + (b+c)V - bc} \quad (2.28)$$

Unlike the Joffe-Zudkevitch modification, however, the a and b in Heyen's modification are well-behaved, continuous functions of temperature, a result of using three parameters. As in the case of Wilson's and Soave's modifications, however, the prediction of B is inferior to that with the original RK EOS.

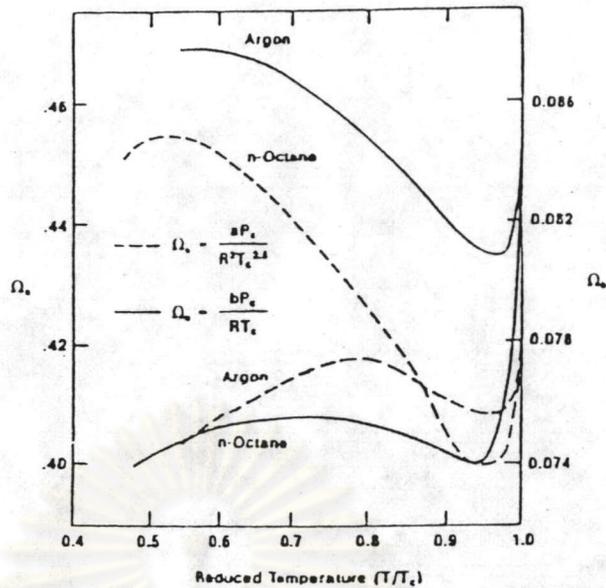


Figure 2.8 Temperature-dependent a and b parameters in Redlich-Kwong EOS (Tsonopoulos et al. (62)).

2.3.3. Modifications of The Attractive Term

Redlich and Kwong modified the attractive term of the van der Waals EOS. The more recent modifications of the attractive term are frequently called Redlich-Kwong modifications, even though they actually are modifications of the van der Waals EOS. However, RK equation "showed the way," and therefore it is appropriate that the RK EOS is considered the starting point for later modifications.

The most important modification of the attractive term that uses only two parameters is the Peng-Robinson (3) EOS.

$$P = \frac{RT}{(V-b)} - \frac{a}{V(V+b) + b(V-b)} \quad (2.18)$$

The addition of the $b(V-b)$ term in the denominator of the attractive term resulted in an improved prediction of the liquid density without

making b a function of temperature . The Peng-Robinson EOS uses Equation (2.26) for α ,but m is given by

$$m = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad (2.29)$$

The Peng-Robinson EOS is generally similar to Soave's for VLE, but better than Soave's for liquid density. However, the Peng-Robinson or any other two-parameter EOS cannot simultaneously improve the vapor density. To do that, a third parameter must be added .

Three-parameter EOS make it possible to have a component specific Z_c . Even though the experimental Z_c has been used, an adjusted Z_c that is typically 10-15 % larger than experimental Z_c has been found to improve overall EOS performance.

Schmidt and Wenzel (20) recommended an attractive term that introduces the acentric factor explicitly as a third parameter:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2 + (1 + 3\omega)bV - 3\omega b^2} \quad (2.30)$$

a similar form was proposed by Harmens and Knapp (21).

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2 + cbV - (c-1)b^2} \quad (2.31)$$

It is interesting to note that this EOS reduces to the Redlich-Kwong, for $c = 1$, or the Peng-Robinson, for $c = 2$.

Heyen (19) used a different form:

$$P = \frac{RT}{(V-b)} - \frac{a}{V^2 + (b+c)V - bc} \quad (2.28)$$

Equations (2.28), (2.30) and (2.31) were developed for VLE calculations; accordingly, they focus on the fit of vapor pressure and liquid density with one or two (in the case of Equation 2.28) temperature-dependent parameters. As can be seen, the Schmidt-Wenzel and Harmen-Knapp forms use very similar adjusted Z_c 's. It is also shown that the acentric factor dependence incorporated in the Schmidt-Wenzel EOS interpolates between the RK ($\omega=0$) and Peng-Robinson ($\omega=0.333$) EOS, when each EOS is at its best. All modifications of the attractive term have one common feature: they have generally degraded the prediction of B compare to the original RK.

The discussion in this section has highlighted the research on modifying the attractive term; the repulsive term has been kept in the form proposed by van der Waals. The next section considers modifications of the van der Waals repulsive term.

2.3.4. Modifications of The Repulsive Terms

In the last two decades there has been much interest in modifying the van der Waals repulsive term. If consider a hard-sphere fluid, then there is no attractive term and the van der Waals EOS becomes

$$P_{hs} = \frac{RT}{V} \cdot \frac{1}{(1-b/V)} \quad (2.32)$$

This is a considerable improvement over the ideal-gas EOS, which also is the first term in the virial and Benedict-Webb-Rubin EOS:

$$P_{hs} = \frac{RT}{V} \quad (2.33)$$

However, application of statistical mechanics to the presentation of the hard-sphere EOS suggests that Equation (2.32) is a crude approximation.

Thiele (22) developed the first successful, closed-form hard sphere EOS :

$$\begin{aligned} P_{hs} &= \frac{RT}{V} \cdot \frac{1-y^3}{(1-y)^4} \\ &= \frac{RT}{V} \cdot \frac{1+y+y^2}{(1-y)^3} \end{aligned} \quad (2.34)$$

where $y = b/4V$.

Carnahan and Starling (4) improved upon Thiele's expression by adding the term $(-y^3)$ in the numerator:

$$P_{hs} = \frac{RT}{V} \cdot \frac{1+y+y^2-y^3}{(1-y)^3} \quad (2.35)$$

The ideal gas, van der Waals, and Carnahan-Starling $Z_{h,s}$ are plotted on Figure 2.9. What is most striking is the enormous difference between Carnahan-Starling, the presumed correct result, and van der Waals. What makes this difference more perplexing is that, when an attractive term is added to the Carnahan-Starling EOS, no significant improvement results in describing the real-fluid behavior. This issue has not yet been fully considered.

Some recent investigations have proposed approximate forms for the hard-sphere EOS so that the complete EOS could maintain a cubic form. Ishikawa et al. (8) used Scott's (23) approximate hard-sphere EOS together with the RK attractive term, but VLE predictions with the resulting EOS are similar to those with the Joffe-Zudkevitch modification of the RK EOS. As shown in Figure 2.9, Scott's hard-sphere EOS is in excellent agreement with Carnahan-Starling up to $y = 0.3$.

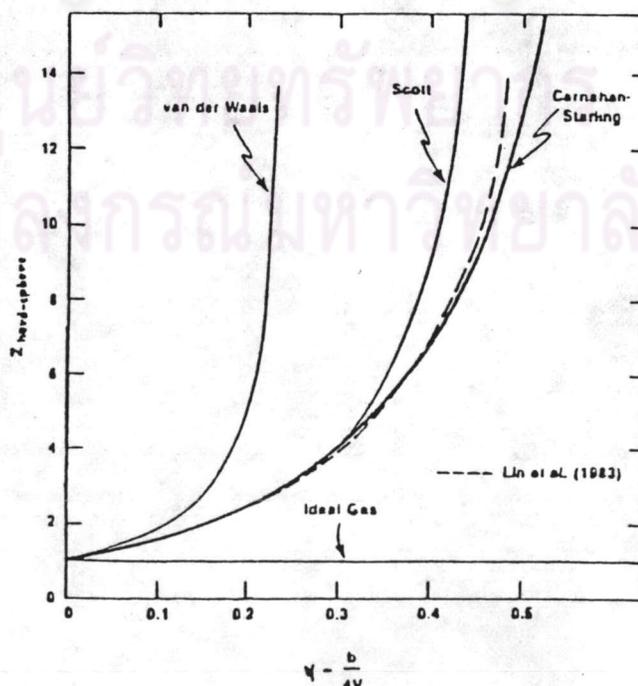


Figure 2.9 Compressibility factor of hard-sphere fluid (Tsonopoulos et al. (62)).

2.4 Perturbed Hard-Sphere Equations of State

Consideration of the forces of repulsion between rigid sphere leads to a virial equation for the repulsion pressure P_R (Ree and Hoover (24)):

$$\begin{aligned} P_R &= \frac{RT}{V} (1 + 4y + 10y^2 + 18.36y^3 + 28.3y^4 + \dots) \\ &= \frac{RT}{V} f(y) \end{aligned} \quad (2.36)$$

where

$$y = b/4V \quad (2.37)$$

and b is a measure of the volumes occupied by the molecules but may be regarded as an empirical parameter.

For real gases the pressure is made up of contributions of forces of attraction as well as repulsion. The Carnahan-Starling (25), the modified van der Waals equation becomes

$$P = \frac{RT}{V} \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - \frac{a}{V^2} \quad (2.38)$$

similarly, the modified Redlich-Kwong equation becomes

$$P = \frac{RT}{V} \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - \frac{a}{T^{0.5} V(V+b)} \quad (2.39)$$

The parameters a and b in these equations may be related to the critical properties by application of the mathematical conditions at the critical point.

Several studies based as perturbed hard-sphere equations of state may be cited.

i) Carnahan-Starling (25) worked with the modified van der Waals and Redlich-Kwong equations. The latter was found to give superior performance for densities and enthalpy deviations of pure substances and some hydrocarbon binaries.

ii) De Santis et al. (5) made an attempt to develop a hard-sphere repulsion compressibility factor of Carnahan-Starling (4) with a simple expression for the attractive term for VLE calculations. De Santis et al. hard-sphere EOS :

$$P = \frac{RT}{V} \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - \frac{a}{V(V+b)} \quad (2.40)$$

The parameters a and b were correlated as linear functions of the temperature for twenty-one substances.

The proposed hard-sphere EOS yields good results, for the case of pure components, in the range spanning ideal gas to saturated liquids. Extension to mixtures to predict vapor-liquid equilibria of Pitzer fluids allows good accuracy in a wide range of temperatures and pressures.

iii) Nagata and Yasuda (6) applied the Carnahan-Starling-Redlich-Kwong equation to saturated vapors.

iv) Nakamura, Breedveld, and Prausnitz (7) studied the hard-sphere equation in the form

$$P = \frac{RT}{V} \frac{(1 + y + y^2 - y^3)}{(1 - y)^3} - \frac{a}{V(V+c)} \quad (2.41)$$

where

$$a = \alpha + \beta / T \quad (2.42)$$

$$y = \frac{1}{4V} \exp \left(\frac{1}{\delta + \delta T} \right) \quad (2.43)$$

where parameter c is independent of temperature but is characteristic of the substance, being zero for nonpolar and slightly positive for the few polar substances tested. For mixtures, binary interaction parameters are required for evaluation of the α 's. Constants for fourteen substances are given.

v) A simple form of the perturbed hard-sphere repulsion term was adopted by Ishikawa, Chung and Lu (8). They made a study on the representation of pure component properties by means of the vdW and the RK equations of state together with their twelve variants. These variants were obtained by replacing the $RT/(V-b)$ term with the analytical expressions of the hard sphere compressibility factor proposed by Thiele (22), Scott (23) and others, in addition to that suggested by Carnahan-Starling (4). The results of the study indicate that the variant which combines the hard sphere compressibility factor

of Scott and the RK empirical attractive term

$$P = \frac{RT}{V} \frac{(2V+b)}{(2V-b)} - \frac{a}{T^{0.5} V(V+b)} \quad (2.44)$$

appears to be superior to all the other variants of the vdW and the RK equations mentioned above for representing pure component properties which are relevant to VLE calculations. The pure component properties selected for the evaluation included vapor pressure, saturated liquid and vapor volumes, latent heat of vaporization and second virial coefficient. It should be mentioned, however, that the parameters of the variants were considered as universal constants in all of the calculations.

Equation (2.44) is very attractive from the viewpoint that it is simple to use. It contains only two parameters and remains a cubic equation in terms of volume. The purpose of this study is to evaluate the feasibility of improving Equation (2.44) for representing pure component properties by considering the two temperature and substance dependent parameters, and to evaluate the applicability of Equation (2.44) to calculating and predicting VLE using these modified parameters.

The quantities a and b of Equation (2.44) are related to the critical properties as follows :

$$a = \Omega_a R^2 T_c^{2.5} / P_c \quad (2.45)$$

and

$$b = \Omega_b R T_c / P_c \quad (2.46)$$

Equations (2.45) and (2.46) were obtained by applying the two conditions, $(\partial P / \partial V)_{T_c} = 0$ and $(\partial^2 P / \partial V^2)_{T_c} = 0$, to the critical point. The parameters Ω_a and Ω_b were evaluated from vapor pressures and saturated liquid densities for twenty two arbitrarily selected pure compounds following a procedure similar to that proposed for modifying the RK equation (Chung and Lu (26)). The calculated Ω_a and Ω_b values were further correlated by means of Equations (2.47) and (2.48) :

$$\Omega_a = \sum_{i=0}^3 a_i T_r^{-i} \quad (2.47)$$

and

$$\Omega_b = \sum_{i=0}^3 b_i T_r^{-i} \quad (2.48)$$

The values of the coefficients a_i and b_i of these two equations are also reported in Table 2.6.

Table 2.6 Values of the Coefficients a_i and b_i of Equations (2.47) and (2.48)

	a_0	a_1	a_2	a_3	b_0	b_1	b_2	b_3
Methane	0.19650	1.16856	-1.38439	0.47037	0.13356	0.12888	-0.26165	0.19262
Ethane	0.20176	1.31256	-1.67980	0.61622	0.11802	0.17279	-0.31486	0.12735
Propane	0.24104	1.25456	-1.64596	0.59878	0.11493	0.17712	-0.31397	0.12452
n-butane	0.23612	1.35573	-1.81164	0.66445	0.10786	0.19593	-0.32967	0.12712
n-pentane	0.35919	0.85241	-1.09198	0.32006	0.12727	0.07994	-0.14135	0.03378
n-hexane	0.29758	1.19570	-1.62966	0.57754	0.09861	0.19188	-0.29559	0.10457
n-heptane	0.24812	1.40351	-1.87158	0.65585	0.02042	0.47134	-0.63328	0.24004
n-octane	-0.20696	3.10569	-3.93178	1.46918	-0.12905	1.00409	-1.26511	0.48801
i-butane	-0.18450	2.89176	-3.65663	1.39674	-0.03957	0.75459	-1.02007	0.40746
i-pentane	0.10878	1.81070	-2.34577	0.86703	0.02509	0.49251	-0.68086	0.26953
Ethylene	0.44641	0.30161	-0.29444	-0.00538	0.14054	0.07086	-0.15209	0.04310
Propylene	0.11730	1.63895	-2.02328	0.71485	0.05773	0.37461	-0.53234	0.20234
1-butene	-0.22174	2.85561	-3.41073	1.21951	-0.00685	0.56951	-0.72161	0.25950
Acetylene	1.15110	-2.24265	2.82209	-1.28905	0.33084	-0.67414	0.78921	-0.34625
Benzene	0.38936	0.65177	-0.78790	0.18743	0.11547	0.13103	-0.21122	0.06496
Carbon dioxide	-0.96550	5.68232	-6.94321	2.67340	-0.31758	1.71076	-2.11569	0.82464
Carbon monoxide	0.16664	1.47391	-1.92735	0.74838	0.10783	0.24471	-0.42244	0.17596
Nitrogen	0.79071	-1.07156	1.52277	-0.79841	0.26291	-0.38945	0.44179	-0.21436
Oxygen	0.46326	0.12814	-0.01032	-0.13075	0.19070	-0.10512	0.06006	-0.04248
Argon	0.22914	1.02460	-1.16633	0.36604	0.12583	0.16172	-0.29468	0.11138
Sulfur dioxide	0.03616	2.08022	-2.69963	0.98686	0.02529	0.47173	-0.64978	0.25346
Ammonia	-0.12433	2.43358	-3.10164	1.21720	0.01133	0.45682	-0.63062	0.25746

The calculated results are reported in Table 2.7. Furthermore, the calculated results obtained from the cubic equation recently proposed by Peng-Robinson and De Santis et al. were also included in Table 2.7 for the purpose of comparison. The overall averages obtained are shown in Table 2.7, indicating that the proposed (ICL) equation gives smaller deviations between the calculated and the literature values than the more complicated equation of De Santis et al. for all of the four saturated properties studied. The Peng-Robinson equation gives larger deviations than the ICL equation in the calculated values of vapor pressure and saturated liquid volume but gives slightly smaller deviations in the calculated values of saturated vapor volume and latent heat of vaporization. However, the ICL equation would give smaller average deviations than the Peng-Robinson equation in all of the four properties studied if calculated results for ammonia were excluded in the comparison.

Table 2.7 A summary of deviations between calculated and literature values of four saturated properties, Average Absolute Deviations, %

Compound	N	$\Delta P/P$ _{av}		$\Delta V^L/V^L$ _{av}		$\Delta V^V/V^V$ _{av}		$\Delta h_v/h_v$ _{av}					
		PR	De Santis	This work	PR	De Santis	This work	PR	De Santis	This work			
Methane	29	1.63	5.10	0.48	3.26	7.12	1.82	7.73	8.05	0.54	3.44	4.50	1.60
Ethane	27	1.09	4.06	0.31	2.27	8.21	1.04	6.68	3.62	2.23	4.14	5.72	0.64
Propane	31	1.04	0.81	0.31	2.28	2.22	0.88	8.75	0.91	1.07	3.70	2.46	1.19
n-butane	28	0.97	0.87	0.22	1.50	2.95	2.06	4.59	1.13	0.91	2.42	3.52	2.64
n-pentane	30	0.32	0.58	0.18	1.10	3.65	2.57	4.71	0.78	0.74	1.72	4.41	3.78
n-hexane	43	1.43	2.25*	0.28	1.33	7.27*	3.31	4.10	1.33*	0.42	2.54	5.96*	4.13
i-butane	29	1.47	2.06	0.04	2.35	3.53	0.70	5.09	1.63	0.43	2.34	7.09	4.31
Ethylene	21	1.15	3.44	0.77	1.58	6.63	1.82	6.45	2.29	0.38	1.40	4.58	2.50
Propylene	26	0.58	0.87	0.07	1.39	2.64	1.75	5.26	0.79	0.27	1.97	3.07	2.18
Acetylene	22	1.57	1.53	0.32	0.97	5.49	3.59	5.00	1.36	0.51	4.37	3.56	3.37
Benzene	47	0.91	1.09†	0.16	2.80	2.79†	3.21	4.39	0.84†	0.29	3.20	2.96†	3.25
Carbon dioxide	32	0.65	2.24	0.18	1.31	5.27	2.69	4.62	2.00	0.36	4.09	7.30	4.65
Carbon monoxide	24	1.45	6.36**	0.20	2.97	10.58**	3.16	8.49	4.24**	0.34	2.68	5.40**	2.60
Nitrogen	18	1.41	7.01	0.74	4.36	10.86	3.18	8.12	4.50	0.88	4.10	8.06	4.72
Ammonia	29	0.54	2.85	0.28	5.27	7.57	9.55	15.40	1.72	0.65	4.35	9.65	11.56
Average		1.08	2.74	0.30	2.32	5.84	2.76	6.43	2.15	0.67	3.10	5.22	3.56

* N=37.
† N=44.
** N=22

Application of Equation (2.44) to mixtures requires the definition of two quantities, a_m and b_m , which replace a and b in Equations (2.44), (2.45) and (2.46). The conventional mixing rules

$$a_m = \sum_i \sum_j y_i y_j a_{ij} \quad (2.49)$$

and

$$b_m = \sum_i y_i b_i \quad (2.50)$$

were used for gas mixtures. The same rules were used for liquid mixtures with x replacing y in these equations. The mixing rule for a_{ij} as proposed by Redlich and Kwong (1) was modified by Joffe and Zudkevitch (18).

$$a_{ij} = (a_{ii} a_{jj})^{0.5} (1 - C_{ij}) \quad (2.51)$$

The calculated results for eleven binary systems at fifty-three isothermal conditions, indicate that the ICL equation is suitable for VLE calculations as shown in figure 2.10 and 2.11.

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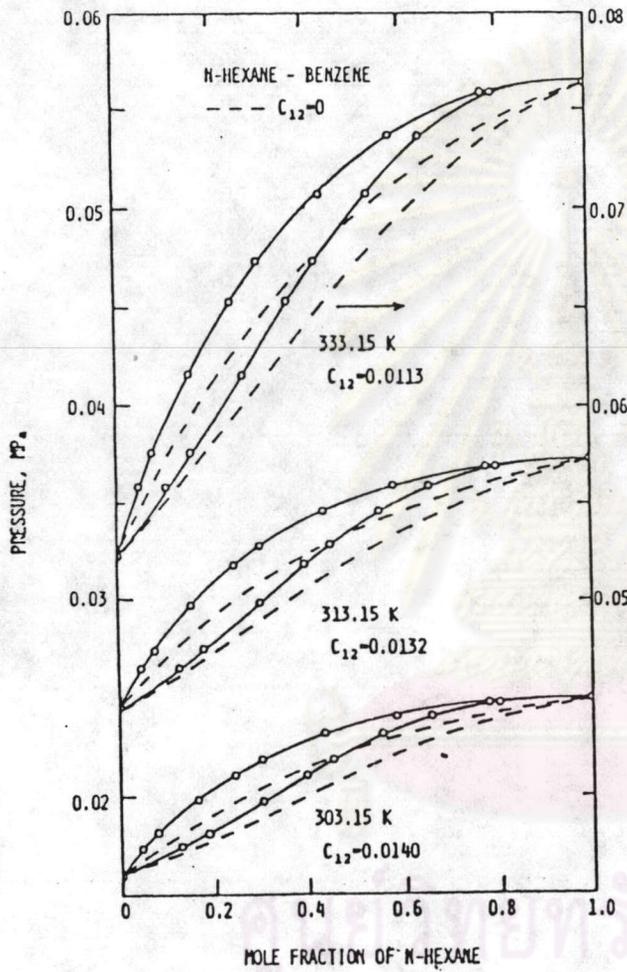


Figure 2.10 Calculated and experimental VLE values for ethane-propane system (---, —, calculated).

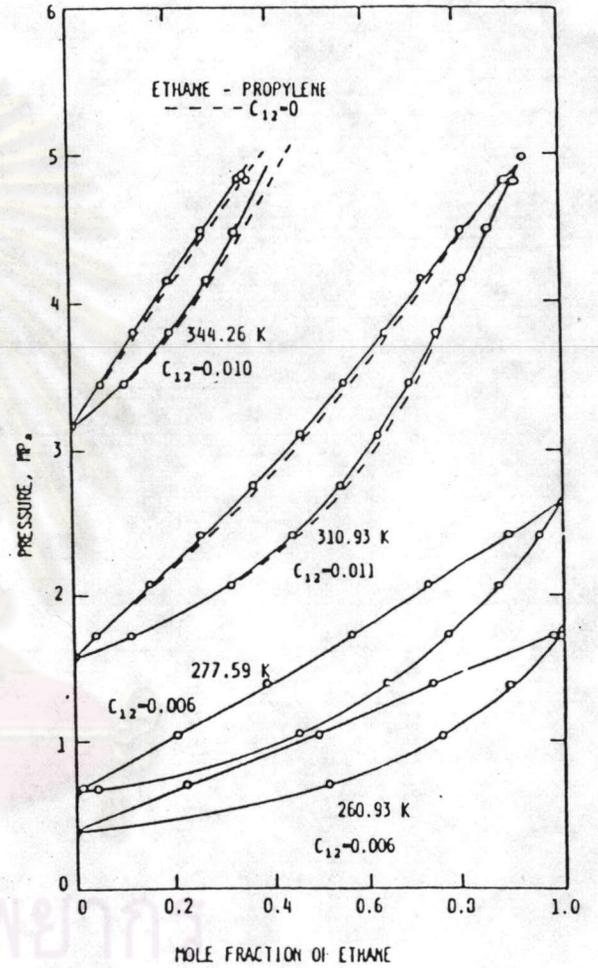


Figure 2.11 Calculated and experimental VLE values for n-hexane-benzene system (---, —, calculated)