Modifying the Redlich-Kwong-Soave Equation of State

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Abstract: The Redlich-Kwong-Soave equation of state for real gases and liquids has been modified in order to improve the match of calculated liquid molar volumes with measured data by allowing the *b*-parameter to be a function of the temperature and molar volume of real gases and liquids. Molecular dynamics simulations of the noble gas krypton, using the hard-sphere potential for a large number of krypton atoms, were performed to evaluate how the *b*-parameter varies with gas molar volume. The results of these simulations were applied when modifying the original Redlich-Kwong-Soave equation of state. In the modified Redlich-Kwong-Soave equation of state, the *a*-parameter is kept constant. Also, in this modified version, the measured critical molar volume is employed as well as the measured critical temperature and critical pressure values in parameter determination at the critical point. From this determination of parameters for a number of real gases, the same parameters can be approximately calculated using the measured critical compressibility factor avoiding numerical procedures. This results in an equation of state that matches closely with the measured critical point for many gases as well as improving the match between the model and measured liquid molar volumes.

Introduction

The first equation of state developed to model real gases at relatively high temperatures and low pressures is the ideal gas equation:

$$PV = nRT \tag{1}$$

P is the pressure of the gas, V is the volume of the gas, n is the number of moles of the gas, T is the temperature of a gas in absolute temperature scale, and R is the ideal gas constant. If one divides through the ideal gas equation with the number of moles of gas, one has the general expression below in terms of gas molar volume v.

$$Pv = RT \tag{2}$$

The gas molar volume v is the unit volume occupied by one mole of a gas and is equal to the gas volume V divided by the number n of moles of gas.

$$v = V/n \tag{3}$$

However, at low temperatures and high pressures, real gases deviate from the ideal gas expression given in Equation 1. At sufficiently low temperatures and high pressures, any real gas will condense into the liquid phase and an equilibrium situation takes place between the liquid and gas phases of any pure substance. The first attempt to model real gases and liquids was accomplished by van der Waals using the following mathematical relation.

$$P = nRT/(V - nb_{\mathrm{vdW}}) - a_{\mathrm{vdW}}\, n^2/V^2 \tag{4}$$

In the van der Waals expression, Equation 4, b_{vdW} is the molar volume of space occupied by individual gas atoms, in the case of a noble gas, or gas molecules which is much less than the volume of the gas itself at relatively low pressures. It is this space occupied by gaseous particles which prevent any real gas volume going to zero at extremely large pressures. The a_{vdW} term represents the weak attractive forces amongst gaseous atoms or molecules which is responsible for the liquid phase at temperatures below the critical temperature value T_c of any pure gas. Above the critical temperature value, it is impossible to liquefy any gas, because only below the critical temperature both the liquid and vapor phases coexist. In theory, above the critical temperature, the average kinetic energy of gas atoms or molecules is sufficient to overcome the weak attractive forces that occur when two gas atoms or molecules come into close contact (Barrow, 1979). Above the critical temperature value, it is impossible to liquefy any gas due to the average kinetic energy of gas atoms or molecules successfully overcoming the weak attractive forces that occur when two gas atoms or molecules come into close contact. If one substitutes Equation 3 into Equation 4, then the van der Waals equation of state can be more conveniently represented as a function of gas molar volume v instead.

$$P = RT/(v - b_{\mathrm{vdW}}) - a_{\mathrm{vdW}}/v^2 \qquad (5)$$

Unlike the ideal gas equation, one must experimentally determine the numerical values of parameters a_{vdW} and b_{vdW} in the van der Waals expression. The exact values of these two parameters depend upon the chemical composition of any pure gas. To determine their values, one has to use differential calculus and the definition of the critical point of a real gas. The critical point takes place when a real gas is at its critical temperature value T_c and its pressure value P is equal to its critical pressure value P_c. The critical pressure value P_c is that value the equilibrium vapor pressure of a pure liquid approaches to in the limit of the critical temperature, and likewise in the limit of the temperature approaching the critical temperature value at the critical pressure value, the liquid molar volume v of the liquid approaches its critical molar volume v_c. Or, at the critical temperature and pressure, the molar volume of the liquid is equal to that of its gas molar volume instead of being less than the gas molar volume. At the critical point of any pure gas, the first and second derivative of the van der Waals expression, Equation 5, with respect to the molar volume v are both equal to zero.

$$(\partial P/\partial v) = 0 \quad (\text{At } T = T_c,\ P = P_c \text{ and } v = v_c) \qquad (6)$$

$$(\partial^2 P/\partial v^2) = 0 \quad (\text{At } T = T_c,\ P = P_c \text{ and } v = v_c) \qquad (7)$$

By using Equations 6 and 7 along with the following expression one can determine the numerical values of a_{vdW} and b_{vdW}:

$$P_c = RT_c/(v_c - b_{\mathrm{vdW}}) - a_{\mathrm{vdW}}/v_c^{\,2} \qquad (8)$$

When van der Waals first studied real gases in the early part of the 20th century, it was practically impossible to measure the critical molar volume v_c of a liquid with the technology available at that time. When solving for parameters a_{vdW} and b_{vdW}, they were determined to be the following two functions of the measured critical pressure and critical temperature values.

$$a_{\mathrm{vdW}} = (27/64)\, R^2\, T_c^{\,2} / P_c \qquad (9)$$

$$b_{\mathrm{vdW}} = RT_c/(8P_c) \qquad (10)$$

And the estimated critical molar volume v_c is three times the numerical value of the van der Waals *b*-parameter.

$$v_c = 3b_{\mathrm{vdW}} \qquad (11)$$

The first error in the van der Waals expression is that it overly estimates the values of most measured critical molar volumes determined with today's technology. Also, it over-estimates the pressures of most real gases as compared to high pressure data measured at temperatures above the critical temperature value where condensation is unable to take place. To improve this model, Redlich and Kwong later on developed the following expression.

$$P = RT/(v - b) - a/\{T^{1/2}\ [v(v + b)]\} \qquad (12)$$

Division by the square root of the absolute temperature T compensates for the increase of overcoming weak intermolecular forces of attraction with an increase of temperature. With the inclusion of the b parameter in the Redlich-Kwong equation of state for real gases and liquids, Equation 12, in the subtraction term, Equation 12 can be rearranged to similar format of the original van der Waals equation into the following equation.

$$P = RT/(v - b) \; - \; \{a/[T^{1/2}(1 + b/v)\,]\} \;/\; v^2 \quad (13)$$

Thus, by the Redlich-Kwong equation of state, the van der Waals a_{vdW} parameter is the following function of temperature and molar volume.

$$a_{\mathrm{vdW}} \; = \; a/[T^{1/2}(1 + b/v)\,] \quad (14)$$

Thus, in view of Equation 13, the decrease in molar volume allows the van der Waals a_{vdW} parameter approach zero in the limit of zero molar volume because at sufficiently low molar volumes, atoms and molecules then would begin to overlap their electron clouds. This equation will then model decreasing attractive forces of gaseous atoms and molecules in the limit of zero molar volume along with the positive term in the original van der Waals equation of state. Again using the differential calculus given in Equations 6 and 7, the a and b parameters and the critical molar volume are approximately equal to the following expressions given below to a limited number of significant figures.

$$a \; = \; 0.42748\, R^2\, T_{\mathrm{c}}^{\,2}/P_{\mathrm{c}} \quad (15)$$

$$b \; = \; 0.08664\, R\, T_{\mathrm{c}}\,/P_{\mathrm{c}} \quad (16)$$

$$v_{\mathrm{c}} \; = \; 0.38473\, b \quad (17)$$

When using differential calculus for the Redlich-Kwong equation, numerical techniques must be utilized in a computer program in order to evaluate the fractions given in Equations 15 to 17. The Redlich-Kwong expression yielded a much improved model when comparing the measured high pressure data of a real gas at temperatures above the measured critical temperature value. Yet, still the calculated critical molar volume v_{c} by the Redlich-Kwong equation of state given in Equation 17 over predicts the measured values, but closer than that by the van der Waals equation. Another problem with the Redlich-Kwong function is that with the a parameter divided by the square-root of the absolute temperature scale over estimates the weak attractive forces amongst gas atoms below the critical temperature value, especially as the temperature drops below the freezing point of any substance.

To avoid this problem for low temperatures concerning the Redlich-Kwong equation, Soave modified the Redlich-Kwong equation in the following expression referred to as the Redlich-Kwong-Soave equation of state (Prausnitz et al., 1998).

$$P = R\,T\,/\,(v - b) \; - \; a(T,\omega)\,/\,\; [v\,(v \; + b)] \quad (18)$$

For this expression, $a(T,\omega)$ is the next function of the absolute temperature T, the measured critical pressure value P_{c}, the measured critical temperature value T_{c}, and the measured acentric factor ω of a real gas or liquid:

$$a(T,\omega) = [0.42748\, R^2\, T_{\mathrm{c}}^{\,2}\,/\,P_{\mathrm{c}}]\{1 + [0.480 + 1.574\omega \; - \; 0.176\omega^2][1 - \;(T/T_{\mathrm{c}})^{1/2}]\}^2 \quad (19)$$

However, the b parameter and the critical molar volume v_{c} in the Redlich-Kwong-Soave equation of state are still defined by Equations 16 and 17. Thus, the calculated critical molar volumes are larger than that observed experimentally. By definition (Prausnitz et al., 1998), the measured acentric factor ω is equal to the following equation involving the observed equilibrium liquid-vapor pressure value P_{equil}, at an absolute temperature value equal to 70% of the measured critical temperature value T_{c} of any pure substance, and the measured critical pressure value P_{c}:

$$\omega \;\; = \;\; -\log_{10}(P_{\mathrm{equil}}/P_{\mathrm{c}}) \;\; - \;\; 1$$

$$(\mathrm{At}\ T = 0.7\ T_{\mathrm{c}}) \quad (20)$$

For noble gases, the acentric factors are nearly equal to zero, but for other gases and liquids acentric factors are measured to be greater than zero. The measured acentric factor is useful in observing non-ideal properties of gases and liquids in general, such that larger the value of the acentric factor less ideal gas behavior of real gases and liquids. When utilizing the Redlich-Kwong-Soave equation of state, Equation 18, the model still matches well with observed high pressure data, and the *a* value will not approach infinity in the limit as the temperature goes to absolute zero. However, the value of *a* will reach a zero value at sufficiently high temperatures and then approach infinity as the temperature goes to infinity. Another important disagreement between the previously discussed models is that they all also over predict the measured liquid molar volumes of liquids studied because the *b* parameter is held constant. This is a common error in all the three previous models of real gases and liquids discussed thus far. An additional modification is needed to take into account how the *b* parameter is a function of both the gas molar volume and absolute temperature.

The Modified Redlich-Kwong-Soave Equation of State for Real Gases and Liquids

In theory, the *b*-parameter includes the space occupied by gas atoms or molecules, and the space they cannot occupy due to hindrance during collisions in space. The numerical value of the *b* parameter should decrease with increasing molar density and approach a constant value greater than zero in the limit of infinite pressures if the atoms making up the gas are hard-spheres. However, atoms that make up matter are not hard spheres but atoms behave instead like spheres with a soft outer periphery and a nearly incompressible inner spherical core. Thus, for real gases, the *b* parameter is a function of the absolute temperature as well as the gas molar density. The next function presented in Equation 21 is the modified Redlich-Kwong-Soave equation which matches measured liquid molar volumes below the critical temperature as well as high pressure data above critical temperature value:

$$P = RT / \{v - b_0 - b_1(T)\, exp[-k(T)/v]\} - a / [v\,(v + b_0)] \qquad (21)$$

In this modified version, the effective atomic or molecular molar volume *b* of the original Redlich-Kwong-Soave equation has been replaced by the following negative exponential function of temperature and molar volume *v*:

$$b(T) = b_0 + b_1(T)\, exp[-k(T)/v] \qquad (22)$$

In Equation 22, $b_1(T)$ and $k(T)$ are evaluated functions of temperature derived from analyzing listed liquid-vapor equilibrium data below critical temperatures and high pressure data above the critical temperature values for a number of pure substances (Green and Southhard, 2018). The substitution of the constant *b*-parameter with a function of temperature and molar volume, Equation 22, is originally based upon the study of computer simulations for the noble gas krypton using the hard-sphere potential (See the next section titled "The Modification with Regards to the *b*-Parameter."). In this modified version of the Redlich-Kwong-Soave equation (Equation 21), the *a*-parameter is assumed to be constant and also the b_0-parameter. To best match up with measured liquid molar volume values, the b_0-parameter is set equal to 0.2632 times the measured critical molar volume v_c of any real gas or liquid:

$$b_0 = 0.2632\, v_c \qquad (23)$$

Furthermore, at the critical temperature value T_c the parameters $b_1(T_c)$ and $k(T_c)$ were observed approximately to be the following functions of the critical compressibility factor Z_c and measured critical molar volume v_c:

$$b_1(T_c) \cong v_c\,[-2030.1Z_c^4 + 1983.8Z_c^3 - 738.11Z_c^2 + 121.16Z_c - 6.2489] \qquad (24)$$

$$k(T_c) \cong v_c\,[-22.92\, Z_c^4 + 19.098Z_c^3 - 6.1684Z_c^2 + 0.7599Z_c + 1.0437] \qquad (25)$$

This was accomplished by curve-fitting the evaluated b_0-, $b_1(T_c)$-, $k(T_c)$-, and a-parameters from measured critical point data of real gases and liquids using expressions given in Equations 46 to 47 as well as Equation 23. The data utilized are listed in Perry's Chemical Engineer's Handbook, 6th Edition. Referring to Equations 24 and 25, the critical compressibility factor Z_c is the following function of the measured critical pressure P_c, the measured critical temperature T_c, and the measured critical molar volume v_c at the critical point including the ideal gas constant R:

$$Z_c = P_c v_c /(RT_c) \tag{26}$$

Concerning the a-parameter, from the analyses performed it is observed to be nearly modeled by the following function of the measured critical pressure and measured critical temperature including the experimental critical compressibility factor and ideal gas constant R (Figure 1):

$$a \cong [(R\,T_c)^2/P_c][-881.16Z_c^4 + 848.14Z_c^3 - 318.38Z_c^2 + 55.96Z_c - 3.1858] \tag{27}$$

At and above the measured critical temperature value, the evaluated high pressure data of the noble gases neon, argon, krypton, and xenon reveal that $b_1(T)$ and $k(T)$ approximately follow the two next functions of temperature (Figure 2):

$$b_1(T) \cong b_1(T_c)\{0.1691 + 0.8247exp[-0.6928(T/T_c)] + 0.4611exp[-0.09207\,(T/T_c)]\}/1.002135 \tag{28}$$

$$k(T) \cong k(T_c)\{0.4871 + 0.2138exp[-0.5003(T/T_c)] + 0.4138exp[-0.05789(T/T_c)]\}/1.007263 \tag{29}$$

For temperatures below the critical temperature value ($T < T_c$) in the liquid-vapor region, the $b_1(T)$ and $k(T)$ functions were observed to approximately match up with the following cubic and quadratic functions of temperature, respectively, for non-polar and polar substances both (Figure 3):

$$b_1(T) \cong b_1(T_c)\,[\beta_0 + \beta_1\,(T/T_c) + \beta_2\,(T/T_c)^2 + \beta_3\,(T/T_c)^3]/[\,\beta_0 + \beta_1 + \beta_2 + \beta_3] \tag{30}$$

$$k(T) \cong k(T_c)\,[\kappa_0 + \kappa_1\,(T/T_c) + \kappa_2\,(T/T_c)^2]\,/\,[\,\kappa_0 + \kappa_1 + \kappa_2] \tag{31}$$

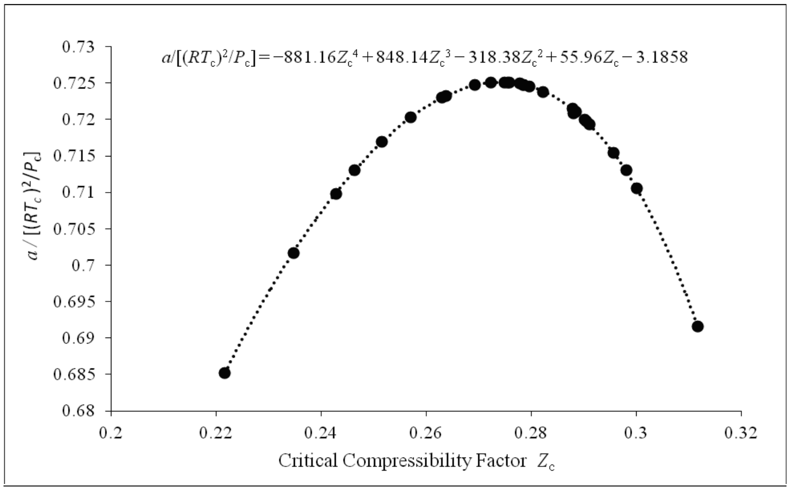

Figure 1. Evaluated $a/[(R\ T_c)^2/P_c]$ ratios for a number of non-polar and polar molecular compounds at the measured critical point using Perry's Chemical Engineers' Handbook (Green and Southard, 2018). The dotted line is the displayed fit to the data points.

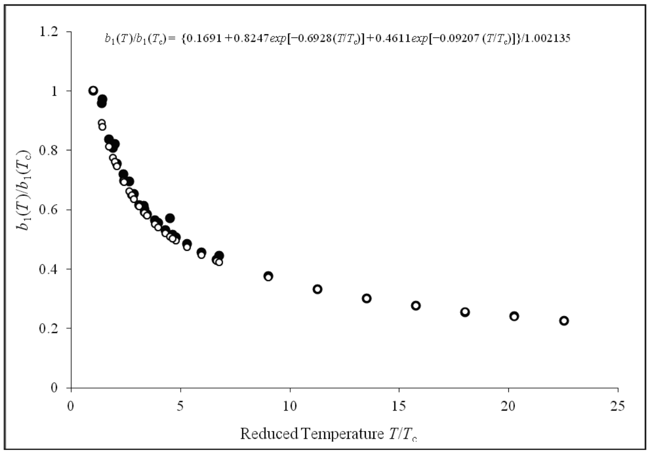

Figure 2. Evaluation of the $b_1(T)/b_1(T_c)$ ratios from the measured high-pressure data of the noble gases neon, argon, krypton, and xenon at temperatures above the critical temperature value using Perry's Chemical Engineers' Handbook (Green and Southard, 2018). The filled in circles (●) are from the data, and the open circles (o) are from the negative exponential fit of the data points.

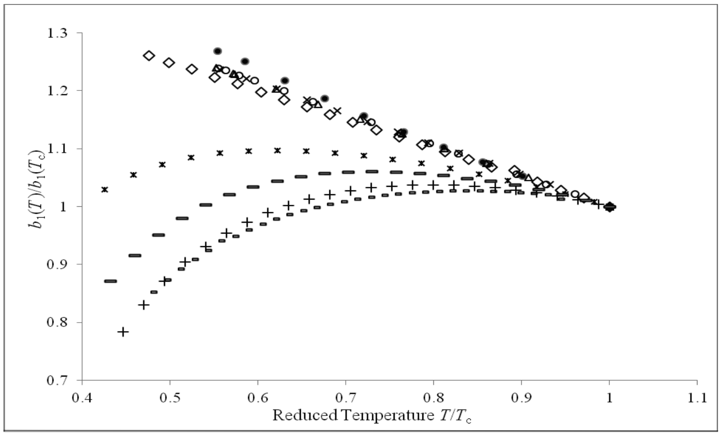

Figure 3. Evaluated $b_1(T)/b_1(T_c)$ ratios from measured liquid-vapor equilibrium data of noble gases neon, argon, krypton, xenon; hydrocarbons methane, ethane, propane, and butane; and water using Perry's Chemical Engineers' Handbook (Green and Southard, 2018). The filled-in circles (•) represent data for neon; circles (o) represent data for argon; triangles (Δ) represent data for krypton; crosses (×) represent data for xenon; diamonds (◊) represent data for methane; asterisks (*) represent data for ethane; long dashes (–) represent data for propane; pluses (+) represent data for butane; and short dashes (-) represent data for water.

The β_0-, β_1-, β_2-, and β_3-parameters in the cubic expression of Equation 30 for non-polar compounds were observed to approximately equal the following linear functions of the acentric factor ω (Figure 4):

$$\beta_0 \cong -11.393\,\omega + 1.4017 \quad (32)$$

$$\beta_1 \cong 32.772\,\omega - 0.0942 \quad (33)$$

$$\beta_2 \cong -32.655\,\omega - 0.5220 \quad (34)$$

$$\beta_3 \cong 11.282\,\omega + 0.2158 \quad (35)$$

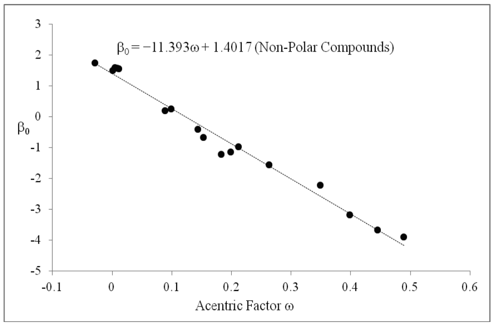

Figure 4. Evaluated β_0 values for a number of non-polar compounds using Perry's Chemical Engineers' Handbook (Green and Southard, 2018). The dotted line is the linear fit to the data, and the non-polar compounds analyzed were the hydrocarbons stated in the text, and all the noble gases except helium.

And for polar substances, the following approximate linear expressions of the acentric factor apply instead:

$$\beta_0 \cong -7.062\,\omega + 1.7997 \tag{36}$$

$$\beta_1 \cong 22.000\,\omega - 2.2642 \tag{37}$$

$$\beta_2 \cong -24.101\,\omega + 2.7785 \tag{38}$$

$$\beta_3 \cong 9.199\,\omega - 1.3223 \tag{39}$$

Because non-polar and polar substances experience different types of intermolecular interactions, it is not surprising that different numerical constants result in linear functions of the acentric factor. The κ_0-, κ_1-, and κ_2-parameters in the quadratic expression of Equation 31 for non-polar compounds are similarly approximately equal to the following linear functions of the acentric factor ω (Figure 5):

$$\kappa_0 \cong -2.089\,\omega + 1.1043 \tag{40}$$

$$\kappa_1 \cong 4.346\,\omega - 0.0688 \tag{41}$$

$$\kappa_2 \cong -2.276\,\omega - 0.0355 \tag{42}$$

And for polar substances, the following approximate similar linear expressions apply.

$$\kappa_0 \cong -1.355\,\omega + 1.1620 \tag{43}$$

$$\kappa_1 \cong 2.685\,\omega - 0.1886 \tag{44}$$

$$\kappa_2 \cong -1.337\,\omega + 0.0268 \tag{45}$$

Due to the slight curvature of the $k(T)$ parameter, a quadratic expression was utilized instead of a cubic function. For non-polar substances, data from all noble gases except helium were analyzed, and the hydrocarbons whose measured data were studied are linear saturated hydrocarbons methane to butane and heptane to decane, and also ethylene, propylene, isobutene, benzene and toluene. Concerning polar substances, data from ammonia, carbon monoxide, chloromethane, and water were studied.

Concerning the critical point at P_c, T_c, and v_c, the numerical value of the b_0-parameter was calculated using Equation 23, and then the numerical values of the a-parameter and the temperature dependent parameters $b_1(T_c)$ and $k(T_c)$ were initially evaluated using the following three expressions:

$$P_c = R\,T_c / \{v_c - b_0 - b_1(T_c)\,exp[-k(T_c)/v_c]\} - a / [v_c\,(v_c + b_0)] \tag{46}$$

$$(\partial P_c/\partial v_c)_T = 0 \quad (\text{at } T = T_c) \tag{47}$$

$$(\partial^2 P_c/\partial v_c{}^2)_T = 0 \quad (\text{at } T = T_c) \tag{48}$$

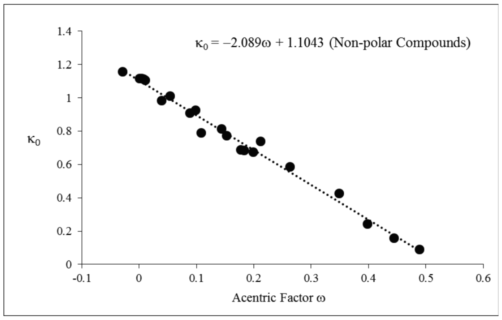

Figure 5. Evaluated κ_0 values for non-polar noble gases and hydrocarbons using Perry's Chemical Engineers' Handbook (Green and Southard, 2018). The dotted line is the linear fit to the data, and the non-polar compounds analyzed were the hydrocarbons stated in the text, and all the noble gases except helium.

In addition, for any particular real gas concerning the evaluated values of b_0-, $b_1(T_c)$-, and $k(T_c)$-parameters, there is the hypothetical minimum molar volume $v_{\min}$ at the limit of infinite pressures:

$$v_{\min} - \{ b_0 + b_1(T_c)\, exp[-k(T_c)/v_{\min}]\} = 0 \quad (\text{at } T = T_c) \tag{49}$$

For the expressions given in Equations 46 to 48, there is the complication that with three equations of state there are four parameters to be evaluated: a, b_0, $b_1(T_c)$, and $k(T_c)$. The fourth mathematical condition used was the expression in Equation 23 to calculate the constant b_0-parameter as a linear function of the measured critical liquid molar volumes. A number of gases in the liquid phase were evaluated by variation of the b_0-parameter to obtain the best calculated liquid molar volumes in comparison to experimental values. The constant value which yielded the best overall averages is the value of 0.2632 in Equation 23 for the constant b_0-parameter as a linear function of the measured critical molar volume v_c.

Of course, a computer program is necessary to evaluate the parameters a, $b_1(T_c)$, $k(T_c)$, and $v_{\min}$ at the critical point due to the complexity of the non-linear functions in Equations 46 to 48. Yet, from the evaluation of a number of real gases and liquids, curve fitting of these parameters obtained from numerical analyses of data in Equations 46 to 48 resulted in the expressions given in Equations 24, 25, and 27. Table 1 displays how closely the modified Redlich-Kwong-Soave equation of state matches measured critical point data when utilizing Equations 24, 25, and 27 for the measured critical point data to evaluate the a-parameter and parameters $b_1(T_c)$ and $k(T_c)$. Concerning the minimum volume $v_{\min}$ in the limit of infinite pressure, minimum molar volume varies slightly with temperature when using the modified Redlich-Kwong-Soave equation of state for temperatures below and above the critical temperature value. In theory, the value of $v_{\min}$ hypothetically should be constant or nearly constant.

Concerning the liquid phase, Figure 6 displays how well the modified Redlich-Kwong-Soave expression matches up with measured liquid molar volume data for the hydrocarbon butane at different temperatures as compared to the original Redlich-Kwong-Soave equation. With regards to high pressures above the critical temperature, Figure 7 displays the same comparison for high pressure data of butane at 500 Kelvin. The matches for both versions of the Redlich-Kwong-Soave equations of state are equally well at high pressures for temperatures above the critical temperature value.

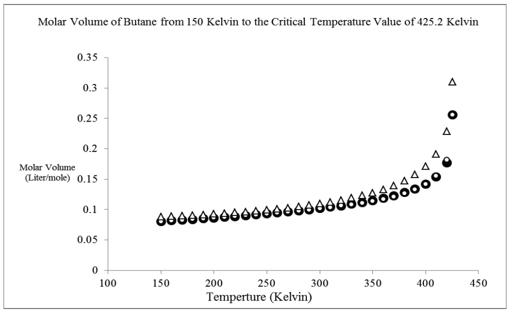

Figure 6. Liquid molar volume of butane from 150 Kelvin up to the critical temperature value of 425.2 Kelvin. The black circles are from experimental measurements, white triangles calculated values from the Redlich-Kwong-Soave equation of state, and the white circles from calculated liquid molar volumes using the modified Redlich-Kwong-Soave equation of state.

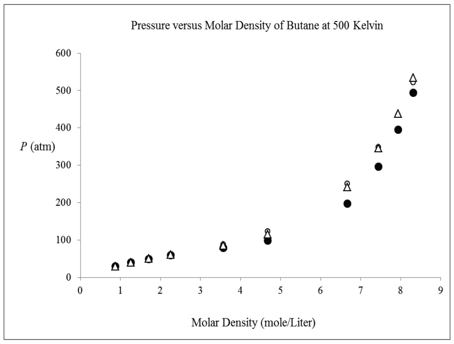

Figure 7. High pressure data of butane at 500 Kelvin. The black circles are from experimental measurements, white triangles from Redlich-Kwong-Soave equation of state, and the white circles from the modified Redlich-Kwong-Soave equation of state.

In addition to the evaluation of $b_1(T_c)$, $k(T_c)$ and a using measured critical point data, the other mathematical challenge was how to determine the general temperature variations of parameters $b_1(T)$ and $k(T)$ below and above the critical temperature value in order to derive general expressions in Equations 28 to 45. A series of iterations and algorithms in FORTRAN were developed to evaluate the b_1 and k values at different temperatures in both the liquid-vapor region and high pressure data above the critical temperature, for each real gas or liquid studied (Press et al., 1992). In all instances, not only was the b_0-parameter kept constant calculated using Equation 23, but also the minimum molar volume v_{min} was assumed to be constant when calculated by Equation 49 from the value of for a, $b_1(T_c)$, and $k(T_c)$ in Equations 46 to 48. Determining values of $b_1(T)$ and $k(T)$ for high pressure data above critical temperature value was accomplished simply by curve fitting experimental high pressure data observed at different measured molar gas volumes at different constant temperature values. At a given temperature, the $b_1(T)$ value determined was the number which yielded a minimum chi-square value while keeping v_{min} evaluated at the critical temperature constant, and the value of $k(T)$ was evaluated using the next expression from rearranging Equation 49.

$$k(T) = -v_{min} \log_e[(v_{min} - b_0) / b_1(T)] \qquad (50)$$

However, evaluation for the $b(T)$ value below the critical temperature incorporated the following integral set equal to zero.

$$\int_{v_{liq}}^{v_{gas}} (P_{equil} - P_{mRKS})\, dv = 0 \qquad (51)$$

P_{equil} is the measured equilibrium liquid-vapor pressure at a measured temperature value below the critical temperature, and P_{mRKS} is the modified Redlich-Kwong-Soave expression in Equation 21. Theoretically, this integral is equal to zero between the lower limit, the liquid molar volume v_{liq}, and the upper limit being the vapor molar volume v_{gas}, because the molar Gibbs free energy value of both liquid and vapor phases are equal at equilibrium conditions (Hirschfelder et al., 1954). The algorithm varied the value of $b_1(T)$, determining the value of $k(T)$ using the expression in Equation 50 by again assuming

Table 1. Comparison between measured critical point data along with that calculated using the modified Redlich-Kwong-Soave equation incorporating parameter derivation using measured critical compressibility factors in Equations 24, 25, and 27.

Gas	Measured T_c (Kelvin)	Calculated T_c (Kelvin)	Measured P_c (Atm)	Calculated P_c (Atm)	Measured v_c (Liter/mole)	Calculated v_c (Liter/mole)
Neon	44.4	44.4	26.18	26.23	0.04177	0.04177
Argon	150.9	151.0	48.34	48.42	0.07458	0.07457
Krypton	209.39	209.54	54.24	54.34	0.09201	0.09199
Xenon	289.7	289.9	57.45	57.50	0.1194	0.1194
Methane	190.6	190.7	45.39	45.47	0.1000	0.09998
Ethane	305.3	305.5	48.07	48.16	0.1471	0.1471
Butane	425.2	425.5	37.46	37.54	0.2560	0.2559
CO_2	304.2	304.4	72.86	73.02	0.09440	0.09438
O_2	154.77	154.82	50.20	50.23	0.07885	0.07887
N_2	126.25	126.34	33.52	33.58	0.09216	0.09215
Water	647.31	647.52	218.31	218.50	0.05711	0.05712
Ammonia	405.4	405.6	111.5	111.7	0.07246	0.07247
CO	132.91	133.01	34.50	34.56	0.09347	0.09346

the hypothetical minimum molar volume v_{min} is constant, until the integral expression in Equation 51 is equal to zero. Then for any particular real gas or liquid, the values of $b_1(T)$ and $k(T)$ at different temperatures were compared to the $b_1(T_c)$ and $k(T_c)$ values calculated using Equations 24 to 25 from measured critical point data. This resulted in the data shown in Figure 3, and a closer analysis of data below the critical temperature values resulted in an observation of the linear dependence of the β_i ($i = 0$ to 3) and κ_i ($i = 0$ to 2) values upon the acentric factor ω when curve fitting the data.

Concerning high pressure data for butane, the calculated pressures using the modified Redlich-Kwong-Soave equation was accomplished simply by applying Equations 21 to 25 and 27 to 29 for each measured gas molar volume and likewise Equations 18 and 19 for the original version. However, for the calculated liquid molar and vapor molar volumes in both the original Redlich-Kwong-Soave equation and the modified version, the expression in Equation 51 was used.

The Modification with Regards to the *b*-Parameter

In the Redlich-Kwong-Soave equation of state, the *b*-parameter represents the atomic or molecular molar volume of a real gas which is due to the gas atoms and molecules occupying space, or a small fraction of the gas volume at low pressure since atoms are not point masses. In theory [3], this *b*-parameter is not constant but dependent upon the gas molar density and absolute temperature as well. By assuming this parameter *b* is constant at all gas densities and temperature values, the Redlich-Kwong-Soave equation does not match up well with measured liquid molar volumes at temperatures below the critical temperature value. Therefore, it was necessary to determine how this parameter varies with gas molar density at least by using the hard-sphere model. This was accomplished by developing a FORTRAN computer program that models the collision dynamics of a monatomic gas contained within a cubic gas volume simulating gas atoms as hard spheres. A large number of simulations were performed for the noble gas krypton at different molar densities with a simulation temperature equal to 300 Kelvin. In addition, at each specific molar density simulated at 300 Kelvin, the number of krypton atoms was also varied. It was necessary to do simulations at constant temperature and constant molar density using a different large number of krypton atoms in order to obtain correct extrapolations to an extremely large number of gas atoms such as Avogadro's number.

For a single simulation, there is first the input value N for a large number of gas atoms, from several hundred to over ten-thousand, to be encased within a microscopically sized cubic volume that has edge lengths on the order from less than 100 to more than 1,000 Ångstroms (1Ångstrom = 10^{-10} meter) . Then, the atoms are initially positioned in the face-centered cubic unit cell arrangement, with the separation distances amongst the atoms established by the specific molar density input value. Afterwards, a Gaussian random number generator (Press et al., 1992) is utilized to establish a Maxwellian velocity distribution for the assigned gas temperature value. Then the simulation begins and continues until a very large number of inter atomic collisions take place. When the simulation is completed, the pressures at each of the six flat square walls are evaluated. The average simulation pressure value $< P >$ is determined by calculating the averages of the simulation pressures P_{i} at all six flat square walls:

$$< P > \;=\; \sum_{\mathrm{i}=1}^{6} P_{\mathrm{i}} / 6 \qquad (52)$$

And for the final determined simulation pressure value $< P >$, the standard deviation was calculated to get an estimated uncertainty in the atomic molar volume b. When figuring out the numerical value of the *b*-parameter at a given molar density and temperature value using the hard-sphere model, it is necessary to take edge effects into account since the number of gas atoms in any simulation is much less than Avogadro's number. When doing so, the pressure observed at any of the six flat walls of the cube is computed as:

$$P_i = \left(\sum_{j=1}^{N_i} 2\,m v_j / t\right) / (l - 2r)^2 \qquad (53)$$

In Equation 53, l is the edge length of the microscopic cubic gas volume of the simulation, r is the hard-sphere atomic radius, m is the mass of the hard-sphere, v_j is the velocity component of the colliding atom whose direction is perpendicular to the flat square wall, N_i is the total number of collisions at the wall, and t is the total simulation time.

For the hard sphere model, the equation of state of such a hypothetical gas is the following mathematical expression:

$$P = R\,T / (v - b) \qquad (54)$$

In Equation 54, the effective atomic molar volume b for one mole of hard-spheres is the following function of gas pressure P, temperature T, and molar volume v:

$$b = v - R\,T / P \qquad (55)$$

If one divides Equation 55 by Avogadro's number N_A, one obtains the effective atomic volume v_{eff} for a hard-sphere atom:

$$v_{eff} = v_{atom} - (R/N_A)\,T / P \qquad (56)$$

In Equation 56, the term v_{atom} represents the gas volume in units of Liters per atom. Since edge effects must be taken into account because the number of gas atoms in a single simulation is much less than Avogadro's number, Equation 56 becomes the following expression when using the average simulation pressure value $< P >$:

$$v_{eff} = (l - 2r)^3/N - (R/N_A)\,T / < P > \qquad (57)$$

The next challenge was then to determine how to extrapolate the simulation results to that for Avogadro's number of hard spheres where there are practically no edge effects. At zero moles per Liter or zero molar density, theoretically (Hirshfelder et al., 1954) the ratio of the effective atomic volume v_{eff} and atomic volume v_{atom} for hard-spheres is exactly equal to four:

$$v_{eff}/v_{atom} = 4 \qquad (58)$$

Theoretically this ratio decreases in value with increasing molar density until maximum molar density is attained at nearly infinite pressures, and for the face-centered cubic unit cell arrangement, this ratio at maximum molar density is about 1.35 at extremely large pressure values:

$$v_{eff}/v_{atom} = (3 \times 2^{1/2})/\pi \cong 1.35$$

(In the limit of infinite pressure) (59)

For the noble gas krypton using the hard-sphere model, the atomic volume v_{atom} is calculated by setting the atomic diameter equal to the sigma-parameter in the Lennard-Jones potential evaluated from viscosity data (Bird et al., 2006):

$$v_{atom} = (4\pi/3)\,(\sigma/2)^3 = (4/3)\,\pi r^3 \qquad (60)$$

It was observed that the ratio of the effective atomic volume and atomic volume (v_{eff}/v_{atom}) increases in value with the ratio $(l - 2r)^3/l^3$. The smallest number in one simulation was 172 atoms, and then additional simulations were performed at 365, 666, 1099, 1688, 2457, 3430, 4631, 6084, and 7813 atoms with molar density of 15 moles per Liter at 300 Kelvin. A plot of the ratio v_{eff}/v_{atom} versus the ratio $(l - 2r)^3/l^3$ can be fitted with a polynomial. Logically, if there is one mole of hard-spheres, Avogadro's number, the ratio $(l - 2r)^3/l^3$ will be nearly equal to one. Hence, extrapolation to one yields the simulation ratio of v_{eff}/v_{atom} for an astronomically large number of hard spheres. Once this value is determined, then the b-parameter at the simulation molar density can be evaluated for the expression in Equation 55. After a large number of simulations were performed and extrapolations done, the ratio of the effective atomic volume and atomic volume (v_{eff}/v_{atom}) versus molar density ($1/v$) at 300 Kelvin for krypton using the hard-sphere potential was observe to follow a negative exponential function. The simulation data revealed that the effective atomic molar volume b in the hard-sphere model is approximately modeled by the following negative exponential cubic function of the gas molar density:

$$b = b_0 + b_1\, exp[\, -(k_1/v - k_2/v^2 + k_3/v^3)\,] \quad (61)$$

And the numerical values of the constants in Equation 61 have to be determined from curve fitting the simulation data of a gas when using the hard-sphere model. Of course, the values of these constants depend upon the size of the hard-sphere and what type of initial arrangement was employed when beginning the simulations.

Because atoms are not hard-spheres but behave more like spheres with a soft, penetrable outer periphery and an infinitely hard inner spherical core, the negative exponential function in Equation 22 was employed to best match experimental data of real gases when modifying the Redlich-Kwong-Soave equation of state.

Conclusion: Why not modify the van der Waals Equation of State for Real Gases and Liquids?

The first equation of state developed for real gases and liquids is the van der Waals equation. Thus, one may ask the question why not apply the same variation of the b-parameter for this first equation of state.

$$P = RT / \{v - b_0 - b(T)\,\exp[-k(T)/v)]\} - a / v^2 \quad (62)$$

There is a serious problem when applying this modification to the tradition van der Waals equation of state for real gases and liquids, because for some polar liquids, such as methyl alcohol and others, instead of having one critical point, there are two instead. In reality, real gases and liquids only have one critical point.

However, the modified Redlich-Kwong-Soave gas equation can be rearranged mathematically to the following expression resembling a modified van der Waals expression.

$$P = RT / \{v - b_0 - b_1(T)\, exp[-k(T)/v]\} - [a/(1 + b_0/v)] / v^2 \quad (63)$$

In Equation 63, the numerator in the subtraction term represents the fact that the van der Waals a-parameter in the modified Redlich-Kwong-Soave equation has dependence upon the gas molar volume v such that in the limit of zero molar volume, the term in the numerator approaches zero for this subtraction term. In theory, this correlates with the fact that at such high pressures gaseous atoms or molecules will begin to overlap their electron clouds enhancing repulsive forces. Thus, the repulsive forces for real gaseous atoms and molecules are not completely represented by the positive first term only in both the van der Waals and Redlich-Kwong-Soave equations of state.

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