INVESTIGATION of the CORRELATIONS P- V- T of COMPRESSED LIQUIDS at HIGH PRESSURES

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by

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CERTIFICATION

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ABSTRACT

Prediction of the accurate values of molar volume of compressed liquids is very important in process design calculation and other industrial applications. Experimental measurements of molar volume V for compressed fluids are very expensive , so in order to obtain accurate V values, attention has been turned to calculate it from equation of state Alto and Kiskinen[1] equation for pure non polar component, using correlations to Tait equation for polar component, and modification of Rackett equation are used for mixtures.

In this study five types of equations of state were used to calculate molar volume V for pure non polar compressed liquid, they are Alto and Kiskinen, Tait, Peng- Robinson, Soave- Redlich- Kowng, Lee- Kesler. These equations were tested against 241 experimental data points of pure non polar compressed liquids and it was found that Aalto and Kiskinen equation is the best compared with the other equations.

The results of Alto and Kiskinen gives the average absolute percent deviation of 11 pure components was 0.6276.

For pure polar compound using four equations of state, Soave- Redlich- Kowng, Peng- Robinson, Alto and Kiskinen, Tait. These equations were tested against 63 experimental data points of polar compressed liquids and it was found that Tait equation is the best compared with the other equations. A new correlation for Tait equation was made to improve its accuracy and this was done by replacing the two terms in Tait equation (pressure and vapor pressure) with reduced pressure P_r and reduced saturated pressure P_{rs} as follows:

$$V = V_s\left(1 - c\ln\frac{\beta + P_r}{\beta + P_{rs}}\right)$$

Prediction using this equation agreed with the experimental data where the average absolute percent deviation for 3 polar compounds with 63 experimental data points was 2.1529.

For mixtures two equations were used to calculate molar volumes of compressed mixtures, Teja equation and Tait equation with HBT mixing rules, the extend of Tait equation to be applicable for mixtures, with Hankinson- Brobst- Thomson (HBT) mixing rules and modified Rackett equation is applied for mixtures to evaluate the pseudo saturated liquid mixtures which can be written as:

$$V_{sm} = \frac{RT_{cm}}{P_{cm}} Z_{cm}^{\left[1+(1-T_{rm})^{2/7}\right]}$$

This equation agreed with the experimental data where the average percent deviation of 291 points for 7 mixtures was 4.9386, thus this new proposed equation has improved the accuracy considerably and may be considered very satisfactory.

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NOMENCLATURE

A B	Constants used in the cubic equation of states	
AK	Aalto and Kiskinen equation	
BWR	Benedict- Webb- Rubin	
c	Constant used in Tait equation	
LK	Lee- Kesler	
HBT	Hankinson- Brobst- Thomson method	
HT	Hankinson- Thomson equation	
m	Constant used in to equations (2-44, 2-46, 2-51)	
P	Pressure	atm
P_c	Critical Pressure	atm
P_r	Reduced Pressure	
P_{rs}	Reduced Saturated Pressure	
P_s	Saturated Pressure	atm
PR	Peng- Robinson equation	
R	Universal gas Constant	atm.cm^3/mol.K
SRK	Soave- Redlich- Kwong equation	
T	Temperature	K
T_c	Critical Temperature	K
T_r	Reduced Temperature	--------
V	Molar volume	cm^3/mol
V_c	Critical Volume	cm^3/mol
V_r	Reduced volume	--------
V_s	Saturated volume	cm^3/mol
V_{rs}	Reduced saturated volume	-------
$V_R^{(0)}$, $V_R^{(\delta)}$	Functions of T_r for HBT correlations,eq.(2-73, 2-74)	cm^3/mol
V^*	Characteristic volume used in AK equation	
x	Mole fraction	
Z	Compressibility Factor	
Z_c	Critical Compressibility Factor	
Z_{RA}	Rackett Compressibility Factor	

GREEK

α	Constant used in the cubic equation of state Riedel s third Parameter eq. (2-37)	
β^s	The isothermal Compressibility of saturated liquid used in Chueh and Prausnitz eq.(2-18)	
ρ	Molar density	mol/cm^3
ρ_c	Critical Molar density	mol/cm^3
ρ_s	Saturated density	mol/cm^3
ρ_{rs}	Reduced saturated density	-----------
Φ	Fugacity coefficient	
ω	Acentric Factor	

Superscript

R1	Simple fluid (eq.2-101)
R2	Reference fluid (eq. 2-101)

Subscript

i	Component i
ij	Component ij
m	Mixture
s	Saturated

CHAPTER ONE

INTRODUCTION

Molar volume is one of the most important thermodynamic properties of a compound. In almost all design calculations, there is a need for the values of molar volume. For saturated liquid or vapor and for gas phase, volume V, is important in high- pressure processing and particularly in the design and operation of high- pressure pumps for all liquids in the chemical process industries. The volume- handing and power characteristics of such pumps are strongly influenced by a liquid's isothermal bulk compressibility, k. All liquids will compress significantly at high pressure [1].

Densities are needed in many engineering problems such as process calculations, simulations, equipment and pipe design, and liquid metering calculations. A good density correlation should be accurate and reliable over the whole liquid region from the freezing point to the critical point. In most practical cases, the fluids of interest are mixtures [2].

This work was made to study the equations which were used for calculating the molar volume of compressed liquids, and shows which equation gives good results than the other equations.

The principal aim of this work is to study the existing equations for calculating the molar volume, and to modify or improve the best equation in order to come out with an equation, or equations, that may predict the molar volume for pure compressed liquid or for mixture of compressed liquids with high accuracy.

This study includes a modification of Tait equation to be accurately applicable to pure polar compressed liquid and introduces new mixing rules for saturated liquid density which is applied to calculate the molar volume of mixtures.

CHAPTER TWO

LITERATURE SURVEY

2.1 Equation of State [3, 4, 5]

An equation of state is an equation that relates pressure, temperature, and specific volume. Many different equations of state have been developed over the years. Some have been purely empirical and others have been based on kinetic theory and/or thermodynamic considerations. However all are empirical in the sense that the constants must be determined from experimental observations, and the equations are valid only for interpolation in the region where experimental data have been obtained. While the equation of state primarily describe gas-phase properties, many modern equations are also useful for prediction of liquid-phase properties of the substance. A thorough understanding of these methods is necessary to understanding of classical thermodynamics. The simplest equation of state is that for an ideal gas.

2.2 Law of Corresponding States [3, 6]

van der Waals in1897 introduced the theorem of corresponding states, which states that different compounds at identical conditions of reduced temperature and reduced pressure will exhibit identical reduced volumes. It was expanded to say that they will have the same compressibility factor (Z).

$$\mathrm{Z} = f(\mathrm{T}_r, \mathrm{P}_r) \qquad (2\text{-}1)$$

However, this approach is only strictly applicable for spherical, nonpolar molecules. For more complex molecules additional parameter(s) are necessary .three parameters approaches have been demonstrated to be successful in correlating properties for non-spherical, nonpolar

Three alternate parameter have been proposed: critical compressibility Factor (Lydersen, Hougen, and Greenkorn) [7], alpha (Riedel)[8], and acentric factor (Pitzer)[6]. Pitzer acentric factor has been widely used, and the law is known as the law of corresponding states of three parameters, i.e.,

$$Z = f(T_r, P_r, \omega) \tag{2-2}$$

Polar molecules add an additional complexity, and four parameter models have been developed. The introduction of law of corresponding states of four parameter was made, with the critical compressibility factor as the fourth parameter [11], i.e.,

$$Z = f(T_r, P_r, Z_c, \omega) \tag{2-3}$$

2.3 The Third Parameter [3, 6]

2.3.1 Critical compressibility Factor (Z_c):

The critical compressibility factor was first proposed to be used as a third parameter by Lydersen, Hougen, and Greenkorn, and defined as:

$$Z_c = \frac{P_c V_c}{R T_c} \tag{2-4}$$

The value of Z_c varies from about 0.23 for water to 0.30 for light gases. Most polar compounds have factor in the range of 0.24 to 0.26, while hydrocarbons are normally in the range of 0.26 to 0.28.

2.3.2 Acentric Factor (ω) [6]:

Pitzer in 1955 postulated that the slope of the reduced vapor pressure curve is the most sensitive property for a third parameter base. Since vapor pressure can be measured with greater accuracy than critical properties, this approach should be superior to the critical compressibility factor. Thus the acentric factor ω, is defined as:

$$\omega = -1 - \log \left[P_r^{sat} \right]_{Tr=0.7} \tag{2-5}$$

where P_r^{sat} is the reduced saturated vapor pressure at reduced temperature ($T_r = 0.7$) (i.e., a temperature near the normal boiling point). This form is chosen to make $\omega = 0$ for simple fluids like (Ar, Kr, and Xe) with simple spherical molecules. Hence acentric factor is a factor for measuring the acentricity or non sphericity of a molecule. However, it should be noted that $T_r = 0.7$ is close to the normal boiling point of most substances, thus the particular choice of $T_r = 0.7$ adopted by Pitzer provides not only numerical simplicity because $\log P_r^{sat} = 1.0$ but also convenience because vapor – pressure data are most commonly available at pressure near atmospheric.

2.4 Polar Compounds **[8]:**

Polar compounds expressed the effect of electrostatic forces between molecules. Polar compounds are alcohol, phenol, water, ketones, aldehydes, ether, and alknitriles. The first three are hydrogen bonding compounds (a bond forms between the hydrogen atom attached to oxygen in one molecule with the oxygen atom of another molecule), this makes their behavior in the vapor different and more complex than that of non-hydrogen bonding compounds (ketones, ect).

2.5 Vapor Pressure **[7]**:

Vapor pressures have been measured for many substances. When reliable measurements are available, Boublik (1984) presents tabulations of experimental data that have been judged to be of high quality for approximately 1000 substances. However, sometimes these vapor pressures are calculated rather than original data and therefore the possibility exists that errors have been introduced in fitting, interpolation, or extrapolation of these data. Many different equations have been presented to correlate vapor pressures as a function of temperature. Two of these, the Antoine and Wagner equations, while the Wagner equation is the best equation for vapor pressure.

2.5.1 Wagner Equation **[7]:**

Wagner used an elaborate statistical method to develop an equation for representing the vapor pressure behavior of nitrogen and argon over the entire temperature range for which experimental data were available. The resulting equation is:

$$\ln P_{vpr} = (a\tau + b\tau^{1.5} + c\tau^{3} + d\tau^{6}) / T_r \qquad (2\text{-}6)$$

P_{vpr} is the reduced vapor pressure, T_r is the reduced temperature, and τ is $1\text{-}T_r$. The constants in eq. (2-6) have been given by McGarry for 250 fluids.

2.6 Critical Properties **[9]:**

The critical point is the state at which liquid and vapor in equilibrium becomes indistinguishable from one another i.e. at which all of the properties of the two phases (density, enthalpy .etc) become identical .For a pure substance the critical point is the highest temperature and pressure at which liquid and vapor phases can coexist in equilibrium. The horizontal inflection exhibited by the critical isotherm at critical point implies the two mathematical conditions:

$$\left(\frac{\partial \mathrm{P}}{\partial V}\right)_{T,Cr} = 0 \qquad (2\text{-}7)$$

$$\left(\frac{\partial^2 \mathrm{P}}{\partial V^2}\right)_{T,Cr} = 0 \qquad (2\text{-}8)$$

where subscript Cr denotes the critical state . These critical properties are used as special constants for each substance, in addition to the other physical and chemical constants such as boiling and freezing points, molecular weight...etc. where Tc represents the critical temperature and Pc, Vc represent the critical pressure and volume respectively.

The most generalized correlation are based on the observation that data for different fluids exhibit a remarkable uniformity when the thermodynamic coordinates are expressed basis for the theorem of corresponding states. Thus the reduced conditions are [10].

$$\left.\begin{aligned} T_r &= \frac{T}{T_c} \\ P_r &= \frac{P}{P_c} \\ V_r &= \frac{V}{V_c} \end{aligned}\right\} \qquad (2\text{-}9)$$

2.7 Compressed Liquid [12]

On a pressure – temperature diagram, often called a phase diagram, the saturation curves might appear as shown in figure 2-1. It is seen that the liquid – vapor saturation curves ends at the critical point. Every pure substance has a critical point .At any point not on the saturation curve, the substance can exist only in one phase: solid, liquid, or gaseous. If the temperature of the substance in the liquid phase is less than the saturation temperature for the given pressure, the substance is called a sub cooled liquid. Under the same conditions, the substance may also be called a compressed liquid to indicate that its pressure is greater than the saturation pressure required for the existing temperature

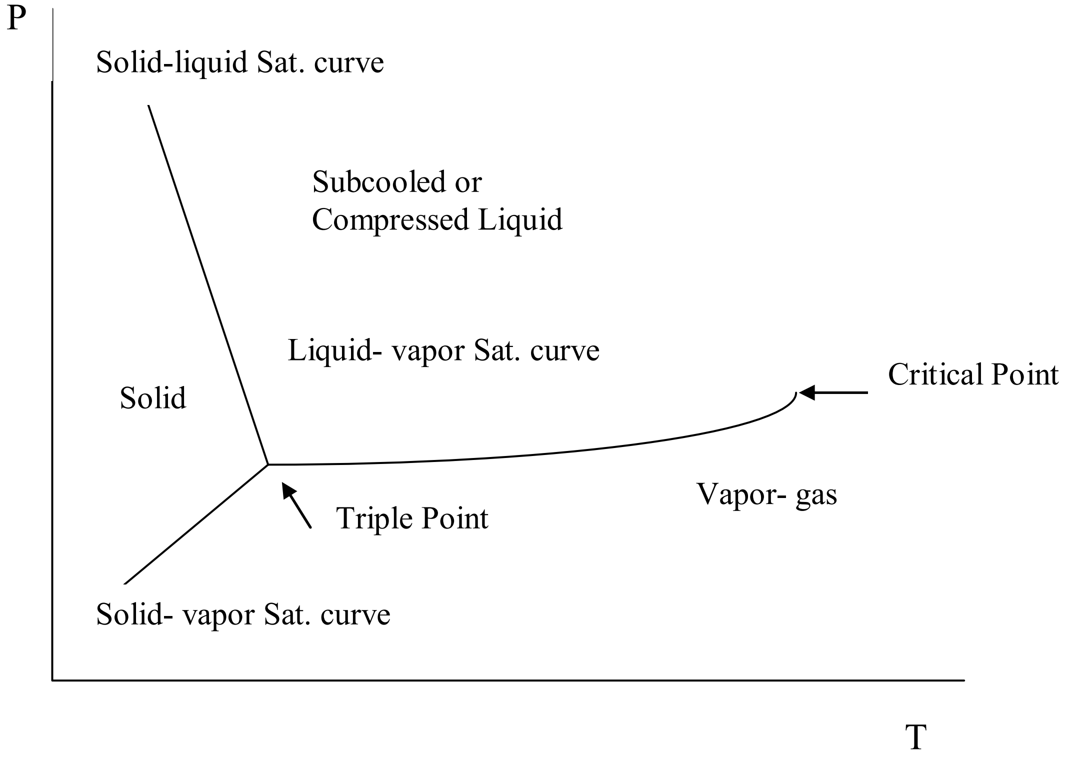

Figure 2-1: Pressure- Temperature Diagram

Consider the saturation curves shown in figure 2-2. A liquid existing at state 1 is not on the liquid – vapor saturation curve. It is at actual pressure P_1, and at liquids temperature T_1 which is below the saturation temperature for P_1, and is above the saturation pressure P_3 for T_1, and it can also be thought of as a compressed liquid.

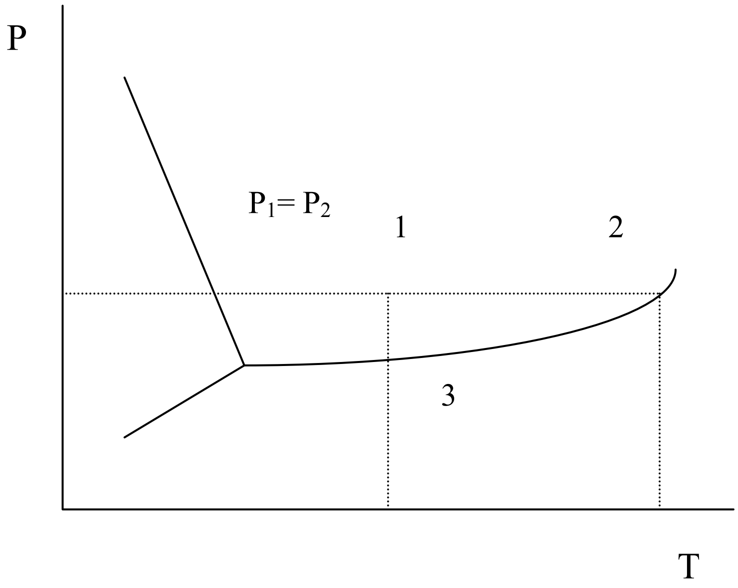

Figure 2-2: Saturation curve

2.8 Alternative Analytical Methods [13]:

2.8.1 Yen and Woods Correlation

Yen and Woods [14] defined the density of a compressed liquid in reduced quantities as:

$$\rho_r - \rho_{rs} = (\Delta\rho_r)_{27} + \delta_{Z_C} \qquad (2\text{-}8)$$

Here ($\rho_r - \rho_{rs}$) is the isothermal pressure effect on the reduced density based on the saturated reduced density, ρ_{rs}, and $(\Delta\rho_r)_{27}$ represents the reduced density increase for compounds with a Z_C of 0.27 when the pressure is increased from the equilibrium vapor pressure to the pressure of interest. The term $\delta_{ZC,}$ which equals zero for compounds having Z_C of 0.27, further corrects the isothermal pressure effect on density for compounds with other Z_C values. It was recommended that the reduced saturated liquid density be calculated by the following equation:

$$\rho_{rs} = 1 + A(1-T_r)^{1/3} + B(1-T_r)^{2/3} + D(1-T_r)^{4/3} \qquad (2\text{-}9)$$

The A, B and D in this equation have been correlated as polynomial functions of Z_C. The value of $(\Delta\rho_r)_{27}$ is calculated from

$$\left(\Delta\rho_r\right)_{27} = E + F\ln\Delta P_r + Ge^{H\Delta P_r} \tag{2-10}$$

Here ΔP_r is the reduced pressure increase from the vapor pressure to the pressure of interest and E, F, G, and H are given by complicated functions ot T_r. Similarly, δ_{ZC} is given as a function of ΔP_r:

$$\delta_{Z_C} = 1 + J\ln\Delta P_r + Ke^{L\Delta P_r} \tag{2-11}$$

where I, J, K, and L are defined functions of T_r and Z_C. The critical density must be known or estimated. Needless to say, these calculations are extremely tedious and intended exclusively for computer applications.

2.8.2 A Generalized Correlation for the Compressibilities of Normal Liquids

Much attention has been given to the volumetric properties of normal fluids in the gas phase and it is possible to estimate with good accuracy the compressibility of nonpolar (or slightly polar) gases. In this work one can report a correlation for the isothermal compressibility β is defined by

$$\beta = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T \tag{2-12}$$

For a given liquid, β is a function of both temperature and pressure (or density). As suggested by Wada [16] the effect of density ρ is given to a good approximation by

$$\rho\beta^{1/n} = \rho^s\left(\beta^s\right)^{1/n}$$

$$= \text{constant which depends on temperature} \tag{2-13}$$

where superscript s stands for saturation and n is an empirical constant. Substituting equation (2-13) into equation (2-12), gives:

$$-\frac{d\ln v}{dP} = \beta^s \left(\frac{v}{v^s}\right)^n \qquad (2\text{-}14)$$

Rewriting and integrating equation (2-14) we have

$$\int_{y^s}^{y} \frac{dy}{y^2} = -n\frac{\beta^s}{y^s}\int_{P^s}^{P} dP \qquad (2\text{-}15)$$

where $y = v^n$.

from equation (2-15)

$$\rho^n = \left(\rho^s\right)^n \left[1 + n\beta^s\left(P - P^s\right)\right] \qquad (2\text{-}16)$$

The compressibility of saturated liquid, β^s depends only on temperature.

To obtain a generalized correlation, the reduced experimental compressibility data for argon, methane, nitrogen, benzene, and n-heptane are used. From these data the empirical reduced equation is as follows

$$\frac{R\beta^s T_C}{v_C} = \left[1.0 - 0.89\omega^{1/2}\right]\left[\exp\begin{pmatrix} 6.9547 - 76.2853T_R + 191.3060T_R{}^2 \\ -203.5472T^3{}_R + 82.7631T^4{}_R \end{pmatrix}\right] \qquad (2\text{-}17)$$

where $T_R=T/T_C$, T_C is the critical temperature, v_c is the critical volume, ω is Pitzer's centric factor and R is the gas constant. Equation (2-17) holds for the interval $0.4 \le T_R \le 0.98$.

To calculate densities (or volumes) of compressed liquids equation (2-16) and (2-17) together with the correlation of Lyckman and Eckert [11] for volumes of saturated liquids are used. Wada [16] has suggested that for normal fluids n = 7. However, the studies suggest that somewhat better results are obtained with n = 9. Chueh and Prausnitz [15] suggested that ρ is not strongly sensitive to n if equation (2-16) in logarithmic form so they obtained generalized correlation for compressibilities of normal liquids in the following form:

$$\log\rho = \log\rho^s + \frac{1}{n}\log\left[1 + n\beta^s\left(P - P^s\right)\right] \qquad (2\text{-}18)$$

where β^s is the compressibility at saturation given as a function of T_r and ω. The equation of Lyckman is the recommended equation for calculating the saturated liquid density, ρ_s. This equation has the form:

$$\rho_C/\rho_s = V_r = V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)} \tag{2-19}$$

The $V_r^{(i)}$, s are generalized functions of T_r and ω is the acentric factor. Again, the critical density must be known or estimated. The accuracy of the correlations for the density of liquids under pressure depends strongly on the value of the saturated liquid density used.

Yen and Woods and Chueh and Prausnitz [14, 15] examined the results which presented of 32 components of 2590 data point and got an over all absolute average percent deviation 2.95 and 5.52 for molar volumes of compressed liquids of Yen and Woods and Chueh and Prausnitz respectively, and when they used Rackett equation (2-20) instead of equations (2-9), (2-19) the accuracy was improved to 2.29 and 1.75, so Rackett equation can be written in form:

$$Vs = \frac{RTc}{Pc} Z_{RA}^{[1+(1-Tr)^{2/7}]} \tag{2-20}$$

Its an equation to estimate saturated volumes which was developed by Rackett and later by Spencer and Danner [6, 7]. Z_{RA} is a unique constant for each compound, if a value of Z_{RA} is no available, it may be estimated by:

$$Z_{RA} = 0.29056 - 0.08775\omega \tag{2-21}$$

If one experimental density is available at reference temperature T^R, the recommended form of the Rackett equation is:

$$V_s = V_s{}^R Z_{RA}{}^{\Phi} \tag{2-22}$$

where $$\Phi = (1-T_r)^{2/7} - (1-T_r{}^R)^{2/7} \tag{2-23}$$

2.9.1 van der Waals Equation:

Derivation of the ideal gas law assumes that the volume of molecules is infinitesimal compared with the total volume. Actually, the volume in which a molecule can move is less than the total volume by some amount, which takes into account the finite size of the molecules and the repulsion between molecules. The force of attraction between molecules, called the van der Waals forces, is also neglected in the ideal-gas law. This force reduces the pressure below the value calculated from ideal-gas law by pulling molecules together. Kinetic theory shows this pressure to be inversely proportional to the molar volume squared. Using this observation, the van der Waals equation has been derived as

$$\left(P+\frac{a}{V^2}\right)(V-b)=RT \qquad (2\text{-}24)$$

or

$$P=\frac{RT}{V-b}-\frac{a}{V^2} \qquad (2\text{-}25)$$

where a and b are characteristics of each compound and are called the van der Waals constants. Values of a and second derivatives of pressure with respect to volume equal to zero:

a and b can be calculated from critical properties by applying the van der Waals equation to the critical point using the fact that at the critical point constant:

$$a=\frac{27R^2{T_C}^2}{64P_C} \qquad (2\text{-}26)$$

$$b=\frac{RT_C}{8P_C} \qquad (2\text{-}27)$$

The van der Waals equation is a simple although somewhat inaccurate equation but it provides a starting point for many more sophisticated formulations[3].

2.9.2 Redlich – Kwong Equation:

The two- constant Redlich-Kwong equation of state has been determined to be one of the most useful equations, it has been proposed in the century following van der Waals, work. The equation is:

$$P = \frac{RT}{V-b} - \frac{a}{T^{1/2}V(V+b)} \tag{2-28}$$

Constant a and b can be most accurately determined by fitting the constants, using experimental PVT data. However, as this information is not usually available, the criteria of the critical point (at the critical point the first and second derivatives of pressure with respect to volume equal to zero) are used to determine values for a and b as a function of the critical temperature and critical pressure of the compound concerned. The results of this derivation are

$$a = \frac{0.42748 R^2 T_C{}^{2.5}}{P_C} \tag{2-29}$$

$$b = \frac{0.08664 R T_C}{P_C} \tag{2-30}$$

These generalized parameters can then used with the Redlich-Kwong equation to determine PVT properties. The Redlich-Kwong equation is also often written as a compressibility equation:

$$Z = \frac{1}{1-h} - \frac{A}{B}\frac{h}{1+h} \tag{2-31}$$

where

$$h = \frac{b}{V} = \frac{BP}{Z} \tag{2-32}$$

$$B = \frac{bP}{RT} \tag{2-33}$$

$$A = \frac{aP}{R^2 T^{2.5}} \tag{2-34}$$

This equation will allow values of Z to be determined by iterative solution of the equation. Such a procedure would set a value of Z (say 1), calculate h, and then calculate a new value for Z. The process would be repeated until the assumed Z and calculated Z agree with certain limits.

Equation (2-25) can be written in terms of compressibility factor as:

$$Z^3 - Z^2 + (A - B - B^2)Z - AB = 0 \tag{2-35}$$

Any cubic equation will give three roots for Z. The largest is the vapor compressibility factor, the smallest is the liquid compressibility factor, and the intermediate root has no physical significance[3, 4].

2.9.3 Wilson Equation:

Wilson equation is a modification of Redlich-Kwong equation. Wilson redefined the equation in another way as:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)} \tag{2-36}$$

where

$$a = a_C \alpha \tag{2-37}$$

$$a_C = \frac{0.42784(RT_C)^2}{P_C} \tag{2-38}$$

He also defined a parameter g, which is equivalent to α / T_r, and made a parameter as a function of reduced temperature T_r, and acentric factor ω, as follows:

$$\alpha = T_r g(T_r, \omega) \tag{2-39}$$

$$g = 1 + (1.57 + 1.62\omega)\left(T^{-1}{}_r - 1\right) \tag{2-40}$$

$$\alpha = T\left[1 + (1.57 + 1.62\omega)\left(T_r^{-1} - 1\right)\right]_r \qquad (2\text{-}42)$$

In deriving the above equation, Wilson used the PVT behavior observation that the vapor pressure curve is continuous with the critical isochors at the critical point. Soave, on the other hand, used vapor pressure data and the definition of the acentric factor in obtaining the α expression[4].

2.9.4 Soave Equation:

Soave also defined α as a function of T_r and ω, but in a much different way to Wilson, Soave calculated the values of α at series of temperatures for a number of pure hydrocarbons, using the equality of vapor and liquid fugacities along the saturation curve. He defined α as:

$$\alpha = \left[1 + m(1 - T_r^{0.5})\right]^2 \qquad (2\text{-}43)$$

$$m = 0.48 + 1.57\omega - 0.176\omega \qquad (2\text{-}44)$$

This is to be used into equation (2-38) with a_C from equation (2-39) and using α into equation (3-37) or to calculate A as in equation (2-45) and use it into equation (2-36).

$$A = \frac{aP}{(RT)^2} \qquad (2\text{-}45)$$

In 1984 Soave [30] redefined m in equation (2-43) as:

$$m = 0.4998 + 1.5928\omega - 0.19563\omega^2 + 0.025\omega^3 \qquad (2\text{-}46)$$

which is restricted by $(0 \le \omega \le 1)$[3, 4, 17].

2.9.5 Peng – Robinson Equation:

Peng and Robinson modified equation (2-37) as follows:

$$P = \frac{RT}{V-b} - \frac{a}{V(V+b)+b(V-b)} \tag{2-47}$$

or in terms of compressibility factor:

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \tag{2-48}$$

where A and B are the same as in equation (2-45) and (2-33) respectively. The difference is in the values of a_C, b, and m. There values are calculated from the following equations[4, 18]:

$$a_C = \frac{0.457235(RT_C)^2}{P_C} \tag{2-49}$$

$$b = \frac{0.077796RT_C}{P_C} \tag{2-50}$$

$$m = 0.37646 + 1.54226\omega - 0.269926\omega^2 \tag{2-51}$$

2.10 Lee - Kesler Correlations:

This method calculates the compressibility factor is as follows:

$$Z = Z^{(0)} + \frac{\omega}{\omega^{(r)}}\left(Z^{(r)} - Z^{(o)}\right) \tag{2-52}$$

This method is based on the law of corresponding state of three parameters. It states that there are two fluids, simple one and reference one and calculated the compressibility factor of any interesting fluid from these two fluids. The compressibility factors of both the simple fluid Z (0) and the reference fluid Z(r) have been represented by the following reduced form of modified BWR equation of state:

$$Z = \left(\frac{P_r V_r}{T_r}\right) = 1 + \frac{B}{V_r} + \frac{C}{V_r^{\,2}} + \frac{D}{V_r^{\,3}} + \frac{c_4}{T_r^{\,3} V_r^{\,2}}\left(\beta + \frac{\gamma}{V_r^{\,2}}\right)\exp\left(-\frac{\gamma}{V_r^{\,2}}\right) \tag{2-53}$$

$$B = b_1 - b_2 / T_r - b_3 / T_r^{\,2} - b_4 / T_r^{\,3} \tag{2-54}$$

$$C = c_1 - c_2 / T_r + c_3 / T_r^{\,3} \tag{2-55}$$

$$D = d_1 + d_2 / T_r \tag{2-56}$$

Table 2-1: Constants for equation (2-53)

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

To calculate Z for the liquid of interest, given T and P, first calculating the appropriate values of T_r (T/T_c) and P_r (P/P_c) using critical properties of the from the simple fluid constants in table 2-1 equation (2-53), solving for V_r. When V_r is applied in the first equality of equation (2-53), $Z^{(0)}$ is calculated for the simple fluid. The next step is identical to the first except that the reference fluid constants of table 2-1 are used, but with the same T_r and P_r values of the fluid of interest that were determined in the first step. The result of the second step is $Z^{(r)}$. Finally, with $Z^{(0)}$ from the first step and $Z^{(r)}$ from the second, the compressibility factor Z for the fluid of interest is determined from equation (2-52) where $\omega^{(r)} = 0.3978$. knowing that the reference fluid is n-octane[6, 9].

2.11 Tait Equation for non polar compressed Liquids [6, 7, 20]:

One of the most general and useful equation for estimation of V is the Tait equation. This equation is generally applicable to nonpolar and moderately polar compounds, such as hydrocarbons and common solvents, but overestimates V for alcohols and diols at high pressures mainly because it does not account for these compounds of relatively large acentric factors, extreme polarities and strong hydrogen bonds. Compressed liquid density measurements were performed at pressure up to 68 MPa and at reduced temperature $T_r \leq 0.95$.

The obtained results were fitted to a generalized Tait equation in the form proposed by [18]:

$$V = V_{sat}\left(1 - c\ln\frac{\beta + P}{\beta + P_{sat}}\right) \qquad (2\text{-}57)$$

where V is the molar volume, V_{sat} is the saturated molar volume, P the pressure and P_{sat} the vapor pressure which was determined from eq. (2-6) by multiplying P_{vpr} with P_c.

P_C = critical pressure, in bars

Thomson et al. [6] presented generalized correlations for β and c in terms of T_c, P_c and ω, and obtained from the following equations:

$$\beta = P_C\left[-1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + d(1-T_r) + e(1-T_r)^{4/3}\right] \qquad (2\text{-}58)$$

$$e = \exp\left(f + g\omega_{SRK} + h\omega_{SRK}{}^2\right) \qquad (2\text{-}59)$$

$$c = j + k\omega_{SRK} \qquad (2\text{-}60)$$

Here ω is the acentric factor calculated through the basic equation:

$$\omega = -\log_{10} P_{rsat(at T_r = 0.7)} - 1 \qquad (2\text{-}61)$$

where $P_{rsat} = P_S / P_C$

The a - k coefficients, regressed on the base of experimental data, are given in table 2-2.

Table 2-2: Coefficients of the generalized Tait equation.

Coefficient	*Numerical value*	*Coefficient*	*Numerical value*
a	-9.070217	b	62.45326
d	-135.1102	f	4.79594
g	0.250047	h	1.14188
j	0.0861488	k	0.0344483

The ability to predict saturated liquid densities for elements and compounds continues to play an important role in the treatment of thermodynamic properties. Although the calculation of such densities is possible through the use of an equation of state more often than not. An equation to estimate saturated volumes was given also by Spencer and Danner [6, 7] (2-20).

2.12 Compressed Liquid densities based on Hankinson-Thomson saturated liquid density

2.12.1 Hankinson-Brobst-Thomson model [21]

Thomson et al. [22] proposed a method (HBT) to calculate the compressed liquid density. This model first calculates the saturated liquid density using equations (2-73)-(2-75). The effect of pressure is then taken into account using the generalized Tait equation. This method needs the pure component vapor pressure (experimental value or from a correlation equation like Antoine or Wagner equation) and the pure component critical pressure.

Alto et al. [23] have shown that this generalized Tait equation is limited to reduced temperature of 0.95. Therefore this method is to be replaced with newer and more accurate methods described next.

2.12.2 Alto et al. equation **[7, 21]**

Alto et al. [23, 24] have presented a compressed liquid density calculation method that first calculates saturated liquid density using HT model, and then the effect of pressure is taken into account by a modification of equation of Chang - Zhao [25] (1990) to T_r =1.

$$V = V_S \frac{AP_c + C^{(D-T_r)^B}\left(P - P_{vp}\right)}{AP_c + C\left(P - P_{vp}\right)} \tag{2-62}$$

A and B are polynomials in T/T_c and ω, respectively. Alto et al. (1996) modified the Chang - Zhao model by the HT model: V^*, T_C and ω_{SRK}. This model is quite accurate as discussed by Poling et al. [30]. The formation of A and B:

$$A = a_0 + a_1 T_r + a_2 T_r^{\,3} + a_3 T_r^{\,6} + a_4/T_r \tag{2-63}$$

$$B = b_0 + \omega_{SRK} b_1 \tag{2-64}$$

The constants of Alto et al. (1996) are shown in table 4-3.

Table 4-3: Constants for Alto, et al. (1996) Correlation for Compressed Liquids of eqs. (2-63) and (2-64)

a_0	a_1	a_2	a_3	a_4	b_0	b_1	C	D
-170.335	-28.578	124.809	-55.5393	130.01	0.164813	-0.0914427	Exp(1)	1.00588

The drawback of this model is that data used in the general model parameter fitting was limited to 20 MPa as maximum. The model has been found to have systematic errors (density under prediction) in pressures higher than 25 MPa and it is recommended only for the pressure range it was initially fitted, I, e. maximum pressure for this model is 20 MPa.

2.12.3 Alto and Keskinen equation [21]

Alto and Keskinen [26, 27] (AK) improved the equation of Alto et al. [23, 24] for compressed liquids. The data used in fitting the general model parameters extended up to 800 MPa. A lot of data points were also located near the critical temperature. Thus the AK model can be used with excellent accuracy up to extremely high pressures. The AK model also applies with good accuracy to the critical temperature giving also the liquid compression at the critical temperature when pressure is higher than critical pressure. The AK model was compared to the model of Alto et al. [23, 24] and was found to be of nearly the same accuracy in the pressure range from saturation pressure to 20 MPa. Therefore the AK model is better recommended than the model of Alto et al. The AK model, using V_S from the HT model, is as follows:

$$V = V_S \frac{A + C^{(D-T_r)^B}\left(P_r - P_{s,r}\right)^E}{A + C\left(P_r - P_{s,r}\right)} \tag{2-65}$$

$$A = a_0 + a_1 T_r + a_2 {T_r}^3 + a_3 {T_r}^6 + a_4 / T_r \tag{2-66}$$

$$B = b_0 + \frac{b_1}{b_2 + \omega_{SRK}} \tag{2-67}$$

$$C = c_1 (1 - T_r)^{c_2} + \left[1 - (1 - T_r)^{c_2}\right] \exp\left[c_3 + c_4 \left(P_r - P_{s,r}\right)\right] \tag{2-68}$$

The general model parameters for equations (2-65) - (2-68) are

$a_0 = 482.85416$ $a_1 = -1154.2977$ $a_2 = 790.09727$ $a_3 = -212.14413$

$a_4 = 93.4904$ $b_0 = 0.0264002$ $b_1 = 0.42711522$ $b_2 = 0.5$

$c_1 = 9.2892236$ $c_2 = 2.5103968$ $c_3 = 0.5939722$ $c_4 = 0.0010895002$

$D = 1.00001$ $E = 0.80329503$

Reduced temperature is obtained from,

$$T_r = \frac{T}{T_C} \qquad (2\text{-}69)$$

and reduced pressure P_r and reduced pressure of saturated vapor S_{pur} are

$$P_r = \frac{P}{P_C} \qquad (2\text{-}70)$$

$$P_{r,s} = \frac{P_S}{P_C} \qquad (2\text{-}71)$$

The AK model uses the same pure component parameters as the HT model: V^*, T_C and ω_{SRK}. In addition to that the critical pressure and saturated liquid vapor pressure are needed. The saturated liquid molar volume, V_S is computed in the Hankinson- Thomson HT model [13].

2.12.4 Hankinson-Thomson model for saturated liquid density [21, 7]:

One of the most successful saturated liquid density models is the Hankinson-Thomson (HT) model, often called *COSTALD*. It is accurate for pure compounds from triple point to the near-critical region, and it has been successfully extended to mixtures. Moreover, a large collection of pure- component parameters has already been published. HT was developed mainly for hydrocarbons and other organic compounds, but it is also accurate for many other types of compounds. The Hankinson-Brobst-Thomson (HBT) model is an extension of the HT model to the compressed liquid region, HBT is applicable both for pure compounds and mixtures. Later, many new methods for compressed liquid density calculation have been proposed. Many of those utilize a concept similar to HBT model. First, the saturated liquid density is obtained, and then the effect of pressure is described using another model. HT has often been selected for the saturated liquid density predictions in these compressed liquid density model due to its good accuracy. The saturated liquid molar volume, *Vs,* is computed in the Hankinson-Thomson model from:

$$\frac{V_S}{V^*} = V_R{}^{(0)}\left[1 - \omega_{SRK} V_R{}^{(\delta)}\right] \qquad (2\text{-}72)$$

$$V_R{}^{(0)} = 1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + c(1-T_r) + d(1-T_r)^{4/3} \qquad (2\text{-}73)$$

when 0.25< T_r<095

$$V_R{}^{(\delta)} = (e + fT_r + gT_r{}^2 + hT_r{}^3)\big/(T_r - 1.00001) \qquad (2\text{-}74)$$

when 0.25<T_r < 1.0

$$T_r = \frac{T}{T_C} \qquad (2\text{-}75)$$

for equations (2-73) - (2-74) the general parameters are as the following:

$a = -1.52816$ $\quad b = 1.43907$ $\quad c = -0.81446$ $\quad d = 0.190454$

$e = -0.296123$ $\quad f = 0.386914$ $\quad g = -0.0427258$ $\quad h = -0.0480645$

The pure - component specific parameters are the following: characteristic volume V^*, slightly adjusted critical temperature T_c and the SRK acentric factor ω_{SRK}. These are tabulated for many compounds in *Appendix A* and the uses of these special parameters are recommended to get best accuracy. Although equation (2-74) was originally stated to apply only at range 0.25<T_r< 0.95 , Alto et al, Alto and Keskinen and also Nasrifar et al [28], and Nasrifar and Mosfeghian[29] found it to hold reasonably well up to the critical temperature Poling et al. [30], discussed the need for the special parameter V^* ,T_c and ω_{SRK}. They state that real T_c can be used in place of T_c, but remind that the same value of T_c should be used with the model that was used in the fitting of the V^* and ω_{SRK}. Poling et al. Also stated that with a little loss of accuracy, V^* can be set equal to V_c and correspondingly ω_{SRK} can be substituted by the normal Riedel acentric factor ω.

2.13 Mixing Rules

The methods reviewed above are for pure components calculations. To extend the methods to mixtures, they must be modified to include the additional variable of composition. In essentially all cases, the inclusion is accomplished by averaging pure component constants to obtain constants which hopefully characterize the mixtures. Equations that do this are called mixing rules [6].

2.13.1 The Hankinson – Brobst - Thomson (HBT) [31]:

This mixing rules that are recommended for compressed liquids, are as follows:

$$T_{Cm} = \frac{\sum_i \sum_j x_i x_j V_{ij}^* T_{Cij}}{V_{cm}^*} \tag{2-82}$$

$$V_{ij}^* T_{Cij} = \left(V_i^* T_{Ci} V_j^* T_{Cj} \right)^{1/2} \tag{2-83}$$

$$V_{cm}^* = \frac{1}{4}\left[\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*^{2/3}} \right)\left(\sum_i x_i V_i^{*^{1/3}} \right) \right] \tag{2-84}$$

$$\omega_m = \sum_i x_i \omega_i \tag{2-85}$$

$$P_{Cm} = \frac{(0.291 - 0.080\omega_m) R T_{Cm}}{V_m^*} \tag{2-86}$$

2.13.2 An Improved Correlation for Densities of compressed Liquids and liquid Mixtures [31]:

The Tait equation has been extended and generalized to permit the calculation of densities of compressed liquids and their mixtures to a pressure of 680 atm using only critical temperature, critical pressure, Soave- Redlich- Kwong acentric factor, saturation pressure, and saturated volume for a pure liquid or the corresponding mixture parameters for a liquid mixture. This correlation, together with the correlation developed by Hankinson and Thomson (1979) for saturated liquid densities, comprises *COSTALD* (Corresponding States Liquid Density), an integrated method for estimating densities of nonpolar and slightly polar fluids and mixtures. This new correlation gave 0.446 average absolute percent error for 6338 data points for nonpolar liquids, 2.57 for 1352 data points for polar and quantum liquids, 0.369 for 319 data points for LNG/LPG mixtures, and 1.61 for all mixtures tested. with regard Tait equation (2-57), Cutler et al. (1958), Neece and Squire (1968), McDuffie et al. (1969), Benson and Winnick (1971), and Kumagai et al. (1976) treated the constant β as a linear or quadratic function of temperature, decreased as the temperature increased. Cutler et al. Nanda and Simha (1964), McDuffie et al; and Zordan and Henry (1975) treated C as a constant while Ginell (1961), Neece and Squire; and Kumagai considered it to be a weak function of temperature. Snyder and Winnick (1970) selected the values for β and C which fitted their data best. They did not discuss the temperature dependence of the constants.

Since β has the units of pressure, it is reduced by dividing it by P_c as in equation (2-57), Tait C is dimensionless and it is considered to be independent of temperature. It is generalized by making it a linear function of the SRK acentric factor as in equation (2-61).

In sense, mixing rules were not developed for the Tait equation. But the mixing rules for the saturated and the compressed liquid density mixtures were developed by (*COSTALD*) and these mixing ruled were also used for density correlation of mixture using Tait equation. The equations used are:

$$T_{Cm} = \frac{\sum_i \sum_j x_i x_j V_{ij}^{*} T_{Cij}}{V_m^{*}} \qquad (2\text{-}82)$$

$$V_{ij}^{\ *}T_{Cij} = \left(V_i^{\ *}T_{Ci}V_l^{\ *}T_{Cj}\right)^{1/2} \tag{2-83}$$

$$V_m^{\ *} = \frac{1}{4}\left[\sum_i x_iV_i^{\ *} + 3\left(\sum_i x_iV_i^{\ *^{2/3}}\right)\left(\sum_i x_iV_i^{\ *^{1/3}}\right)\right] \tag{2-84}$$

and

$$\omega_m = \sum_i x_i\omega_i \tag{2-85}$$

Mixture critical pressures are calculated as

$$P_{cm} = \left(Z_{cm}RT_{cm}\right)/V_m^{\ *} \tag{2-86}$$

Where V_m^* comes from Eq. (2-86) and Z_{cm} as

$$Z_{cm} = 0.291 - 0.080\omega_{SRKm} \tag{2-87}$$

The saturation pressure of the mixture, P_{sm}, is equal to the product of P_{rm} and P_{cm}.P_{rm} is calculated from the generalized Riedel vapor pressure equation with constants determined in experimental,

$$\log P_{rm} = P_{rm}^{\ (0)} + \omega_{SRK}P_{rm}^{\ (1)} \tag{2-88}$$

$$P_{rm}^{\ (0)} = 5.8031817\log T_{rm} + 0.07608141\alpha \tag{2-88a}$$

$$P_{rm}^{\ (1)} = 4.86601\beta \tag{2-88b}$$

$$\alpha = 35.0 - 36.0/T_{rm} - 96.736\log T_{rm} + T_{rm}^{\ 6} \tag{2-89}$$

$$\beta = \log T_{rm} + 0.03721754\alpha \tag{2-90}$$

where $T_{rm} = T/T_{cm}$

Hankinson and Thomson gave values of ω_{SRK} and V^* for 200 compounds.

Alto, et al. (1996, 1997) have extended eq. (2-57) to mixtures eqs. (2-82) and (2-84) for T_{cm} and V^*_m. They calculated P_{cm} as:

$$P_{cm} = \frac{\left(0.291 - 0.080\omega_{SRKm}\right)RT_{cm}}{V_m^{\ *}} \tag{2-91}$$

$$\omega_{SRKm} = \left(\sum_i x_i \omega_{SRKi}^{1/2} \right)^2 \tag{2-92}$$

Alto et al [7]. (1996) recommended that the vapor pressure used to calculate P_{vpr} in eq. (2-57) be obtained from generalized Riedel vapor pressure equation which, with some algebraic manipulation, can be put in the form

$$\ln P_{vpr} = P^0{}_{vpr} + \omega P^1{}_{vpr} \tag{2-93}$$

$$P^0{}_{vpr} = 6.13144 - \frac{6.30662}{T_{rm}} - 1.55663 \ln T_{rm} + 0.17518 T^6{}_{rm} \tag{2-93a}$$

$$P^1{}_{vpr} = 2.99938 - \frac{3.08508}{T_{rm}} + 1.26573 \ln T_{rm} + 0.08560 T^6{}_{rm} \tag{2-93b}$$

As previously mentioned, eqs. (2-82) and (2-84) do not represent estimates of the true T_{cm} and V^*_m. Thus, eq. (2-91) is not an estimate of the true P_{cm}, but is rather a pseudocritical pressure, and in the same way, the P_{vp} value predicted by eqs. (2-93) is not an estimate of the true bubble point pressure, but is rather a pseudo vapor pressure associated with the pseudocritical values of T_{cm} and P_{cm}. As a result, the Aalto method does not predict the correct volume at the bubble point unless the correct point pressure is used in eq. (2-57) instead of P_{vpr} from eqs. (2-93).

2.14.3 Densities of liquid at their Bubble Point

In order to extend equations such as eq. (2-20) to mixtures, mixing rules are required. Li [32] (1973) and Spencer and Danner [6] recommended

$$V_{sm} = R \left(\sum_i \frac{x_i T_{ci}}{P_{ci}} \right) Z_{RAm}^{\left[1+(1-T_r)^{2/7}\right]} \tag{2-94}$$

$$Z_{RAm} = \sum x_i Z_{RAi} \tag{2-95}$$

with the relation of Yamada and Gunn (1973)

$$Z_{RAi} = 0.29056 - 0.08775\omega_i \tag{2-96}$$

Spencer and Danner (1973) recommend the mixing rules of Chueh and Prausnitz [33]

$$T_{cm} = \sum_i \sum_j \phi_i \phi_j T_{cij} \tag{2-97}$$

$$\phi_i = \frac{x_i V_{ci}}{\sum_j x_j V_{cj}} \tag{2-98}$$

$$T_{cij} = \left(1 - k_{ij}\right)\left(T_{ci} T_{cj}\right)^{1/2} \tag{2-99}$$

Li's method sets $k_{ij} = 0$ for eq. (2-99).

2.15 Higher Parameter and Alternative CSP Approaches **[7]**

One method to extend *Corresponding States Principle (CSP)* to substances more complex than normal fluids is to use more terms in eq. (2-100) with new characteristic parameters to add for the effects of polarity and association.

$$Z = Z^{(0)}\left(T/T_c, P/P_c\right) + \omega Z^{(1)}\left(T/T_c, P/P_c\right) \tag{2-100}$$

Most of these correlations were not very successful though the approach (2-101) Wilding (Wilding and Rowley, 1986 and Wilding, et al., (1987) showed reasonable accuracy. This lack of reliability may be due to the polar and associating forces affecting not only the volumetric behavior as the model tries to treat, but also the critical properties. The result is that to use them for dimensionless scaling is inconsistent with the molecular theory basis for CSP (Hakala, 1967).

Alternative expansions of eq (2-100) have also appeared. Rather than using simple fluids as a single reference, multiple reference fluids can be used. For example, Lee and Kesler (1975) and Teja, et al. (1981)

developed CSP treatments for normal fluids that give excellent accuracy. The concept is to write Z in two terms with two reference substances having acentric factors $\omega^{(R1)}$ and $\omega^{(R2)}$, $Z^{(R1)}$ (T_r, P_r, $\omega^{(R1)}$) and $Z^{(R2)}$ (T_r, P_r, $\omega^{(R2)}$). The expression is

$$Z(T_r, P_r, \omega) = Z^{(R1)}\left(T_r, P_r, \omega^{(R1)}\right) + \frac{\omega - \omega^{(R1)}}{\omega^{(R2)} - \omega^{(R1)}}\left[Z^{(R2)}\left(T_r, P_r, \omega^{(R2)}\right) - Z^{(R1)}\left(T_r, P_r, \omega^{(R1)}\right)\right] \quad (2\text{-}101)$$

Typical reference fluids to provide properties are simple fluids as R1 and a larger hydrocarbon such as n-octane for R2. It is also possible to use more reference fluids to extend CSP to more complex substances. For example, Golobic and Gaspersic (1994) use three reference fluids (simple fluids, n-octane and water) with modification of the second term in eq. (2-101) and an additional term, both of which include another characteristic parameter. The properties have been provided in tables rather than analytic equations. Golobic and Gaspersic compared 20 different models for saturated vapor and liquid volumes with their method. Their comparisons with eight strongly polar alcohols and others were the most reliable, giving errors that were rarely more than any of the others and with maximum errors less than twice the average. Platzer and Maurer (1989) also used a three- reference fluids approach but with an equation for the EoS. For the 24 normal and 18 polar and associating fluids for which they obtained T_c, P_c, ω, and a polar factor, the correlation was as good as other methods available [7].

CHAPTER THREE

INVESTIGATION AND DISCUSSION

3.1 Introduction to Investigation

Liquid densities can be calculated from equations of state (EOS). Normally, the accuracy of liquid density predictions with EOS is not sufficient, and therefore special correlations for liquid density are used. Many accurate correlations are available for saturated liquid densities of pure fluids. The accuracy of many models is not good enough for mixtures, mainly due to the problems in formulating the mixing rules.

A good discussion of saturated and compressed liquid density calculation methods can be found in Poling et al. [30]. For density of saturated pure liquids, they recommended the Daubert et al. [32] version of the (modified Rackett) equation proposed by Spencer and Danner [33]. That model is applicable only for pure compounds. Reid et al. [34] recommended Spencer and Danner [33] and Hankinson- Thomson [35] (HT) models. They also recommended compressed liquid densities to be calculated using the Hankinson- Brobst- Thomson (HBT) model [22], in which HT is used for saturated liquid density. Poling et al. [32] recommended the model by Alto et al. [23, 24] for accurate compressed liquid density; the model by Alto et al. [23, 24] uses the HT model as basis and is applicable both for pure compounds and mixtures to predict compressed liquid densities. Aalto and Keskinen [26, 27] published an improved version of Alto et al. [23, 24] model. The new model is applicable for pure components and liquid mixtures and at extremely high pressures and gives better density prediction near critical temperature. The Alto and Keskinen [26, 27] model also uses the HT model as the basis for saturated density.

Based on the above discussion it can be stated that one of the most successful saturated liquid density calculation models is the Hankinson-Thomson model. The HT model was reviewed, with regard general and pure-component model parameters that are needed, and whether they are available and how to fit the parameters from experimental data.

Three notable paths have been evolved from industrial applications view point [60], as follows:

Path 1. van der Waals ⟶ Redlich- Kowng ⟶ Wilson ⟶ Lee-Edmister ⟶ Soave ⟶ Peng- Robinson.

Path 2. Beattie- Bidgeman ⟶ Benedict- Webb- Rubin ⟶ Starling ⟶ Starling Han ⟶ Lee- Kesler.

Path 3. Tait equation

Path 4. Hankinson- Brobst- Thomson (HBT) ⟶ Alto ⟶ Alto-Kiskinen

The development of two paths 3 and 4 was empirical, with goals for immediate applications of industrial problems. For most calculations, the empirical approach is as good as, often better than, theoretical approach of path 2 as Lee- Kesler approach, but the accuracy of Lee- Kesler equation which is designed for vapor phase only, and therefore path 2 is not to be taken into account in this work. Cubic equation of state is represented by the path 1 only with Soave- Redlich- Kwong equation (SRK) and Peng- Robinson (PR) which were used to calculate the molar volume of compressed liquid, but the results were not as good as in path 3 and 4. Path 3 represented by Tait equation which gives good results for pure components. However this equation does not work at $T_r > 0.95$ and the deviation in the region are large, and also the deviations increase where P_r nearly close to 10 as shown in tables 3-7 and 3-8, So Alto and Keskinen model was used in path 4 for refrigerant systems at reduced temperature up to $T_r = 1$.

3.2 Pure Component

3.2.1 Experimental Data:

It is well known fact that the evaluation of any correlation or prediction method is done by comparison of the results with the results of experimental dependable data. The deviation between the experimental results and the results of prediction or correlation method determines the accuracy of the method. The experimental data of the molar volume of compressed liquids, obtained from literature for the purpose of this investigation consists of 298 data points of eleven non polar pure components and there polar compounds as shown in table 3-1. These experimental data at condition of temperature up 250 C and pressure up to 680 atm.

Table 3-1: The Pure Component Molar Volume Data

No.	***Component***	***No. of Point***	***Reference Data***
1	*n- Pentane*	25	[45]
2	*n-Nonane*	24	[47]
3	*Propylene*	19	[39]
4	*n-Octane*	23	[46]
5	*Isobutane*	27	[36]
6	*n-Heptane*	26	[38]
7	*Ethylene*	20	[43]
8	*1-Butene*	18	[47]

9	*n-Butane*	21	[44]
10	*n-Decane*	19	[49]
11	*Propane*	13	[37]
12	*Ammonia*	20	[41]
13	*Water*	24	[52]
14	*Acetone*	19	[47]
	Σ	298	

3.2.2 Equations of States:

For pure component molar volume of compressed liquid using equation of state like Soave, Peng- Robinson, Lee- Kesler, Tait, and Aalto- Kiskinen equations, it is seen that when using Lee- Kesler equation the results were not good and acceptable. For example of two liquids 1-Butene, and n- Nonane which have Average Absolute Percent Deviation (AA%D) of 10.52, 9.643 respectively. As shown in table 3-2.

Table 3-2: Results of Lee- Kesler Equation

No.	***Component***	***No. of Point***	***AA%D***
1	*1- Butene*	19	10.52
2	*n- Nonane*	24	9.643
	Over all AA%D	*42*	*10.01885*

For Soave equation calculating molar volume of compressed liquids the results showed rather high deviations from the experimental data. For example calculating the molar volume of three components n-heptane, isobutane, and propylene gave (AA%D) of 10.552, 4.132, and 6.717

respectively, table 3-3 shows the results of 91 data point by using Soave equation for three the component .

Table 3-3: The Results of using Soave Equation

No.	*Component*	*No. of Point*	*AA%D*
1	*n- Heptane*	26	10.552
2	*Isobutane*	27	4.132
3	*Propylene*	19	6.717
	Over all AA%D	91	5.643

When Peng- Robinson equation was used to calculate the molar volume of compressed liquids for the three components n-heptane, isobutane, and propylene, the results were not good so but the deviations were less than using the two previous equations of Lee- Kesler, and Soave. Table 3-4 shows the results of calculating the molar volume for three components using Peng-Robinson equation.

Table 3-4: The Results of using Peng- Robinson

No.	*Component*	*No. of Point*	*AA%D*
1	*n- Heptane*	26	1.427
2	*Isobutane*	27	6.795
3	*Propylene*	19	5.180
	Over all AA%D	91	3.559

Another equation of state was Tait equation that was used to calculate the molar volume of compressed liquids for 11 pure component of 241 data point and gives good results and much less deviations from the experimental data as shown in table 3-5. Table 3-5 shows that the maximum deviation from the experimental data was 1.6118% for n- octane and the minimum deviation was 0.2323% for propylene.

Table 3-5: Results of Tait Equation

	Component	***No. of Data point***	***%Av.Dev.of Tait***
1	*n-Pentane*	25	0.9195
2	*n-Nonane*	24	0.7076
3	*Propylene*	19	0.2323
4	*n-Octane*	23	1.6118
5	*Isobutane*	27	0.3778
6	*n-Heptane*	26	0.8365
7	*Ethylene*	20	0.3358
8	*1-Butene*	18	0.944
9	*n-Butane*	21	0.7240
10	*n-Decane*	19	1.2894
11	*Propane*	19	0.2266
	Total % av.dev.	***241***	***0.73378***

A gain by using another equation which was Aalto and Kiskinen method this equation was used to calculate the molar volume of compressed liquids of 11 pure component of 241 data points and gives better results even when compared with Tait equation as shown in table 3-6. Table 3-6 shows the maximum deviation from experimental point is 1.3126 % for ethylene and the minimum deviation is 0.1633 % for n- Decane.

Table 3-6: Results of Alto and Kiskinen method

No.	***Component***	***No. of Data point***	***%Av.Dev.of (AK)***
1	*n-Pentane*	25	0.5129
2	*n-Nonane*	24	1.2366
3	*Propylene*	19	0.2243
4	*n-Octane*	23	0.8511
5	*Isobutane*	27	0.2731
6	*n-Heptane*	26	0.4523
7	*Ethylene*	20	1.3126
8	*1-Butene*	18	0.8410
9	*n-Butane*	21	0.4879
10	*n-Decane*	19	0.1633
11	*Propane*	19	0.5807
	Total % av.dev.	***241***	***0.62876***

At the end of this investigation it is clear appeared that Aalto and Kiskinen equation gives more accurate results those obtained by using other equations.

3.2.3 Comparison between Tait and Aalto -Kiskinen equations

A- For $T_r < 0.95$

When calculating the molar volume of compressed liquid region, there are two variables that affect the value of liquid volume, namely the pressure and temperature. High values of pressure and different values of temperature were used in this work. No influence of temperature was noticed in the region where T_r was less than 0.95 on both Tait and AK equations, however the pressure or the reduced pressure affects the deviation from experimental value, but still the AK equation showed less deviation than Tait equation for the same value of reduced pressure as shown in table 3-7.Table 3-7 shows the results of calculating molar volumes of pure components by Tait and AK equations for 4 pure components at reduced temperature less than 0.95 and different reduced pressures from 7 up to 27 where it appears that the maximum deviation in Tait equation for n-nonane is 2.006 %, and in AK method is 0.1414 % for P_r = 30.1005, and minimum deviation in Tait equation 1.059 %, and AK equation is 0.3435 % for P_r = 21.070 of n-nonane.

Table 3-7: The effect of Reduced Pressure on Tait & AK equations
At different temperatures

	Component	***Pr***	***Vexp. (cm^3/mol)***	***AK Equation***		***Tait Equation***	
				Vcal. (cm^3/mol)	***% Dev.***	***Vcal. (cm^3/mol)***	***% Dev.***
1	1-Butene	7.7158	101.88092	100.6449	1.171	100.6449	1.213
		8.5732	100.88209	99.52683	1.343	99.57532	1.295
		10.2878	99.19656	97.7811	1.426	97.6999	1.508
		12.0024	97.69831	96.21792	1.515	96.09279	1.643
		13.7171	96.26249	94.86848	1.448	94.68674	1.636
		15.431	95.01395	93.68548	1.398	93.437	1.659
2	n-Butane	18.139	93.45327	93.4295	0.0254	92.44383	1.072
		18.139	100.25782	100.1319	0.1256	98.96558	1.288
3	n-Nonane	21.070	196.02090	195.3475	0.3435	198.0979	1.059
		24.0803	193.52381	193.381	0.0738	195.95316	1.255
		27.0904	194.77235	196.1669	0.5286	200.38080	1.577
		30.1005	194.77235	196.9903	0.1414	201.22793	2.006
4	n-Heptane	6.9181	140.71054	140.7845	0.0525	139.12302	1.128
		7.547	140.46083	140.5657	0.0746	138.83024	1.1607
		8.8049	150.44916	150.53	0.0537	148.73298	1.1407
		10.0627	149.70003	149.8658	0.1107	147.93160	1.1813
		11.3206	148.95091	149.2351	0.1908	147.17005	1.195
		12.5785	148.45149	148.6338	0.1228	146.4446	1.351

In order to show the effect of reduced pressure on molar volume of compressed liquids, figures 3.1, 3.2, and 3.3 were plotted. The figures are molar volume against reduced pressure for the experimental data and for those calculated by Tait and AK equations for the pure components of heptane, n-nonane, and 1-butene. The figures indicate that generally speaking as reduced pressure P_r increases the deviation of the curve calculated using Tait equations from that of experimental data is increased. Thus it can be said that in the region where $T_r < 0.95$ and P_r up to 30 AK equation gives better results than Tait equation.

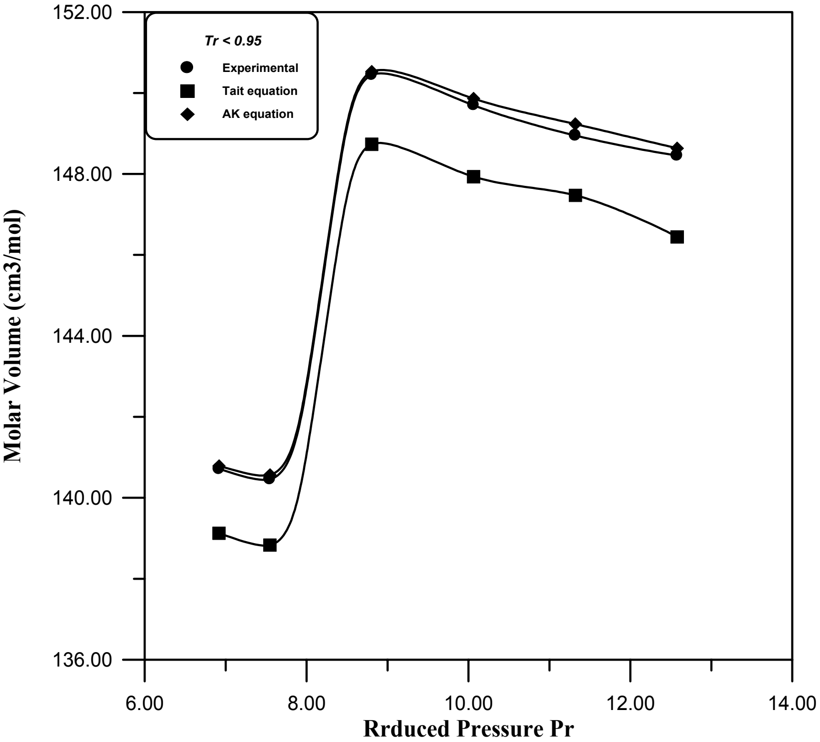

Figure 3.1 The effect of Pr on Tait &AK equations at T_r less than 0.95 for n-Heptane

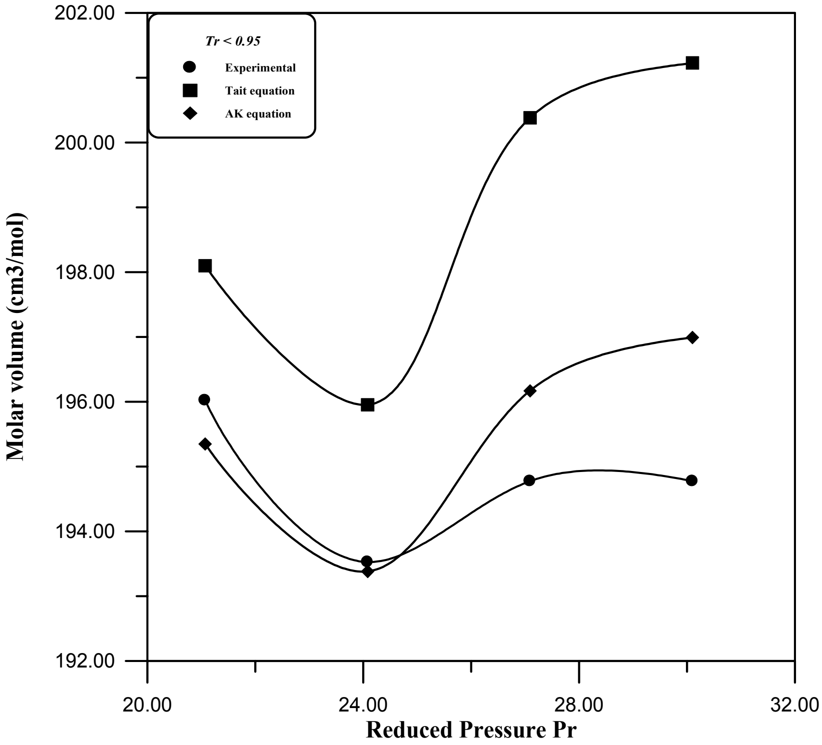

Figure 3.2 The effect of Pr on Tait &AK equations at Tr less than 0.95 for n-Nonane

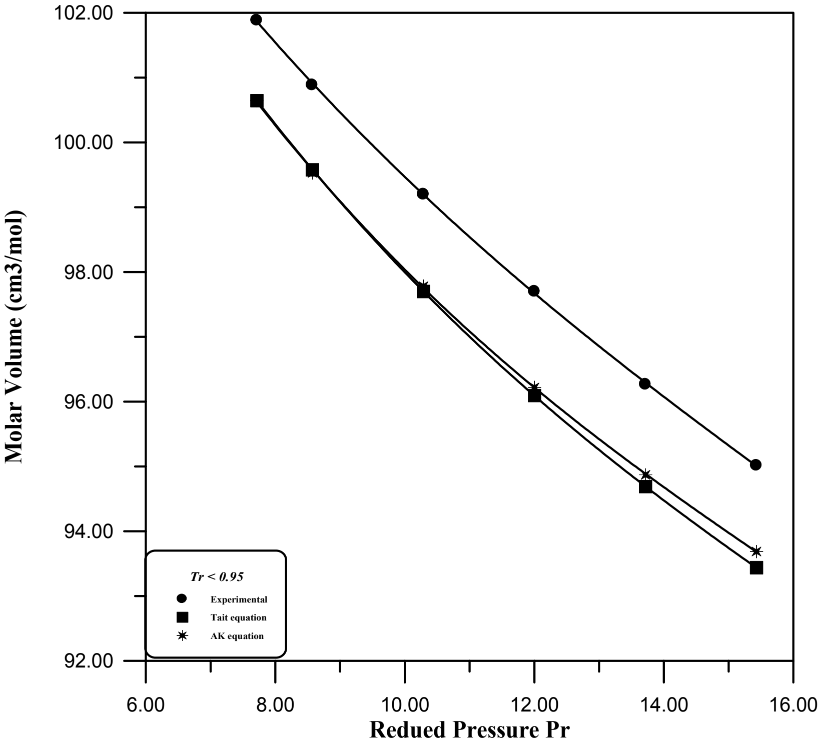

Figure 3.3 The effect of Pr on Tait &AK equations at Tr less than 0.95 for 1-Butene

B- For $T_r > 0.95$

In this region the effect of reduced temperature is clearly appeared in the results for each of the calculating equation Tait and AK, as shown in table 3-7. Table 3-8shows a comparison between Tait and AK equations for five components with different reduced temperatures from 0.95 up to 1, the deviation of molar volume calculated by Tait equation at $T_r = 0.95$ is very high and when $T_r = 0.99$ Tait equation did not give any results as shown in ethylene at Tr = 0.9915 and propane at Tr = 0.9901, while the deviation of molar volume of Aalto and Kiskinen equation is still satisfactory.

Table 3-8: Comparison between Tait & AK equations at Tr > 0.95

	Component	***T (K)***	***Tr***	***Vexp. (cm3/mol)***	***AK Equation***		***Tait Equation***	
					Vcal. (cm3/mol)	***% Dev.***	***Vcal. (cm3/mol)***	***% Dev.***
1	*Ethylene*	270	0.95609	51.08228	52.1923	2.178	49.74623	2.61
				51.081908	52.3543	1.876	49.94479	2.812
		276	0.9773	50.986266	52.9585	3.872	37.9942	25.478
				50.704524	52.7640	4.066	37.65484	25.733
		280	0.9915	50.983706	54.8896	8.327	---------	------
				51.554065	55.1383	6.957	---------	------
2	*n-Pentane*	444.26	0.9459	126.52212	124.5788	1.535	124.2132	1.824
				125.48621	123.748	1.384	123.1405	1.869
				124.58542	122.980	1.287	122.1327	1.968
				123.14409	121.5995	1.254	120.2836	2.322
				122.55850	120.974	1.292	119.43079	2.552
3	*n-Butane*	410.92	0.9664	134.97315	136.4531	1.100	132.7790	1.621
				111.24984	110.6236	0.5585	108.4972	2.469
				102.13509	102.8316	0.6863	101.0492	1.058
4	*1-Butene*	410.92	0.9793	109.87136	107.0222	2.593	83.0519	24.403
				108.24826	105.6009	2.445	81.1504	25.033
				106.87487	104.3969	2.318	79.4658	25.645
				104.68992	102.4522	2.137	76.59412	26.837
5	*Propane*	366.15	0.99012	121.17063	122.0069	0.6901	---------	------
				111.17999	109.0138	1.948	----------	-----
				111.04003	108.6902	2.116	-----------	-------
				107.07622	104.1725	2.711	-----------	-------
				102.90310	97.60979	5.143	-----------	-------

In order to illustrate this fact, figures were drawn of molar volumes against pressure for five components. Figure 3.4 for ethylene, figure 3.5 for n-pentane, figure 3.6 for n-butane, figure 3.7 for 1-butene and figure 3.8 for propane.These figures show that when the pressures increase the deviation increases also especially for $T_r = 0.95$ and higher, as in fig.3.6 and 3.7. The results of AK equation are much better than those by Tait equation. Thus Aalto and Kiskinen equation is used to calculate molar volume of compressed liquids up to $T_r = 1$, with very satisfactory deviations, Thus it can be considered that AK equation is the best equation in this range of T_r.

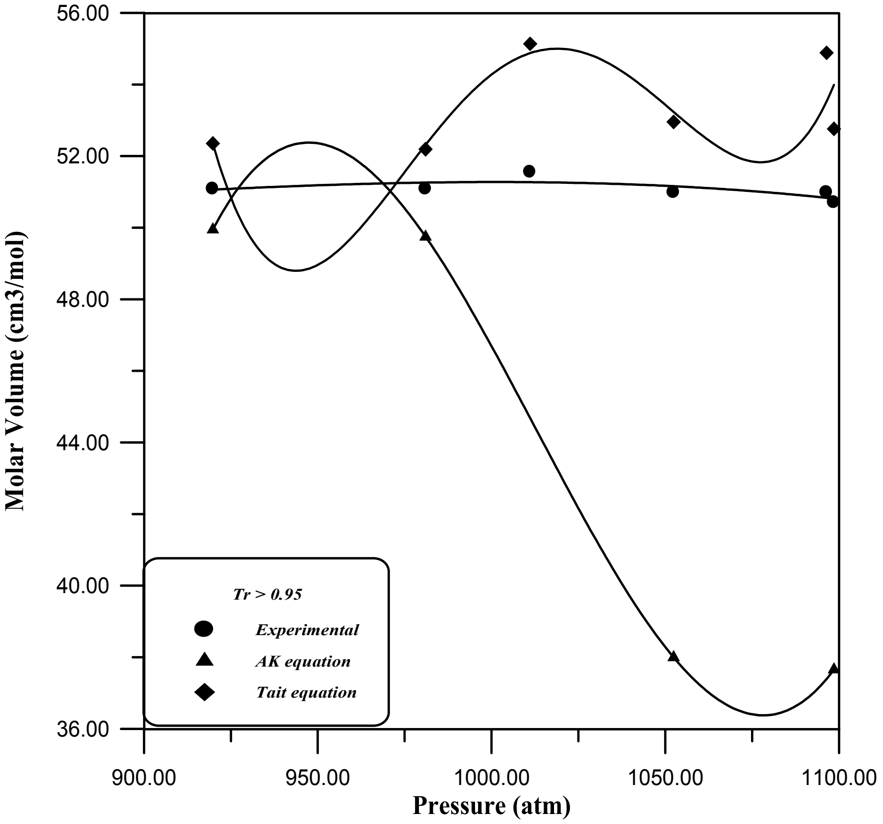

Figure 3.4 Ethylene at reduced temperature over 0.95

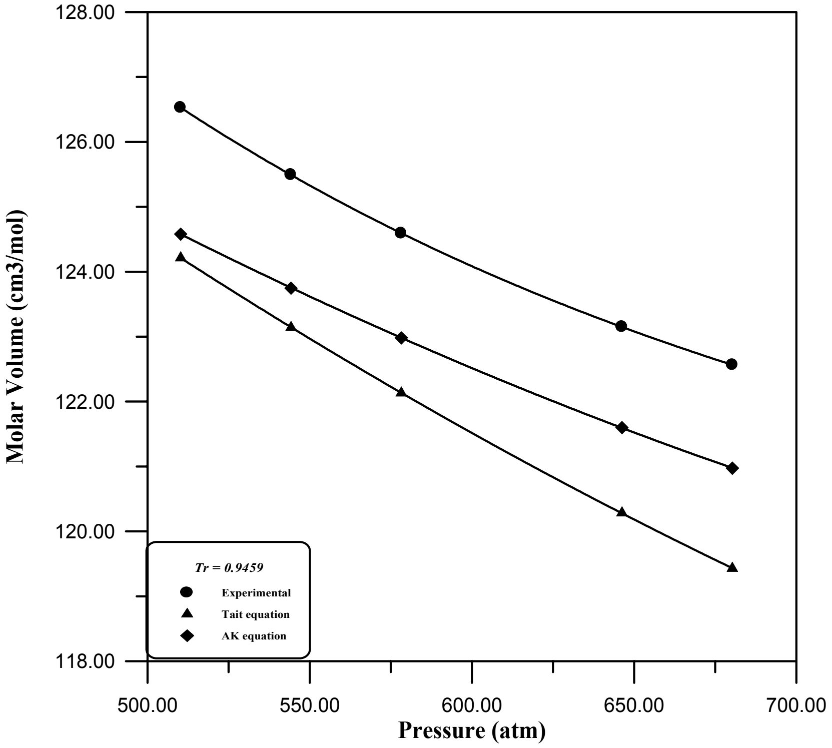

Figure 3.5 n- Pentane at reduced temperature 0.95

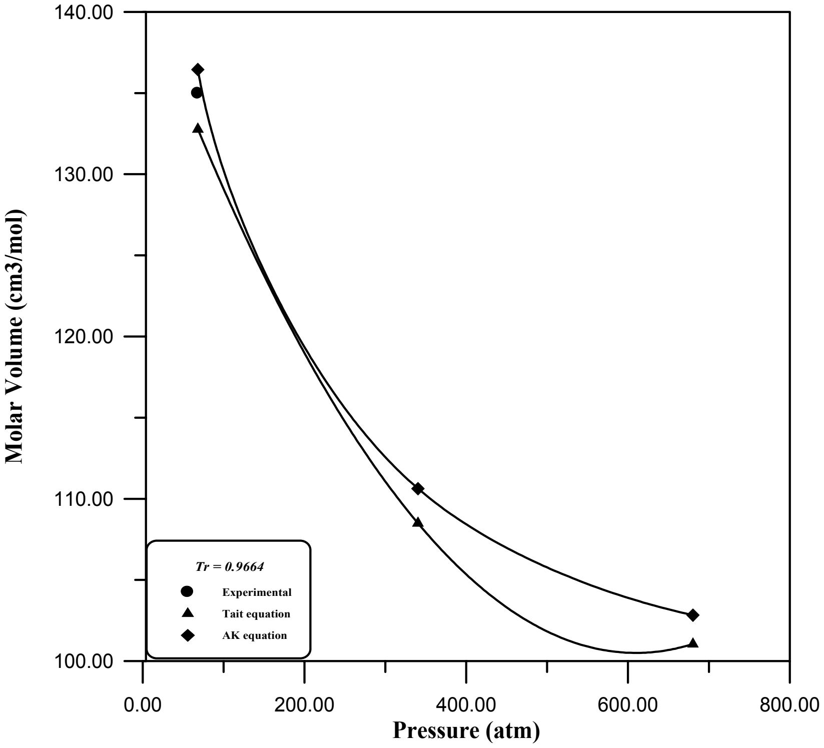

Figure 3.6 n-Butane at reduced temperature 0.9664

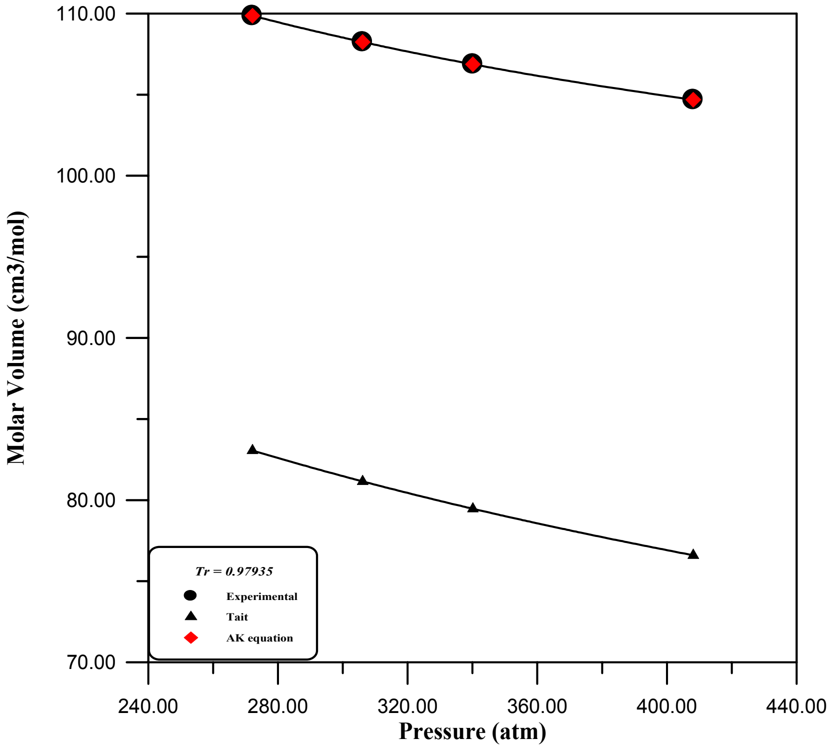

Figure 3.7 1-Butane at reduced temperature 0.97935

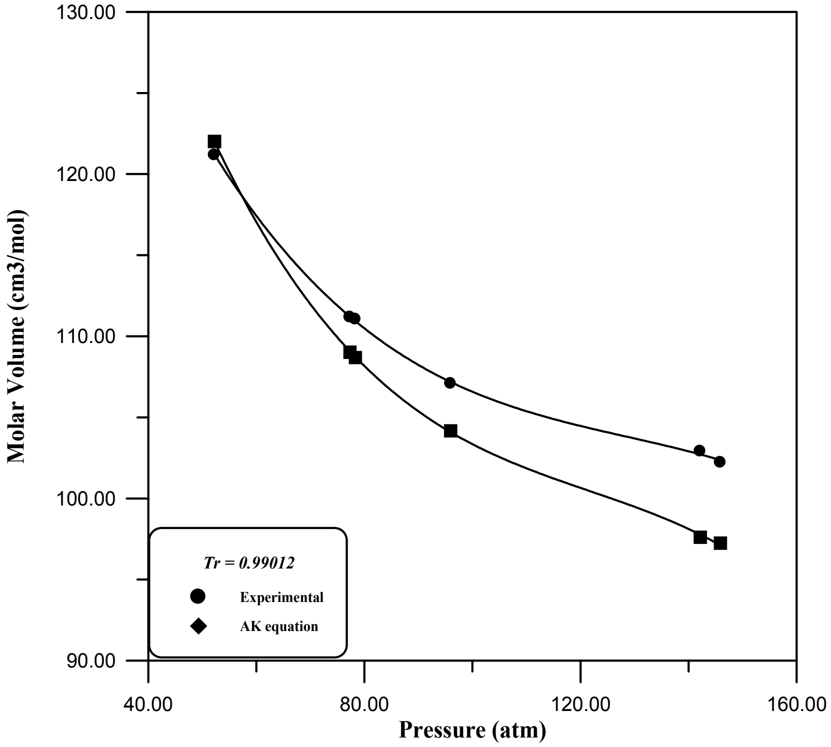

Figure 3.8 Propane at reduced temperature 0.99012

3.3 Summary of the Investigation

The following steps of investigation were carried out:

1- Soave- Redlich- Kwong (SRK) equation was used for calculating molar volume of compressed liquids for example n-heptane, isobutane and propylene experimental data. It was found that Average Absolute Percent Deviation (AA%D) is 5.643 for 91 data point.

2- Peng- Robinson (PR) equation was also used to calculate molar volume of compressed liquids for example n-heptane, isobutane and propylene experimental data. It was found that Average Absolute Percent Deviation (AA%D) is 3.559 for 91 data point.

3- Lee- Kesler (LK) equation again was employed for the same purpose as the authors claimed that their equation is suitable for prediction of molar volume of compressed liquids [19], and the (AA%D) was 10.0188 for 42data point of 1-butene and n-nonane.

4- Tait equation was once more used to calculate molar of volume compressed liquids for all experimental data. It was found that the (AA%D) is 0.73378 for pure non polar molar volume of compressed liquids and for all the 241 data point.

5- Aalto and Keskinen (AK) equation was once again used to calculate the molar volume of compressed liquids for all experimental data. It was found that the (AA%D) is 0.62876 for pure non polar molar volume of compressed liquids for all the 241 data point.

6- Comparison of Tait and AK equations at $T_r < 0.95$ and $T_r > 0.95$.

3.4 Sample of Calculation of Volume of Compressed liquid for Pure Components by Aalto and Kiskinen equation

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Calculation of molar volume for n-Decane at 344.261 K and 238.095 atm.

For n-Decane $T_c = 617.7$ K $P_c = 20.922$ atm

$\omega_{SRK} = 0.4916$ $V^* = 619.2\ cm^3/mol$

$$T_r = \frac{T}{T_c} = \frac{344.261}{617.7} = 0.55733$$

$$P_r = \frac{P}{P_c} = \frac{238.095}{20.922} = 11.3801$$

To calculate the vapor pressure using Wagner equation:

$$\ln\left(\frac{P_{vp}}{P_c}\right) = (1-\tau)^{-1}\left[A(\tau) + B(\tau)^{1.5} + C(\tau)^3 + D(\tau)^6\right]$$

where

$$\tau = 1 - T_r$$

$$\tau = 1 - 0.55733 = 0.44267$$

The Constants of Wagner equation

A = -8.56523 B = 1.97756

C = -5.81971 D = -0.29982

$$\ln\left(\frac{P_{vp}}{P_c}\right) = (1-0.44267)^{-1}\begin{bmatrix}(-8.56523)\times(0.44267)+(1.97756)\times(0.44267)^{1.5}\\ +(-5.81971)\times(0.44267)^{3}+(-0.29982)\times(0.44267)^{6}\end{bmatrix}$$

$$\ln\left(\frac{P_{vp}}{P_c}\right) = -6.66961$$

$$\left(\frac{P_{vp}}{P_c}\right) = 1.26954\times10^{-3}$$

$$P_{vp} = 1.26954\times10^{-3}\times 20.922$$
$$P_{vp} = 0.02654 atm$$

$$P_{sr} = \frac{0.02654}{20.922} = 1.2709\times10^{-3}$$

Using HT method to calculate saturated molar volume:

$$\frac{V_s}{V^*} = V_R^{(0)}\left[1-\omega_{SRK}V_R^{(\delta)}\right]$$

$$V_R^{(0)} = 1 + a(1-T_r)^{1/3} + b(1-T_r)^{2/3} + c(1-T_r) + d(1-T_r)^{4/3}$$

$$V_R^{(\delta)} = \left(e + fT_r + gT_r^{\,2} + hT_r^{\,3}\right)/(T_r - 1.00001)$$

$a = -1.52816$
$b = 1.43907$
$c = -0.81446$
$d = 0.190454$
$e = -0.296123$
$f = 0.386914$
$g = -0.0427258$
$h = -0.0480645$

$$V_R^{(0)} = 1+\begin{bmatrix}(-1.52816)\times(1-0.44267)^{1/3}+(1.43907)\times(1-0.44267)^{2/3}\\ +(-0.81446)\times(1-0.44267)+(0.190454)\times(1-0.44267)^{4/3}\end{bmatrix}$$

$$V_R^{(0)} = 0.3749$$

$$V_R^{(\delta)} = \left[\begin{array}{l}(-0.296123)+(0.386914)\times(0.44267)+(-0.0427258)\times(0.44267)^2 \\ +(-0.0480645)\times(0.44267)^3\end{array}\right]/(0.44267-1)$$

$$V_R^{(\delta)} = 0.230592$$

$$\frac{V_s}{619.2} = 0.3749[1-0.4916(0.230592)]$$

$$V_s = 205.768195 cm^3/mol$$

Aalto and Kiskinen equation

$$V = V_s \frac{A + C^{(D-T_r)^B}\left(P_r - P_{s,r}\right)^E}{A + C\left(P_r - P_{s,r}\right)^E}$$

$$A = a_0 + a_1 T_r + a_2 T_r^{\ 3} + a_3 T_r^{\ 6} + a_4 / T_r$$

$$B = b_0 + \frac{b_1}{b_2 + \omega_{SRK}}$$

$$C = c_1(1-T_r)^{c_2} + \left[1-(1-T_r)^{c_2}\right]\exp\left[c_3 + c_4\left(P_r - P_{s,r}\right)\right]$$

$$A = (482.85416) + (-1154.2979)T_r + 790.09727(T_r)^3 + (-212.14413)(T_r)^6$$
$$+ 93.4904/T_r$$

$$A = 137.6903$$

$$B = (0.0264002) + \frac{0.42711522}{(0.5 + 0.4916)}$$

$$B = 0.45713$$

$$C = 9.2892236(1 - 0.44267)^{2.510396} + \left[1 - (1 - 0.44267)^{2.510396}\right] \times \exp\begin{bmatrix} 0.5939722 + \\ 0.0010895(11.3801 - 0.00127) \end{bmatrix}$$

$$C = 2.7975$$

$$E = 0.80329503$$

$$D = 1.00001$$

$$V = 205.768195\left[\frac{137.6791 + (2.7975)^{(1-0.44267)^{0.45713}}(11.3801 - 0.00127)^{0.80329503}}{137.6971 + (2.7975) \times (11.3801 - 0.00127)^{0.80329503}}\right]$$

$$V = 198.7754 cm^3 / mol$$

The experimental molar volume ***= 198.74654 cm³/mol***

$$A\%D = \left|\frac{V_{Experimental} - V_{Calculated}}{V_{Experimental}}\right| \times 100$$

$$A\%D = \left|\frac{(198.74654) - (198.7754)}{(198.74654)}\right| \times 100$$

$$= 0.01451\%$$

3.5 Improvement of Tait equation for Polar component of pure liquids in this work

Soave- Redlich- Kowng, and Peng- Robinson equations were use to calculate the molar volume of compressed liquids for polar components but the results were not good, for example the (AA%D) for water calculated by SRK, and PR are 11.872, 25.674 and for ammonia 20.281, 12.359 respectively, as shown in table 3-9.

Table 3-9: Results of SRK &PR equations of state

No.	*Component*	*No. of Data Point*	*(AA%D)SRK equation*	*(AA%D)PR equation*
1	*Water*	24	11.872	20.281
2	*Ammonia*	20	25.674	12.359
	Over All % dev.	***44***	***18.145***	***16.6801***

Although AK method seemed to be better than Tait equation and other equations which were used for predication of molar volume of compressed liquids; we think there is still room for improving Tait equation for the polar components because Tait equation used for nonpolar and slightly polar component, while AK equation used for nonpolar component only.

For polar compounds the improvement was made by calculating the molar volume of compressed liquids and comparing it with the actual value, considering each parameters in Tait equation as constant except the pressure P and vapor pressure P_{vp} parameters. The new development was to replace the pressure with reduced pressure P_r and vapor pressure with reduced saturated pressure P_{rs}, and thus Tait equation can be written as:

$$V = V_s \left(1 - c \ln \frac{\beta + P}{\beta + P_s} \right) \qquad (2\text{-}57)$$

With modification of this work becomes:

$$V = V_s \left(1 - c \ln \frac{\beta + P_r}{\beta + P_{rs}} \right) \qquad (3\text{-}1)$$

The equation (3-1) gives good results with Average Absolute Percent Deviation (AA%D) of 2.1529 for 63 data points of three components. Table 3-4 summarizes the comparison of AA%D for molar volumes by using Tait equation, AK equation and the modification of Tait equation for all 63 data point.

Table 3-10: Comparison of the results of polar component

	Equations	***AA%D of 63 data point***
1	*Tait equation*	4.1163
2	*AK equation*	10.3157
3	*Modified of Tait in this work*	2.1529

Figures 3.9, 3.10 show the deviation from experimental data with the five equations for each polar compound (Water, Ammonia, and Acetone), Peng- Robinson show highest deviation from the experimental curve and followed by Aalto and Kiskinen equation, then Soave- Redlich- Kowng equation Tait equation, and modified Tait equation of this work which gives the least deviation than all the others.

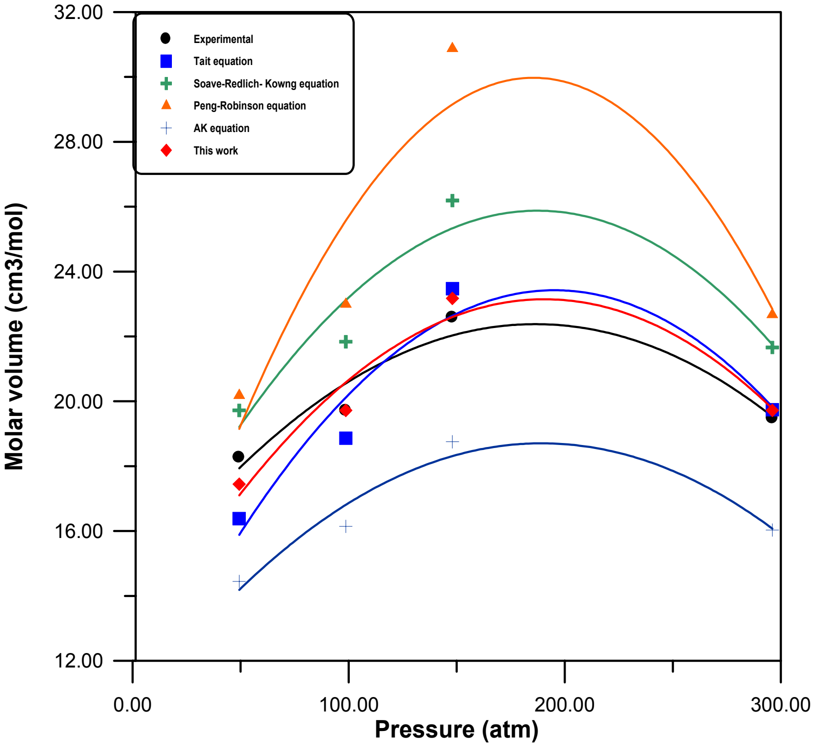

Figure 3.9 the deviation of molar volume of Water for different equations

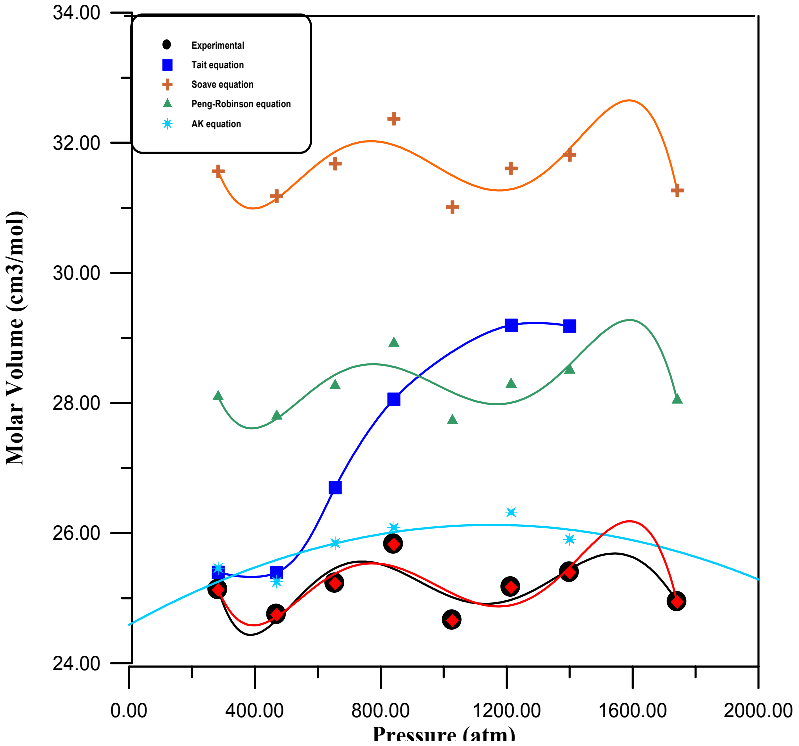

Figure 3.10 the deviation of molar volume of Ammonia for different equations

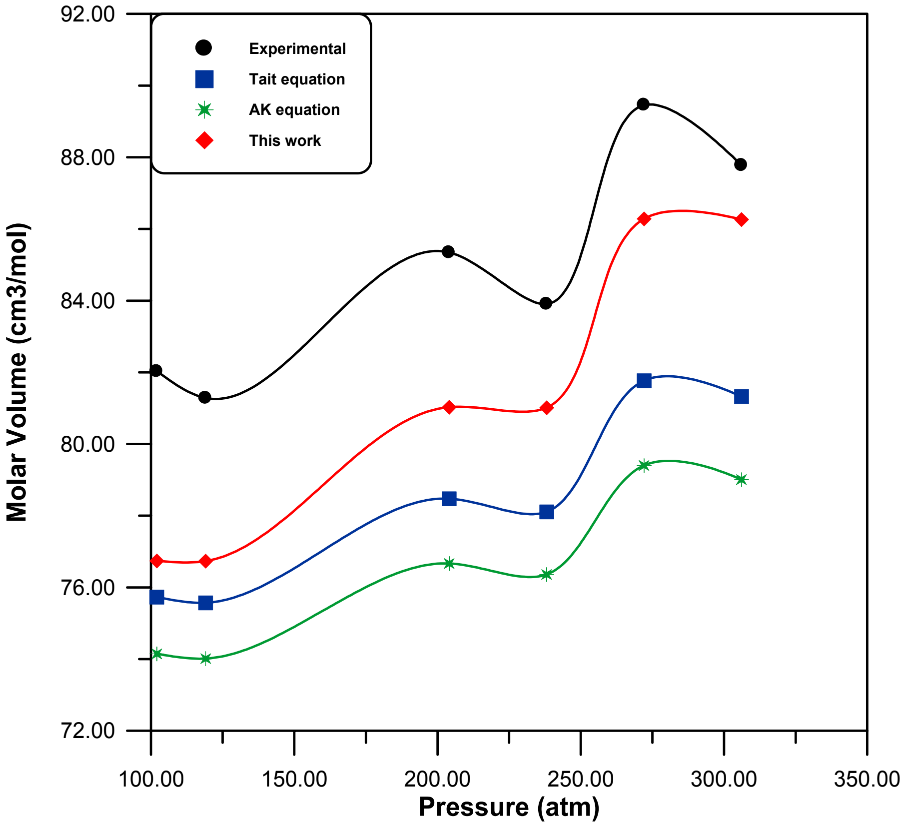

Figure 3.11 the deviation of molar volume of Acetone for different equations

3.6 Sample of calculation for Polar Compounds by Modified Tait equation

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Calculation of molar volume for Water at 433.15 K and 98.691 atm.

For Water

$T_c = 647.37$ K $P_c = 218.307$ atm

$\omega_{SRK} = 0.3852$ $Z_{RA} = 0.2338$

$$T_r = \frac{T}{T_c} = \frac{433.15}{647.37} = 0.6691$$

$$\begin{aligned} \tau &= 1 - T_r \\ &= 1 - 0.6691 = 0.33083 \end{aligned}$$

$$P_r = \frac{P}{P_c} = \frac{98.691}{218.307} = 0.45207$$

$$\ln\left(\frac{P_{vp}}{P_c}\right) = (1-\tau)^{-1}\left[A(\tau) + B(\tau)^{1.5} + C(\tau)^3 + D(\tau)^6\right]$$

The constants of Wagner equation

A = -7.76451 C = -2.77580

B = 1.45838 D = -1.23303

$$\ln\left(\frac{P_{vp}}{P_c}\right) = (1-0.33083)^{-1}\begin{bmatrix}(-7.76451)\times(0.33083)+(1.45838)\times(0.33083)^{1.5} + \\ (-2.77580)\times(0.33083)^3 + (-1.23303)\times(0.33083)^6\end{bmatrix}$$

$$P_{vp} = P_s = 6.10565$$

$$P_{rs} = \frac{P_s}{P_c} = \frac{6.10565}{218.307} = 0.02796$$

$$R = 82.057 cm^3 .atm / mol.K$$

$$V_s = \frac{RT_c}{P_c} Z_{RA}^{[1+(1-T_r)2/7]}$$

$$V_s = \frac{(82.057)\times(647.37)}{218.307}(0.2338)^{\left[1+(1-0.33083)^{2/7}\right]}$$

$$V_s = \frac{82.057(647.37)}{218.307}(0.2338)^{1.72903}$$

$$V_s = 19.71813 cm^3 / mol$$

Modified Tait equation:

$$V = V_s\left(1 - c\ln\left(\frac{\beta + P_r}{\beta + P_{rs}}\right)\right)$$

$$\beta/P_c = -1 + a(\tau)^{1/3} + b(\tau)^{2/3} + d(\tau) + e(\tau)^{4/3}$$

$$e = \exp\left(f + g\omega_{SRK} + h\omega_{SRK}{}^2\right)$$

$$c = j + k\omega_{SRK}$$

The constants a-k can be taken from chapter two

$$e = \exp\left[4.7954 + 0.250047(0.3852) + 1.14188(0.3852)^2\right]$$

$$e = 157.8569$$

$$\beta/P_c = -1 + (-9.070217)\times(1-0.3308)^{1/3} + (62.45326)\times(1-0.3308)^{2/3} + (-135.1102)\times(1-0.3308) + (157.8569)\times(1-0.3308)^{4/3}$$

$$\beta = 3061.032 atm$$

$$c = 0.0861488 + (0.0344483)\times(0.3852)$$

$$c = 9.9918\times10^{-2}$$

$$V = 19.71813\left(1 - 0.09991\ln\left(\frac{3061.032 + 0.45207}{3061.032 + 0.02796}\right)\right)$$

$$V = 19.71813\left(1.37733\times10^{-5}\right) = 19.71786 cm^3 / mol$$

*The experimental molar volume =**19.71453 cm^3/mol***

$$A\%D = \left|\frac{V_{Experimental} - V_{Calculated}}{V_{Experimental}}\right|\times100$$

$$A\%D = \left|\frac{(19.71453)-(19.71786)}{(19.71453)}\right|\times100 = 0.16872\%$$

3.7 Applications to Mixtures

3.7.1 Teja equation

Teja equation which was derived to calculate the compressibility factor for mixture. It is tested primarily on hydrocarbons for both vapor and liquid phases for calculating molar volume of mixture. Teja method needs to evaluate the compressibility factor for two reference pure fluids which combined binary systems, therefore the two compressibility factors Z^{R1}, and Z^{R2} can be calculated from any equation of state for pure compressed liquids like Tait equation or Aalto and Kiskinen equation but at the same reduced temperature T_{rm} and reduced pressure P_{rm} of the mixture. The Teja equation:

$$Z = Z^{(R_1)} + \frac{\omega - \omega^{(R_1)}}{\omega^{(R_2)} - \omega^{(R_1)}}\left(Z^{(R_2)} - Z^{(R_1)}\right) \qquad (2\text{-}102)$$

3.7.2 Investigation to the Mixtures

Two methods where used to calculate molar volumes of compressed liquid mixtures, there are Teja equation and Tait equation.

1. In this work we have two lines to calculate the molar volume of compressed liquid mixtures by using Teja with Tait equation or Teja equation with AK equation.

2. Tait equation which was developed to calculate the molar volume of mixtures by using mixing rules of HBT and with any of the two equations for evaluating saturated liquid mixtures are:
   a. Hankinson- Thomson method

$$\frac{V_S}{V^*} = V_R^{(0)}\left[1 - \omega_{SRK} V_R^{(\delta)}\right] \qquad (2\text{-}72)$$

b. Rackett equation

$$V_s = \frac{RT_c}{P_c} Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]} \tag{2-20}$$

The experimental data used to evaluate the accuracy of prediction consisted of 192 experimental literature data on 7 binary mixtures, as shown in table 3-11.

Table 3-11: The Mixtures Molar volume Data

	Mixture Systems	***No. of compositions***	***No. of data point***	***Data Reference***
1	*Propane- Benzene*	6	24	[47]
2	*Methane- n-Pentane*	3	22	[50]
3	*Acetone-1- Butene*	5	25	[47]
4	*Propane- Acetone*	2	30	[47]
5	*Propane-n- Decane*	3	24	[49]
6	*Propane- 1- Butene*	4	42	[48]
7	*Methane- Propane*	3	24	[51]
	Σ	26	192	

The following steps were tried:

1- Using Teja equation as it is with Tait equation to determine the molar volume of compressed liquid for pure component references 1and 2 at the same T_r & P_r as of the mixture and then calculating the molar volume of compressed liquid mixtures. The Average Absolute Percent Deviation of 168 data point (AA%D) is 6.07305.

2- Using Teja equation as it is with Aalto and Keskinen equation to determine the molar volume of compressed liquid for pure component references 1 and 2 at the same T_r & P_r as of mixture and then calculating the molar volume of the compressed liquid mixtures. The

Average Absolute Percent Deviation of 192 data point was (AA%D) 5.8160.

3- Using Tait equation as it is with HBT mixing rule to determine molar volume compressed of liquid mixtures. The (AA%D) of 192 is 5.5034.

4- Using Tait equation as it is with HBT mixing rule to determine the molar volume of compressed liquid mixtures, except that the equation which used to determine the mean saturated liquid molar volume was replaced with Teja equation with two references 1&2 at the same T_r & P_r as of the mixture, but this method failed to give good results.

5- Using the two equations of state which represented by Soave- Redlich-Kwong and Peng- Robinson equations with mixing rules but this step gave a large deviations from the experimental data.

3.8 Development Method for Mixture in this work:

As the five methods tried above did not lead to any successful results, a new approach consists of using Tait equation for predicting the molar volume of pure component to develop it for mixture by using mixing rules.

In this work using the HBT mixing rules as written in chapter two as they are except the equation of estimating saturated liquid densities for mixtures. Rackett equation was used with a new mixing rules different from the mixing rule which written in chapter two and this difference was made by replacing the parameters in Rackett equation which are the critical temperature, critical pressure, and compressibility factor with pseudo critical temperature, critical pressure, and pseudo critical compressibility factor using HBT mixing rules, so equation (2-20) represent the Racket equation before the modifications, while equation (3-2) represented the modified of this work:

$$V_s = \frac{RT_c}{P_c} Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]} \tag{2-20}$$

$$V_{sm} = \frac{RT_{cm}}{P_{cm}} Z_{cm}^{\left[1+(1-T_{rm})^{2/7}\right]} \tag{3-2}$$

$$Z_{cm} = 0.291 - 0.08\omega_{SRKm} \tag{3-2}$$

$$\omega_{SRKm} = \sum x_i \omega_{SRKi} \tag{2-85}$$

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j V^*_{ij} \; T_{cij}}{V_m^*} \tag{2-82}$$

$$V_{ij}^* T_{cij} = \left(V_i^* T_{ci} V_j^* T_{cj}\right)^{1/2} \tag{2-83}$$

$$V_m^* = \frac{1}{4}\left[\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*2/3}\right)\left(\sum_i x_i V_i^{*1/3}\right)\right] \tag{2-84}$$

$$P_{cm} = \frac{Z_{cm} RT_{cm}}{V_m^*} \tag{2-86}$$

where $T_{rm} = T/T_{cm}$.

The modification of Rackett equation mixing rule which derived for determining molar volume of compressed liquid for mixtures gives Average Absolute Percent Deviation (AA%D) of 4.9386 which is lower than the other methods.

Table 3-12 shows a comparison of over all Average Absolute Percent Deviation for molar volumes of 7 mixtures of compressed liquids by various methods.

Table 3-12: Comparison of the results of mixtures

Equation used	***AA%D of 192 data point***
Teja- Tait	6.07305
Teja- AK	5.8160
Tait mixing rule	5.5034
Tait modified mixing rule	4.9386

3.9 Sample of Calculation for Mixture of Liquid

Calculation of the molar volume for mixture of 90 mol% Propane with 10 mol% Benzene at 310.927 K and 680.272 atm.

Data required:

Compound	*Propane*	*Benzene*
x	0.9	0.1
T_c *(K)*	369.8	562.2
P_c *(atm)*	41.944	48.26
ω_{SRK}	0.1532	0.2137
V^* *(cm³/mol)*	200.1	256.4

Applying Hankinson- Brobst- Thomson (HBT) mixing rule:

$$T_{cm} = \frac{\sum_i \sum_j x_i x_j V^*_{ij}\ T_{cij}}{V_m^*}$$

$$V_{ij}^* T_{cij} = \left(V_i^* T_{ci} V_j^* T_{cj}\right)^{1/2}$$

$$= \left[(0.9)\times(200.1)(0.1)\times(256.4)\right]^{1/2}$$

$$= 103278.8584$$

$$\sum_i^2 \sum_j^2 x_i x_j V_{ij}^* T_{Cij} = x_1^2 V_1^* T_{C1} + x_2^2 V_2^* T_{C2} + 2x_1 x_2 \left(V_1^* T_{C1} V_2^* T_{C2}\right)^{1/2}$$

$$= (0.9)^2 \times (200.1)\times(369.8)$$

$$+ (0.1)^2 \times (256.4)\times(562.2)$$

$$+ 2(0.9)\times(0.1)\times(103278.8584)$$

$$= 79969.23$$

$$V_m^* = \frac{1}{4}\left[\sum_i x_i V_i^* + 3\left(\sum_i x_i V_i^{*2/3}\right)\left(\sum_i x_i V_i^{*1/3}\right)\right]$$

$$\sum x_i V_i^* = 0.9\times(200.1) + 0.1\times(256.4)$$

$$= 205.73 cm^3$$

$$\sum_i x_i V_i^{*2/3} = 0.9 \times (200.1)^{2/3} + 0.1 \times (256.4)^{2/3}$$
$$= 34.8257 cm^3$$

$$\sum_i x_i V_i^{*1/3} = 0.9 \times (200.1)^{1/3} + 0.1 \times (256.4)^{1/3}$$
$$= 5.88893 cm^3$$

$$V_m^* = 1/4[205.73 + 3 \times 34.8257 \times 5.88893]$$
$$= 205.5209 cm^3$$

$$T_{Cm} = \frac{79969.23}{205.5209} = 389.105K$$

$$\omega_{SRKm} = \sum x_i \omega_{SRKi} = x_1 \omega_{SRK1} + x_2 \omega_{SRK2}$$
$$= 0.9 \times (0.1532) + 0.1 \times (0.2317)$$
$$= 0.15925$$

$$Z_{cm} = 0.291 - 0.08\omega_{SRKm}$$
$$= 0.291 - 0.080 \times (0.15925)$$
$$= 0.27826$$

$$P_{Cm} = \frac{(0.27826) \times (82.057) \times (389.105)}{205.5209} = 43.2292 atm$$

$$T_{rm} = \frac{T}{T_{cm}} = \frac{310.927}{389.105} = 0.79908$$

By generalizing Riedel vapor pressure equation:

$$\log P_{Rm} = P_{Rm}^{(0)} + \omega_{SRK} P_{Rm}^{(1)}$$

$$P_{Rm}^{(0)} = 5.8031817 \log T_{rm} + 0.07608141\alpha$$

$$P_{Rm}^{(1)} = 4.86601\beta$$

$$\alpha = 35.0 - 36.0 / T_{rm} - 96.736 \log T_{rm} + T_{rm}^{6}$$

$$= 35.0 - 36.0/0.79908 - 96.736\log(0.79908) + (0.79908)^6$$
$$= -0.368427$$

$$\beta = \log T_{rm} + 0.03721754\alpha$$
$$= \log(0.79908) + 0.03721754(-0.368427)$$
$$= -0.1111205$$

$$P_{Rm}^{(1)} = 4.86601 \times (-0.1111205) = -0.54071$$

$$P_{Rm}^{(0)} = 5.8031817\log(0.79908) + 0.07608141 \times (-0.368427)$$

$$= -0.593309$$

$$\log P_{Rm} = -0.593309 + 0.15925 \times (-0.54071)$$
$$= -0.679418$$

$$P_{Rm} = 0.209209$$

$$P_{Rm} = \frac{P_{sm}}{P_{cm}} = 0.209209 = \frac{P_{sm}}{43.2292}$$

$$P_{sm} = 43.2292 \times 0.209209$$

$$= 9.043965 atm$$

$$e = \exp\left(f + g\omega_{SRK} + h\omega_{SRK}^{\ 2}\right)$$
$$e = \exp\left(4.79594 + 0.250047 \times (0.15925) + 1.14188 \times (0.15925)^2\right)$$

$$= 129.6344$$

$$\beta/P_c = -1 + a(\tau)^{1/3} + b(\tau)^{2/3} + d(\tau) + e(\tau)$$

$$\tau = 1 - T_r$$

$$\beta/P_c = -1 + (-9.070217)\times(1 - 0.79908)^{1/3} + (62.45326)\times(1 - 0.79908)^{2/3} +$$
$$(-135.1102)\times(1 - 0.79908) + (157.8569)\times(1 - 0.79908)^{4/3}$$
$$\beta = 139.2216 atm$$

$$c = 0.0861488 + (0.0344483)\times(0.79908)$$

$$= 9.1634 \times 10^{-2}$$

$$V = V_{sm}\left(1 - c\ln\left(\frac{\beta + P}{\beta + P_{sm}}\right)\right)$$

$$V_{sm} = \frac{RT_{cm}}{P_{cm}} Z_{cm}^{\left[1+(1-T_{rm})^{2/7}\right]}$$

$$= \frac{82.057 \times (389.105)}{43.2292}(0.27826)^{[1+(1-0.79908)]}$$

$$= 91.54432 cm^3 / mol$$

$$v = 91.54432 \times \left(1 - 9.16346 \times 10^{-2} \ln\left(\frac{139.2216 + 680.272}{139.2216 + 9.04396}\right)\right)$$

$$= 77.20242 cm^3 / mol$$

*The experimental molar volume =77****.47534 cm^3/mol***

$$A\%D = \left|\frac{V_{Experimental} - V_{Calculated}}{V_{Experimental}}\right| \times 100$$

$$A\%D = \left|\frac{(19.71453) - (19.71786)}{(19.71453)}\right| \times 100 = 0.16872\%$$

3.10 DISCUSSION

- The usual method available for predicting the molar volume of compressed liquids for pure components and mixtures is by using the equation of state:

1- Lee- Kesler equation was used to calculate the molar volume of compressed liquid. The results that are shown in chapter three indicate that this equation worked only in the gas phase and not for liquids, and especially for compressed liquid the reason for this is that the values of the compressibility factors for compounds in liquid phase are usually much smaller than those in the vapor phase, and any small error in the compressibility factor causes a large error in molar volume. The AA%D is 10.0185 for 42 data point of 1-butene, and n-nonane.

2- Soave- Redlich- kowng equation and Peng- Robinson equation were used also to calculate the molar volume of compressed liquids. The results shown that the error was high but less than that of Lee- Kesler equation. This is also can be explained as it is due to the sensitivity of small values of compressibility values Z. For 91 data point of three components (n-heptane, isobutane, and propylene) AA%D are 5.643 and 3.559 for SRK and PR equations respectively.

3- By applying Tait equation to calculate the molar volume of compressed liquid for pure compounds. It seems as shown in table 3-7 that this equation works very nicely with very much less deviations from experimental data than the equations mentioned above. Mainly for pure components at T_r up to 0.95 and dose not work at T_r higher than 0.95. This is because of the parameter which exists in Tait equation and that is β, where β is a function of temperature and when T_r = 0.95 and higher, the sign of β is negative. This negative sign will affect the value of this term $\left(\ln\frac{\beta+P}{\beta+P_s}\right)$ where the value of P_s is very small in comparison with the value of the whole term which becomes negative and when applying (ln) to this term it becomes zero, and this dose not give any result in this case. The effect of reduced pressure P_r on the deviation of Tait equation the deviation from experimental data was not so large as compared with the effect of reduced temperature above 0.95 as shown in tables 3-6, 3-7. Figures 3.12, 3.13 shown the effect of T_r and P_r on n-pentane and 1-butene.

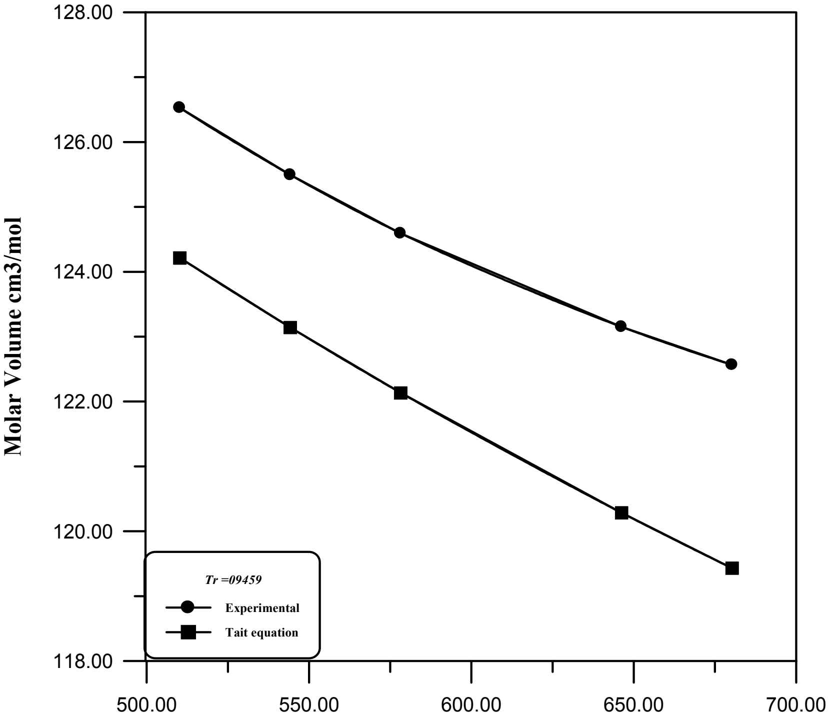

Figure 3.12 n- Pentane at reduced temperature 0.95

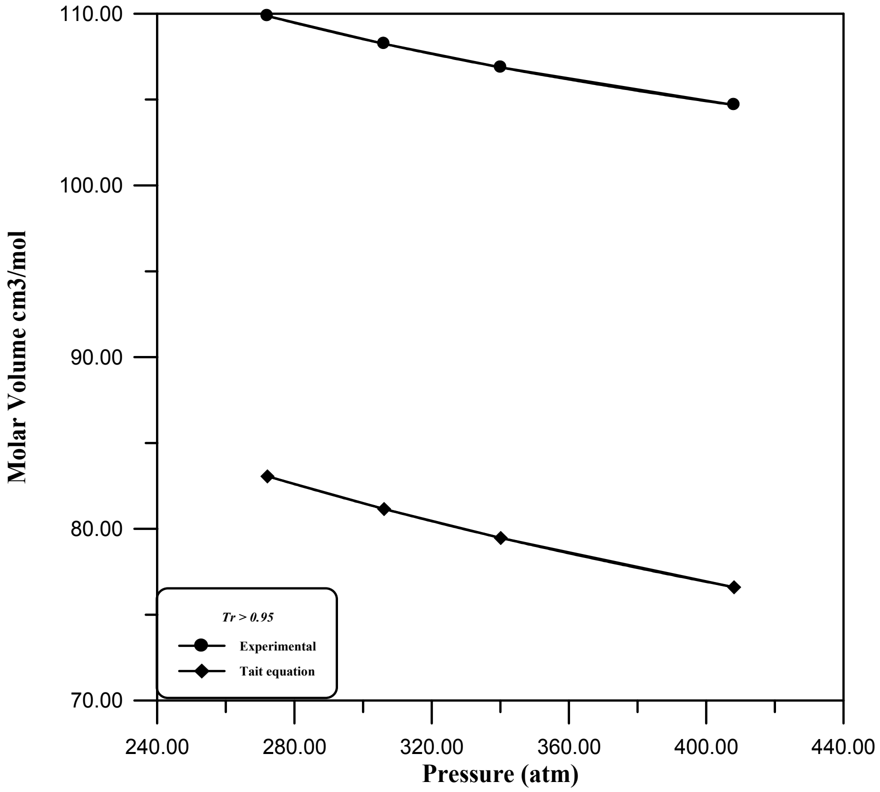

Figure 3.13 The effect of Pr on Tait equation at Tr less than 0.95 for 1-Butene

4- For pure components AK equation proves to be the best equation for calculating the compressed volume of pure liquid than all other equations used in this work. It shows the least deviations from experimental data. Thus very satisfactory results obtained at T_r up to one and $P_r > 30$. Figures 3.14 and 3.15 show the effect of T_r and P_r on molar volumes of n-pentane, and 1-butene using AK equation.

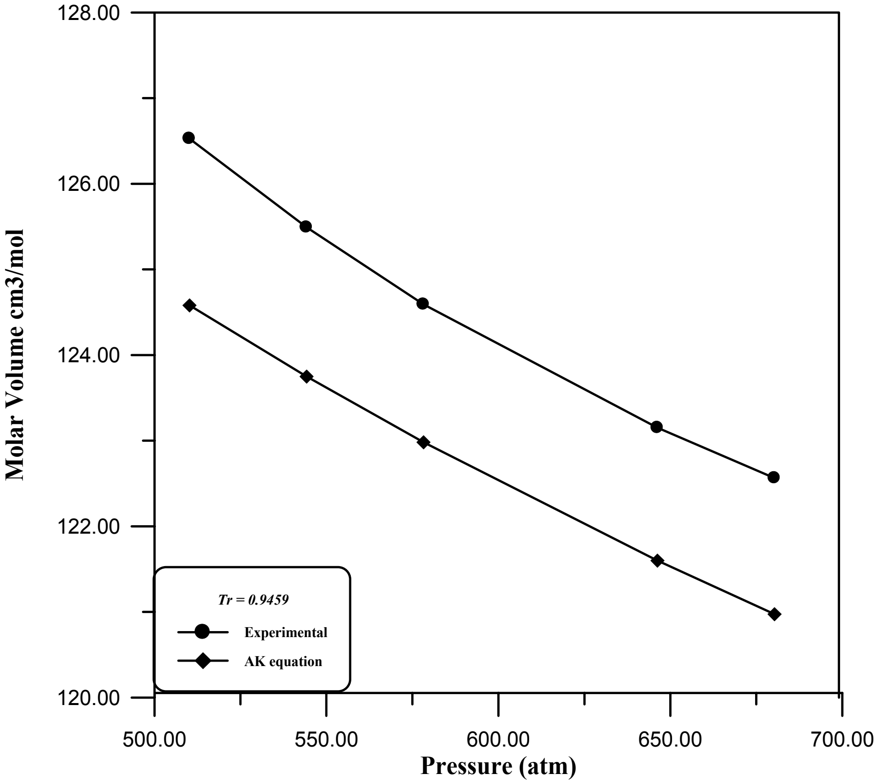

Figure 3.14 n- Pentane at reduced temperature 0.95 on AK equation

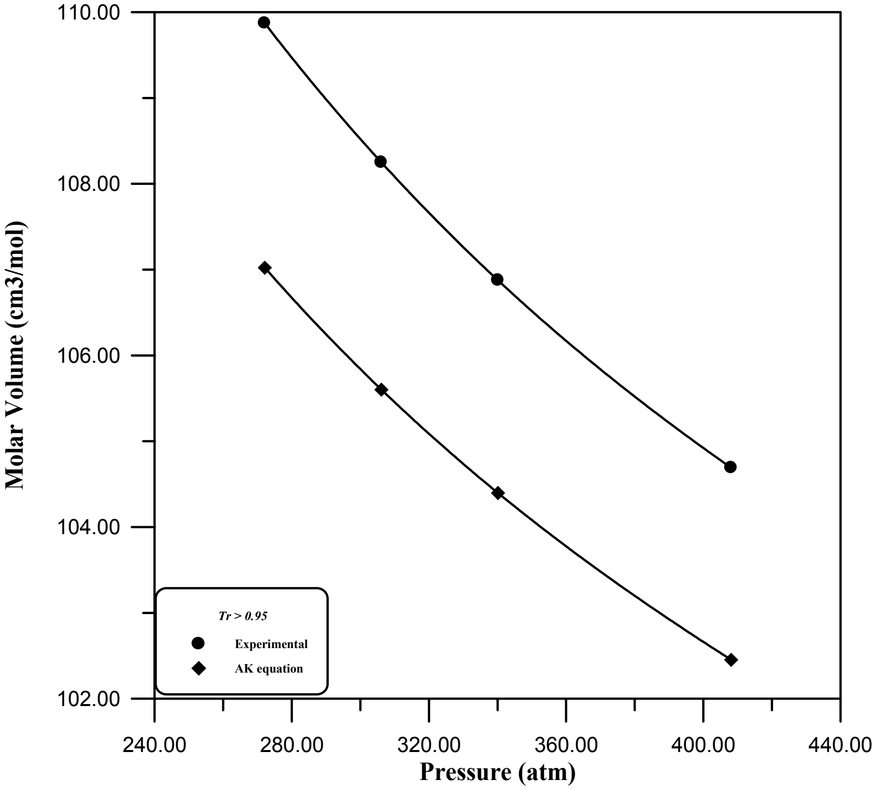

Figure 3.15 The effect of Pr on AK equation at Tr less than 0.95 for 1-Butene

Table 3-13 shows the summarized results obtained for the eleven pure compressed liquid components calculated both by Tait and AK equations. As seen from the table, the over all percent deviation of 241 data points of 11 pure compressed liquids using Aalto and Keskinen equation, is 0.62876 % for molar volume, while when using Tait equation the AA%D is 0.73378.

Table 3-13: Summary of Results of Pure Components

No.	***Component***	***No. of Point***	***Tait Equation***	***AK Equation***
1	*n- Pentane*	25	0.9195	0.5129
2	*n-Nonane*	24	0.7076	1.2366
3	*Propylene*	19	0.2323	0.2243
4	*n-Octane*	23	1.6118	0.8511
5	*Isobutane*	27	0.3778	0.2731
6	*n-Heptane*	26	0.8365	0.4523
7	*Ethylene*	20	0.3358	1.3126
8	*1-Butene*	18	0.944	0.8410
9	*n-Butane*	21	0.7240	0.4879
10	*n-Decane*	19	1.2894	0.1633
11	*Propane*	19	0.8803	0.5807
	Over All %Av.Dev.	***241***	***0.73378***	***0.62876***

- For polar component of compressed liquids Tait equation shows better results (more accuracy) than AK, SRK, and PR equations.

Table 3-14 shows the results obtained for the three polar components for compressed liquids calculated by SRK, PR, AK, Tait equations and also by the proposed modified Tait equation in this work. The table shows the over all deviation of 63 data points for 3 polar components for compressed liquids for the five equations. The AA%D in our proposed modified Tait equation is 2.1529 % for molar volume of compressed liquid. Comparing these results with those in table 3-4 shows that our proposed method improves the accuracy for molar volume of compressed liquids by 15.9921% as compared with Soave- Redlich- Kowng equation for 44 data points and 14.527% as compared with Peng- Robinson for the same number of data points, it is also improves the accuracy for molar volume of compressed liquid by 8.1682% and 1.9634% as compared with AK and Tait equations respectively.

Table 3-14: Results of Pure Polar Compounds

Component	*No. of Point*	*SRK AA%D*	*PR AA%D*	*AK AA%D*	*Tait AA%D*	*This work AA%D*
Ammonia	20	11.872	20.281	3.067	1.1514	1.155
Water	24	25.674	12.359	18.0778	4.0900	2.125
Acetone	19	------	------	8.1414	6.0587	3.2387
Over All %Av.Dev.	*63*	*18.145*	*16.6801*	*10.3157*	*4.1163*	*2.1529*

- There are four methods used to calculate the molar volumes of compressed liquid mixtures.

  Method 1: Using Tait equation with its own mixing rules except in this work Rackett equation with HBT mixing rules are used to calculate the saturated density in Tait equation.

  Method 2: Using Tait equation with its own mixing rules except using Hankinson- Thomson equation (HT) with HBT mixing rules to calculate the saturated density in Tait equation.

  Method 3: Using Teja equation to calculate the molar volume of compressed liquid for mixtures with Tait equation to calculate the compressibility factor of the reference fluids R_1, R_2.

  Method 4: Using Teja equation to calculate the molar volume of compressed liquid for mixtures with AK equation to calculate the compressibility factor of the reference fluids R_1, R_2.

Comparing these results with those in table 3-11 shows that our proposed method improves the accuracy for molar volume of compressed liquid mixtures by 1.1344 % as compared with Teja- Tait method for the same number of data points. It is also improve the accuracy of molar volume of compressed liquid by 0.8774 % as compared with Teja- AK method. It further improves the accuracy for molar volume $V_{mix.}$ by 0.6817 % as compared with Tait equation mixing rules by using V_s for HT method for the same data points. Table 3-15 shows comparison of the percent deviation of molar volumes of 7 binary mixtures of compressed liquids by Teja- Tait, Teja- AK, Tait mixing rule methods and our proposed method. It is seen from table that when using Teja-Tait method for methane- propane system does not gives any results and that was because of the value of T_r of propane which equal to 0.99 so that Tait equation proved that in this case did not work. The table indicates that the accuracy was increased considerably by our proposed method especially for molar volume compressed liquid mixtures. The over all percent accuracy has been increased by 4.9386 for molar volume of mixtures of 192 data points of mixtures of compressed liquids by our proposed method compared to of these three other methods.

Table 3-15: Summary of Results of Mixtures

No	***Mixture Systems***	***No. of Data***	***Tait Mix. Rule.***		***AA%D Teja (Tiat)***	***AA%D Teja (AK)***
			AA%D VsHT	***AA%D (This work) Vs Rackett***		
1	*Propane-Benzene*	24	1.1982	1.0945	0.695	2.4116
2	*Methane-n-Pentane*	22	2.024	1.4947	0.6453	0.8026
3	*Acetone-1-Butene*	25	2.5304	6.8969	5.4692	6.9814
4	*Propane-Acetone*	30	9.448	9.843	8.0932	7.7302
5	*Propane-n-Decane*	24	2.6055	1.9636	9.600	8.6134
6	*Propane-1-Butene*	42	8.2503	8.001	9.0350	8.3066
7	*Methane-Propane*	24	9.485	11.079	-----------	3.296
	Over All AA%D	***192***	***5.5034***	***4.9386***	***6.07305***	***5.8160***

To show the comparison between the four methods for evaluating the molar volumes of compressed liquid mixtures. Figure 3.16 shows the `deviation from the experimental data and it seems that the curve that represents the modification of the Rackett equation when applied for mixtures is the nearest curve to the experimental.

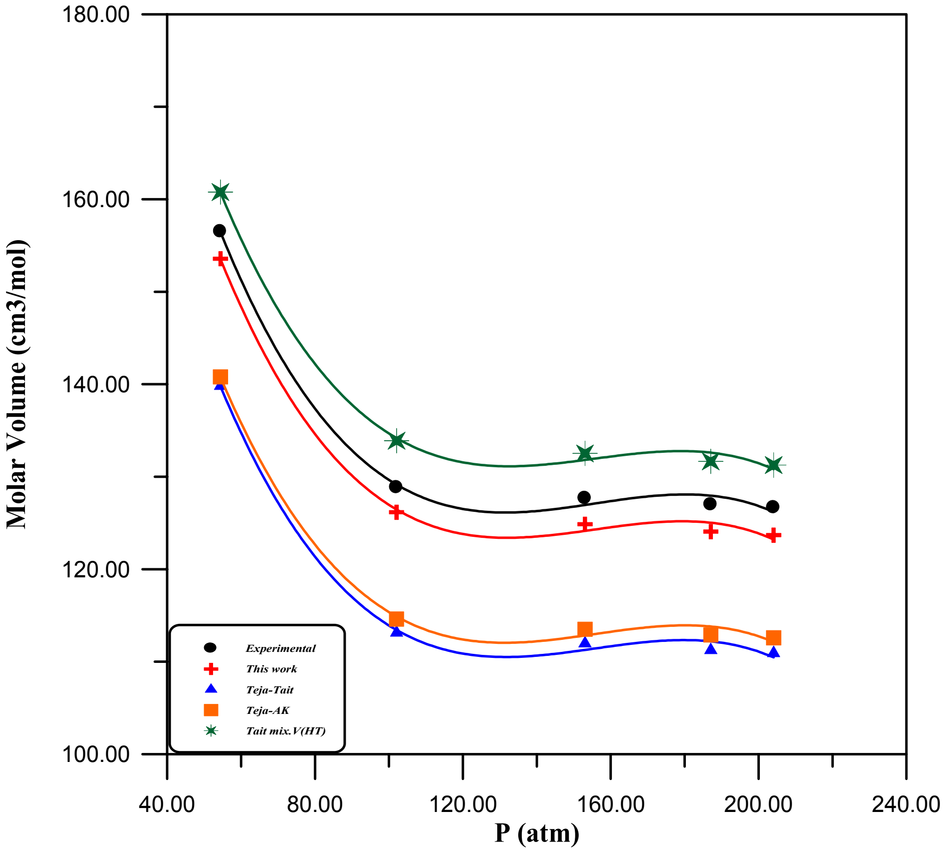

Figure 3.16 Comparison between four methods for Propane-n-Decane System

CHAPTER FOUR

4.1 CONCLUSION

1. Using equations of state to calculate the molar volume of compressed liquids it is found that equations (Lee- Kesler, SRK, PR) are not suitable to use for calculation of compressed liquid volume for pure components or mixtures since they produce large deviation from experimental data, as shown in the results of using these equation shown in table 4-1.

Table 4-1: The Results of using Equations of State

Equation	*No. of point*	*AA%D*
Lee- Kesler	42	10.0185
SRK	91	5.643
PR	91	3.559

2. Tait and AK equations can be used for calculating the molar volume of compressed liquid which gave relatively low deviations.

3. Tait equation is good for calculating molar volume of compressed liquids at T_r up to 0.95 while AK equation is satisfactory at T_r up to one. Aalto and Kiskinen equation reduces the maximum deviation of 26.837% to 2.137% as the effect of T_r and reduces the maximum deviation from 1.659% to 1.398% as the effect of P_r, so as shown in table 4-2 for 1-butene with different reduced pressures and temperatures.

Table 4-2: Comparison between Tait and AK for $T_r < 0.95$ and $P_r < 10$ for 1-Butene.

P_r	Tait	AK	T_r	Tait	AK
	AA%D	AA%D		AA%D	AA%D
10.2878	1.508	1.426	0.9793	24.403	2.593
12.0024	1.643	1.515		24.033	2.445
13.7171	1.636	1.448		25.645	2.318
15.431	1.659	1.398		26.837	2.137

3. Anew correlation has been developed to predict molar volume of pure polar liquids. This correlation is a modification of Tait equation for compressed liquids. The modification was made by replacing the pressure with reduced pressure and the term of vapor pressure with reduced saturated pressure as follows:

$$V = V_s\left(1 - c\ln\frac{\beta + P_r}{\beta + P_{rs}}\right) \tag{3-1}$$

The new correlation seems to be superior to Tait, SRK, PR, AK equations. The over all AA%D for 63 points of three polar pure compounds obtained from this correlation was 2.1529 % in comparison with those obtained from SRK, PR, Tait, and AK where they are 18.1456 %, 16.6802 %, 4.1163%, and 10.3157% respectively.

4. Applying Rackett equation for saturated liquids of pure components to the mixtures by using pseudo critical temperature, pressure, and compressibility factor for mixture, so that Rackett equation becomes:

$$V_s = \frac{RT_c}{P_c} Z_{RA}^{\left[1+(1-T_r)^{2/7}\right]} \tag{2-20}$$

$$V_s = \frac{T_{cm} R}{P_{cm}} Z_{cm}^{\left[1+(1-T_{rm})^{2/7}\right]} \tag{3-2}$$

This new method was compared with HT equation for saturated liquid volume mixtures, and the over all AA%D of 192 points of 7 binary mixtures is 4.9386 % for Tait equation mixing rules by using the modified Rackett equation of this work.

4.2 Recommendation

For those who would carry future studies on related subject, the following recommendations may be considered:

1. Applying the polar correlation for other polar compounds.
2. . Applying those methods to study other thermodynamic properties of compressed liquids such as enthalpy and entropy.
3. Studying the possibility of applying this method to ternary compressed liquid mixtures.

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Appendix A: Some Properties of Pure Components

Table A-1-1: Properties of Pure Component

No.	***Component***	T_c ***(K)***	P_c ***(bar)***	ω	ω_{SRK}	V^* ***(cm³/mol)***	Z_{RA}
1	*n- Pentane*	469.7	33.7	0.251	0.2522	311.3	0.2684
2	*n-Nonane*	594.6	22.9	0.445	0.4478	552.9	0.2543
3	*Propylene*	364.9	46.0	0.144	0.1455	182.9	0.2779
4	*n-Octane*	568.8	24.9	0.398	0.3998	490.4	0.2571
5	*Isobutane*	408.2	36.5	0.183	0.1825	256.8	0.2754
6	*n-Heptane*	540.3	27.4	0.349	0.3507	430.4	0.2604
7	*Ethylene*	282.4	50.4	0.089	0.0882	131.0	0.2815
8	*1-Butene*	419.6	40.2	0.191	0.1921	237.7	0.2736
9	*n-Butane*	425.2	38.0	0.199	0.2008	254.4	0.2730
10	*n-Decane*	617.7	21.2	0.489	0.4916	619.2	0.2507
11	*Propane*	369.8	42.5	0.153	0.1532	200.1	0.2766
12	*Ammonia*	405.5	113.5	0.250	0.2620	70.1	0.2465
13	*Water*	647.3	221.2	0.344	0.3852	43.6	0.2338
14	*Acetone*	508.1	47.0	0.304	0.3149	208.0	0.2477
15	*Benzene*	562.2	48.9	0.212	0.2137	256.4	0.2698
16	*Methane*	190.4	46.0	0.011	0.0074	99.4	0.2892

Table A-2-1: Constants of Wagner Vapor Pressure Equation

No.	***Component***	***a***	***b***	***c***	***d***
1	*n- Pentane*	-7.28936	1.53679	-3.08367	-1.02456
2	*n-Nonane*	-8.24480	1.57885	-4.38155	-4.04412
3	*Propylene*	-6.64231	1.21857	-1.81005	-2.48212
4	*n-Octane*	-7.91211	1.38007	-3.80435	-4.50132
5	*Isobutane*	-6.95579	1.50090	-2.52717	-1.49776
6	*n-Heptane*	-7.67468	1.37068	-3.53620	-3.20243
7	*Ethylene*	-6.32055	1.16819	-1.55935	-1.83552
8	*1-Butene*	-6.88204	1.27051	-2.26284	-2.61632
9	*n-Butane*	-6.88709	1.15157	-1.99873	-3.13003
10	*n-Decane*	-8.56523	1.97756	-5.81971	-0.29982
11	*Propane*	-6.72219	1.33236	-2.13868	-1.38551
12	*Ammonia*	45.327	4104.67	-5.146	615.
13	*Water*	-7.76451	1.45838	-2.77580	-1.23303
14	*Acetone*	-7.45514	1.20200	-2.43926	-3.35590
15	*Benzene*	-6.98273	1.33213	-2.62863	-3.33399
16	*Methane*	-6.00435	1.18850	-0.83408	-1.22833

Appendix B: Results for Pure Liquids

Table B-1-1: n-Pentene

	P(atm)	*T(K)*	*V exp. (cm^3/mol)*	*Vcalc.(AK) (cm^3/mol)*	*% Deviation*
1	54.421	310.927	117.33367	117.0006	0.2838
2	68.027	310.927	117.01835	116.6667	0.3004
3	85.034	310.927	116.61245	116.2747	0.2896
4	102.040	310.927	116.20766	115.9051	0.2603
5	119.047	310.927	115.847103	115.5541	0.2529
6	153.061	344.261	120.93365	120.4643	0.3881
7	204.081	344.261	119.49533	119.1487	0.2901
8	238.095	344.261	118.63992	118.3528	0.2419
9	272.108	344.261	117.78412	117.6098	0.1479
10	306.122	344.261	117.01841	116.9121	0.0908
11	272.108	377.594	123.27904	122.4572	0.6666
12	340.136	377.594	121.43250	120.562	0.7168
13	374.149	377.594	120.66678	119.7116	0.7915
14	408.163	377.594	119.90105	118.9151	0.8223
15	442.176	377.594	119.22546	118.1662	0.8884
16	408.163	410.927	124.72048	123.3370	1.108
17	442.176	410.927	123.77465	122.3896	1.119
18	476.190	410.927	122.29456	121.5089	0.6423
19	544.217	410.927	121.43250	119.9188	1.246
20	612.244	410.927	119.99117	118.516	1.229
21	510.204	444.261	126.52212	126.048	0.3747
22	544.217	444.261	125.48621	125.1959	0.2313
23	578.231	444.261	124.58542	124.4074	0.1429
24	646.258	444.261	123.14409	122.9899	0.1251
25	680.272	444.261	122.55850	122.3486	0.1712
					%average deviation = 0.5129 %

Table B-1-2: n-Pentene (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***% Deviation***
1	54.421	310.927	117.33367	116.85523	0.4077
2	68.027	310.927	117.01835	116.46513	0.4727
3	85.034	310.927	116.61245	115.99580	0.5288
4	102.040	310.927	116.20766	115.54526	0.6344
5	119.047	310.927	115.847103	115.11208	0.5700
6	153.061	344.261	120.93365	120.18628	0.6179
7	204.081	344.261	119.49533	118.67654	0.6852
8	238.095	344.261	118.63992	117.76642	0.7362
9	272.108	344.261	117.78412	116.92066	0.7330
10	306.122	344.261	117.01841	116.13070	0.7585
11	272.108	377.594	123.27904	122.63897	0.5191
12	340.136	377.594	121.43250	120.64974	0.6446
13	374.149	377.594	120.66678	119.75934	0.7520
14	408.163	377.594	119.90105	118.92631	0.8129
15	442.176	377.594	119.22546	188.14385	0.9072
16	408.163	410.927	124.72048	124.13048	0.4730
17	442.176	410.927	123.77465	123.13321	0.5182
18	476.190	410.927	122.29456	122.20111	0.0763
19	544.217	410.927	121.43250	120.50185	0.7663
20	612.244	410.927	119.99117	118.98362	0.8396
21	510.204	444.261	126.52212	124.21320	1.8249
22	544.217	444.261	125.48621	123.14051	1.8692
23	578.231	444.261	124.58542	122.13275	1.968
24	646.258	444.261	123.14409	120.28366	2.322
25	680.272	444.261	122.55850	119.43079	2.552
%average deviation= 0.9195 %					

Table B-2-1: n-Nonane

No.	*P(atm)*	*T(K)*	*V exp. (cm^3/ mol)*	*V calc.(AK) (cm^3/ mol)*	*%Deviation*
1	54.421	310.927	180.72627	179.7472	0.5417
2	68.027	310.927	180.41414	179.4146	0.5540
3	85.034	238.705	183.22335	166.6082	9.068
4	102.040	238.705	182.84879	166.3751	9.009
5	119.047	344.261	185.65801	184.697	0.5176
6	136.054	344.261	185.15859	184.2659	0.4821
7	136.054	360.927	180.52965	187.6145	3.924
8	153.061	360.927	187.90538	188.9739	0.5686
9	170.068	377.594	191.02673	190.045	0.5139
10	187.074	377.594	190.40246	189.5502	0.4476
11	204.081	394.261	192.89954	192.3898	0.2642
12	238.095	394.261	191.65100	191.3536	0.1551
13	272.108	410.927	194.14808	193.493	0.3374
14	272.108	427.594	197.26944	196.62	0.3291
15	306.122	410.927	192.89954	192.4563	0.2297
16	340.136	427.594	194.77235	194.3463	0.2187
17	408.163	444.261	195.39663	194.9442	0.2315
18	476.19	460.927	196.02090	195.3475	0.3435
19	544.217	460.927	193.52381	193.381	0.0738
20	544.217	477.594	196.64517	195.6908	0.4853
21	612.244	477.594	194.77235	193.7928	0.5029
22	612.244	494.261	197.26944	196.1669	0.5286
23	680.272	494.261	194.77235	194.3617	0.2108
24	680.272	510.927	197.26944	196.9903	0.1414
% average deviation = 1.2366%					

Table B-2-2: n-Nonane (Tait Equation)

No.	***P(atm)***	***T(K)***	***V exp. (cm^3/ mol)***	***V calc.(Tit) (cm^3/ mol)***	***%Devation***
1	54.421	310.927	180.72627	179.76983	0.5292
2	68.027	310.927	180.41414	179.42048	0.5507
3	85.034	238.705	183.22335	182.22614	0.5442
4	102.040	238.705	182.84879	181.76556	0.5924
5	119.047	344.261	185.65801	184.64032	0.5481
6	136.054	344.261	185.15859	184.15595	0.5415
7	136.054	360.927	180.52965	187.62046	0.4822
8	153.061	360.927	187.90538	187.09789	0.4297
9	170.068	377.594	191.02673	190.14395	0.4621
10	187.074	377.594	190.40246	189.59497	0.4241
11	204.081	394.261	192.89954	192.70246	0.1021
12	238.095	394.261	191.65100	191.55050	0.0443
13	272.108	410.927	194.14808	194.09845	0.0255
14	272.108	427.594	197.26944	197.89508	0.3171
15	306.122	410.927	192.89954	192.97177	0.0374
16	340.136	427.594	194.77235	195.47116	0.3587
17	408.163	444.261	195.39663	196.81010	0.7233
18	476.19	460.927	196.02090	198.09797	1.0596
19	544.217	460.927	193.52381	195.95316	1.255
20	544.217	477.594	196.64517	199.30537	1.3527
21	612.244	477.594	194.77235	197.17380	1.232
22	612.244	494.261	197.26944	200.38080	1.5772
23	680.272	494.261	194.77235	198.25797	1.789
24	680.272	510.927	197.26944	201.22793	2.006
% average deviation=0.7076%					

Table B-3-1: Propylene

No.	*P(atm)*	*T(K)*	*V exp. (cm^3/mol)*	*V calc.(AK) (cm^3/mol)*	*%Deviation*
1	68.027	310.927	83.69593	83.41688	0.3334
2	102.040	310.927	82.01664	81.90645	0.1343
3	47.408	299.816	82.50981	81.47308	1.256
4	108.843	294.261	78.28350	78.15034	0.1700
5	85.034	327.594	87.66004	87.53285	0.1450
6	60.952	293.15	79.39470	79.3905	0.0528
7	61.925	333.15	91.47433	91.54367	0.0758
8	62.891	323.15	87.66629	87.50151	0.1879
9	68.027	327.594	89.08338	88.743	0.3820
10	72.564	273.15	75.14342	75.21972	0.1015
11	82.244	303.15	80.92416	80.85968	0.0796
12	85.034	310.927	82.82819	82.6236	0.2470
13	89.013	283.15	76.51057	76.61043	0.1305
14	99.659	313.15	82.50981	82.54692	0.0449
15	102.040	294.261	78.28350	78.34142	0.0739
16	105.442	293.15	77.92142	78.03367	0.1440
17	106.428	333.15	87.66629	88.0149	0.3976
18	108.843	277.594	75.22458	75.2197	0.06490
19	132.557	273.15	73.82621	74.07887	0.224
% average deviation = 0.224%					

Table B-3-2: Propylene (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***%Deviation***
1	68.027	310.927	83.69593	83.79525	0.1186
2	102.040	310.927	82.01664	82.13949	0.1497
3	47.408	299.816	82.50981	82.78905	0.3384
4	108.843	294.261	78.28350	78.33020	0.0594
5	85.034	327.594	87.66004	87.60798	0.0594
6	60.952	293.15	79.39470	80.82834	0.4458
7	61.925	333.15	91.47433	79.74866	0.1624
8	62.891	323.15	87.66629	91.62291	0.16808
9	68.027	327.594	89.08338	87.81361	0.1706
10	72.564	273.15	75.14342	75.417730	0.3650
11	82.244	303.15	80.92416	81.17394	0.3086
12	85.034	310.927	82.82819	82.92439	0.1161
13	89.013	283.15	76.51057	76.80036	0.3787
14	99.659	313.15	82.50981	82.77806	0.3251
15	102.040	294.261	78.28350	78.54576	0.3349
16	105.442	293.15	77.92142	78.21976	0.3828
17	106.428	333.15	87.66629	87.79626	0.1482
18	108.843	277.594	75.22458	74.05195	0.3057
19	132.557	273.15	73.82621	75.30236	0.1034
% average deviation= 0.2323 %					

Table B-4-1: n-Octane

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc.(AK) (cm^3/ mol)***	***%Deviation***
1	50	734.15	206.5314	206.5526	0.0102
2	100	498.15	209.7299	209.086	0.3062
3	100	523.15	220.2392	219.5331	0.3206
4	150	498.15	204.0183	203.1894	0.4062
5	150	523.15	212.8142	211.6745	0.5355
6	200	473.15	192.9378	192.4352	0.2604
7	200	548.15	215.0988	213.0351	0.9594
8	250	373.15	170.0914	170.876	0.4612
9	250	423.15	179.4584	179.8977	0.2447
10	300	398.15	173.1757	173.9117	0.4249
11	300	448.15	182.3142	182.3743	0.0329
12	100	473.15	201.0483	200.5345	0.2555
13	150	473.15	196.5932	196.0417	0.2805
14	200	473.15	192.9378	192.4352	0.2604
15	200	498.15	199.5633	198.6624	0.4514
16	250	498.15	195.7936	195.0073	0.2487
17	300	498.15	192.5951	191.9586	0.3304
18	100	523.15	220.2392	219.5331	0.3206
19	150	523.15	212.8142	211.6745	0.5355
20	200	523.15	207.2168	205.9865	0.5937
21	200	548.15	215.0988	213.0351	0.9594
22	250	548.15	209.5014	186.432	11.011
23	300	548.15	205.0464	204.295	0.3660
% average deviation = 0.8511 %					

Table B-4-2: n-Octane (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/ mol)***	***%Deviation***
1	50	734.15	206.5314	208.98134	1.186
2	100	498.15	209.7299	214.38693	2.221
3	100	523.15	220.2392	225.96090	2.600
4	150	498.15	204.0183	208.68110	2.286
5	150	523.15	212.8142	218.01394	2.445
6	200	473.15	192.9378	196.46101	1.826
7	200	548.15	215.0988	214.54306	0.2582
8	250	373.15	170.0914	170.38086	0.1717
9	250	423.15	179.4584	180.95725	0.8413
10	300	398.15	173.1757	173.86554	0.3967
11	300	448.15	182.3142	184.70537	1.312
12	100	473.15	201.0483	204.31470	1.624
13	150	473.15	196.5932	200.03327	1.749
14	200	473.15	192.9378	196.46151	1.826
15	200	498.15	199.5633	204.11119	2.278
16	250	498.15	195.7936	200.29758	2.300
17	300	498.15	192.5951	197.02560	2.300
18	100	523.15	220.2392	225.96271	2.598
19	150	523.15	212.8142	218.01862	2.445
20	200	523.15	207.2168	211.98611	2.301
21	200	548.15	215.0988	214.54306	0.258
22	250	548.15	209.5014	208.01925	0.7076
23	300	548.15	205.0464	202.70334	1.142
% average deviation = 1.6118 %					

Table B-5-1: Isobutane

	P(atm)	T(K)	V exp. (cm^3/mol)	V calc.(AK) (cm^3/mol)	%Deviation
1	54.421	310.927	105.7569	106.156	0.3773
2	68.027	310.927	105.1447	105.6244	0.4562
3	85.034	310.927	104.445	105.6244	0.5409
4	102.040	310.927	103.8299	104.4398	0.5874
5	119.047	310.927	103.2581	103.9055	0.6270
6	136.054	310.927	102.8197	103.4016	0.5659
7	170.068	310.927	101.8825	102.4691	0.5757
8	204.081	310.927	101.01494	101.6186	0.5976
9	238.095	310.927	100.1447	100.8348	0.6890
10	136.054	344.261	109.9375	110.1741	0.2152
11	170.068	344.261	108.3190	108.6272	0.2845
12	204.081	344.261	107.0029	107.2641	0.2441
13	238.095	344.261	105.8917	106.0453	0.1450
14	272.108	344.261	104.8790	104.9435	0.0614
15	306.122	344.261	103.8856	103.9386	0.0509
16	340.136	344.261	103.0750	103.0156	0.0576
17	408.163	344.261	101.6153	101.3705	0.2409
18	476.19	344.261	100.3002	99.93922	0.3598
19	170.068	377.594	116.6914	116.9623	0.2321
20	204.081	377.594	114.6882	114.7497	0.0535
21	238.095	377.594	112.8840	112.8683	0.0139
22	272.108	377.594	111.3060	111.2393	0.0598
23	306.122	377.594	109.8129	109.8080	0.0393
24	340.136	377.594	108.6429	108.5372	0.0973
25	408.163	377.594	106.2595	106.3645	0.0987
26	476.190	377.594	104.5395	104.5623	0.0217
27	544.217	377.594	102.9107	103.0318	0.1176
% average deviation = 0.2731%					

Table B-5-2: Isobutane (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***%Deviation***
1	54.421	310.927	105.7569	106.26342	0.4788
2	68.027	310.927	105.1447	105.66219	0.49703
3	85.034	310.927	104.445	104.95789	0.4912
4	102.040	310.927	103.8299	104.29972	0.4524
5	119.047	310.927	103.2581	103.68194	0.01051
6	136.054	310.927	102.8197	103.09993	0.272
7	170.068	310.927	101.8825	102.02819	0.1429
8	204.081	310.927	101.01494	101.05969	0.0443
9	238.095	310.927	100.1447	100.17629	0.03156
10	136.054	344.261	109.9375	110.22885	0.2653
11	170.068	344.261	108.3190	108.60444	0.2635
12	204.081	344.261	107.0029	107.18809	0.17288
13	238.095	344.261	105.8917	105.93244	0.04121
14	272.108	344.261	104.8790	104.80469	0.07058
15	306.122	344.261	103.8856	103.78114	0.1005
16	340.136	344.261	103.0750	102.84430	0.2238
17	408.163	344.261	101.6153	101.17918	0.4292
18	476.19	344.261	100.3002	99.731938	0.566
19	170.068	377.594	116.6914	116.37729	0.2691
20	204.081	377.594	114.6882	114.17586	0.4467
21	238.095	377.594	112.8840	112.29812	0.5187
22	272.108	377.594	111.3060	110.66103	0.5794
23	306.122	377.594	109.8129	109.20979	0-.5515
24	340.136	377.594	108.6429	107.90638	0.6768
25	408.163	377.594	106.2595	105.64115	0.5820
26	476.190	377.594	104.5395	103.71709	0.7815
27	544.217	377.594	102.9107	102.04448	0.84101
% average deviation= 0.3778%					

Table B-7-1: n-Heptane

	P(atm)	*T (K)*	*V Exp. (cm^3/mol)*	*V calc.(AK) (cm^3/mol)*	*%Deviation*
1	136.054	277.594	141.45966	141.4802	0.0145
2	153.061	277.594	141.20996	141.2407	0.0217
3	170.068	277.594	142.64578	141.0093	1.147
4	187.074	277.594	140.71054	140.7845	0.0525
5	204.081	277.594	140.46083	140.5657	0.0746
6	54.421	310.927	148.45149	142.7792	3.821
7	68.027	310.927	148.13936	142.5392	3.780
8	85.034	310.927	147.76479	147.8797	0.0777
9	102.040	310.927	147.32781	147.5298	0.1371
10	119.047	310.927	147.01567	147.1961	0.1227
11	238.095	344.261	150.44916	150.53	0.0537
12	272.108	344.261	149.70003	149.8658	0.1107
13	306.122	344.261	148.95091	149.2351	0.1908
14	340.136	344.261	148.45149	148.6338	0.1228
15	408.163	377.594	151.82257	152.1999	0.2485
16	476.19	377.594	150.38673	150.8725	0.3229
17	544.217	377.594	149.13819	149.6521	0.3445
18	612.249	377.594	147.88965	148.5218	0.4274
19	272.108	410.927	160.87447	160.7695	0.0652
20	306.122	410.927	159.68836	159.6635	0.0155
21	340.136	410.927	158.56467	158.6309	0.0417
22	408.163	410.927	156.62943	156.7501	0.0770
23	476.19	477.594	164.74495	164.4033	0.2074
24	544.217	477.594	162.56000	162.3163	0.1499
25	612.249	477.594	160.68719	160.4867	0.1247
26	680.272	477.594	158.87681	158.8612	0.0098
%average deviation = 0.4523 %					

Table B-7-2: n-Heptane (Tait Equation)

	P(atm)	***T (K)***	***V Exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***%Deviation***
1	136.054	277.594	141.45966	140.04007	1.0035
2	153.061	277.594	141.20996	139.72731	1.0496
3	170.068	277.594	142.64578	139.42205	1.0911
4	187.074	277.594	140.71054	139.12302	1.128
5	204.081	277.594	140.46083	138.83024	1.1607
6	54.421	310.927	148.45149	147.39804	0.7096
7	68.027	310.927	148.13936	147.04526	0.738
8	85.034	310.927	147.76479	146.61601	0.777
9	102.040	310.927	147.32781	146.19900	0.7662
10	119.047	310.927	147.01567	145.79347	0.8313
11	238.095	344.261	150.44916	148.73298	1.1407
12	272.108	344.261	149.70003	147.93160	1.1813
13	306.122	344.261	148.95091	147.17005	1.195
14	340.136	344.261	148.45149	146.44446	1.351
15	408.163	377.594	151.82257	150.40040	0.936
16	476.19	377.594	150.38673	148.91351	0.979
17	544.217	377.594	149.13819	147.55211	1.063
18	612.249	377.594	147.88965	146.29670	1.0771
19	272.108	410.927	160.87447	160.44866	0.2646
20	306.122	410.927	159.68836	159.27553	0.2585
21	340.136	410.927	158.56467	158.17750	0.2441
22	408.163	410.927	156.62943	156.17222	0.2919
23	476.19	477.594	164.74495	166.10061	0.8228
24	544.217	477.594	162.56000	163.69599	0.6988
25	612.249	477.594	160.68719	161.54669	0.5349
26.	680.272	477.594	158.87681	159.60365	0.4574
					%average deviation = 0.8365%

Table B-7-1: Ethylene

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc.(AK) (cm^3/mol)***	***% Deviation***
1	76.062	110	43.05155	43.36916	0.7377
2	91.438	110	42.99225	43.32817	0.9763
3	114.236	110	42.90922	43.27013	0.8411
4	192.144	120	43.51994	43.85579	0.7717
5	219.126	130	44.18005	44.58833	0.9241
6	287.767	140	44.77885	45.22513	0.9966
7	321.885	150	45.46561	45.97167	1.113
8	349.114	160	46.18514	46.75454	1.232
9	438.499	170	46.56432	47.30779	1.596
10	490.421	180	47.15738	47.96136	1.704
11	550.525	190	47.75044	48.52591	1.624
12	616.728	200	48.01201	48.97538	2.006
13	672.904	210	48.50580	49.36992	1.781
14	709.937	220	49.08013	49.77998	1.425
15	777.310	231	49.57955	50.01204	0.8723
16	810.530	240	50.02715	50.36666	0.6786
17	874.335	250	50.37986	50.70846	0.6522
18	919.812	260	50.74693	51.37118	1.230
19	981.021	270	51.07967	52.19772	2.188
20	919.812	270	51.07967	52.56007	2.898
%average deviation = 1.312 %					

Table B-7-2: Ethylene (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***% Deviation***
1	76.062	110	43.05155	43.32131	0.626
2	91.438	110	42.99225	43.26138	0.6258
3	114.236	110	42.90922	43.17391	0.6175
4	192.144	120	43.51994	43.62435	0.239
5	219.126	130	44.18005	44.28142	0.2294
6	287.767	140	44.77885	44.77185	0.0156
7	321.885	150	45.46561	45.41698	0.1068
8	349.114	160	46.18514	46.10709	0.169
9	438.499	170	46.56432	46.48704	0.1659
10	490.421	180	47.15738	47.04626	0.2346
11	550.525	190	47.75044	47.55498	0.4092
12	616.728	200	48.01201	48.01450	0.0095
13	672.904	210	48.50580	48.51642	0.0218
14	709.937	220	49.08013	49.11259	0.0653
15	777.310	231	49.57955	49.58080	0.0036
16	810.530	240	50.02715	50.07772	0.1021
17	874.335	250	50.37986	50.42275	0.0851
18	919.812	260	50.74693	50.20526	1.0673
19	981.021	270	51.07967	49.74623	2.61
20	919.812	270	51.07967	50.20526	1.067
%average deviation = 0.3358 %					

Table B-8-1: 1-Butene

	P(atm)	***T (K)***	***V exp. (cm^3/mol)***	***V calc.(AK) (cm^3/mol)***	***%Deviation***
1	54.421	310.927	96.88656	96.507	0.3917
2	68.027	310.927	96.44957	96.11293	0.3490
3	85.034	310.927	95.95016	95.65463	0.3079
4	102.040	310.927	95.45094	95.22659	0.2350
5	119.047	310.927	95.01395	94.82325	0.2007
6	136.054	310.927	94.57696	94.44077	0.1439
7	153.061	344.261	100.75703	99.78911	1.158
8	170.068	344.261	100.13296	99.21818	0.9135
9	187.074	344.261	99.50869	98.67806	0.8347
10	204.081	344.261	98.94685	98.16531	0.7898
11	238.095	344.261	97.94802	97.21127	0.7521
12	272.108	344.261	97.07404	96.33852	0.7576
13	306.122	377.594	101.88092	100.6878	1.171
14	340.136	377.594	100.88209	99.52683	1.343
15	408.163	377.594	99.19656	97.7811	1.426
16	476.190	377.594	97.69831	96.21792	1.515
17	544.217	377.594	96.26249	94.86848	1.448
18	612.244	377.594	95.01395	93.68548	1.398
% average deviation = 0.8410 %					

Table B-8-2: 1-Butene (Tait Equation)

	P(atm)	*T (K)*	*V exp. (cm^3/mol)*	*V calc. (cm^3/mol)*	*% Deviation*
1	54.421	310.927	96.88656	96.52705	0.3710
2	68.027	310.927	96.44957	96.08028	0.3828
3	85.034	310.927	95.95016	95.55093	0.4160
4	102.040	310.927	95.45094	95.05063	0.4193
5	119.047	310.927	95.01395	94.57578	0.4611
6	136.054	310.927	94.57696	94.12542	0.4774
7	153.061	344.261	100.75703	99.8046	0.9452
8	170.068	344.261	100.13296	99.19323	0.9384
9	187.074	344.261	99.50869	98.61725	0.8959
10	204.081	344.261	98.94685	98.07272	0.8834
11	238.095	344.261	97.94802	97.06557	0.9009
12	272.108	344.261	97.07404	96.15098	0.9508
13	306.122	377.594	101.88092	100.6449	1.213
14	340.136	377.594	100.88209	99.57532	1.295
15	408.163	377.594	99.19656	97.6999	1.508
16	476.190	377.594	97.69831	96.09279	1.643
17	544.217	377.594	96.26249	94.68674	1.636
18	612.244	377.594	95.01395	93.437	1.659
% average deviation= 0.944 %					

Table B-9-1: n-Butane

No.	P(atm)	T(K)	V exp. (cm^3/mol)	V calc.(AK) (cm^3/mol)	% Deviation
1	68.027	310.927	101.19909	101.7695	0.5636
2	102.040	310.927	100.18316	100.8537	0.6692
3	136.054	310.927	99.27600	100.0405	0.7700
4	68.027	327.594	105.37684	105.1634	0.2025
5	340.136	327.594	98.26015	98.2974	0.0379
6	680.272	327.594	93.45327	93.4295	0.0254
7	119.047	344.261	105.84360	106.7279	0.8354
8	153.061	344.261	104.50106	105.4542	0.9120
9	187.074	344.261	103.41251	104.3207	0.8782
10	68.027	360.927	113.86691	113.5749	0.2564
11	340.136	360.927	103.12946	102.534	0.5773
12	680.272	360.927	96.761909	96.11956	0.6638
13	136.054	377.594	113.53599	113.8942	0.3154
14	170.068	377.594	111.57665	111.9011	0.2907
15	204.081	377.594	110.16149	110.189	0.0250
16	68.027	394.261	126.16504	126.7058	0.4286
17	340.136	394.261	108.37333	108.0393	0.3082
18	680.272	394.261	100.25782	100.1319	0.1256
19	68.027	410.927	134.96725	136.4725	1.115
20	340.136	410.927	111.24498	110.6266	0.5558
21	680.272	410.927	102.13063	102.8358	0.6904
%average deviation = 0.4879 %					

Table B-9-2: n-Butane (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***% Deviation***
1	68.027	310.927	101.19909	101.68415	0.4792
2	102.040	310.927	100.18316	100.61359	0.4296
3	136.054	310.927	99.27600	99.64965	0.3763
4	68.027	327.594	105.37684	105.23138	0.1376
5	340.136	327.594	98.26015	97.57970	0.6908
6	680.272	327.594	93.45327	92.44383	1.0728
7	119.047	344.261	105.84360	106.80086	0.9043
8	153.061	344.261	104.50106	105.42322	0.882
9	187.074	344.261	103.41251	104.20514	0.7664
10	68.027	360.927	113.86691	113.98552	0.1082
11	340.136	360.927	103.12946	102.52954	0.0581
12	680.272	360.927	96.761909	95.977825	0.8100
13	136.054	377.594	113.53599	114.07205	0.4721
14	170.068	377.594	111.57665	112.03924	0.4146
15	204.081	377.594	110.16149	110.30564	0.1308
16	68.027	394.261	126.16504	126.59766	0.3428
17	340.136	394.261	108.37333	107.61734	0.697
18	680.272	394.261	100.25782	98.96558	1.288
19	68.027	410.927	134.96725	132.77906	1.621
20	340.136	410.927	111.24498	108.49726	2.469
21	680.272	410.927	102.13063	101.049286	1.058
				%average deviation =	0.7240%

Table B-10-1: n-Decane

No.	*P(atm)*	*T(K)*	*V exp. (cm^3/mol)*	*V calc(AK) (cm^3/mol)*	*%Deviation*
1	54.421	310.927	196.21372	196.4356	0.1130
2	68.027	310.927	195.85842	195.0865	0.1164
3	85.034	310.927	195.41445	195.6745	0.0680
4	102.040	310.927	194.97033	195.2841	0.1609
5	119.047	310.927	194.61503	194.9114	0.1522
6	136.054	310.927	194.25973	194.5537	0.1513
7	153.061	310.927	193.99325	194.2091	0.1112
8	170.068	310.927	193.63795	193.8759	0.1228
9	187.074	310.927	193.28266	193.5531	0.1399
10	204.081	310.927	193.01618	193.2396	0.1157
11	238.095	344.261	198.70096	198.7654	0.0324
12	272.108	344.261	198.25684	198.0624	0.0980
13	306.122	344.261	197.54624	197.3925	0.0778
14	340.136	344.261	196.21386	196.7517	0.2741
15	408.163	344.261	194.97033	195.5456	0.2950
16	476.190	344.261	193.90443	194.4249	0.2683
17	544.217	344.261	192.83853	193.3759	0.2786
18	612.244	344.261	191.86146	192.3886	0.2747
19	680.272	344.261	190.97321	191.4549	0.2522
%average deviation = 0.16333 %					

Table B-10-2: n-Decane (Tait Equation)

	P(atm)	***T(K)***	***V exp. (cm^3/mol)***	***V calc. (cm^3/mol)***	***% Deviation***
1	54.421	310.927	196.21372	194.2058	1.032
2	68.027	310.927	195.85842	193.8583	1.0211
3	85.034	310.927	195.41445	193.4323	1.014
4	102.040	310.927	194.97033	193.0151	1.002
5	119.047	310.927	194.61503	192.6063	1.032
6	136.054	310.927	194.25973	192.2056	1.057
7	153.061	310.927	193.99325	191.8128	1.123
8	170.068	310.927	193.63795	191.4274	1.140
9	187.074	310.927	193.28266	191.0493	1.155
10	204.081	310.927	193.01618	190.6781	1.211
11	238.095	344.261	198.70096	196.1139	1.301
12	272.108	344.261	198.25684	195.2962	1.493
13	306.122	344.261	197.54624	194.5093	1.537
14	340.136	344.261	196.21386	193.7508	1.255
15	408.163	344.261	194.97033	192.3118	1.363
16	476.190	344.261	193.90443	190.9654	1.515
17	544.217	344.261	192.83853	189.7004	1.627
18	612.244	344.261	191.86146	188.5076	1.748
19	680.272	344.261	190.97321	187.3791	1.882
%average deviation = 1.2894 %					

Table B-11-1: Propane

No.	*P(atm)*	*T(K)*	*V exp. (cm^3/mol)*	*V calc(AK) (cm^3/mol)*	*%Deviation*
1	90.040	303.15	86.79920	86.78708	0.0139
2	125.95	303.15	85.33769	85.53922	0.2361
3	119.89	303.15	85.2037	85.73827	0.3721
4	54.827	318.15	93.00569	92.56688	0.4718
5	74.343	318.15	91.29192	91.33786	0.0503
6	92.452	318.15	90.63514	90.36086	0.3026
7	132.508	318.15	88.25859	88.52055	0.2968
8	68.324	348.15	102.5441	104.0387	1.457
9	76.142	348.15	101.8807	102.9529	1.052
10	89.271	348.15	100.2591	101.3317	1.069
11	108.869	348.15	98.13929	99.26773	1.149
12	127.113	348.15	97.35921	97.63053	0.2786
13	144.199	348.15	95.52426	96.28581	0.7972
%average deviation = 0.5807 %					

Table B-11-2: Propane (Tait Equation)

No.	**P(atm)**	**T(K)**	**V exp. (cm^3/mol)**	**V calc(AK) (cm^3/mol)**	**%Deviation**
1	90.040	303.15	86.79920	86.81322	0.0211
2	125.95	303.15	85.33769	85.44394	0.1245
3	119.84	303.15	85.42037	85.16964	0.2935
4	54.827	318.15	93.00569	92.75503	0.2695
5	74.343	318.15	91.29192	91.44618	0.1743
6	92.452	318.15	90.63514	90.38448	0.2765
7	132.508	318.15	88.25859	88.41116	0.1791
8	68.0324	348.15	102.5441	103.09251	0.5347
9	76.142	348.15	101.8807	101.91819	0.0367
10	89.271	348.15	100.2591	100.20426	0.0548
11	108.869	348.15	98.13929	98.08311	0.0468
12	127.113	348.15	97.35921	96.43298	0.9470
13	144.199	348.15	95.52426	95.09573	0.4437
%average deviation = 0.2266 %					

Table B-12-1: Ammonia

No.	P(atm)	T(K)	Vexp. (cm^3/mol)	Tait Equation		Modified Tait Equation	
				Vcal.(Tait) (cm^3/mol)	% Devi.	Vcalc. (Mod.Tait) (cm^3/mol)	% Devi.
1	283.1	253.15	25.1275	25.39666	1.071	24.95037	0.7094
2	469.5	253.15	24.74604	25.3937	2.617	24.68965	0.2324
3	654.9	253.15	24.4752	25.39076	3.740	24.45552	0.0849
4	841.4	253.15	24.19594	25.3878	4.925	24.24087	0.1812
5	1027.9	253.15	24.00178	25.38485	5.762	24.043700	0.1701
6	469.5	273.15	25.5168	26.47378	3.567	25.58979	0.1051
7	654.9	273.15	25.2263	26.46995	4.929	25.30523	0.3091
8	1027.9	273.15	24.6574	25.46225	3.264	24.81481	0.6337
9	1400.5	273.15	24.16528	25.45458	5.335	24.40484	0.9867
10	1587.2	273.15	23.95239	24.15075	0.8281	24.22204	1.1213
11	841.4	298.15	25.8258	26.06965	0.9442	24.222043	1.3113
12	1027.9	298.15	25.5073	26.16313	2.571	25.873030	1.429
13	1214.1	298.15	25.1667	25.5746	1.620	25.610001	1.756
14	1587.2	298.15	24.64556	24.74614	0.4081	25.149962	2.041
15	1773.6	298.15	24.4139	25.0405	2.566	24.94673	2.178
16	654.9	313.15	26.94474	27.2242	1.037	27.28579	1.261
17	841.4	313.15	26.47979	27.21664	2.782	26.901829	1.589
18	1214.1	313.15	25.7185	26.2016	1.878	26.264003	2.116
19	1400.5	313.15	25.3949	26.19411	3.147	25.99258	2.348
20	1742.1	313.15	24.9401	25.18044	0.9636	25.55491	2.461
%average deviation				*2.6978%*		*1.1514%*	

Table B-13-1: Water

No.	**P(atm)**	**T(K)**	**Vexp. (cm^3/mol)**	**Tait Equation**		**Modified Tait Equation**	
				Vcal.(Tait) (cm^3/mol)	**% Devi.**	**Vcalc. (Mod.Tait) (cm^3/mol)**	**% Devi.**
1	49.345	333.15	18.26739	16.38581	16.433	17.44439	4.5053
2	49.345	353.15	18.48158	16.82708	5.695	17.8325	3.512
3	49.345	373.15	18.73717	17.30834	3.925	18.24923	2.604
4	49.345	393.15	19.03593	18.37687	3.462	18.69881	1.770
5	49.345	413.15	19.38153	19.16187	2.165	19.18648	1.006
6	98.691	423.15	19.71453	18.86067	4.331	19.71869	0.0210
7	98.691	453.15	20.15731	19.53788	3.072	20.30414	0.7284
8	98.691	473.15	20.66303	21.17847	2.494	20.95384	1.407
9	98.691	493.15	21.24804	21.59794	2.117	21.68279	2.046
10	98.691	513.15	21.93563	22.51854	2.657	22.51201	2.627
11	148.038	533.15	22.58901	23.47176	3.907	23.17176	2.579
12	148.038	553.15	23.55016	24.4962	4.017	24.61037	3.228
13	148.038	333.15	18.15034	17.39825	4.143	17.44424	3.890
14	148.038	353.15	18.35739	17.78055	3.142	17.83233	2.860
15	148.038	373.15	18.59314	18.19039	2.166	18.24904	1.850
16	148.038	393.15	18.89192	18.63177	1.377	18.6986	1.023
17	148.038	413.15	19.21955	19.1096	0.5718	19.18623	0.1733
18	296.076	433.15	19.47692	19.74191	1.360	19.71811	1.238
19	296.076	453.15	19.88372	20.19732	2.080	20.30345	2.111
20	296.076	473.15	20.34270	20.90942	2.785	20.95299	3.000
Ta	296.076	493.15	20.86108	21.39058	3.496	21.68174	3.933
22	296.076	513.15	21.45506	22.15786	4.207	22.51066	4.920
23	493.461	533.15	21.66025	23.46859	8.348	22.74009	4.985
24	493.461	553.15	22.44514	24.6058	9.626	23.6739	5.474
%average deviation				***4.0900%***		***2.125%***	

Table B-14-1: Acetone

No.	***P(atm)***	***T(K)***	***Vexp. (cm^3/mol)***	***Tait Equation***		***Modified Tait Equation***	
				Vcal.(Tait) (cm^3/mol)	***% Devi.***	***Vcalc. (Mod.Tat) (cm^3/mol)***	***% Devi.***
1	102.040	310.92	82.02912	75.72733	7.682	76.7372	6.451
2	119.047	310.92	81.2800	75.56738	7.028	76.73321	5.593
3	136.054	310.92	80.59330	75.41078	6.430	76.72922	4.794
4	153.061	310.92	80.03146	75.25742	5.965	76.72523	4.131
5	170.068	310.92	79.46961	75.10774	5.488	76.72124	3.458
6	187.074	310.92	78.97020	74.95986	5.078	76.71725	2.852
7	204.081	310.92	78.53321	74.81543	4.734	76.71327	2.317
8	204.081	344.26	85.33776	78.47088	8.046	81.02448	5.053
9	238.095	344.26	83.90193	78.10507	6.909	81.01328	3.442
10	272.108	344.26	82.59097	77.7555	5.854	81.00211	1.923
11	306.122	344.26	81.52971	77.42086	5.039	80.99094	0.6608
12	340.136	344.26	80.59330	77.09985	4.334	80.9798	0.4795
13	408.163	344.26	78.97020	76.49465	3.134	80.95755	2.516
14	476.19	344.26	77.59680	75.93271	2.144	80.93536	4.302
15	238.095	377.59	91.39318	82.22971	10.026	86.29465	5.578
16	272.108	377.59	89.45794	81.76422	8.6003	86.27773	3.554
17	306.122	377.59	87.77241	81.32321	7.347	86.26083	1.722
18	340.136	377.59	86.27416	80.90426	6.224	86.24397	0.0350
19	408.163	377.59	83.96436	80.12404	4.573	86.21034	2.674
%average deviation				***6.0587 %***		***3.2387 %***	

Appendix C: Results for Mixtures of Liquids

Table C-1-1: Propane- Benzene System

No.	P(atm)	T(K)	$x_{(propane)}$	Tait Mixing. rule V_s (HT)		Tait Mixing rule V_s (Rackett)	
				Vcalc. (cm^3/mol)	% Devi.	Vcalc. (cm^3/mol)	% Devi.
1	54.412	510.927	0.2	138.5936	3.786	138.5875	2.250
2	68.027	510.927	0.2	131.0534	0.4889	131.0507	0.4868
3	85.034	510.927	0.2	125.1112	1.955	125.1057	1.959
4	102.040	510.927	0.2	120.9062	3.600	120.9009	3.604
5	204.081	444.261	0.5	106.1055	1.243	106.0321	1.311
6	238.095	444.261	0.5	104.108	1.383	104.0359	1.451
7	272.108	444.261	0.5	102.3904	1.436	102.3196	1.505
8	306.122	444.261	0.5	100.8839	1.586	100.814	1.654
9	340.136	410.927	0.6	95.75082	0.6003	95.76463	0.5860
10	408.163	410.927	0.6	93.8539	0.7033	93.86744	0.6889
11	476.190	410.927	0.6	92.23795	0.9076	92.25125	0.8933
12	544.217	410.927	0.6	90.83035	0.9584	90.84344	0.9441
13	136.054	377.594	0.7	98.17892	0.7178	98.23621	0.6598
14	153.061	377.594	0.7	97.32323	0.7055	97.38002	0.6475
15	187.074	377.594	0.7	95.80588	0.7361	95.86178	0.6782
16	204.081	377.594	0.7	95.12619	0.7341	95.18169	0.6761
17	272.108	344.261	0.8	87.64199	0.9979	87.72417	0.9050
18	306.122	344.261	0.8	86.83108	1.076	86.9125	0.9840
19	340.136	344.261	0.8	86.08667	1.0095	86.1674	0.9167
20	408.163	344.261	0.8	84.7592	1.044	84.83868	0.9514
21	476.190	310.927	0.9	79.29034	0.7755	79.40058	0.6376
22	544.217	310.927	0.9	78.41338	0.7878	78.52239	0.6499
23	612.244	310.927	0.9	77.61974	0.7730	77.72766	0.6191
24	680.272	310.927	0.9	76.89497	0.7491	77.00188	0.6111
% Average Deviation				1.198%		1.0945%	

Table C-2-1: Methane- n- Pentane System

No.	P(atm)	T(K)	$x_{(methane)}$	Tait Mixing. rule V_s (HT)		Tait Mixing rule V_s (Rackett)	
				Vcalc. (cm^3/mol)	% Devi.	Vcalc. (cm^3/mol)	% Devi.
1		310.927	0.4635	96.89481	2.874	92.36395	7.416
2		102.040	0.4635	95.87576	3.260	91.39246	0.6603
3	136.054	119.047	0.4635	94.95507	3.294	90.51497	1.535
4	153.061	310.927	0.4635	94.11549	3.254	89.7145	1.573
5	187.074	310.927	0.4635	92.63006	3.227	88.29852	1.599
6	204.081	310.927	0.4635	91.96593	3.150	87.66546	1.673
7	221.088	310.927	0.4635	91.34505	3.120	87.07362	1.702
8	187.074	344.261	0.2933	106.3686	2.314	102.7085	1.205
9	204.081	344.261	0.2933	105.654	2.208	102.0186	1.308
10	221.088	344.261	0.2933	104.983	2.178	101.3707	1.337
11	238.095	344.261	0.2933	104.3507	2.184	100.7601	1.331
12	255.102	344.261	0.2933	103.7527	2.086	100.1827	1.426
13	272.108	344.261	0.2933	103.1856	2.056	99.63507	1.455
14	289.115	344.261	0.2933	102.6462	2.013	99.11429	1.496
15	221.088	377.594	0.1262	118.8417	0.8130	116.7111	0.9942
16	238.095	377.594	0.1262	118.1396	0.8429	116.0216	0.9649
17	255.102	377.594	0.1262	117.4745	0.8697	115.3685	0.9385
18	272.108	377.594	0.1262	116.843	0.8508	114.7482	0.9572
19	289.115	377.594	0.1262	116.2415	0.8977	114.1575	0.9111
20	306.122	377.594	0.1262	115.6674	0.9332	113.5938	0.8762
21	323.129	377.594	0.1262	115.1184	1.027	113.0546	0.7840
22	340.136	377.594	0.1262	114.5924	1.069	112.5379	0.7419
% Average Deviation					**1.4947**		**2.024**

Table C-3-1: Acetone-1- Butene System

No.	P(atm)	T(K)	$x_{(acetone)}$	Tait Mixing. rule V_s (HT)		Tait Mixing rule V_s (Rackett)	
				Vcalc. (cm^3/mol)	% Devi.	Vcalc. (cm^3/mol)	% Devi.
1	54.421	310.927	0.1	94.14078	1.113	93.76574	1.507
2	68.027	310.927	0.1	93.7531	1.067	93.37961	1.4611
3	85.034	310.927	0.1	93.29107	1.032	92.91942	1.427
4	102.040	310.927	0.1	92.85181	0.9743	92.48191	1.368
5	119.047	310.927	0.1	92.43314	0.9592	92.0649	1.353
6	136.054	310.927	0.3	87.75936	2.780	87.27512	3.317
7	153.061	344.261	0.3	92.6436	3.320	92.20723	3.775
8	170.068	344.261	0.3	92.22105	3.130	91.78667	3.586
9	187.074	344.261	0.3	91.81716	2.982	91.38468	3.439
10	204.081	344.261	0.3	91.43031	2.813	90.99965	3.271
11	238.095	344.261	0.5	86.54399	4.127	86.01237	4.716
12	272.108	344.261	0.5	85.99931	3.664	85.47103	4.256
13	306.122	377.594	0.5	89.99633	3.955	89.54727	4.434
14	340.136	377.594	0.5	89.34027	3.498	88.89449	3.980
15	408.163	377.594	0.5	88.15114	2.616	87.71129	3.102
16	476.19	377.594	0.7	83.42191	3.306	82.89547	3.916
17	544.217	377.594	0.7	82.62334	2.539	82.10194	3.154
18	612.244	377.594	0.7	81.89043	1.665	81.3739	2.285
% Average Deviation						**6.8969**	

Table C-4-1: Propane- Acetone

No.	***P(atm)***	***T(K)***	$x_{(acetone)}$	***Tait Mixing. rule V_s (HT)***		***Tait Mixing rule V_s (Rackett)***	
				Vcalc. (cm^3/mol)	***% Devi.***	***Vcalc. (cm^3/mol)***	***% Devi.***
1	54.421	310.927	0.2411	77.19515	13.707	76.63651	14.332
2	68.027	310.927	0.2411	77.02897	13.105	76.47153	13.734
3	85.034	310.927	0.2411	76.82633	11.693	76.27036	13.104
4	102.040	344.261	0.2411	81.00441	16.122	80.47042	16.675
5	119.047	344.261	0.2411	80.73021	15.200	80.1904	15.759
6	136.054	344.261	0.2411	80.46519	14.355	79.93476	14.920
7	153.061	377.594	0.2411	85.1701	17.564	84.7058	18.013
8	170.068	377.594	0.2411	84.80445	16.402	84.34214	16.858
9	187.074	377.594	0.2411	84.45385	15.394	83.99345	15.855
10	204.081	410.927	0.2411	89.70026	17.751	89.35144	18.071
11	238.095	410.927	0.2411	88.74446	15.533	88.39935	15.861
12	272.108	410.927	0.2411	87.7718	13.956	87.53545	14.290
13	306.122	444.261	0.2411	92.09634	14.527	91.88847	14.719
14	340.136	444.261	0.2411	91.00163	13.230	90.79624	13.426
15	408.163	444.261	0.2411	89.09711	11.352	88.896	11.552
16	119.047	310.927	0.6289	81.06502	3.524	80.74188	3.909
17	136.054	310.927	0.6289	80.72697	3.135	80.40517	3.526
18	153.061	310.927	0.6289	80.40289	2.869	80.08239	3.256
19	170.068	344.261	0.6289	85.41502	4.385	85.15656	4.675
20	187.074	344.261	0.6289	84.96273	4.020	84.70564	4.310
21	204.081	344.261	0.6289	84.53315	3.621	84.27736	3.913
22	238.095	360.927	0.6289	86.44992	3.832	86.23264	4.073

23	272.108	360.927	0.6289	85.56039	3.071	85.34535	3.315
24	306.122	360.927	0.6289	84.75066	2.401	84.53764	2.646
25	340.136	377.594	0.6289	86.43063	2.362	86.2459	2.570
26	408.163	377.594	0.6289	84.85537	1.359	84.67401	1.569
27	476.19	377.594	0.6289	83.50124	0.6254	83.32277	0.8378
% Average Deviation							

Table C-5-1: Propane- n-Decane System

No.	***P(atm)***	***T(K)***	$x_{(propane)}$	***Tait Mixing. rule V_s (HT)***		***Tait Mixing rule V_s (Rackett)***	
				Vcalc. (cm^3/mol)	***% Devi.***	***Vcalc. (cm^3/mol)***	***% Devi.***
1	54.421	277.594	0.3	160.7673	2.723	153.5688	1.875
2	68.027	277.594	0.3	160. 4608	2.732	153.276	1.867
3	85.034	277.594	0.3	160.0856	2.697	152.9176	1.9006
4	102.040	277.594	0.3	159.719	2.626	152.5674	1.968
5	119.047	277.594	0.3	159.3605	2.602	152.225	1.991
6	136.054	277.594	0.3	159.0098	2.541	151.89	2.049
7	153.061	277.594	0.3	158.6666	2.485	151.5621	2.103
8	170.068	277.594	0.3	158.3305	2.433	151.2411	2.153
9	102.040	310.927	0.6	133.8852	3.908	126.1547	2.091
10	119.047	310.927	0.6	133.41	3.891	125.707	2.106
11	136.054	310.927	0.6	132.9514	3.837	125.2749	2.157
12	153.061	310.927	0.6	132.5082	3.795	124.8572	2.198
13	170.068	310.927	0.6	132.0794	3.763	124.4548	2.226
14	187.074	310.927	0.6	131.6642	3.947	124.062	2.295

15	204.081	310.927	0.6	131.2616	3.629	123.6826	2.354
16	238.095	310.927	0.6	130.4916	3.531	122.9571	2.446
17	272.108	344.261	0.9	100.4467	1.644	97.38593	1.453
18	306.122	344.261	0.9	99.42879	1.576	96.39906	1.518
19	340.136	344.261	0.9	98.49932	1.533	95.49792	1.560
20	408.163	344.261	0.9	96.85226	1.468	93.90104	1.623
21	476.19	344.261	0.9	95.42511	1.297	92.51737	1.788
22	544.217	344.261	0.9	94.16601	1.236	91.29664	1.848
23	612.244	344.261	0.9	93.03943	1.179	90.20439	1.903
24	680.272	344.261	0.9	92.02032	1.448	89.21633	1.642
% Average Deviation					***2.6055***		***1.9636***

Table C-6-1: Propane- 1-Butene System

No.	***P(atm)***	***T(K)***	$x_{(propane)}$	***Tait Mixing rule V_s (Rackett)***	
				Vcalc. (cm^3/mol)	***% Devi.***
1	54.421	310.927	0.1705	91.14168	1.9350
2	68.027	310.927	0.1705	90.45409	1.921
3	85.034	310.927	0.1705	89.66541	1.892
4	102.040	310.927	0.3315	89.93923	1.514
5	119.047	310.927	0.3315	89.32596	1.544
6	136.054	310.927	0.3315	88.7532	1.516
7	153.061	310.927	0.6905	90.95559	9.763
8	170.068	310.927	0.6905	90.50934	9.701
9	187.074	310.927	0.6905	90.08445	9.665

10	204.081	310.927	0.8174	90.75063	12.281
11	238.095	310.927	0.1874	90.01443	12.161
12	272.108	310.927	0.8174	89.3341	12.068
13	170.068	344.261	0.1705	93.47635	2.7007
14	187.074	344.261	0.1705	92.64415	2.685
15	204.081	344.261	0.1705	91.8766	2.693
16	238.095	344.261	0.3315	91.65034	1.149
17	272.108	344.261	0.3315	90.52154	1.075
18	306.122	344.261	0.3315	89.5093	1.097
19	340.136	344.261	0.6905	91.63121	9.429
20	408.163	344.261	0.6905	90.15931	9.516
21	476.190	344.261	0.6905	88.8795	9.559
22	544.217	344.261	0.8174	88.94516	12.044
23	612.244	344.261	0.8174	87.94789	12.102
24	680.272	344.261	0.8174	87.04225	11.975
25	102.040	377.594	0.3315	98.42941	10.148
26	119.047	377.594	0.3315	95.71278	10.645
27	136.054	377.594	0.3315	93.48198	11.058
28	153.061	377.594	0.6905	105.3403	9.409
29	170.068	377.594	0.6905	104.1724	9.389
30	187.074	377.594	0.6905	103.1126	9.379
31	204.081	377.594	0.8174	103.1308	12.331
32	238.095	377.594	0.8174	101.5135	12.258
33	272.108	377.594	0.8174	100.0988	12.183
34	340.136	377.594	0.6905	88.45822	2.759
35	408.163	377.594	0.6905	85.84253	3.469

36	476.190	394.261	0.6905	83.65979	4.045
37	544.217	394.261	0.8174	91.69257	8.375
38	612.244	394.261	0.8174	90.15498	8.131
39		394.261	0.8174	88.78365	7.963
% Average Deviation				***8.001***	

Table C-7-1: Methane- Propane System

No.	**P(atm)**	**T(K)**	$x_{(propane)}$	**Tait Mixing. rule V_s (HT)**		**Tait Mixing rule V_s (Rackett)**	
				Vcalc. (cm^3/mol)	**% Devi.**	**Vcalc. (cm^3/mol)**	**% Devi.**
1	54.421	277.594	0.5	81.69807	49.216	83.82961	47.891
2	68.027	277.594	0.5	77.7422	28.429	79.77055	26.562
3	85.034	277.594	0.5	74.5263	7.384	76.47072	4.966
4	102.040	277.594	0.5	72.21651	6.254	74.10066	3.809
5	119.047	277.594	0.5	70.41273	6.241	72.24982	3.794
6	136.054	277.594	0.5	68.93268	6.817	70.73116	4.386
7	153.061	277.594	0.5	67.67765	7.102	69.44339	4.679
8	170.068	277.594	0.5	66.58817	7.247	687.32548	4.827
9	204.081	310.927	0.3	74.70554	6.435	76.18725	4.580
10	238.095	310.927	0.3	73.03078	6.784	74.47927	4.935
11	272.108	310.927	0.3	71.60926	7.043	73.02955	5.199
12	306.122	310.927	0.3	70.37428	7.3702	71.77007	5.533
13	340.136	310.927	0.3	69.28255	7.668	70.65669	5.837
14	408.163	310.927	0.3	68.618	6.453	68.75523	6.266

15	476.19	310.927	0.3	65.86225	8.258	67.16855	6.438
16	544.217	310.927	0.3	64.52724	8.446	65.80708	6.630
17	272.108	344.261	0.1	78.37868	9.739	79.19823	8.795
18	306.122	344.261	0.1	76.94735	10.095	77.75193	9.155
19	340.136	344.261	0.1	75.68273	10.396	76.47409	9.459
20	408.163	344.261	0.1	73.52429	10.977	74.29308	10.046
21	476.190	344.261	0.1	71.72423	11.348	72.4742	10.421
22	544.217	344.261	0.1	70.18031	11.688	70.91413	10.765
23	612.244	344.261	0.1	68.82863	12.077	69.54832	11.158
24	680.272	344.261	0.1	67.62656	12.426	68.33369	11.510
% Average Deviation				***11.0793***		***9.485***	

الخلاصة

أن التنبوء بالقيمة الصحيحة لحجم السوائل المضغوطة له أهمية كبيرة في الحسابات التصميمية وبعض التطبيقات الصناعية الأخرى. أن التجارب العملية لحساب حجم السائل المضغوط تكون مكلفة جدا ولهذا فقد تحول الأهتمام الى حسابها من معادلات الحالة، لذلك أستعمل معادلة Aalto and Kiskinen للسوائل النقية وتعديل معادلة Tait للمواد القطبية وأستخدام معلدلة Tait مع طريقة الخلط.

في هذه الدراسة أستعملت خمس من معادلات الحالة بهدف حساب حجم السائل النقي الغير قطبي وهي: معادلة Aalto and Kiskinen ، معادلة Tait، معادلة Peng- Robinson ، معادلة Soave- Redlich- Kwong، مع معادلة Lee-Kesler. وقد جربت هذه الطرق على ٢٤١ نقطة مختبرية للسوائل المضغوطة النقية وقد وجد أن معادلة Aalto and Kiskinen هي أفضل من المعادلات الأخرى.

من أستخدام معادلة Aalto and Kiskinen تطابقت مع النتائج المختبرية فقد كان المعدل المطلق للانحراف لاحد عشر مركب نقي مع ٢٤١ نقطة كان ٠,٦٢٧٦ لحجوم السوائل النقية.

أما للمواد القطبية فقد استخدمت ٤ معادلات من معادلات الحالة وهي : معادلةSoave- Redlich- Kwong، معادلة Peng- Robinson، معادلة Aalto and Kiskinen و معادلة Tait. هذه الطرق قد جربت على ٦٣ نقطة مختبرية للسوائل القطبية المضغوطة وقد وجد أن معادلة Tait هي الافضل مقارنة بالمعادلات الاخرى. لذلك أجري تعديل على معادلة Tait لتحسين دقتها وذلك من خلال ابدال متغيرين في معادلة Tait هي الضغط و ضغط البخار مع الضغط المتبقي وضغط البخار المتبقي وكما يلي:

$$V = V_s\left(1 - c\ln\frac{\beta + P_r}{\beta + P_{rs}}\right)$$

النتائج المستحصلة من أستخدام هذه الطريقة تطابقت مع النتائج المختبرية فقد كان المعدل المطلق للانحراف لثلاث مركبات قطبية مع ٦٣ نقطة كان ٢,١٥٢٩ للحجم المضغوط.

لخليط من السوائل المضغوطة هناك طريقتين قد أستخدمت لحساب حجوم المخاليط المضغوطة وهي معادلة Teja ومعادلة Tait مع معادلات الخلط.

لأمكانية أستمرارية تطبيق معادلة Tait للخلائط مع أستخدام طريقة Hankinson- Brobst- Thomson (HBT) للخلائط مع تطوير معادلة Rackett لتطبيقها على الخليط لحساب معدل الحجوم المشبعة للخليط ولذلك هذه المعادلة يمكن كتابتها كما يلي:

$$V_{sm} = \frac{RT_{cm}}{P_{cm}} Z_{cm}^{\left[1+(1-T_{rm})^{2/7}\right]}$$

هذه الطريقة تطابقت مع النتائج المختبرية فقد كان المعدل المطلق للانحراف ٢٩١ نقطة مأخوذة من ٧ خليط ثنائي وجد أنه 4.9386. أن هذه الطريقة المقترحة قد حسنت الدقة كثيرا ويمكن اعتبارها طريقة مقبولة جدا.

شكر

أود أن أعبر عن خالص شكري و تقديري للمشرف الأستاذ الدكتور محمود عمر عبد الله لما قدمه لي من معلومات و وقت وفير و متابعة خلال فترة البحث.

أقدم شكري الى الاستاذ الدكتور قاسم جبار محمد السليمان رئيس قسم الهندسة الكيمياوية لمساعدته لي وتشجيعي.

ولا أنسى أن أتقدم بالشكر و الامتنان إلى أعز من في الوجود إلى أبي و أمي و جميع أفراد عائلتي فلهم جزيل الشكر و التقدير.

ايجاد معادلة مصححة للمتغيرات P- V- T للسوائل المضغوطة في ضغط عالي

رسالة
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في الهندسة الكيمياوية

من قبل
نور صبيح مجيد القزاز
بكالوريوس في الهندسة الكيمياوية ٢٠٠٢

ربيع الأول ١٤٢٦
نيسان ٢٠٠٥