# INVESTIGATION OF THE CORRELATIONS FOR PREDICTION OF SATURATED VAPOR VOLUME FOR PURE COMPONENTS AND MIXTURES

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**in**
**Chemical Engineering**

**by**

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# ABSTRACT

The prediction of molar volume of saturated vapor can be calculated from many equations of state, some of these equations applied for both gas and liquid phase ,and some of them applied for gas phase only . The accuracy of these equations are different . For pure compounds the molar volume of saturated vapor can be calculated from many equations ,such as Lee-Kesler equation that gave a very high deviation from the molar volume calculated from the PVT data , it is used to calculate the molar volume of three compounds (72 data points polar and non-polar ) with (average absolute percent deviation) AAD% 62.432%, and when its deviation found to be very high there is no need to used this equation for other compounds . Redlich –Soave equation was the second equation of state that used to calculate the deviation of the molar volume in this project , it gave AAD% 15.3125 for 299 data points for 14 compounds polar and non-polar . Peng –Robinson equation of state was used in this project and applied for 299 data points and gave AAD% 14.3476% which is relatively better than that obtained from Redlich-Soave equation .And finally Virial equation of state that can be used to calculate the molar volume with Virial truncated to second term and Virial truncated to third term ,the use of Virial equation truncated to second term gave AAD% 7.5525% for 299 data points (polar and non-polar ) this relatively high deviation is because of the ranges of pressures of some compounds in this project was relatively high ,and the second term of Virial equation is used for pressures relatively low 9not accede 15 bar) .While Virial equation truncated to third term gave better deviation the AAD% is 1.0955% this because it can be used for pressure range greater than that of second term (up to 50 bar) .

From the above comparison, it is Easley considered that the truncated Virial equation is the best equation that can be used to calculate the molar volume of the saturated vapor ,and it is clearly showed that the Virial truncated to third coefficient is much better than second term for the conditions of this project (temperatures and pressures ). Correlations must be done on these coefficients of Virial equation in order to reduce the deviation of the calculated molar volume. For second Virial coefficient and by using statistical methods, the correlation was developed and this correlation modified the percent deviation from 7.5525% to 3.5209% by using 89data points for 4 compounds (Cyclo propane, propanol, i-Butane, R.245) and then applied this correlation to 210 data points

The correlation developed to modify the percent deviation of the calculated molar volume of saturated vapor by using Virial truncated to third term gave a relatively acceptable deviation and reduce the deviation from 1.0955% to 0.7899% this correlation developed by using 60 data points for 3 compounds polar and non-polar and applied for 239 data points for 11 compounds (polar and non-polar).

For binary mixtures ,the calculation of the molar volume of saturated vapor done by using three methods .The first method is done by using Virial equation truncated to second term with Virial mixing rule and this gave relatively high deviation from the molar volume obtained from the PVT data the AAD% is 8.3919% for 142 data points for 6 mixtures .The second method is done by using Teja equation with Virial mixing rule ,where the compressibility factor calculated from Teja equation and the pseudo critical properties of each compounds calculated from Virial mixing rule and this gave AAD% is 3.4669% for 142 data points for 6 mixtures ,and this is relatively better than that obtained from the modified Virial truncated to second term .The third method is done by using the modified Virial equation truncated to third term with Virial mixing rule and this method gave the lowest deviation and the best accuracy than other two methods used to calculate the molar volume of saturated vapor for binary mixtures ,the AAD% is 1.4967% for 142 data points (6 mixtures ).

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# CHAPTER ONE

# INTRODUCTION

The saturated vapor density (volume) of the substance represents a point on the saturated vapor envelope of a PVT surface and therefore depicts the limiting value of a gaseous isotherm just before condensation is initiated .Thus ,the saturated vapor state becomes the point of intersection between a super heated gas isotherm and the corresponding vaporizing liquid isotherm .There are many equations of states that calculate the saturated vapor density (volume) . The equations of state are widely used in the prediction of thermodynamic properties of pure fluids and fluid mixtures.

The term equation of state is used to describe an empirically derived function which provides a relation between pressures, temperature, molar volumes and (for mixtures) composition.

Many equations of state can represent the properties of the gas phase, some of them are applicable for the liquid phase only, but the most important category of equations of state that applied in the same form to both gaseous and liquid phases.

Peng and Robinson and Soave –Redlich Kowing equations of states are applicable for both liquid and vapor phases ,and can be used for calculating the molar volumes by calculating the compressibility factor .The accuracy of these equations is good at low ranges of temperatures and pressures but this accuracy is decreased when the ranges of temperatures and pressures are increased .

Virial equation is one of the equations of state that provides a method of describing the gas behavior, it is an important equation for the gas phase because it is not applicable for the liquid phase and its coefficients are related to intermolecular potential energy.

The form of the Virial equation is a power series in the reciprocal molar volume, (1/v).

$$z = 1 + \frac{B}{V} + \frac{C}{V^2} + ... \qquad ...(1.1)$$

Where B,and C are the second and third Virial coefficients respectively.

So, there are many equations to calculate the molar volumes, the methods to be used in this work are based on the experimental data and fitting these data to the equations in terms of suitable parameter.

Pure gases are classified as polar and non polar gases. Non polar gases are classified as:

1. Simple fluids that have zero acentric factor.
2. Quantum gases that have negative acentric factor.
3. Other non polar gases that have positive acentric factor.

Polar gases are classified as:

1. Non hydrogen bonding components as aldehydes.
2. Hydrogen bonding components as water.

The aim of this work is to calculate the molar volume of saturated vapor using many equations and find the best one that gives the lowest deviation (and highest accuracy) and then efforts will be done to modify this equation to obtain if possible an expression that increases the accuracy as much as possible at moderate conditions and ranges of temperatures and pressures, this modification will be tried by using a statistical methods. The same procedures are used for the multi component mixtures.

The saturated vapor volume is necessary for many chemical engineering applications such as separation and distillation and the vapor liquid application processes.

# CHAPTER TWO

# Literature Review

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## 2.1 : THE P-V-T BEHAVIOR OF FLUIDS : [46],[18]

A pure fluid is an equilibrium state when two intensive variables are fixed and all properties are uniform throughout .the PVT behavior of a fluid is usually displayed on a PV diagram on which constant temperature curves, isotherms are drawn, Fig 2.2 shows the general behavior of a pure fluid on these coordinates .Three isotherms are shown ,the critical temperature ,one higher temperature and one lower temperature . Above the critical temperature where no liquid phase can exist ,pressure in monotonic fashion . Below the critical temperature isotherms show discontinuity at the two-phase envelope. To the left of this envelope is the liquid region where it is seen that isotherm is nearly a vertical line showing that the volume of a liquid changes only slightly with large changes in pressure .As the temperature, where liquid and vapor become indistinguishable ,the length of the horizontal segment ,Vg-Vl, approaches zero .This means that at the critical point the critical isotherm exhibits as a point of inflection as in equation (2.1),(2.2).

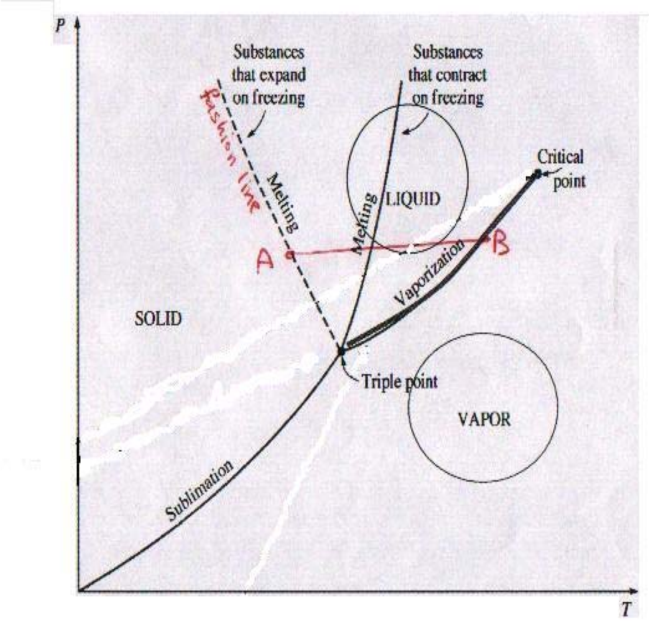
$$\left(\frac{\partial P}{\partial V}\right)_{Tc} = 0 \qquad (2.1)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{Tc} = 0 \tag{2.2}$$

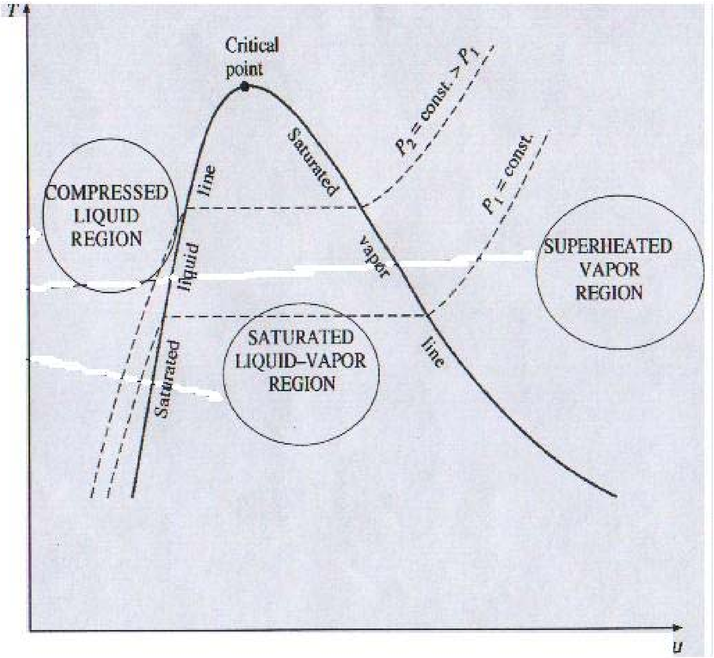
Some times PVT data are plotted as isochors ,lines of constant density ,on a P-T diagram .Fig.(2.1) shows the general behavior of pure fluid on such a plot .

The heavy curve terminating at the critical point C is the vapor pressure curve which separates the vapor and liquid regions .

The experimental determination of PVT data usually follows one of two courses :measurements of pressure as a function of temperature at a series of fixed volume ,and the second course is the measurement of temperature as a function of volume at a series of fixed pressures. .



Figer 2.1 The P-T behavior of the fluid



Figer 2.2 The P-V behavior of the fluid

## 2.2 Saturated vapor density : [7]

The saturated vapor density of a substance represents a point on the saturated vapor envelope of a PVT surface and therefore depicts the limiting value of gaseous isotherm just before condensation is initiated .Thus the saturated vapor state becomes the point of intersection between a superheated gas isotherm and the corresponding vaporizing liquid isotherm **.**

## 2.3 Models for calculating the saturated molar volume of Pure component :

### 2.3.1Caillet and Mathias (1886):

Caillet and Mathias [3] attempted to relate the saturated vapor density with temperature ,their efforts resulted in the formulation of the empirical "rectilinear diameter rule " which states that the mean saturated density is linearly dependent on temperature as follows :

$$\frac{1}{2}(\rho_L + \rho_V) = mT + K \qquad (2.3)$$

Where m and K are constants .

## 2.3.2 Bendict – Web – Rubin model :[42] ,[8]

Using Bendict-Web-Rubin equation of state to give analytical expression for the volume . The vapor pressure data calculated from the modified Antoine equation :

$$P = \frac{RT}{V} + \frac{B0RT - A0 - (C0/T^2)}{V^2} + \frac{bRT - a}{V^3} + \frac{C}{T^2V^3} * \left[ \left( 1 + \frac{\gamma}{V^2} \right)^{\frac{-\gamma}{V^2}} \right] \qquad (2.4)$$

Constants for the B-W-R equation have been determined by using least squares method [47].

Comparison between the density from experimental data and the density resulted from this equation ,for example for i-Pentane the deviation agrees very well ,within 0.2% maximum difference .

## 2.3.3 Hirschfelder model (1958) : [46]

The three expressions reported by Hirschofelder constitute a generalized approach where each relationship is valid over particular region of PVT surface . For 2601 selected values ,this equation of state reproduces the densities with average deviation of 0.48% .These deviations represent considerable improvement over corresponding values obtained from the BWR equation of state and compare with those resulting from the model proposed by Stewart (1981) .This model is qualitatively correct and qualitatively exact and offers the most complete representation for the PVT behavior of fluid.

The compressibility factor of this model is given by the following form :

$$z = 1 + (0.99769Zc - 1)Tr^{0.4} \exp(-0.6161(1 - Tr)^{0.2809}) \qquad \textbf{(2. 5)}$$

Wilsok **(**1982),suggested the following reduced vapor pressure equation:

$$\ln P_R = 4.6334 - \frac{4.5397}{Tr} - \frac{0.22715}{Tr^2} + 0.13114 * Tr^{5.7406} \qquad \textbf{(2.6 )}$$

The two equations above are capable of reproducing the experimental density measurements with an average deviation of 0.83%

## 2.3.4 EDWARD AND THODOS MODEL : [7]

A Relationship was developed between saturated vapor density and reduced temperature, reduced pressure and critical compressibility factor capable of predicting saturated vapor density.

For 276 points considered an average deviation of 1.9% resulted for Tr up to 0.985 .

The equation of EDWARD AND THODOS (1974) for saturated vapor density is :

$$\rho_{rv} = \frac{\Pr}{Tr}\left[ zc + 0.26\Pr + \frac{0.74 - Zc}{(2-\Pr^{3})^{6.33}} \right] \qquad \textbf{(2. 7)}$$

## **2.3.5 HALL AND EUBANK MODEL: [46]**

HALL AND EUBANK (1976) have applied a vapor density equation of the form :

$$\rho_{rs} = 1 \mp k_1 \left|\Delta T\right| \beta + k_2 \mathrm{H} T + k_3 \left|\Delta T\right| (1-\alpha) \qquad (2.8)$$

where k1,k2,and k3 are material constants .The minus sign corresponds to the vapor boundary ,the plus sign corresponds to the liquid boundary .

## **2.3.6 DAVIS and RICE MODEL : [9],[10]**

Experimental values of the density ,together with the saturated vapor densities ,were fitted to a differential regional of Bendict-web-Rubin (DR-BWR) EOS .The method proposed by DAVIS and Rice (1977) is given as :

$$(\rho_{sl} + \rho_{sv}) = a1 + b1(\rho_{sl} + \rho_{sv})^{3} \qquad (2.9\ )$$

where a1 and b1 are different values for each compound and these values are listed in tables .

This equation was tested with many experimental data of saturated densities of many compounds such that for n-butane and n-pentane ,with experimental data from saturated vapor and liquid density measurements of Kay (1945)near the critical point and Liquid and vapor density measurements of Sliwinski (1942)) and the results were acceptable with its error limits to 1% .

### 2.3.7 Peneloux MODEL (1982): [5]

One method that has become quite popular to improve the density prediction from cubic equations of state is called volume shifting and it is a correction to the calculated molar volume .

$$V_{corrected} = V_{EOS} + C \tag{2.10}$$

In this case C is constant . If C is properly selected, then the corrected volume should be an improved estimate of the true molar volume .

### 2.3.8 Mathias MODEL : [5]

Mathias (1989) noted that the volume –shift method of Peneoloux improved the prediction of the density only up to reduced temperatures of about 0.85 .

To improve the prediction over the entire range, Mathias (1989)[9] proposed the following equation:

$$V_{corrected} = V_{EOS} + S + fc\left[\frac{0.41}{0.41 + \delta}\right] \qquad (2.11)$$

where S is constant and $\delta$ is defined as :

$$\delta = -\frac{V^2}{RT}\left(\frac{\partial p}{\partial V}\right)_T \qquad (2.12\ )$$

Finally the function fc was chosen such that the volume shifting procedure calculated the true critical point .for the PR equation this function is given by the following expression:

$$fc = Vc - (3.946\ b + s) \qquad (2.13)$$

### 2.3.9 Riaza and Mansoori MODEL : [14]

The RK equation that is a modification of the Van der Waals equation ,was a considerable improvement over other equations of relatively simple forms at the time of its introduction .Riaza and Mansoori (1993) stated that parameter b for the RK equation is more effective for the volume of the molecules . They modified the parameter b of RK equation by $\beta$ ,that depends on the refractive index of the compound .

$$Z = \frac{v + \gamma b}{v - b} - \frac{av / RT}{T^{\varepsilon}(v + \eta c)(v + \lambda c)} \qquad (2.14\ )$$

where

$$a = \Omega a \alpha R^2 Tc^{(3+\varepsilon)} / pc \quad (2.15)$$

$$b = c = \Omega b * \beta RTc / Pc \quad (2.16)$$

### 2.3.10 ANCILLARY MODEL : [24]

The saturated vapor density is represented by the Ancillary equation (1985) :

$$\frac{\bar{\rho}}{\rho_c} = 1 + N1\theta^{0.38} + N2\theta^{1.22} + N3\theta^{3.3} + N4\theta^{6.9} \quad (2.17)$$

where N1,N2,N3,and N4 are constant values for each refrigerant **.**

The accuracy of this equation tested and compared with accuracy of the equation of state and found its deviation was approximately 0.3% .

This comparison based on the experimental data for many refrigerants such as R-125 where :

N1=-2.8403 ,N2=-7.2738

N3=-21.890 , N4 =-58.82

### 2.3.11 KYONG KUHN PARK MODEL : [31 ]

A saturated vapor density correlation, which relates logarithmic density to the inverse of temperature, is used to fit the saturated vapor density data for 41 pure substances .The equation with 4 terms in it yields an average AAD OF 0.12%,which compares with 0.27% of 5 term conventional equation ,so the performance is improved while the number of terms is reduced . This equation is valid over the entire temperature range from critical point to the triple point.

$$ln\left(\frac{\rho_g}{\rho_c}\right) = \sum_{i=1}^{N} C_i \theta^{ki} \tag{2.18}$$

$$\text{Where } \theta = \frac{1-T}{T_c} \tag{2.19}$$

The four term equation is :

$$\ln\left(\frac{\rho_g}{\rho_c}\right) = C_1\theta^{k1} + C_2\theta^{k2} + C_3\theta^{k3} + C_4\theta^{k4} \tag{2.20}$$

Where $K1 = 1/3 < K2 < K3 < K4$

There are many tables that give the values of K2,K3 and K4 as shown in reference [26] .There is another form of this equation :

$$ln(\frac{\rho_g}{\rho_c}) = \sum_{i=1}^{N} C_i \tau^{ki} \tag{2.21}$$

$$\text{Where } \tau = \frac{T_c}{T-1} \tag{2.22}$$

Four term equation :

$$\ln\left(\frac{\rho_g}{\rho_c}\right) = C_1\tau^{v3} + C_2\tau^{k2} + C_3\tau^{k3} + C_4\tau^{k4} \qquad (2.23)$$

## 2.4 Molar volume for gas mixtures : [38]

No comprehensive tests have been made of all estimation techniques. Generally, errors were found to be less than 2 to 3 percent, except near the critical point or for mixtures containing high polar components in significant concentrations .Recommendations to estimate the molar volume of hydrocarbon gas mixtures (including those component associated with natural gas ,as CO2 and H2S ) , are essentially the same as for pure gases . for small deviations from ideal-gas behavior , the truncated Virial equation is satisfactory . Otherwise values of binary interaction coefficients (Kij's) determined from VLE data can be used in volume calculations. Mixtures molar volume is much less sensitive to Kij values than are VLE calculations .

There are many models that are developed to calculate the molar volume of saturated vapors as follows :

### 2.4.1 Models for truncated Virial equation :

#### 2.4.1.1 PITZ CURL model : [4]

There are many mixing rules that can be used to calculate the molar volume of binary mixtures . Pitz Curl calculated the density of binary mixtures of hydrocarbon gases according to a aforementioned method by using Virial equation truncated to third term .

$$\rho_{cal} = \frac{P}{RT(1 + B_{mix} * \rho_{exp} + C_{mix} * \rho_{exp}^2} \qquad (2.24)$$

### 2.4.1.2GERG method [4]:

This equation is based on three-term truncated Virial equation, it predicts the density of mixtures up to 13 common components of natural gas with an estimated uncertainty of 0.1% :

$$Z = 1 + B_{mix} * \rho_{exp} + C_{mix} * \rho_{exp}^{2} \tag{2.25}$$

$$\rho_{cal} = \frac{P}{ZRT} \tag{2.26}$$

\

## 2.4.2 Methods based on volume –shifting method :

### 2.4.2.1 Peneloux model for mixture :[ 5]

To apply this method to the mixtures, it is assumed that C for the mixture, C mix is the mole fraction weighted as average of the parameters for the pure components.

$$C_{mix} = \sum_{i=1}^{Nc} x_i * C_i \tag{2.27}$$

Then substituting this in the Peneoloux equation:

$$V_{\substack{corrected \\ formixtures}} = V_{EOS} + C_{mix} \tag{2.28}$$

## 2.4.2.2 Mathias model for mixture: [5]

To apply this method to mixtures, it is assumed that:

$$S_{mix} = \sum_{i=1}^{Nc} X_i * S_i \tag{2.29}$$

Then substituting this value in the Mathias equation :

$$V_{\substack{corrected \\ formixture}} = V_{EOS} + S_{mix} + f_c \left[ \frac{0.41}{0.41 + \delta} \right] \tag{2.30}$$

# CHAPTER THREE

# Theories and Definitions

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## 3.1 Equation of state :[ 46],[38]

The term equation of state means an equation that relates volume to pressure and temperature .

The simplest equation of state is ideal gas equation :

$$PV=nRT \qquad (3.1)$$

This equation is only true at zero pressure .

Many equation of state of varying degrees of complexity have been proposed and while a few have some basis in molecular theory ,all are used empirically .the advantages offered by equation of state are mainly data reduction and ease of use in subsequent calculations .

A large number of PVT equations have been developed to describe non-ideal or real gas behavior.

## 3.2 Classification of Equations of state : [4]

The need for accurate prediction of the thermodynamic properties of many fluids and mixtures has led to the development of equations of state with different forms .before proceeding with the discussion of specific equations of state it is useful to make some general classification in to which they may fall.

The main types of equation of state may be classified conveniently according to their mathematical form as follows:

### 3.2.1 :Standerd P-V-T forms :

This type of equation of state may be written for a pure fluid as :

$$P=p(T,V_m) \text{ or } Z=Z(T,V_m) \qquad (3.2)$$

a. Truncated Virial equation in which p is given by polynomial in $1/V_m$ with temperature and composition dependent coefficients.

b. Complex empirical equations: which represent p by some combination of polynomial and other term (e.g. BWR and related equations).

It is also possible to invert the functional relationships to give $V_m$ or Z in terms of T,P and the composition variables .However ,although this choice of independent variables may be convenient in the analysis of experimental data for a single fluid phase ,it is almost never used in thermodynamic modeling .

### 3.2.2 Fundamental form :

A fundamental equation gives one of the state functions in terms of its natural independent variables .The most common choice is the molar Helmoltz energy Am as a function of temperature and the molar volume .

$$A_m = A_m \ (T,V_m) \qquad (3.3)$$

In order to achieve a precise representation of the experimental data over a wide range of conditions ,the structure of the functional relationship is often very complicated ,Am is split into perfect gas and residual parts which are parameterized separately .

Although accurate fundamental equations of state exist for only about twenty of the most important pure fluids ,one or more of these may form the basis of a corresponding states treatment of the residual properties of a wide variety of other fluids including mixtures .

## 3.3 Law of corresponding states :[38]

The principle of corresponding states establishes a connection between the configuration integrals of different substances and thereby allows each of configurationally and residual thermodynamic properties are related in a very simple way .

The assumption in applying corresponding states is that the PVT behavior of the mixture will be the same as that of pure component whose critical temperature and pressure are equal to the pseudo critical temperature and pressure of the mixture .

To apply the corresponding states to the mixture ,one must determine appropriate scaling factor.

### 3.3.1 Two parameter correlations (spherical molecules): [ 38],[4]

The non ideality of the gas is conveniently expressed by the compressibility factor z .

The compressibility factor is often correlated with Tr,Pr as :

Z=f(Tr,Pr) (3.4)

equation (3.6) is an example of the law of corresponding states in this equation Vr is not defined in the usual manner ,that is ,(V/Vc),but instead is an "ideal reduced volume "given by :

$$Vri = \frac{V}{RTc / pc} \tag{3.5}$$

This law ,though not exact ,suggest that reduced properties of all fluids are essentially the same if compared at equal reduced temperature and pressures :

for PVT properties ,this law gives :

$$V_{r=} \frac{V}{V_C} = \frac{(Z / Z_C)(T / T_C)}{p / p_C} = f_1(\text{Tr,Pr}) \tag{3.6}$$

$$Z = Zc\ f_2(\text{Tr,Pr}) \tag{3.7}$$

Except for monatomic gases ,highly polar fluids ,and fluids composed of large molecules ,value of zc for most organic compounds range form .27 to .29 if it is assumed to be a constant .

## 3.3.2 Three parameter correlations (non spherical molecules):[ 51],[39]

In general successful Eos have included one or more dimensionless characteristic parameters in to the function the first step in accomplishing this is to introduce a third parameter ; usually it is related to the vapor pressure ,Pvp ,or volumetric property at or near the critical point .

Historically several different third parameters were introduced at about the same time but the most popular have been zc (lyderson,1955) and the acentric factor w(Pitzer and Curl 1955,1057 ab).Lyderson and later revision by Hougan ,et .al.(1959) tabulated z (and reduced thermodynamic properties ) at increment of (Tr) and (Pr)for different values of zc in practice, this correlation has been used only occasionally ,such as by Edward and Thodos (1974)for estimating saturated vapor densities of non polar compounds .

The much more commonly used third parameter is the acentric factor . for example the compressibility factor was given as :

$$z = z0\,(Tr\ ,\ \mathrm{Pr}) + \omega\, z1\,(Tr\ ,\ \mathrm{Pr}) \tag{3.8}$$

## 3.3.3 Four parameter model (polar molecules) :[ 4]

WU and Stiel[52]modified the Lee-kesler[24]scheme by incorporating the polar substance water as a third reference fluid .The compression factor is given by :

$$z = z0 + \omega z1 + \gamma z2 \tag{3.9}$$

Where $\gamma$ is a fourth parameter characteristic of polar molecules . Here ,z0 and z1 are given by the original Lee-kesler scheme ,while z2 was defined in terms of the compression factor Zw of water by means of the equation :

$$z2 = z\omega - (z0 + \omega wz1) \tag{3.10}$$

In which $\omega$ =0.344 is the acentric factor of the water .

This definition ensures that for non-polar systems ,the compression factor reverts to the Lee-Kesler formulation while ,for $(\gamma = 1)$ ,eq .(3.9) reduced to the compression factor zw of water .

WU and Stile argued that a definition based on the molar volume of the saturated liquid at specified reduced temperature had the desired properties .thus they defined $\gamma$ by means of equation :

$$vr\sigma = .1326 - .0547 - .0222\gamma \tag{3.11}$$

Where $V_r^{\delta} = V_m^{\delta}(\frac{P_C}{RT_C})$ (3.12)

## 3.4 Van der waals Equation : [22]

Undoubtedly ,the best known equation of state is the Van der Waals equation :

$$p = \frac{RT}{V - b} - \frac{a}{V^2} \tag{3.13}$$

according to Van der Waals derivation .The term (a/v2)accounts for attractive forces between molecules ,and b is a correction for the volume occupied by the molecules themselves .This equation is cubic in v ,and at temperatures below the critical there are three real root ,as indicated in fig (2.1) it can be shown that the segment of the isotherm lying between A and B represents unstable state ,and therefore in the pressure range PA to PB there are only two values of v which correspond to stable states.

While this suggests the application of Van der waals equation to calculations in the two phase region ,the form of the equation is far too simple to be capable of closely representing the isotherm in this region.

When an equation of state contain only two parameters in the term of critical temperature and pressure. Evaluating these derivatives and the equation of state at the critical point results in three equations involving a,b,tc,pc and Vc .Because Vc is not always available .It can be eliminated at the remaining equations solved for a ,and b in terms of Tc and Pc .for Van der waals equation this results in :

$$a = \frac{27R^2T_C^2}{64P_C}$$

$$, \ b = \frac{RTc}{8Pc} \qquad (3.14)$$

Because Tc and Pc are known as for many substances ,it is convenient to evaluate parameters in this manner .

## 3.5 Lee-kesler Equation : [38] ,[2]

This is one of the equations of state that calculates the compressibility factor as :

$$z = z0 + \frac{\omega}{\omega(r)}(z(r) - z(0)) \tag{3.15}$$

The equation is based on the law of corresponding states of three parameter it states that there are two fluids ,simple one and reference one ,and the compressibility factor of any interesting fluid z(0) and the reference fluid z ( r) have been represented by the following reduced form of a modified BWR equation of state :

$$Z = \frac{\Pr * Vr}{Tr} = 1 + \frac{B}{Vr} + \frac{C}{Vr^2} + \frac{D}{Vr^3} + \frac{c4}{Tr^3 * Vr^2}(B + \frac{\gamma}{Vr^2}) * \exp(-\frac{\gamma}{Vr^2}) \tag{3.16}$$

$$B = b1 - \frac{b2}{tr} - \frac{b3}{tr^2} - \frac{b4}{tr^3} \tag{3.31}$$

$$C = c1 - \frac{c2}{tr} + \frac{c3}{tr^3} \tag{3.32}$$

$$D = d1 + \frac{d2}{tr} \tag{3.33}$$

## 3.11 REDLICH –KWONG EQUATION OF STATE : [49],[28]

Redlich and Kwong were very much concerned about the limiting behavior of the EOS .They wanted correct representation at low density and at high density and proposed the following equation :

$$\alpha(T) = a_C / T^{0.5}, ac = \Omega aR^2Tc^{2.5} / Pc, \tag{3.34}$$

$$\Omega a = .4278, \Omega b = .0867 \tag{3.35}$$

$$b = \Omega bRTc / Pc \tag{3.36}$$

This equation did not have strong theoretical background but proved to give good results for many gaseous systems ,it should be also mentioned that ,when Redlich and Kwong proposed their celebrated equation of state they were inserted in developing a good equation for gases only .

## 3.12 SOAVE EQUATION OF STATE : [4],[16]

soave modification of Redlich –kowing equation involved replacing the term $(a/T^{0.5})$ by amore complicated function of temperature ,$a\alpha(T)$ ,incorporating the acentric factor ,the form of the cubic equation of state is as follow :

$$p = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + \omega b^2} \tag{3.37}$$

an equivalent form of equation is :

$$Z^3 - (1 + B^* - UB^*)Z^2 + (A^* + \omega B^{*2} - 2UB^{*2} - 2UB^*)Z - A^*B^* - \omega B^{*2} - \omega B^{*3})$$

Where $A^* = \frac{aP}{R^2T^2}$ (3.38 )

And $B^* = \frac{bp}{RT}$ (3. 39)

U=1 , $\omega = 0$ (3. 40)

$$b = \frac{0.08664RTc}{Pc} \tag{3.41}$$

and $a = \frac{0.42748 \ * R^2 \ * Tc^2}{Pc} \left[1 + \ fw(1 - Tr^{0.5})\right]^2$ (3.42)

$fw = 0.48 + 1.574\omega - 0.176\omega^2$ (3.43 )

The form of this function was devised primarily to obtain a good representation of the vapor pressure curve for a number of hydrocarbons .Subsequently ,this term was modified further by Graboski and Daubert

## 3.13Peng -Robinson equation of state : [4],[52]

Peng and Robinson equation is structurally rather similar to the RKS equation ,requires only the critical constants and the acentric factor for its application to pure fluids .

The form of the cubic equation as follows :

$$p = \frac{RT}{V - b} - \frac{a}{V^2 + ubV + \omega b^2} \tag{3. 44}$$

and the equivalent form :

$$z^3 - (1 + B* - uB*)z^2 + (A* + \omega B*^2 - uB* - uB*^2)z - A*B* - \omega B*^2 - \omega B*^3 = 0$$

(3.45 )

wfere $A* = \frac{aP}{R^2T^2}$ (3. 46)

and $B* = \frac{bP}{RT}$ (3.47 )

u=2, $\omega = -1$ (3.48 )

$$a = \frac{0.07780RTc}{Pc} \tag{3. 49}$$

$$b = \frac{0.45724R^2Tc^2}{Pc}\left[1 + \ fw(1 - Tr^{0.5})\right]^2 \tag{3.50 }$$

$$fw = 0.37464 + 1.5226\omega - 0.26992\omega^2 \qquad (3.51)$$

Soave equation together with that of peng-Robinson are today probably the two most widely used equations of state. Because of the way in which the attractive term have been tailored to achieve a fit to vapor pressure data ,and the incorporation of the acentric factor ,these equations usually permit VLE calculations to be made with acceptable accuracy.

## 3.14VIRIAL EQUATION OF STATE : [ 4],[46],[2],[43]

Virial equation of state is one of the most important equations of state which are used to describe the PVT properties of the fluids ,and it is initially developed in 1901 by Kamerlingh Onnes .

The coefficients of the Virial series ,known as Virial coefficients ,they are function of temperature and composition but not of density .the form of Virial equation is as follows:

$$z = \frac{pv}{RT} = 1 + \frac{B}{v} + \frac{C}{v2} + .... \qquad (3.52)$$

this equation gives a great use at low to moderate pressure where it can be safely truncated after the second term .

Many other equations of state have been proposed for gases ,but the Virial equation is the only one having a firm basis in theory .the methods of statistical mechanics allow derivation of the Virial equation and provide physical significance to Virial coefficients .

### 3.14.1 Second Virial coefficients: [38],[39],[2],[48]

Second Virial coefficient can be determine from experimental data mostly complied by Dymond and smith (1968) or calculated with a suitable correlation.

It is well known that accurate procedures are required for the calculation of second Virial coefficient of gases .One of the correlations used to compute the second Virial coefficient is that based on semi empirical equations, this semi empirical estimation has the major advantage when theoretical approaches are tedious. Though it is possible to derive correlations from the original and modified Redlich kowing equations and molecular theory ,such expressions are usually more complicated than those cited ,even for simple substances ,and so they have not been evaluated ,we give an explanation for one of the practical techniques for estimating values for most types of pure substances (Tsonpoulos,1974).

#### 3.14.1.1 Tsonpolous correlation :

A new correlation of second Virial coefficient of both polar and non polar system is presented :

$$\frac{BPc}{RTc} = B0 + \omega B1 + B2 \qquad (3.53)$$

$$B0 = .1445 - \frac{0.33}{Tr} - \frac{0.1385}{Tr^{2}} - \frac{0.0121}{Tr^{3}} - \frac{0.000607}{Tr^{8}} \qquad (3.54)$$

$$B1 = 0.0637 + \frac{0.331}{Tr^2} - \frac{0.423}{Tr^3} - \frac{0.008}{Tr^8} \qquad (3.\ 55)$$

where the polar term B2 is given by :

$$B2 = \frac{a}{Tr^6} \qquad (3.56\ )$$

This Equation can be applied only for non-hydrogen bonding compounds .in the case of ketones ,a is best expressed as a linear function of MR :

a= -0.00020483* MR (3.57)

And for ethers :

a=-12.63147+2.09681*ln MR (3.58 )

For alcohols ,a is constant and equal to 0.0878 .

For hydrogen bonding compounds the polar term contains two parameters :

$$B2 = \frac{a}{Tr^6} - \frac{b}{Tr^8} \qquad (3.59)$$

The value of a for non hydrogen bonding compounds and the value of a and b for hydrogen bonding compounds are given in tables .

The value of b for hydrogen bonding compound is expressed as function of MR as :

B=0.00908+0.0006957*MR (3.60 )

CROSS COEFFICIENTS FOR MIXTURES :

The second Virial cross coefficient Bij has the same temperature dependence that Bii and Bjj have ,but the parameters to be used are Tcij, $\omega ij$ ,aij and bij .

The mixing rule are given below :

$$Tcij = (1 - Kij)\sqrt{Tci.Tcj} \qquad (3.\ 61)$$

$$Pcij = \frac{4Tcij\left[\frac{Pci*Vci}{Tci} + \frac{Pcj*Vcj}{Tcj}\right]}{(Vci1/3 + Vcj^{1/3})^{3}} \qquad (3.62\ )$$

$$\omega ij = 0.5(\omega i + \omega j) \qquad (3.63\ )$$

For polar/non polar binary mixture ,Bij is assumed to have no polar term :aij=0 (3.64 )

bij=0 (3.65 )

For polar/polar binary mixtures, the polar contribution to bij is calculated by assuming that :

aij= 0.5(ai+aj) (3.66 )

bij=0.5(bi+bj) (3.67 )

### 3.14.2 Third virial coefficient: [39],[30],[17]

It is possible to derive the third Virial coefficient correlations from molecular theory ,but these are not very successful .

The principle theoretical problem is that the trio intermolecular potential includes significant contributions that can not be determined from their pair potentials that describe second Virial coefficients .Thus ,CSP is also used for calculating c ,though the range of substances considered has been much more limited .

This means that the users often must choose to use a complete equation of state .

For high pressure above 15 bar ,eq.(3.52 ) may be truncated after three terms .There are many correlations for third Virial coefficient such that Orbey Vera correlation .

## 3.14.2.1ORBEY VERA CORRELATION : [39]

An empirical correlation for the third coefficient of non polar gases was developed .the correlation required acknowledge of the critical temperature ,critical pressure ,acentric factor of the component for the prediction of the third Virial coefficient in the absence of the experimental data . The third Virial coefficient C was correlated as a function of acentric factor :

$$\frac{CcPc^{2}}{(RTc)^{2}} = 0.03526 + 0.02566\ \omega \qquad (3.68)$$

$$C0(Tr) = 0.399 + \frac{.68972}{Tr^{2.8}} - \frac{.08872}{Tr^{10.5}} \qquad (3.69)$$

$$\overline{C} = \omega * (-0.037 + \frac{0.04}{Tr^{3}} - \frac{0.003}{Tr^{6}}) \qquad (3.70)$$

Combination of the two equations above gives the final form for the generalized empirical correlation :

$$\frac{Cc*Pc^{2}}{(RTc)^{2}}=C0+\omega\overline{C} \tag{3. 71}$$

Where

$$C0 = 0.01407 + \frac{0.02432}{Tr^{\,2.8}} - \frac{0.00313}{Tr^{\,10.5}} \tag{3. 72}$$

$$\overline{C} = -0.02676 + \frac{0.0177}{Tr^{\,2.8}} + \frac{0.04}{Tr^{\,3}} - \frac{0.003}{Tr^{\,6}} - \frac{0.00228}{Tr^{\,10.5}} \tag{3. 73}$$

The correlation applied in this work may be applied to quantum gases ,the following temperature dependent effective critical parameter :

$$Tc = \frac{Tc\ 0}{1+\frac{21\ .8}{mt}} \tag{3. 74}$$

$$Pc = \frac{Pc\ 0}{1+\frac{44\ .2}{mt}} \tag{3.75 }$$

For mixture :

The third coefficient of a mixture was given by the following rigorous expression :

$$C = \sum_i \sum_j \sum_k yi * yj * yk * Cijk \tag{3.76}$$

## 3.15 MIXING RULES : [4]

### 3.15.1Mixing rule for Virial coefficients :

The second Virial coefficient of multicomponent gas mixture is given exactly by quadratic expression in the mole fractions :

$$Bmix(T) = \sum_{i=1}^{v}\sum_{j=1}^{v} xi.xjBij(T) \tag{3.77}$$

For binary mixture this reduced to :

$$Bmix\ (T) = x_{12} B_{11}(T) + 2x_1 x2 B_{12}(T) + x_{22} B_{22}(T) \tag{3.78}$$

Bij is defined as the second Virial coefficient corresponding to the potential energy function $\phi\ ij\ (r)$ which describes the interaction of one molecule of species I with one of species j .Bij is also referred to as the cross Virial coefficient ,the cross Virial coefficient ,or the mixed Virial coefficient .

To calculate the mixture interaction Virials Bij ,combination rules must be devised to obtain Tcij ,Pcij,and wij .this problem have been discussed from a theoretical point of view by land and Chappelear [25] and Ramaiah and Stiel [35] .For typical engineering calculations involving normal fluids ,the following simple rules are useful [44]:

$$Tc_{ij} = (Tc_i.Tc_j)^{0.5} * (1 - K_{ij}) \tag{3.79 }$$

$$Vcij = \left[ \frac{Vci^{1/3}.Vcj^{1/3}}{2} \right]^2 \quad (3.80)$$

$$Zcij = \frac{Zci + Zcj}{2} \quad (3.81\ )$$

$$\omega\, ij = \frac{\omega\, i + \omega\, j}{2} \quad (3.82)$$

$$Pcij = \frac{ZcijRTcij}{Vcij} \quad (3.\ 83)$$

$$Kij = 1 - \frac{8(Vci.Vcj)^{0.5}}{(Vci^{1/3} + Vcj^{1/3})^3} \quad (3.\ 84)$$

The third Virial coefficient of multicomponent mixture is cubic in the mole fractions and given by :

$$Cmix(T) = \sum_{i=1}^{v} \sum_{j=1}^{v} \sum_{k=1}^{v} xi.xj.xk.Cijk(T) \quad (3.85)$$

Here , Ciii is the third Virial coefficient of pure I ,and Cijk is the contribution that arises from the interaction of one molecule of species I ,one molecule of species j and one molecule of species k .

Depending upon the availability of experimental data ,one of two general approaches may be adopted when dealing with multicomponent mixtures .one can fit the experimental data to the viral equation truncated to the third coefficient and obtain each of the possible pure component and interaction Virial coefficients .

This requires experimental data for each of the possible binary and ternary combinations of the components .

### 3.15.2 Teja equation mixing rule:[38]

Teja equation which was derived to calculate the compressibility factor for mixture .its used primarily on hydrocarbons for both vapor and liquid phases for calculating molar volumes of mixtures . Teja method needs to evaluate the compressibility factor Zr1,Zr2 can be calculated from any equation of state for pure saturated vapors like Virial equation but at the same reduced temperature (Trm) and reduced pressure (Prm) of mixture The Teja equation is :

$$Z = Zr1 + \frac{\omega - \omega_{r1}}{\omega_{r2} - \omega_{r1}}(Zr2 - Zr1) \qquad (3.86\ )$$

# CHAPTER FOUR

# Investigation and Development

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## 4.1 investigation of the equations of state :

Vapor densities can be calculated from equations of state. Usually the accuracy of some equations of state to calculate the saturated molar volumes of pure components is not satisfactory . on the other hand the accuracy of many models of equations of state are not good enough for mixtures, mainly due to the problems in formulating the mixing rule .

It is well known fact that the evaluation of any correlation or prediction method is done by comparison of the results obtained from the correlation with those results obtained from the experimental data which will measure the accuracy of this prediction .The experimental data needed in this prediction is PVT data for pure components and PVTX for mixtures at saturation conditions .

Table 4.1 :Non-polar compounds PVT experimental data.

| Compounds | Temp.range(k) | Press.range(bar) | No.of data points | Ref. |
|---|---|---|---|---|
| n-pentane | 469.8-305.37 | 33.1-.7605 | 11 | 8 |
| Carbon dioxide | 304.2-212.94 | 73.815-4.3701 | 10 | 7 |

| | | | | |
|---|---|---|---|---|
| Carbon monoxide | 131.705-73.26 | 31.202-.3415 | 12 | 7 |
| Ref.410 | 173.15-204.15 | 0.037-0.382 | 32 | 19 |
| n-butane | 272.67-420 | 1.01325-34.946 | 25 | 8 |
| Neopentane | 282.628-431 | 1.01325-30.632 | 23 | 36 |
| Cyclo propane | 357.03-380.46 | 44.4155-71.058 | 28 | 26 |
| i-pentane | 255.372-365.92 | 0.1502-601980 | 21 | 7 |
| Ref.245 | 232.59-333.705 | 0.3493-3.005 | 16 | 42 |
| i-butane | 261.32-400 | 1.01325-301927 | 21 | 8 |

Table 4.2 :Polar compounds PVT experimental data .

| Compound | Temp.range(k) | Press.range(bar) | No.of data points | Ref. |
|---|---|---|---|---|
| Water | 263.15-305.37 | 0.00286-1.0505 | 23 | 6 |
| Propanol | 304.2-212.94 | 0.02683-41.255 | 24 | 29 |
| Propyl alcohol | 277.59-377.59 | 0.08-19.078 | 20 | 25 |
| ammonia | 357.03-394.91 | 45-94 | 33 | 13 |

There are several equations of state that are used to describe the thermodynamic properties of the fluids ,such as Lee-Kesler ,Soave ,Peng Robinson ,Truncated Virial equation, and many other equations of state

.These equations are considered the most important and accurate equations that are used to determined the thermodynamic properties of the fluids (liquid and vapor phases ) .

### 4.1.1 Lee-Kesler equation of state :

The use of Lee-Kesler equation in this moderate conditions is not accurate, the accuracy of this equation can be much better at expanded ranges of temperatures and pressures . The results obtained from this equation are listed in table 4.3 for 3 pure compounds only because the absolute average deviation obtained from this equation is very high as shown in table 4.3 :

Table 4.3 : The AAD% of Lee-Kesler from the experimental data .

| compounds | No.of data points | AAD% |
|---|---|---|
| Water | 23 | 70.0209 |
| Cyclo propane | 28 | 55.1232 |
| i-pentane | 21 | 63.8654 |
| | | AAD%=62.432 |

### 4.1.2 : Soave equation of state .

Soave equation (1972) is a modification of Redlich-Kwong equation . It is derived primarily to obtain a good representation of vapor pressure curve for a number of hydrocarbons without any constraints on the densities of the co-existing phases . This equation reforms best for height by hydrocarbons and other small non-polar molecules . The results obtained when using this equation to calculate the molar volumes of saturated vapor of pure non-polar compounds were not very satisfactory , however they were better than when using Lee-Kesler method . The results using this equation are shown in table 4.4.

Table 4.4 :The AAD% of Soave from the experimental data .

| compounds | No.of data points | AAD% |
|---|---|---|
| n-pentane | 11 | 38.8108 |
| Carbon monoxide | 10 | 34.3104 |
| Ref.410 | 12 | 0.7255 |
| Carbon dioxide | 32 | 1.7775 |
| Water | 23 | 0.4275 |
| n-Butane | 25 | 15.1264 |
| n-Propanol | 24 | 5.6818 |
| Propylalcohol | 20 | 1.5026 |
| Neopentane | 23 | 43.084 |
| Cyclopropane | 28 | 25.8715 |
| I-pentane | 21 | 2.4031 |
| Ref.245 | 16 | 3.5006 |
| Ammonia | 33 | 24.4484 |
| I-butane | 21 | 26.6583 |
| **AA%D** | **299** | **15.3125** |

### 4.1.3 Peng-Robinson equation of state :

Peng Robinson equation (1976) is structurally rather similar to the RKS equation and like the RKS, requires only the critical constants and the acentric factor for the application to a pure fluid. The Soave and Peng – Robinson equations are roughly of equal reliability although the representation of PVT data in vicinity of the critical point is better with the Peng –Robinson equation. The results of using Peng –Robinson equation to calculate the molar volumes of saturated vapor for pure non-polar compounds are shown in table 4.5. The table indicates that the overall average deviation is somewhat better than in case of using RKS equation but still was not very satisfactory.

Table 4.5 :The AAD% of Peng –Robinson from the experimental data .

| compounds | No.of points | AAD% | |
|---|---|---|---|
| n-pentane | 11 | 18.0767 | |
| Carbon monoxide | 10 | 33.0754 | |
| Ref.410 | 12 | 0.5528 | |
| Carbon monoxide | 32 | 11.0508 | |
| Water | 23 | 0.4414 | |
| n-Butane | 25 | 15.072 | |
| n-Propanol | 24 | 6.5217 | |
| Propyl Alcohol | 20 | 1.14222 | |
| Neopentane | 23 | 32.0546 | |
| Cyclo propane | 28 | 26.191 | |
| I-pentane | 21 | 1.14222 | |
| Ref.245 | 16 | 1.6895 | |
| Ammonia | 33 | 24.3876 | |
| I-butane | 21 | 24.1598 | |
| AA%D | 299 | 14.3476 | |

### 4.1.4 Truncated Virial equation of state :

Truncated Viral equation is one of the most important equations of state that are used to describe the PVT properties of the vapor phase .It is found that truncated Virial equation is the best equation to calculate the molar volumes of the saturated vapor, Virial equation truncated to the second coefficient,and Virial equation truncated to the third coefficient gives very accurate results that reduced the average deviation from the previous equations of state as considered in table 4.6 .

Table 4.6 : The AAD% of Virial truncated to second and third coefficient from the experimental data .

| compounds | No.of Data points | AA%D truncated at B | AA%D truncated at C |
|---|---|---|---|
| n-pentane | 11 | 9.9576 | 0.9088 |
| Carbon monoxide | 10 | 6.190603 | 1.5539 |
| Carbon dioxide | 12 | 25.7386 | 0.5922 |
| Ref.410 | 32 | 0.42185 | 0.6737 |
| Water | 23 | 0.5425 | 0.1884 |
| n-Butane | 25 | 15.072 | 1.1236 |
| n-Propanol | 24 | 6.5217 | 1.4087 |
| Propylalcohol | 20 | 1.1945 | 0.8735 |
| Neopentane | 23 | 32.0546 | 1.7228 |
| Cyclopropane | 28 | 9.2764 | 1.8200 |
| I-pentane | 21 | 0.3274 | 1.6740 |
| Ref.245 | 16 | 0.9546 | 0.50607 |
| Ammonia | 33 | 3.4504 | 0.9296 |
| I-butane | 21 | 2.9531 | 1.19848 |
| **AA%D** | **299** | **7.5525** | **1.0955** |

The comparison in appendix C indicates that Soave and Peng – Robinson accuracy increase when temperature and pressure range decreases and the equation losses the accuracy when calculating for higher temperatures and pressures . This finding is shown clearly when observing that the Virial equation results are closer to the experimental PVT data. It was found that the accuracy gain is dependent on the number of terms in the truncated Virial equation used in the calculations .

The compressibility factor explicit Virial equation of state ,truncated after the second Virial coefficient is a useful expression for the calculation of thermodynamic properties of gases at conditions such that the reduced volume is greater than 2 . The addition of the third Virial coefficient extended the applicability of the Virial equation to conditions of temperatures and pressures for which the reduced volume is greater than 1.3 .(31)

## 4.2 CHOICE OF THE VIRIAL EQUATION :

It is known that there are many forms of Virial equation .it Is not easy to choose any form of them. Some of these forms can not be utilized and require the availability of the experimental data that enables to fit the forms of the equations to be constructed .Other forms of the Virial equation mentioned were so mathematically complicated as to render the control on its form or coefficients is very difficult.

However, one of these forms depends on the law of corresponding states was found relatively easy. Particular instances of this form is of Orbey and Tsonpoulos which were applied to compounds at moderate condition .This form is used in this work.

## 4.3 DEVELOPMENT OF THE CORRELATION :

The results indicate clearly that when using Virial equation of state to predict the saturated vapor volume of the compounds ,the deviations from experimental data are much less (more accurate results ) than when using other equations .

In order to build a general idea about the results obtained from the Virial equation ,it was applied to some of the compounds that are listed in table (4.1) and (4.2) .It was found that the effect of including third Virial coefficient results in increasing the accuracy for higher ranges of temperatures and pressures . It means that the second Virial coefficient is very accurate at pressure range up to 15 bar , when the pressure increases the accuracy when using only the second Virial coefficient (B) decreases . When including also the third Virial coefficient (C) the accuracy remains good at higher pressure ranges .The effect of the pressure on the accuracy of Virial equation is illustrated in appendix C .

### 4.3.1 CORRELATION OF SECOND VIRIAL COEFFICIENT:

Table (4.6) indicates that for most of the compounds, the deviations occurred while introducing the third Virial coefficient (C) is generally less than when retaining the second coefficient (B) only .For the second Virial coefficient the generalized correlation of Tsonpoulos was developed:

$$B = \left(\frac{R * Tc}{Pc}\right)(B0 + \omega B1) \qquad \ldots(4.1)$$

Where :

$$B0 = 0.1445 - \frac{0.33}{Tr} - \frac{0.1385}{Tr^2} - \frac{0.0121}{Tr^3} - \frac{0.000607}{Tr^8} \qquad \ldots(4.2)$$

$$B1 = 0.0637 + \frac{0.331}{Tr^2} - \frac{0.423}{Tr^3} - \frac{0.008}{Tr^8} \qquad \ldots(4.3)$$

Using experimental data to calculate B(eq.4.1) and then B0 (eq.4.2),writing B0 as function of polynomial series :

$$B0 = A1 + \frac{A2}{Tr^{A3}} + \frac{A4}{Tr^{A5}} + \frac{A6}{Tr^{A7}} + \frac{A8}{Tr^{A9}} \qquad \ldots(4.4)$$

With R=0.9988 ,where R is the correlation coefficient of this fitting .

Substituting B0 values obtained from experimental data and Tr , the coefficients A1,A2,A3,A4,A5,A6,A7,A8 and A9 were evaluated using statistical methods .

TABLE 4.7 : Values of coefficients in equation 4.4 obtained from experimental data

| Coefficient | Value | Coefficient | value |
|---|---|---|---|
| A1 | 0.1258 | A5 | 2.311 |
| A2 | -0.3017 | A6 | -0.00574 |
| A3 | 1 | A7 | 7.85 |
| A4 | -0.1258 | | |

Using the same procedure to evaluate the coefficients n equation 4.5

$$B^1 = A1 + \frac{A2}{Tr^{A3}} + \frac{A4}{Tr^{A5}} + \frac{A6}{Tr^{A7}} \tag{4.5}$$

TABLE 4.8: Values of coefficients in equation 4.5 obtained from experimental data .

| Coefficient | Value | Coefficient | value |
|---|---|---|---|
| A1 | 0.05257 | A5 | 3 |
| A2 | 0.3575 | A6 | -0.002184 |
| A3 | 1.8 | A7 | 7.85 |
| A4 | -0.47155 | | |

About 70 data points for three compounds were used in this fitting ,(I-Pentane ,Cyclo Propane , and I-Butane ),they contain 28 points for polar compounds and 42 points for non-polar compounds .

### 4.3.3 Correlation of third Virial coefficient :

The third Virial coefficient was taken from Orbey and Vera correlation as follows:

$$C = \left( \frac{R * Tc}{Pc} \right)^2 (C0 + \omega C1) \qquad \ldots(4.6)$$

Where:

$$C0 = 0.01407 + \frac{0.02432}{Tr^{2.8}} - \frac{0.00313}{Tr^{10.5}} \qquad \ldots(4.7)$$

$$C1 = -0.02676 + \frac{0.0177}{Tr^{2.8}} + \frac{0.04}{Tr^{3}} - \frac{0.003}{Tr^{6}} - \frac{0.00228}{Tr^{10.5}} \qquad \ldots(4.8)$$

C can be calculated from experimental data, and C0 obtained as:

$$C = \left(\frac{RTc}{Pc}\right)^{2} * \left(C0 + \omega c1\right)$$

Inserting the values of C0 from experimental data and Tr of 46 points in the computer program and by using statistical methods calculating the coefficients of the following equation can be determined :

$$c0 = A1 + \frac{A2}{Tr^{A3}} + \frac{A4}{Tr^{A5}} + \frac{A6}{Tr^{A7}} \qquad (4.9)$$

TABLE 4.9: Values of coefficients in equation 4.9 obtained from experimental data .

| Coefficient | Value | Coefficient | Value |
|---|---|---|---|
| A1 | -42.98302 | A5 | 0.01 |
| A2 | 0.15025 | A6 | -0.00369 |
| A3 | 2 | A7 | 10 |
| A4 | -0.507 | | |

By using the same procedure to calculate the coefficients of the following equation were calculated :

$$C1 = A1 + \frac{A2}{Tr^{A3}} + \frac{A4}{Tr^{A5}} + \frac{A6}{Tr^{A7}} \qquad (4.10)$$

TABLE 4.10: Values of coefficients in equation 4.10 obtained from experimental data .

| coefficient | Value | Coefficient | Value |
|---|---|---|---|
| A1 | 0.022501 | A5 | 5.5 |
| A2 | 1.26968 | A6 | -0.75663 |
| A3 | 5 | A7 | 4.4 |
| A4 | -0.507 | | |

The modified Virial equations truncated to second Virial coefficient with :

$$B0m = 0.1258 - \frac{0.3017}{Tr} - \frac{0.1258}{Tr^{2.31}} - \frac{0.01325}{Tr^{3.21}} - \frac{0.005748}{Tr^{7.85}}$$

$$B1m = 0.05257 + \frac{0.3575}{Tr^{1.8}} - \frac{0.47155}{Tr^{3}} - \frac{0.002184}{Tr^{7.85}}$$

And the modified Virial equation truncated to third Virial coefficients with :

$$C0 = 0.01407 + \frac{0.02432}{Tr^{2.8}} - \frac{0.00313}{Tr^{10.5}}$$

$$C1m = 0.022501 + \frac{1.265968}{Tr^{5}} - \frac{0.507}{Tr^{5.5}} - \frac{0.75663}{Tr^{4.4}}$$

These modified Virial equations can be considered as generalized equations to predict the molar volume of saturated vapor for pure polar and non-polar compounds .

Table 4.6 : The AAD% of modified Virial truncated to second and third coefficient from the experimental data .

| compounds | No.of points | AA%D truncated at B | AA%D truncated at C |
|---|---|---|---|
| n-pentane | 11 | 9.9576 | 0.9088 |
| Carbon monoxide | 10 | 6.190603 | 0.5922 |
| Carbon dioxide | 12 | 25.73869 | 0.67376 |
| Ref.410 | 32 | 0.42185 | 0.9537 |
| Water | 23 | 0.542523 | 0.1884 |
| n-Butane | 25 | 5.0164 | 1.1236 |
| n-Propanol | 24 |  | 1.4087 |
| Propylalcohol | 20 | 1.1044 | 0.8735 |
| Neopentane | 23 | 5.9473 | 0.6157 |
| I-pentane | 21 | 0.3274 |  |
| Ammonia | 33 | 1.6786 | 1.8750 |
| **%AAD** | **299** | **3.5209** | **0.7899** |

## 4.4 Investigation to the mixtures :

It is well known fact that the calculations of the thermodynamic properties of the mixtures are not as easy as the calculations for pure components. This is because of finding the critical constants that represents the mixture from critical constants of pure components and this is done by using what is called mixing rules . The mixing rules are not very accurate due to difference in chemical structures of the components .Usually adjustable parameter or parameters are needed to calculate any thermodynamic property of mixture very accurately .

In this work the prediction of the molar volume of saturated vapors for binary mixtures are done by using two methods :

The first method is by using Virial equation for calculating the compressibility factor and Virial mixing rule. The second method is by using Teja equation for calculate the compressibility factor and Virial mixing rule the results obtained from these two methods are listed in table (4.11).

Comparison of the results obtained from the Virial mixing rule (Virial equation truncated to second and Virial equation truncated to third coefficient ) and the results obtained fromTeja -Virial mixing rule are listed in appendix D.The accuracy of Virial mixing rules (truncated to the third coefficient ) is much better than that of Teja -Virial mixing rules as listed in table 4.11 .

Many developments were done in order to increase the accuracy of this equation by using statistical program using the following form :

$$Z = a1 + a2 * \exp(x1 * Zcal)^{a3} + a4 * \exp(x2 * Zcal)^{a5}$$

It is found that this correlations were accurate for some mixtures and not accurate for some mixtures ,this may be due to the fact that some of the mixtures are consisting of polar and non-polar compounds ,So it is clearly that the form of Virial mixing rule truncated to third coefficient is acceptable and gives accurate results .

Table (4.11) : The molar volume of saturated vapor for binary mixtures.

| Mixture | No.of points | AAD%by Virial(truncated to B) mixing rule | AAD%Virial (truncated to C)mixing rule | AA%D Virial-Teja mixing rule |
|---|---|---|---|---|
| Propane – n-Octane | 34 | 21.6112 | 2.2192 | 7.0232 |
| n-Butane-n-Octane | 18 | 21.51446 | 1.565104 | 5.70306 |
| Nitrogen-Heluim | 50 | 0.52387 | 0.1999 | 0.9357 |
| Carbon dioxide-Etheylene | 17 | 2.19566 | 2.195 | 0.2224 |
| H2s-Methane | 13 | 5.10206 | 2.2303 | 5.58004 |
| Hydrogen-Methane | 10 | 7.4038 | 5.6559 | 8.32369 |
| AAD% | 142 | 8.39192 | 1.4967 | 3.4669 |

# CHAPTER FIVE

# Discussion and Conclusions

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## 5.1 Discussion

### 5.1.1 Equation of state used :

There are many equations of state that are used to calculate the molar volume of fluids. In this research the equations of state used to calculate the molar volume of saturated vapor of compounds were: Lee-Kesler, Redlich-Soave, Peng-Robinson and Virial equations truncated to second and to third terms.

Tables 5.1 and 5.2 indicate the molar volume of saturated vapor in these moderate ranges of temperatures and pressures. The molar volume calculated by using Lee-Kesler equation is not accurate .The AAD% is 62.432% for 3 compounds (polar and non-polar)and 72 data points .Usually Lee-Kesler equation gives good results in superheated region and this accuracy decreases when using this equation for saturated region .

The average percent deviation for 10 non-polar compounds of Redlich-Soave equation and 201 data points is 18.6292 .and the AAD% is 16.1791 when using Peng-Robinson equation for 10 non-polar compounds 201 data points .On the other hand the average percent deviation for 4 compounds and 110 data points for polar compounds is 7.7664%when using Soave equation and 7.5256% when using Peng Robinson equation . However these two equations (Soave and Peng-Robinson) gave very accurate results when they were used to calculate the molar volume of saturated vapor of water. This is probably due to their methods of derivation. However Peng Robinson equation can be considered better than Redlich –Soave equation to predict the molar volume of saturated vapors.

The generalized Virial equation truncated to two terms and Virial equation truncated to three terms are considered to be more accurate than all the previous equations mentioned as shown in tables 5.1 and 5.2 . Virial equation truncated to third term gave relatively better results than those obtained from Virial equation truncated to second term.

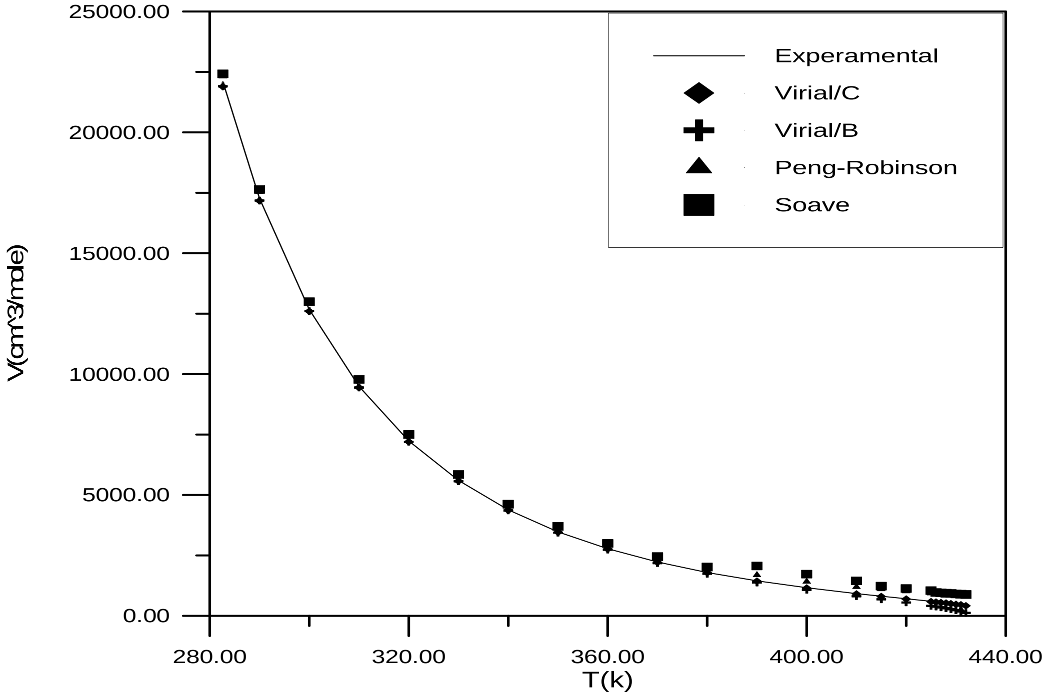
After these comparisons one can conclude that the generalized Virial equations truncated to second term and truncated to third term are the most suitable equations to calculate the molar volume of saturated vapor. Thus efforts were directed to modify these equations to increase their accuracy (decrease the deviation from the experimental data).The average percent deviation for 10 non-polar compounds and 201 data points is 11.8566% when using Virial equation truncated to second term and 1.4620% for Virial equation truncated to third term .For 4 polar compounds and 114 data points the AAD% of Virial equation truncated to second term is 1.7645% and for Virial equation truncated to third term is 1.1085% .Figers 5.1 to 5.7 show the deviations from experimental data using the equations : Redlich –Soave equation , Peng –Robinson equation ,Virial equation truncated to B and Virial equation truncated to C after these comparison one can conclude that the generalized Virial equation truncated to third term is the most suitable equations to calculate the molar volume of saturated vapor. Thus efforts were directed to modify this equation to increase its accuracy (decrease the deviation obtained from experimental data).These figures is clearly indicate that Virial equation truncated to C is the best equation for the moderate conditions studied in this research.

Table 5.1 Comparison of the calculated molar volume obtained from different equations for non-polar compounds.

| . Compound | No. of points | AAD% Lee-Kesler Eq. | AAD% Redlich-Soave Eq. | AAD% PR Eq. | AAD% Virial truncated to B | AAD% Virial truncated to C |
|---|---|---|---|---|---|---|
| **n-Pentane** | **11** | | **38.8108** | **18.0767** | **9.7192** | **1.318** |
| **Carbon dioxide** | **12** | | **34.3104** | **33.0754** | **29.498** | **1.4013** |
| **Ref.410** | **32** | | **0.72559** | **0.5528** | **0.2918** | **1.1643** |
| **Carbon monoxide** | **10** | | **17.0017** | **11.0508** | **8.5177** | **1.5526** |
| **n-Butane** | **25** | | **15.12** | **15.072** | **15.0724** | **1.886** |
| **Neopentane** | **23** | | **43.0845** | **43.0928** | **32.054** | **1.7225** |
| **Cyclopropane** | **28** | **55.1232** | **25.8715** | **26.191** | **9.2764** | **1.820** |
| **I-Pentane** | **21** | **63.8654** | **2.4031** | **1.1422** | **1.6678** | **0.8822** |
| **Ref.245** | **16** | | **3.5765** | **1.6895** | **0.9497** | **0.9546** |
| **I-Butane** | **21** | | **26.6583** | **24.159** | **11.4591** | |
| **AAD%** | | **58.8698** | **18.6292** | **16.1791** | **11.8566** | **1.4620** |

Table 5.2 Comparison of the calculated molar volume obtained from different equations for polar compounds

| compounds | No.of points | AAD%Lee-Kesler eq. | AAD% Redlich-Soave eq. | AAD% Peng-Robinson eq. | AAD%Virial eq.truncated to B | AAD% Virial truncated to C |
|---|---|---|---|---|---|---|
| **H2O** | **23** | **70.0209** | **0.4275** | **0.4414** | **0.1595** | **0.763** |
| **n-Propanol** | **24** | | **5.6818** | **6.5217** | **2.7508** | **1.61** |
| **Propyl Alcohol** | **20** | | **1.5026** | **1.1448** | **1.1945** | **1.25** |
| **Ammonia** | **47** | | **24.448** | **24.3876** | **3.4504** | **0.9296** |
| **AAD%** | | **70.0209** | **7.7664** | **7.5256** | **1.7645** | **1.1085** |



**Figer 5.1 Molar volume of saturated Vapor vs.Saturated temperature for Neopentane by using Different equations.**

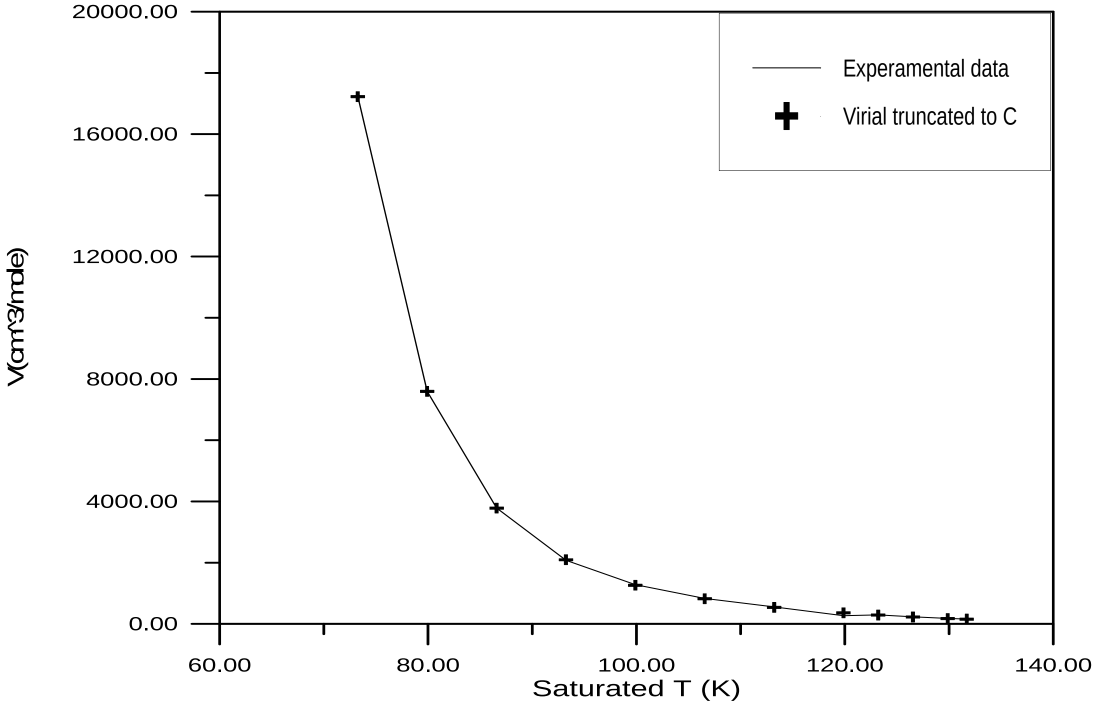


**Figure 5.2 Molar volume of saturated vapor vs. saturated temperature for Carbon monoxide using Virial equation truncated to C**

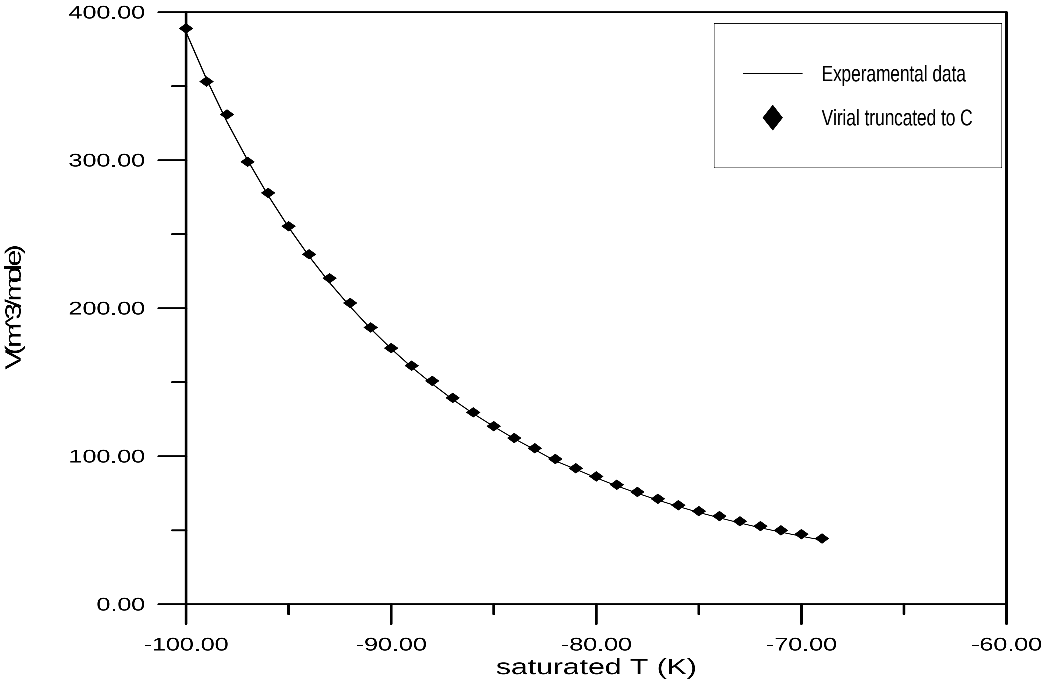


Figure 5.3 Molar volume of saturated vapor vs. saturated temperature for REF.410 using Virial equation truncated to C

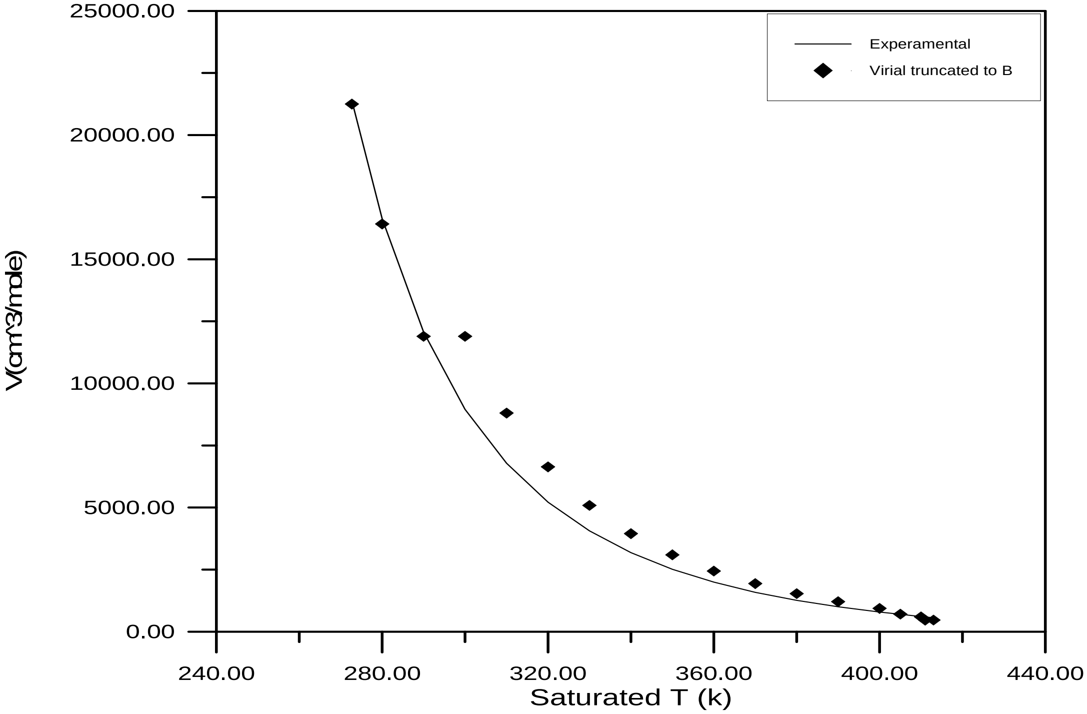


Figure 5.4 Molar volume of saturated vapor vs. saturated temperature for Carbon monoxide using Virial equation truncated to B

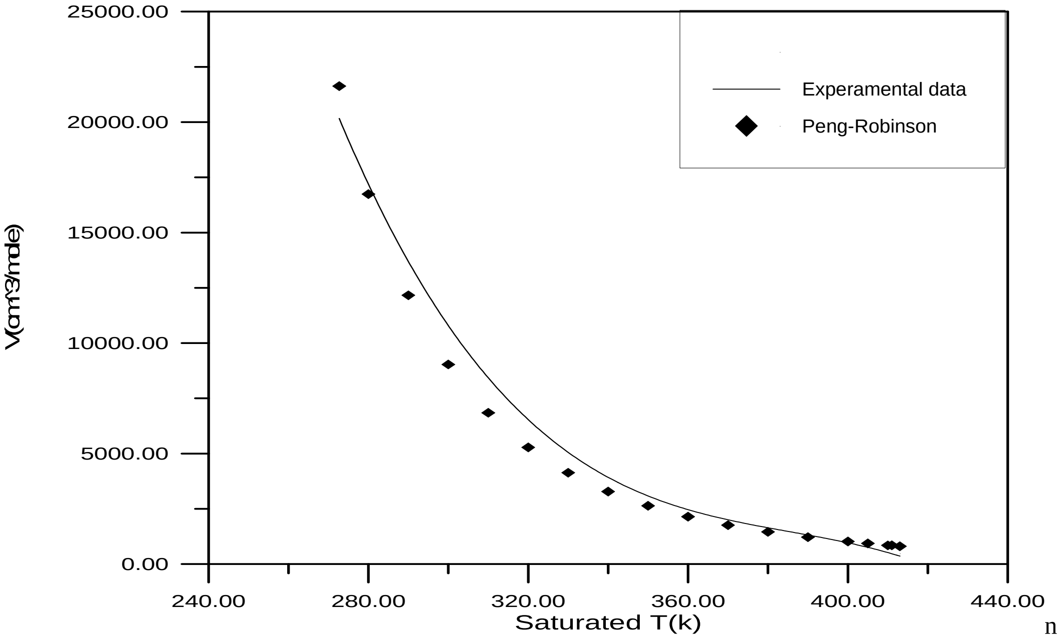


**Figure 5.5 Molar volume of saturated vapor vs. saturated temperature for n-Butane using peng-Robinson equation**

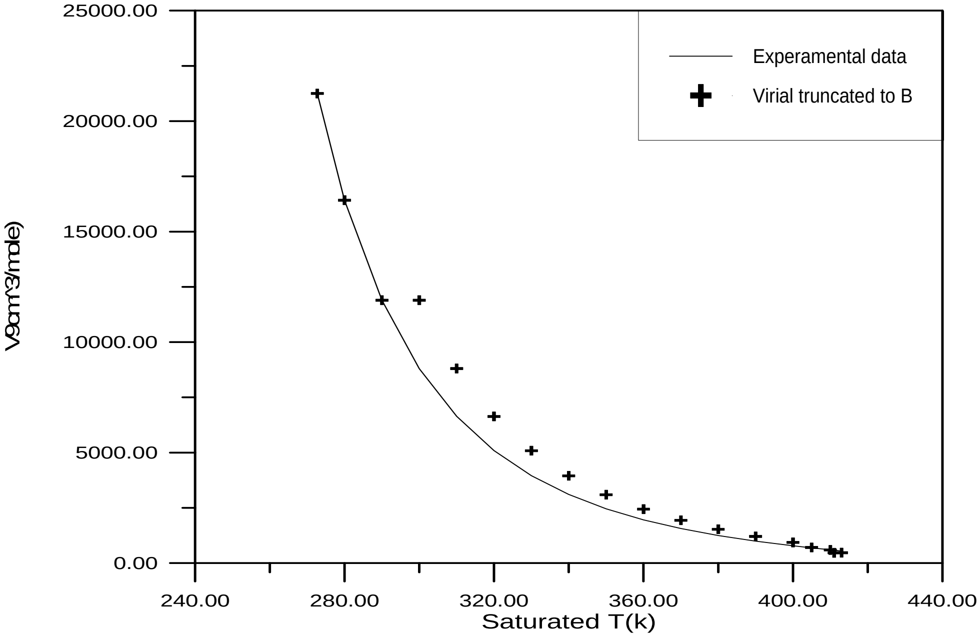


**Figure 5.6 Molar volume of saturated vapor vs. saturated temperature for n-Butane using Virial equation truncated to B**

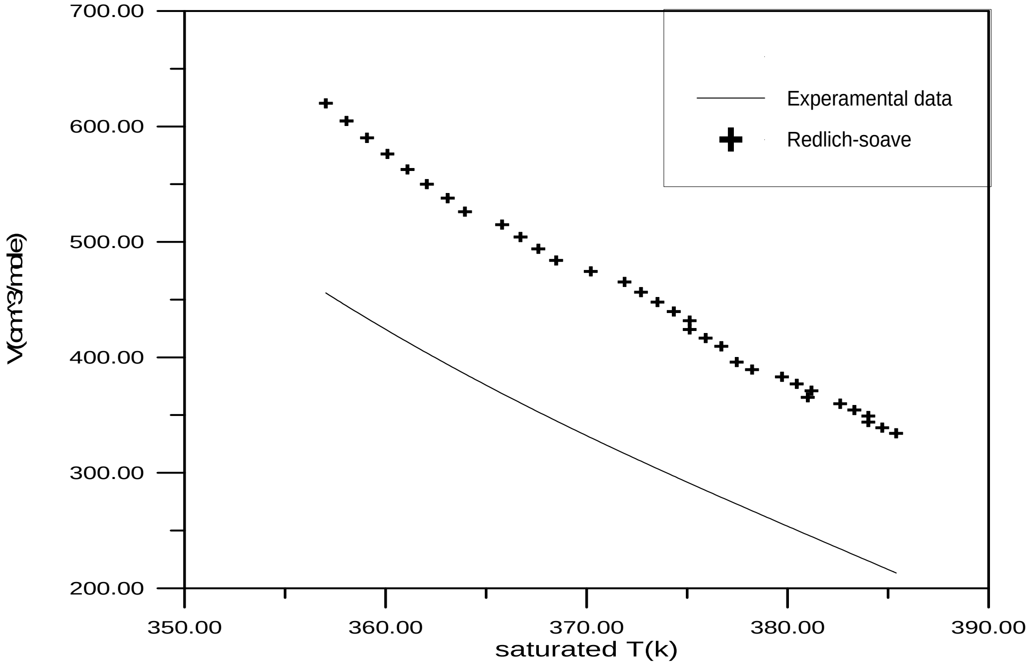


**Figure 5.7 Molar volume of saturated vapor vs. saturated temperature for Ammonia using Redlich-Soave equation.**

## 5.1.2 : The developed correlation :

After concluded that the best equation that calculates the molar volume of vapor for saturation conditions (temperatures and pressures) was Virial equation , efforts were tried to modify the two different forms of Virial equation (truncated to second term and to the third term)to decrease the percent deviation as much as possible ,this may done by using a statistical program and statistical methods that give the best form of the correlation . Two modifications were developed in this thesis , the first modification was developed to correlate Virial equation truncated to second term where the AAD% was 7.5535 for 14 pure compounds (299 data points) which is relatively high deviation .Many attempts were done to modify this equation in order to reduce the percent deviation as much as possible , this modification was applied for 10 compounds (210 data points ) polar and non-polar compounds and it is reduced the percent average absolute deviation from

7.5535% to 3.5209% . For example (for carbon dioxide the AAD% by using Virial equation truncated to B is 29.498% , while the AAD% by using the developed Virial equation truncated to B is 25.7386%) and (for n-Butane the AAD% by using Virial truncated to B is 15.0724% where the AAD% by using the modified equation is 5.0164). The second correlation developed in this thesis is for Virial equation truncated to third term .In spite of the good accuracy obtained using this equation where the AAD% 1.0955% for 299 data points polar and non-polar compounds a modification was developed to reduce the average percent absolute deviation for 11 compounds and 229 data points from 1.0955 % to 0.7899% . Thus this modification resulted in an equation which can be considered` as very accurate equation to predict the saturated vapor for polar and non-polar compounds. Table 5.3 show the effect of the correlation developed in this project on the molar volume calculated from many equations .

Table 5.3 The effect of the modifications on the molar volume calculated from different equations .

| Compounds | No.of points | AAD%Virial Truncated to B | AAD% developed virial truncated to B | AAD% Virial truncated to c | AAD%develope Virial truncated to C |
|---|---|---|---|---|---|
| n-Pentane | 11 | 9.7192 | 9.9576 | 1.318 | 0.9088 |
| Carbon Dioxide | 12 | 29.498 | 25.7386 | 1.4013 | 0.5922 |
| Ref.410 | 32 | 0.2918 | 0.42185 | 1.1643 | 0.67376 |
| Carbon monoxide | 10 | 8.5177 | 6.1906 | 1.5526 | 1.2697 |

| | | | | | |
|---|---|---|---|---|---|
| n-Butane | 25 | 15.0724 | 5.0164 | 1.886 | 1.1236 |
| Neopentane | 23 | 32.054 | 5.9473 | 1.7235 | 0.6157 |
| Cyclopropane | 28 | 9.2764 | | 1.820 | |
| i-Pentane | 21 | 1.6678 | 0.3274 | 1.6740 | |
| Ref.410 | 16 | 0.9497 | | 0.8822 | 0.5061 |
| i-Butane | 21 | 11.4591 | | 1.1984 | |
| Water | 23 | 0.1595 | 0.5425 | 0.763 | 0.1884 |
| n-Propanol | 24 | 2.7508 | | 1.61 | 1.4087 |
| Propyl Alcohol | 20 | 1.1945 | 1.1044 | 1.25 | 0.8735 |
| Ammonia | 47 | 2.9531 | 1.6786 | 0.9296 | 1.6785 |
| AAD% | 299 | 7.5535 | 3.5209 | 1.0955 | 0.8769 |

## 5.1.3 : The molar volume of saturated vapor for binary mixtures :

It is well known fact that the calculation of the thermodynamic properties of the mixtures is not as easy as the calculation for pure components . This is because of using the mixing rules to calculate the pseudo critical properties and acentric factor of mixture from the critical properties and acentric factors of pure components .Many of the mixing rules are not quite accurate and need one or more adjustable parameters .

In this research the prediction of the saturated molar volume of binary mixtures were done by using two methods :The first method was done by using Virial mixing rules which is given by the following equations :

$$\omega 12 = \omega 1 * x1 + \omega 2 * x2$$

$$Tc12 = Tc1 * x1 + Tc2 * x2$$

$$Z12 = z1 * x1 + z2 * x2$$

$$Vc12 = \frac{1}{8}(Vc_1^{1/3} + Vc_2^{1/3})^3$$

$$Pc12 = pc1 * x1 + Pc2 * x2$$

These equations were used to calculate the pseudo critical properties and acentric factor for the mixture then using the developed Virial equation truncated to second term and also the developed Virial equation truncated to third term to calculate the compressibility factor of the mixtures .

The second method was accomplished by using the developed Virial equation truncated to second term and the developed Virial equation truncated to third term to calculate the compressibility factor of the mixture from the compressibility factor of the individual component obtained at the same reduced conditions of Tr and Pr as the mixture . The reduced conditions of the mixture were obtained by using properties and acentric factor of the mixture .

This method is Similar to Teja [1] method for calculating the compressibility factor of the mixture from the compressibility factors of individual component.

Table 5.4 shows the results of deviation of saturated molar volume of vapor for binary mixtures from experimental data using the modified Virial equation truncated to second term and modified Virial equation truncated to third term by the two methods motioned above .

Table 5.4 indicates the best deviation (more accuracy) are obtained when using Virial equation truncated to third term and Virial mixing rules .The overall average percent absolute deviation for 6 mixtures and 142 data point is 1.4967 .

For the same 6 mixtures and 142 data point the AAD% is 3.4669 when using Virial equation truncated to third term withTeja method and Virial mixing rules . this AAD% is increased to 8.3919 when using the modified Virial equation truncated to second term and Virial mixing rules .

Table 5.4 indicates clearly that the best method that gives highest accuracy (best deviation) for calculating the saturated molar volume of vapor for binary mixtures is to use the modified Virial equation truncated to third term and Virial mixing rules.

Figers 5.8 to 5.13 show the deviation of the calculated molar volume of saturated vapor for propane-n-Octane system and CO2 –He system by using modified Virial equation truncated to second term with Virial mixing rule and modified Virial equation truncated to third term with Virial mixing rule and Teja equation with Virial mixing rule.

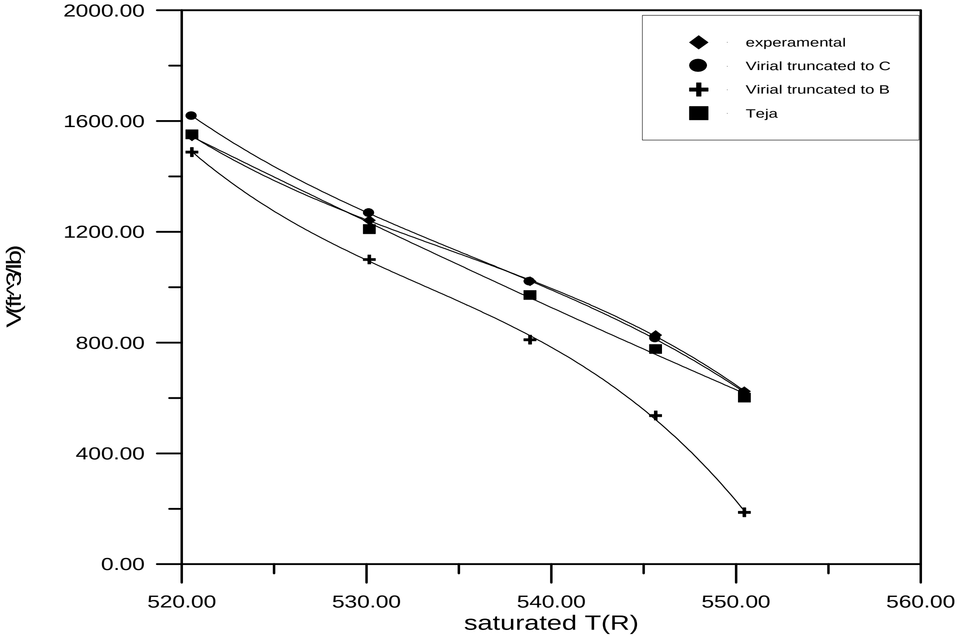
Further attempts were done to possible decrease the deviations further using statistical methods, for example the following form of correlation was used to decreases the deviation:

$$Z = a1 + a2 * \exp(x1 * Zcal)^{a3} + a4 * \exp(x2 * Zcal)^{a5}$$

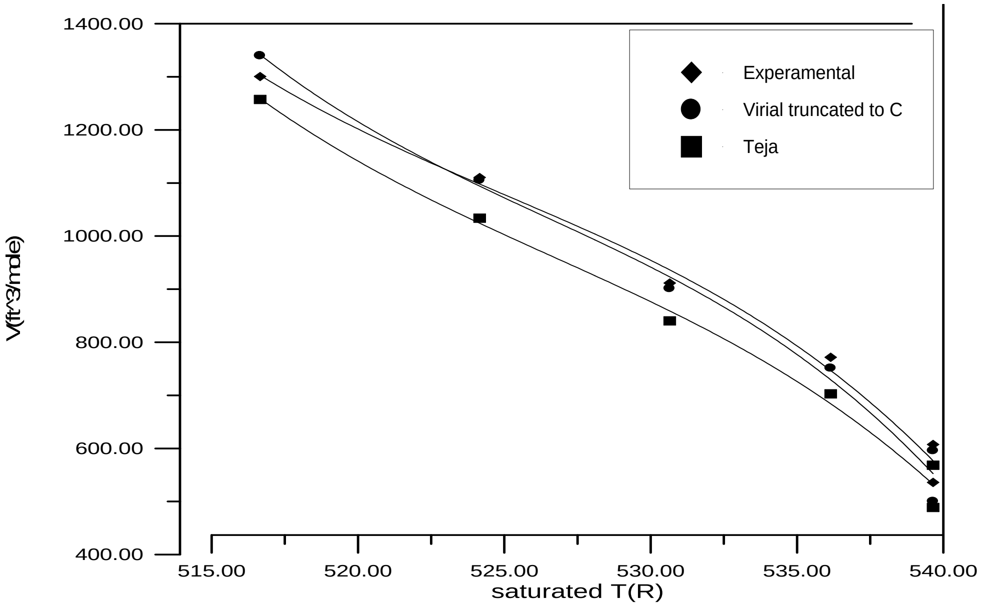
Unfortunately all these attempts did not lead to generalized equation to decrease further deviation than those obtained using developed Virial equation truncated to third term and Virial mixing rules .

Table 5.4 The AAD% of the molar volume of the saturated vapors of binary mixtures calculated from different equations .

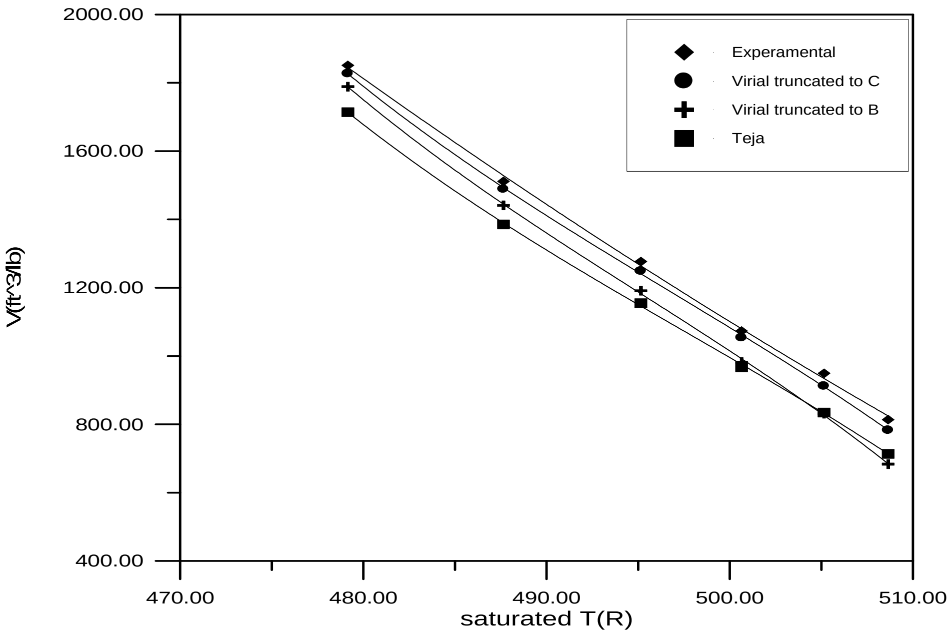
| Mixture | No.of points | AAD%Developed Virial eq.(truncated to B)with Virial mixing rule | AAD%Developed Virial eq.(truncated to C)with Virial mixing rule | AAD%Teja eq. with Virial mixing rule |
|---|---|---|---|---|
| Propane-n-Octane | 34 | 21.6112 | 2.2192 | 7.0232 |
| n-Butane-n-Octane | 18 | 21.5144 | 1.5651 | 5.7031 |
| Nitrogen-Heluim | 50 | 0.5238 | 0.1999 | 0.9357 |
| Carbon Dioxide-ethylene | 17 | 2.19566 | 2.195 | 0.2224 |
| H2S-Methane | 13 | 5.1020 | 2.2303 | 5.5800 |
| Hydrogen-Methane | 10 | 7.4038 | 5.6559 | 8.3236 |
| AAD% | 142 | 8.3919 | 3.4669 | 1.4967 |



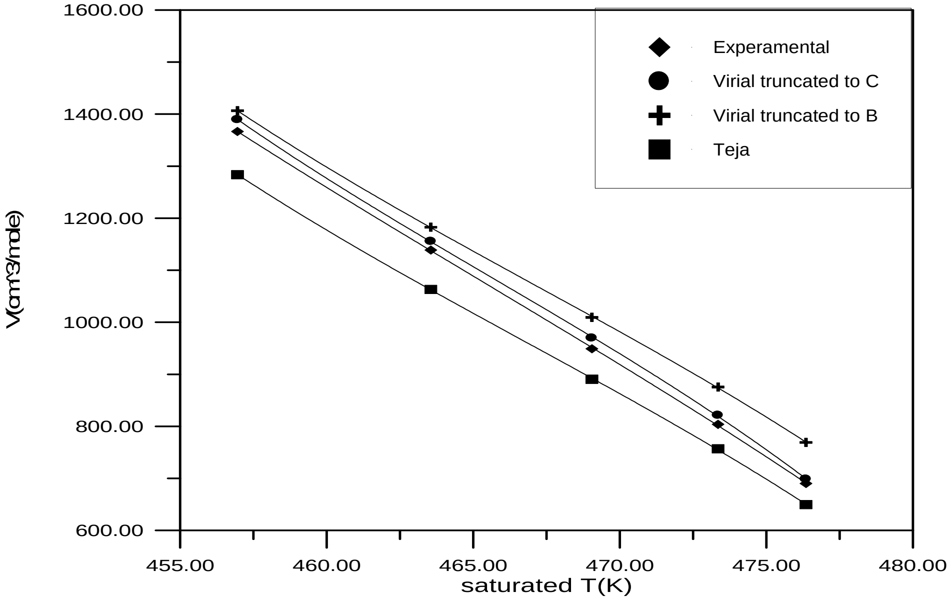
**Figer 5.8 Molar volume of saturated vapor vs. saturated temperature of mixture of 0.2143 mole % Propane and 0.7857 mole % of n-Octane by using three methods.**



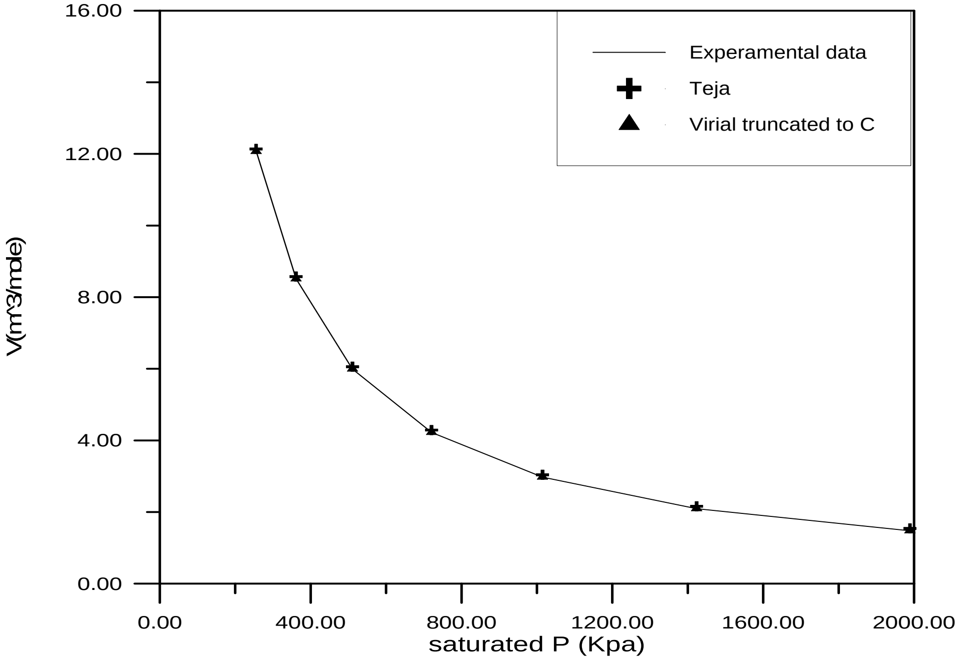
**Figer 5.9 Molar volume of saturated vapor vs. saturated temperature of mixture of 0.3306 mole % Propane and 0.6694 mole % of n-Octane by using three methods**



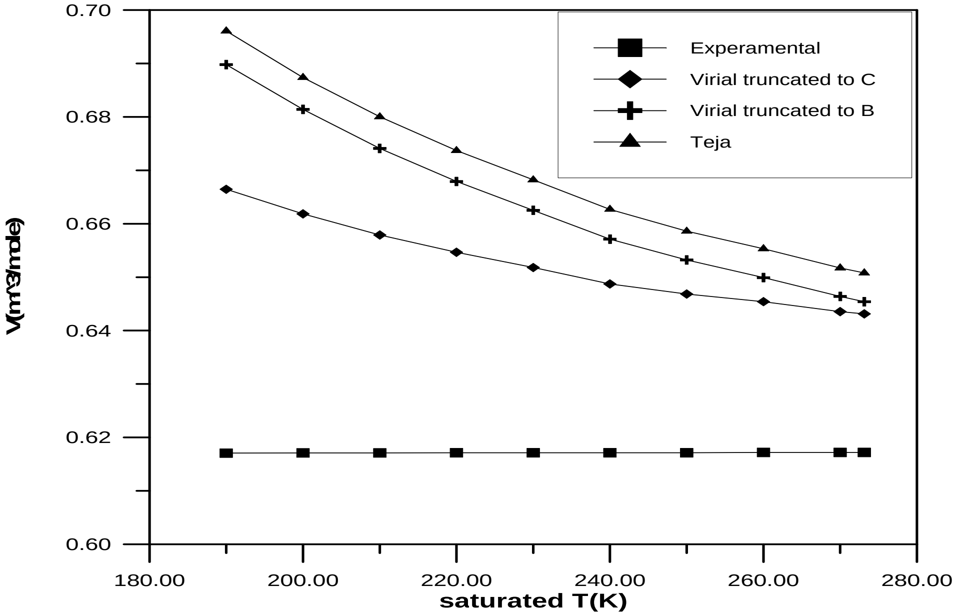
**Figer 5.10 Molar volume of saturated vapor vs. saturated temperature of mixture of 0.5729 mole % Propane and 0.4271 mole % of n-Octane by using three methods**



**Figer 5.11 Molar volume of saturated vapor vs. saturated temperature of mixture of 0.8183 mole % Propane and 0.1817 mole % of n-Octane by using three methods**



**Figer 5.12 Molar volume of saturated vapor vs. saturated temperature of mixture of 0.119 mole % CO2 and 0.881mole % of He by using three methods**



**Figer 5.13 Molar volume of saturated vapor vs. saturated temperature of mixture of 0.15 mole % H2 and 0.85mole % of CH4 by using three methods**

## 5.2Conclusions :

1. There are many equations of state that can be used to calculate the molar volume of saturated vapor .In this research and for these moderate ranges of temperatures and pressures ,four equations of state were used to calculate the molar volume of saturated vapor (polar and non polar). Lee-Kesler equation was applied for 3 compounds (72 data points including polar and non polar) with AAD% 62.432%. Redlich – Soave equation was applied for 14 pure compounds (299 data points polar and non-polar compounds) with AAD% 15.3125%. Peng – Robinson equation was the third equation used to calculate the molar volume of saturated vapor and gave AAD% 14.3476% .These three equations proved to be unsatisfactory although the Peng-Robinson equation gave the best deviations.
2. Truncated Virial equation used in this research, Virial equation truncated to second term that applied for 14 compounds (299 data points) with AAD% 7.5535, while Virial equation truncated to third term gave AAD% is 1.0955%. It is clearly shown that for the same compounds truncated Virial equation truncated to third term is the best equation that can be used to calculate the molar volume of saturated vapor and gave the lowest deviation.

$$Z = 1 + \frac{B}{V\exp} + \frac{C}{V\exp^2} + ....$$

$$B = \frac{R * Tc}{Pc}(B0 + \omega B1)$$

$$B0 = 0.1445 - \frac{0.33}{Tr} - \frac{0.1385}{Tr^2} - \frac{0.0121}{Tr^3} - \frac{0.000607}{Tr^8}$$

$$B1 = 0.0637 + \frac{0.331}{Tr^2} - \frac{0.423}{Tr^3} - \frac{0.008}{Tr^8}$$

And third Virial coefficient :

$$C = \frac{RTc}{Pc}\left(c0 + \omega c1\right)$$

$$c0 = 0.01407 + \frac{0.02432}{Tr^{2.8}} - \frac{0.00313}{Tr^{10.5}}$$

$$c1 = -0.02676 + \frac{0.0177}{Tr^{2.8}} + \frac{0.04}{Tr^3} - \frac{0.003}{Tr^6} - \frac{0.00228}{Tr^{10.5}}$$

3. A statistical program was used to modify the Virial equation truncated to second term and a general correlation was developed (applied for 210 data points for polar and non-polar compounds ).This correlation modified the average deviation obtained from this equation from 7.5535% to 3.5209% . The correlation is given as the following equations :

$$B0m = 0.1258 - \frac{0.3017}{Tr} - \frac{0.1258}{Tr^{2.31}} - \frac{0.01325}{Tr^{3.21}} - \frac{0.005748}{Tr^{7.85}}$$

$$B1m = 0.05257 + \frac{0.3575}{Tr^{1.8}} - \frac{0.47155}{Tr^3} - \frac{0.002184}{Tr^{7.85}}$$

4. The same procedure was used to modify the Virial equation truncated to third term . A general correlation was developed using 70 data point for three compounds and the result equations applied to 11 compounds (polar and non-

polar ). The modified Virial equation truncated to third term reduced the average percent absolute deviation from 1.0955 to 0.7899. The correlation is given as the following equation:

$$C1m = 0.022501 + \frac{1.265968}{Tr^{5}} - \frac{0.507}{Tr^{5.5}} - \frac{0.75663}{Tr^{4.4}}$$

Thus the modified Virial equation truncated to the third term can be considered as the best equation that gives the highest accuracy for prediction the molar volume of saturated vapor .

5. For binary mixtures , the modified Virial equation truncated to second term and truncated to third term ,with Virial mixing rule and with the compressibility factor obtained from Teja equation. For 142 data points (6 mixtures) polar and non-polar the AAD% of the modified Virial equation truncated to second term with Virial mixing rules is 8.39192%. While the AAD% of modified Virial equation truncated to third term with Teja method based on Virial mixing rule is 3.4669%. On the other hand the AAD% for the modified Virial equation truncated to third term with Virial mixing rules is 1.4967%. It can be considered that the modified Virial equation truncated to third term with Virial mixing rule is the best equation for predicting the molar volume of saturated vapor for binary mixture.

## 5.3 Recommendations :

For future work, the following recommendations can be taken in to the consideration:

1. Applying the developed correlation for further available experimental data at saturation conditions (polar and non-polar )
2. Applying these correlations to other thermodynamic properties like Enthalpy , Gibbes free energy for saturated conditions .
3. Studying the possibility of applying Virial mixing rule for ternary mixtures with an acceptable accuracy .

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# APPENDIX A

## PHYSICAL PROPERTIES OF THE COMPONENTS.

---

| COMPONENT | M.WT | Tc(k) | Pc(bar) | W | Zc | Vc(cm3/mole) |
|---|---|---|---|---|---|---|
| n-pentane | 72.151 | 469.7 | 33.7 | 0.251 | 0.263 | 304 |
| n-butane | 58.124 | 425.2 | 38 | 0.199 | 0.274 | 255 |
| i-butane | 58.124 | 408.2 | 36.5 | 0.183 | 0.283 | 263 |
| Carbon dioxid | 44.101 | 304.1 | 73.8 | 0.239 | 0.274 | 93.9 |
| Ref.410 | 120.22 | 345.28 | 36.15 | 0.234 | 0.271 | 211.30 |
| Carbon monoxide | 28.010 | 132.9 | 35.0 | 0.066 | 0.295 | 93.2 |
| Water | 18.015 | 647.3 | 221.2 | 0.344 | 0.235 | 57.1 |
| n-propanol | 60.096 | 536.8 | 51.7 | 0.623 | 0.253 | 219 |
| Propyl alcohol | 60.096 | 508.3 | 47.6 | 0.665 | 0.248 | 220 |
| Neopentane |  | 433.8 | 32 | 0.19 |  |  |
| Cyclopentane | 42.081 | 379.8 | 54.9 | 0.130 | 0.274 | 163 |
| i-pentane | 70.135 | 511.7 | 45.1 | 0.196 | 0.275 | 260 |
| Ref.245 | 134.047 | 685.05 | 456.704 | 0.308 | 0.267 | 291.02 |
| Ammonia | 17.031 | 504.5 | 113.5 | 0.250 | 0.244 | 72.5 |
| Propane | 44.094 | 369.8 | 42.5 | 0.153 | 0.244 | 203 |
| Nitrogen | 28.013 | 126.2 | 33.9 | 0.039 | 0.281 | 89.8 |
| n-Octane | 114.232 | 568.8 | 24.9 | 0.398 | 0.29 | 492.0 |
| Heluim | 4.003 | 5.19 | 2.27 | -0.36 | 0.259 | 57.4 |
| Ethylene | 28.054 | 282.4 | 50.4 | 0.089 | 2.27 | 130.4 |
| H2s | 34.080 | 373.2 | 89.4 | 0.081 | 0.284 | 98.6 |
| Methane | 16.043 | 190.4 | 46 | 0.011 | 0.288 | 99.2 |
| Hydrogen | 2.016 | 33.2 | 13 | -0.21 | 0.306 | 65.1 |

# APPENDIX B

## Computer program for calculating the Volume of saturated vapor .

**This program in QBASIC Language :**

```
CLS
REM "*********************************************"
REM "Computer Program for calculation the molar volume of
pure compounds"
REM "*********************************************"
INPUT "inter the universal Gas constant R=";R
INPUT "inter the critical temperature Tc="; Tc
INPUT "inter the critical Pressure Pc="; Pc
INPUT "inter the A centric factor w="; w
INPUT "inter the Experimental Temperature T="; T
INPUT "inter the Experimental pressure P="; P
INPUT "inter the Experimental volume V="; V
PRINT TAB(11);"**********************************"
PRINT TAB (16);"RESULTS OF COMPUTER PROGRAM
FOR CALCULATION OF MOLAR VOLUME OF
SATURATED VAPOR FROM"
PRINT TAB (32);"VIRIAL EQUATION OF STATE "
PRINT TAB (11);"**********************************"
PRINT TAB (1);"**--------**";TAB(16);"**----------
**";TAB(33);"**--------**";TAB(51);"**-----------
**";TAB(68);"**----------**"
PRINTTAB (4);"Texp";TAB(19);"Pexp";TAB(25);"Vexp";
TAB(36);"Z";TAB(54);"Vcal";TAB (71);"AAD%"
PRINT TAB(1) ;"**--------**";TAB(16);"**--------
**";TAB(33);"**---------**";TAB(51);"**----------
**";TAB(68);"**---------**"
```

```
REM"*****************************************"

REM"CALCULATION        OF        SECOND        VIRIAL
COEFFICIENT "
REM "*****************************************"
B0=0.1445-(0.33/(T/Tc))-(0.1385/(T/Tc)^2)-(0.0121/(T/Tc)^3)-
0.000607/(T/Tc)^8)
B1=0.0637+(0.331/(T/Tc)^2)-(0.423/(T/Tc)^3)-(0.008/(T/Tc)^8)
B=(R*Tc/Pc)*(B0+WB1)
REM"*******************************************"
REM"CALCULATION OF THIRD VIRIAL COEFFICIENT"
REM"******************************************"
C0=0.01407+(0.02432/(T/Tc)^2.8)-(0.00313/(T/Tc)^10.5
C1=-0.02676+(0.0177/(T/Tc)^2.8)+(0.04/(T/Tc)^3-
(0.003/(T/Tc)^6)-(0.00228/(T/Tc)^10.5)
C=(R*Tc/Pc)^2*(c0+wc1)
REM"*******************************************"
REM"CALCULATION OF COMPRESSIBILITY FACTOR "
REM"*******************************************"
Z=1+(B/V)+(C/V^2)
REM"******************************************"
REM"CALCULATION OF MOLAR VOLUME "
Vcal =(Z*R*T/P)
PERCENT=ABS((Vexp-Vcal)/Vexp)*100
REM"*******************************************"
REM "PRINT OF COMPUTER PROGRAM RESULTS"
REM "*****************************************"
PRINT TAB(5);"T=";T
PRINT TAB(17);"P=";P
PRINT TAB(32);"Vcal=";Vcal
PRINT TAB (51);"PERCENT="PERCENT
PRINT
END
```

# Appendix C

## Results of Investigation for Pure Components

### TABLE(C-1) n-propanol

| T(K) | P(bar) | VEXP (cm^3/mole) | DEV SOAVE | DEV PR | DEV VIRIAL/B | DEV VIRIAL/C | DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| 298.1 | .02683 | 87876 | 2.6265 | 3.6798 | 3.4595 | 3.45 | 3.48644 |
| 303.1 | .03711 | 64890 | 3.1165 | 3.18525 | 2.9183 | 2.91 | 2.94795 |
| 313.1 | .06816 | 36720 | 2.3621 | 2.47172 | 2.09183 | 2.08 | 2.12446 |
| 323.1 | .1193 | 21708 | 1.9039 | 2.0709 | 1.5436 | 1.542 | 1.57941 |
| 333.1 | .1999 | 13380 | 1.4666 | 1.7095 | 1.00451 | 1.0026 | 1.03829 |
| 343.1 | .3221 | 85380 | 1.2965 | 1.63637 | .715203 | .71196 | 0.74188 |
| 353.1 | .5017 | 56100 | 1.3983 | 1.8571 | .6730 | .6689 | 0.68692 |
| 363.1 | .7575 | 37920 | 1.5724 | 2.1705 | .67800 | .672 | 0.67032 |
| 373.1 | 1.113 | 26244 | 1.8884 | 2.6435 | 0.7821 | .7766 | 0.74571 |
| 383.1 | 1.594 | 18576 | 2.2900 | 3.2136 | .91720 | .914 | 0.84246 |
| 393.1 | 2.232 | 13362 | 3.1091 | 4.2082 | 1.3590 | 1.365 | 1.23788 |
| 403.1 | 3.059 | 9792 | 3.9859 | 5.2536 | 1.7320 | 1.7601 | 1.55866 |
| 413.1 | 4.1040 | 7308 | 4.9609 | 6.3751 | 2.0324 | 2.1043 | 1.80663 |
| 423.1 | 5.403 | 5538 | 6.1059 | 7.63216 | 2.2626 | 2.414 | 1.9935 |
| 433.1 | 6.991 | 4260 | 7.3084 | 8.8954 | 2.2591 | 2.549 | 1.97314 |
| 443.1 | 8.907 | 3318 | 8.6570 | 10.2405 | 2.0126 | 2.53 | 1.76356 |
| 453.1 | 11.189 | 2064 | 10.568 | 12.0765 | 1.7124 | 2.6032 | 1.5988 |
| 463.1 | 13.878 | 2064 | 12.671 | 14.0109 | .92960 | 2.4071 | 1.12812 |
| 473.1 | 17.878 | 1638 | 15.853 | 16.9270 | .02690 | 2.41 | 0.80336 |
| 483.1 | 20.017 | 1308 | 19.494 | 20.1784 | 1.8804 | 2.06 | 0.13413 |
| | | | **5.681** | **6.5217** | **2.7508** | **1.61** | **1.4087** |

# TABLE (C-2 ) water

| T(c) | P (mmhg) | VEXP (cm^3 / mole) | DEV SOAVE | DEV PR | DEV VIRIAL/ B | DEV VIRIAl /C | DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| -10 | 2.15 | 7627.11 | .0653 | .0657 | .1337 | .071 | .02391 |
| 0 | 4.58 | 3711.34 | .1977 | .1985 | .09965 | .210 | .13377 |
| 5 | 6.54 | 2647.05 | .1777 | .1788 | .0027 | .194 | .09965 |
| 10 | 9.21 | 1914.89 | .09678 | .0982 | .02141 | .119 | .002734 |
| 11 | 9.84 | 1798.20 | .11893 | .1205 | .02312 | .143 | .02141 |
| 12 | 10.52 | 1688.55 | .0779 | .07961 | .0749 | .103 | .02312 |
| 13 | 11.23 | 1585.70 | .1798 | .18166 | .00828 | .446 | .074972 |
| 14 | 11.99 | 1491.30 | .1167 | .11868 | .00827 | .902 | .008283 |
| 15 | 12.79 | 1402.96 | .1100 | .1120 | .00227 | .140 | .002279 |
| 20 | 17.54 | 1040 | .1754 | .17804 | .04246 | .170 | .04246 |
| 25 | 23.76 | 782.608 | .0628 | .05956 | .21773 | .0113 | .21773 |
| 30 | 31.8 | 594.480 | .3348 | .33901 | .12863 | .4011 | .15348 |
| 37 | 47.07 | 410.898 | .3493 | .3551 | .09366 | .4418 | .128689 |
| 40 | 55.3 | 353.129 | .1438 | .1503 | .19139 | .249 | .093662 |
| 60 | 149.4 | 139.058 | .5733 | .5876 | .07429 | .817 | .19139 |
| 80 | 355.1 | 62.0176 | .6283 | .6556 | 1.1978 | 1.123 | .07429 |
| 95 | 634.0 | 36.2111 | 1.9231 | 1.965 | .12219 | 1.592 | 1.19782 |
| 96 | 658.0 | 34.9851 | .8338 | .87669 | .1606 | 1.6512 | .12219 |
| 98 | 707 | 32.7368 | .8828 | .9268 | .2469 | 1.847 | .16061 |
| 99 | 733 | 31.6606 | .9812 | 1.0264 | .2062 | 1.841 | .2469 |
| 100 | 760 | 30.1003 | .9500 | .9963 | .1606 | 1.719 | .20629 |
|  |  |  | **.4275** | **.4414** | **.1595** | **.763** | **.1884** |

## TABLE(C-3) N-PENTANE

| T(K) | P(bar) | VEXP (cm^3 / mole) | DEV SOAVE | DEV PR | DEV VIRIAL/ B | DEV VIRIAL /C | DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| 469.8 | 33.100 | 310.344 | 180.86 | 171.583 | 310.344 | .744 | 1.9822 |
| 462.75 | 29.723 | 564.263 | 71.773 | 66.7532 | 40.787 | 2.198 | 1.8801 |
| 458.05 | 27.813 | 671.742 | 53.857 | 49.6076 | 26.779 | 2.484 | 1.1045 |
| 446.31 | 23.121 | 907.441 | 36.607 | 33.3947 | 13.051 | 1.401 | 1.3768 |
| 434.55 | 19.053 | 1184.52 | 26.594 | 23.9805 | 6.883 | .730 | 1.4139 |
| 422.82 | 15.490 | 1499.25 | 22.626 | 20.3495 | 2.502 | 1.306 | 2.7455 |
| 399.33 | 10.029 | 2482.75 | 12.980 | 11.1469 | 0.314 | .611 | 1.5955 |
| 375.84 | 6.1956 | 4165.70 | 6.8415 | 5.2848 | 0.7616 | .662 | .10468 |
| 352.35 | 3.5641 | 7251.04 | 3.6981 | 2.3617 | 1.157 | 1.284 | .95784 |
| 328.86 | 1.8686 | 13319.5 | 3.3801 | 2.3883 | 0.0385 | .1906 | .029657 |
| 305.37 | 0.8760 | 25862.1 | 7.6971 | 6.9927 | 4.916 | 4.7934 | 0.8974 |
| | | | **38.81** | **35.804** | **37.048** | **1.46** | **0.9088** |

## TABLE(C-4) CARBON DIOXIDE

| T(K) | P(bar) | VEXP (cm^3 / mole) | DEV SOAVE | DEV PR | DEV VIRIAL/ B | DEV VIRIAl /C | DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| 304.2 | 72.85 | 94.2184 | 171.93 | 162.825 | 44.325 | .0873 | 0.5530 |
| 299.63 | 65.93 | 168.247 | 67.77 | 62.7004 | 40.34 | 2.4355 | 0.8966 |
| 296.59 | 61.19 | 196.288 | 54.84 | 50.5391 | 27.5013 | 1.6542 | 0.4408 |
| 288.99 | 50.99 | 269.195 | 35.04 | 31.8440 | 13.4283 | 1.3009 | 0.6258 |
| 281.38 | 42.54 | 351.561 | 23.299 | 20.6745 | 8.5723 | 2.0346 | 0.6783 |
| 273.78 | 34.97 | 446.532 | 17.523 | 15.2505 | 5.5585 | 1.7087 | 0.5528 |
| 258.57 | 22.95 | 7190.24 | 9.723 | 7.8641 | 3.1164 | 1.8064 | 0.8603 |
| 243.36 | 14.21 | 1170.41 | 6.853 | 5.2512 | 1.2183 | 8301. | 0.9492 |
| 228.15 | 8.32 | 2013.24 | 3.0681 | 1.7375 | 1.994 | 1.9471 | 1.0421 |
| 212.94 | 4.313 | 3709.38 | 3.889 | 2.8692 | .2526 | .20899 | 0.1762 |
| | | | **34.310** | **33.0754** | **29.498** | **1.401** | **0.6775** |

## Table (C-5) n-Butane

| T(K) | P (atm) | VEXP (cm^3/ mole) | %DEV SOAVE | DEV PR | DEV VIRIAL/ B | %DEV VIRIAL /C | %DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| 272.67 | 1 | 21384 | 1.003 | 1.151 | .6111 | .6633 | 0.63566 |
| 280.0 | 1.317 | 16636 | 0.4398 | 0.6141 | 1.2986 | 1.35 | 1.3199 |
| 290 | 1.856 | 12070 | 0.5468 | 0.7544 | 1.4505 | 1.51 | 1.4585 |
| 300 | 2.552 | 8958 | 0.5654 | 0.8051 | 1.75 | 1.808 | 1.73625 |
| 310 | 3.430 | 6778 | 0.6699 | 0.9395 | 2.09 | 2.11 | 2.01704 |
| 320 | 4.518 | 5216 | 0.8600 | 1.1555 | 2.49 | 2.45 | 2.3317 |
| 330 | 5.848 | 4056 | 1.5367 | 1.85 | 2.706 | 2.5 | 2.39411 |
| 340 | 7.449 | 3182 | 2.7504 | 3.084 | 2.7838 | 2.43 | 2.24098 |
| 350 | 9.355 | 2511 | 4.6518 | 4.9959 | 2.7686 | 2.107 | 1.86381 |
| 360 | 11.60 | 1992 | 7.2091 | 7.555 | 2.8924 | 1.7162 | 1.42126 |
| 370 | 14.22 | 1584 | 10.668 | 11.009 | 3.2901 | 1.27 | 0.91918 |
| 380 | 17.25 | 1262 | 15.072 | 15.395 | 4.3604 | 9616. | 0.55255 |
| 390 | 20.75 | 1004 | 20.671 | 20.9633 | 6.6545 | 952. | 0.48994 |
| 400 | 24.75 | 790.7 | 27.0803 | 29.0159 | 10.926 | 1.08 | 0.57857 |
| 405 | 26.95 | 696.6 | 27.9380 | 34.6168 | 14.460 | 1.23 | 0.70366 |
| 410 | 29.31 | 609.6 | 30.4160 | 42.2245 | 21.8050 | 1.616 | 1.17478 |
| 411 | 29.79 | 593.732 | 33.2376 | 42.8402 | 20.967 | 1.7126 | 1.9655 |
| 413 | 31.30 | 560.5 | 36.6661 | 43.3613 | 25.2694 | 3.5 | 2.09824 |
| 414 | 31.81 | 543.1 | 46.5925 | 45.5767 | 27.0803 | 3.6 | 2.4508 |
| 415 | 31.81 | 526.0 | 45.435 | 50.9642 | 27.9380 | 2.04 | 2.3408 |
| 416 | 32.33 | 507.7 | 50.831 | 53.8785 | 30.4160 | 2.133 | 2.6382 |
| 417 | 32.86 | 489.6 | 53.755 | 56.9751 | 33.2376 | 2.233 | 3.0216 |
| 418 | 33.40 | 470.6 | 60.544 | 60.6468 | 36.6661 | 2.344 | 2.0123 |
| 419 | 33.94 | 451.1 | 73.183 | 73.2795 | 46.5925 | 1.35 | 1.3981 |
| 420 | 33.49 | 429.3 | 77.5236 | 75.2365 | 46.3068 | 2.5 | 0.9862 |
|  |  |  | **15.12** | **13.116** | **15.072** | **1.886** | **1.1236** |

# TABLE (C-6 ) CARBON MONOXIDE

| T(K) | P(bar) | VEXP (cm^3 /mole) | DEV SOAVE | DEV PR | DEV VIRIAL /B | DEV VIRIAl /C | DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| 129.8 | 29.739 | 174.855 | 69.865 | 65.276 | 27.2517 | 2.5710 | .47517 |
| 126.5 | 25.53 | 232.558 | 56.027 | 51.761 | 14.7807 | 2.5854 | 2.4145 |
| 123.2 | 21.735 | 295.311 | 35.480 | 32.33 | 9.8409 | 2.9062 | 2.4193 |
| 119.8 | 18.181 | 369.139 | 24.273 | 21.789 | 6.6396 | 2.4575 | 2.7453 |
| 113.2 | 12.696 | 553.709 | 18.026 | 16.013 | 4.1261 | 2.5222 | 2.3245 |
| 106.5 | 8.4525 | 826.873 | 10.468 | 8.9213 | 1.3191 | .7750 | 2.3915 |
| 99.9 | 5.4665 | 1281.31 | 8.591 | 7.2868 | 1.6259 | 1.5677 | .66737 |
| 93.24 | 3.2154 | 2076.41 | 5.002 | 3.8676 | 1.0635 | .9383 | 1.4903 |
| 86.58 | 1.725 | 378.433 | 3.7219 | 5.2467 | .1128 | .0285 | .99066 |
| 79.92 | .814 | 7593.73 | 3.194 | 3.0040 | 4677. | .3681 | .00119 |
| 73.26 | .3415 | 17226.5 | .7398 | 2.7045 | 1.2409 | 1.2927 | .38056 |
|  |  |  | **17.025** | **11.05** | **8.5777** | **1.5539** | **1.269** |

## TABLE C-7 Ref.245

| T(R) | P (Psia) | Vexp (ft^3/lb) | DEV SOVE | DEV PR | DEV VIRIAL /B | DEV VIRIAl/C | DEV THIS work |
|---|---|---|---|---|---|---|---|
| 420 | 5.067 | 870.175 | 0.9865 | 0.4331 | 0.5585 | 0.5758 | 0.0181 |
| 430 | 6.742 | 665.560 | 1.1632 | 0.4860 | 0.6007 | 0.6223 | 0.1763 |
| 440 | 8.841 | 516.239 | 1.3614 | 0.5455 | 0.6391 | 0.6651 | 0.2501 |
| 450 | 11.430 | 405.586 | 1.5844 | 0.6154 | 0.6729 | 0.7027 | 0.3356 |
| 460 | 14.584 | 322.424 | 1.8313 | 0.6957 | 0.7062 | 0.7386 | 0.4302 |
| 470 | 18.383 | 259.055 | 2.1202 | 0.8057 | 0.7270 | 0.7596 | 0.4451 |
| 480 | 22.910 | 210.245 | 2.4213 | 0.9173 | 0.7685 | 0.7974 | 0.5602 |
| 490 | 28.253 | 172.143 | 2.7787 | 1.0757 | 0.7985 | 0.8180 | 0.7692 |
| 500 | 34.503 | 142.118 | 3.1748 | 1.2652 | 0.8426 | 0.8843 | 0.7909 |
| 510 | 41.755 | 118.201 | 3.6323 | 1.5095 | 0.8929 | 0.8654 | 0.8058 |
| 520 | 50.656 | 98.972 | 4.1600 | 1.8187 | 0.9566 | 0.8842 | 0.8414 |
| 530 | 59.656 | 83.375 | 4.7694 | 2.2051 | 1.0423 | 0.9038 | 0.9191 |
| 540 | 70.509 | 70.803 | 5.3246 | 2.4182 | 1.3699 | 1.1389 | 1.1075 |
| 550 | 82.773 | 60.098 | 6.0231 | 3.2855 | 1.3103 | 1.9459 | 0.8983 |
| 560 | 96.559 | 51.358 | 6.8325 | 4.0235 | 1.5167 | 1.9711 | 0.7848 |
| 570 | 111.98 | 44.044 | 7.8471 | 4.9322 | 1.7927 | 1.002 | 0.7784 |
|  |  |  | 3.5006 | 1.6895 | 0.9497 | 0.9546 | 0.5061 |

# TABLE C-8 Ref.410

| T(c) | P (KPa) | Vexp (m^3/mole) | DEV SOAVE | DEV PR | DEV VIRIAl /B | DEV VIRIAL /C | DEV THIS WORK |
|---|---|---|---|---|---|---|---|
| -100 | 3.7 | 386.619 | 0.4969 | 0.4335 | 0.0871 | 0.6364 | 0.1473 |
| -99 | 4.1 | 354.785 | 0.6119 | 0.6803 | 1.0349 | 0.4632 | 0.9738 |
| -98 | 4.4 | 325.978 | 1.3656 | 1.2921 | 0.9110 | 1.5261 | 0.9748 |
| -97 | 4.9 | 299.878 | 0.5067 | 0.5857 | 0.9702 | 0.3332 | 0.9060 |
| -96 | 5.3 | 276.191 | 0.4284 | 0.3437 | 0.0619 | 0.6156 | 0.0043 |
| -95 | 5.8 | 254.668 | 0.0734 | 0.0174 | 0.4360 | 0.2747 | 0.3686 |
| -94 | 6.3 | 235.093 | 0.3474 | 0.2502 | 0.1859 | 0.5644 | 0.1170 |
| -93 | 6.8 | 217.268 | 1.1436 | 1.0395 | 0.5814 | 1.3767 | 0.6522 |
| -92 | 7.4 | 201.003 | 1.0039 | 0.8927 | 0.4195 | 1.2542 | 0.4914 |
| -91 | 8.1 | 186.160 | 0.1620 | 0.0435 | 0.4388 | 0.4305 | 0.3664 |
| -90 | 8.8 | 172.595 | 0.033 | 0.1594 | 0.6560 | 0.2546 | 0.5827 |
| -89 | 9.5 | 160.176 | 0.3057 | 0.1711 | 0.3447 | 0.6138 | 0.2702 |
| -88 | 10.2 | 148.803 | 1.0896 | 0.9463 | 0.4062 | 1.4190 | 0.4823 |
| -87 | 11.1 | 138.374 | 0.4096 | 0.2574 | 0.2923 | 0.7616 | 0.2159 |
| -86 | 12 | 128.800 | 0.2942 | 0.1327 | 0.4324 | 0.670 | 0.3553 |
| -85 | 13 | 120.004 | 0.1297 | 0.3011 | 0.8779 | 0.2709 | 0.8005 |
| -84 | 14 | 111.911 | 0.0544 | 0.2359 | 0.8300 | 0.3723 | 0.7521 |
| -83 | 15 | 104.449 | 0.4498 | 0.2576 | 0.0156 | 0.9034 | 0.2803 |
| -82 | 16.2 | 96.8212 | 0.8329 | 0.6279 | 0.7474 | 1.32 | 0.0645 |
| -81 | 17.4 | 91.240 | 0.5702 | 0.1018 | 0.3252 | 0.6266 | 0.6682 |
| -80 | 18.6 | 85.383 | 0.3366 | 0.3434 | 0.5845 | 1.1156 | 0.2454 |
| -79 | 20 | 79.976 | 0.5283 | 0.0974 | 0.4254 | 0.9152 | 0.5047 |
| -78 | 21.4 | 74.961 | 0.6167 | 0.2761 | 0.3684 | 1.1416 | 0.3455 |
| -77 | 22.9 | 70.323 | 0.6390 | 0.3511 | 0.3769 | 1.266 | 0.2886 |
| -76 | 24.5 | 66.026 | 1.0218 | 0.3595 | 0.0398 | 1.326 | 0.2974 |
| -75 | 26.1 | 62.034 | 1.3330 | 0.7279 | 0.2421 | 1.3608 | 0.0477 |
| -74 | 27.8 | 58.333 | 1.2583 | 0.9888 | 0.1364 | 2.1016 | 0.3214 |
| -73 | 29.7 | 54.892 | 1.2162 | 0.9341 | 0.0624 | 2.069 | 0.2151 |
| -72 | 31.7 | 51.684 | 1.4917 | 0.8761 | 0.2993 | 2.07 | 0.1405 |
| -71 | 33.7 | 48.705 | 2.0563 | 1.1353 | 0.8182 | 2.370 | 0.3768 |
| -70 | 35.7 | 45.928 | 1.5069 | 1.6828 | 0.2464 | 2.300 | 0.8953 |
| -69 | 38.2 | 43.344 | 1.4586 | 1.1162 | 0.2254 | 2.500 | 0.3222 |
|  |  |  | 0.7255 | 0.552 | 0.2918 | 1.1643 | 0.6737 |

# TABLE C-9 Propyl Alcohol

| T(R) | P (Psia) | Vexp (ft^3/lb ) | DEV SOVE | DEV PR | DEV VIRIAL /B | DEV VIRIAl /C | DEV THIS work |
|---|---|---|---|---|---|---|---|
| 501 | 0.0890 | 60113.4 | 0.4766 | 0.476 | 0.4475 | 0.447 | 0.476 |
| 511 | 0.1358 | 40175.4 | 0.5029 | 0.50206 | 0.4644 | 0.4644 | 0.502 |
| 521 | 0.2032 | 27363.0 | 0.5256 | 0.5243 | 0.4754 | 0.475 | 0.525 |
| 531 | 0.2986 | 18970.2 | 0.5578 | 0.555 | 0.4930 | 0.493 | 0.557 |
| 541 | 0.4313 | 13372.8 | 0.6027 | 0.600 | 0.5212 | 0.521 | 0.602 |
| 551 | 0.6131 | 9576 | 0.6597 | 0.65 | 0.5579 | 0.557 | 0.659 |
| 561 | 0.8582 | 6959.4 | 0.7293 | 0.72 | 0.6036 | 0.6035 | 0.729 |
| 571 | 1.1841 | 5128.14 | 0.8187 | 0.812 | 0.6653 | 0.665 | 0.818 |
| 581 | 1.6115 | 3828.66 | 0.9300 | 0.912 | 0.7447 | 0.744 | 0.830 |
| 591 | 2.165 | 2893.92 | 1.0602 | 1.0496 | 0.8387 | 0.8386 | 1.060 |
| 601 | 2.8735 | 2212.98 | 1.2143 | 1.2005 | 0.9520 | 0.9518 | 1.114 |
| 611 | 3.76 | 1710.9 | 1.3934 | 1.375 | 1.0856 | 1.058 | 1.093 |
| 621 | 4.891 | 1336.44 | 1.6035 | 1.5814 | 1.245 | 1.245 | 1.035 |
| 631 | 6.2812 | 1054.2 | 1.8432 | 1.815 | 1.4293 | 1.429 | 1.243 |
| 641 | 7.9861 | 839.22 | 2.118 | 2.084 | 1.643 | 1.643 | 1.118 |
| 651 | 10.059 | 673.86 | 2.4309 | 2.388 | 1.8900 | 1.883 | 1.359 |
| 661 | 12.556 | 545.712 | 2.7551 | 2.7037 | 2.142 | 2.14 | 1.525 |
| 668 | 14.696 | 469.452 | 3.0236 | 2.9643 | 2.3526 | 2.35 | 1.023 |
| 671 | 15.54 | 445.08 | 3.1833 | 3.12104 | 2.49 | 2.49 | 1.183 |
| 681 | 19.078 | 365.76 | 3.624 | 3.5498 | 2.85005 | 2.85 | 1.624 |
|  |  |  | 1.502 | 1.1448 | 1.1945 | 1.25 | 0.95 |

# TABLE C-10 Neopentane

| T(K) | P (atm) | Vexp (cm^3 /mole) | DEV SOAVE | DEV PR | DEV VIRIAL /B | DEV VIRIAL /C | DEV THIS work |
|---|---|---|---|---|---|---|---|
| 282.6 | 1 | 22103 | 1.4408 | 0.9716 | 0.8979 | 0.9510 | 0.8369 |
| 290 | 1.295 | 17265 | 2.1341 | 1.6177 | 0.5043 | 0.5620 | 0.4463 |
| 300 | 1.797 | 12670 | 2.552 | 1.9900 | 0.4984 | 0.5530 | 0.4298 |
| 310 | 2.434 | 9490 | 3.0625 | 2.4802 | 0.4870 | 0.5243 | 0.3808 |
| 320 | 3.227 | 7234 | 3.6870 | 3.1100 | 0.488 | 0.481 | 0.3026 |
| 330 | 4.199 | 5597 | 4.4368 | 3.9210 | 0.5430 | 0.4509 | 0.2172 |
| 340 | 5.373 | 4385 | 5.371 | 4.9501 | 0.6659 | 0.4265 | 0.1135 |
| 350 | 6.773 | 3472 | 6.5281 | 6.2622 | 0.9103 | 0.4301 | 0.0082 |
| 360 | 8.425 | 2772 | 7.995 | 7.9390 | 1.3258 | 0.4640 | 0.0999 |
| 370 | 10.357 | 2226 | 9.907 | 10.126 | 1.9830 | 0.5243 | 0.2246 |
| 380 | 12.596 | 1794 | 11.934 | 13.000 | 3.0133 | 0.6190 | 0.3646 |
| 390 | 15.176 | 1446 | 14.953 | 16.870 | 4.644 | 0.7570 | 0.5249 |
| 400 | 18.134 | 1161 | 19.055 | 22.186 | 7.342 | 0.9880 | 0.6748 |
| 410 | 21.513 | 920 | 24.708 | 30.196 | 12.062 | 1.2780 | 0.8885 |
| 415 | 23.377 | 809.6 | 33.237 | 36.147 | 15.958 | 1.4330 | 1.0569 |
| 420 | 25.336 | 706.9 | 39.563 | 43.959 | 21.742 | 1.6440 | 1.2247 |
| 425 | 27.489 | 603.6 | 47.851 | 55.282 | 31.833 | 2.1901 | 1.1386 |
| 426 | 27.931 | 583.4 | 59.868 | 58.095 | 34.614 | 2.3322 | 1.0953 |
| 427 | 28.380 | 561.9 | 62.847 | 61.524 | 37.9985 | 2.4710 | 1.0644 |
| 428 | 28.834 | 540.6 | 66.465 | 65.212 | 41.8682 | 2.651 | 1.0042 |
| 429 | 29.294 | 517.5 | 70.363 | 69.843 | 46.7895 | 2.8226 | 0.9455 |
| 430 | 29.758 | 493.2 | 75.238 | 75.400 | 52.9755 | 3.0276 | 0.8600 |
| 431 | 30.232 | 466.9 | 81.076 | 82.330 | 61.1808 | 3.2923 | 0.7104 |
| 432 | 30.711 | 436.7 | 88.345 | 91.850 | 73.1933 | 4.1833 | 0.4748 |
| 433 | 31.195 | 387.5 | 106.55 | 112.80 | 102.105 | 3.6241 | 0.1209 |
| 433.5 | 31.442 | 366.4 | 116.63 | 123.25 | 119.226 | 4.3697 | 0.4614 |
| 433.7 | 31.545 | 311 | 154.38 | 162.19 | 90.6239 | 3.4713 | 0.9533 |
|  |  |  | 43.084 | 43.09 | 32.054 | 1.722 | 0.615 |

# TABLE C-11 Cyclo Propane

| T(K) | P (bar) | Vexp (cm^3/ mole) | DEV SOAVE | DEV PR | DEV VIRIAL/B | DEV VIRIAl/C |
|---|---|---|---|---|---|---|
| 357.03 | 44.4155 | 456.2605 | 17.9413 | 18.2966 | 0.7848 | 2.1485 |
| 358.06 | 45.3985 | 444.6794 | 18.4609 | 18.8145 | 0.9606 | 2.1323 |
| 359.08 | 46.3854 | 433.6093 | 18.9491 | 19.3008 | 1.1605 | 2.1123 |
| 360.09 | 47.3723 | 422.8797 | 19.4754 | 19.8253 | 1.3543 | 2.1815 |
| 361.08 | 48.3592 | 412.6611 | 19.9804 | 20.3279 | 1.5719 | 2.0854 |
| 362.05 | 49.3462 | 402.6128 | 20.5553 | 20.9008 | 1.7770 | 2.0892 |
| 363.01 | 50.3331 | 393.0755 | 21.0995 | 21.4426 | 2.0066 | 2.0731 |
| 363.95 | 51.3200 | 393.0755 | 21.6511 | 21.9919 | 2.2501 | 2.0518 |
| 364.88 | 52.3069 | 375.0226 | 22.2094 | 22.5476 | 2.2504 | 2.0286 |
| 365.8 | 53.2938 | 366.5071 | 22.7223 | 23.0578 | 2.7863 | 2.0069 |
| 366.71 | 54.2807 | 358.162 | 23.3788 | 23.7117 | 3.0347 | 1.9907 |
| 367.6 | 55.2677 | 350.157 | 23.9743 | 24.3044 | 3.3229 | 1.9639 |
| 368.4 | 56.2543 | 342.4934 | 24.5527 | 24.8799 | 3.6309 | 1.9242 |
| 369.3 | 57.2415 | 334.9998 | 25.1706 | 25.4947 | 3.9428 | 1.8953 |
| 370.2 | 58.2284 | 327.676 | 25.8255 | 26.1466 | 4.2612 | 1.8751 |
| 371.0 | 59.2154 | 320.6937 | 26.4423 | 26.7601 | 4.6117 | 1.82845 |
| 371.8 | 60.2032 | 313.8813 | 27.0930 | 27.4076 | 4.9655 | 1.7934 |
| 372.7 | 61.1892 | 307.2393 | 27.7630 | 28.0750 | 5.3388 | 1.75248 |
| 373.5 | 62.1762 | 300.7675 | 28.4630 | 28.7709 | 5.7195 | 1.7235 |
| 374.3 | 63.1631 | 294.6363 | 29.1075 | 29.4117 | 6.1297 | 1.6656 |
| 375.1 | 64.1500 | 288.5052 | 29.8357 | 30.1364 | 6.5513 | 1.6251 |
| 375.9 | 65.1369 | 282.5443 | 30.5832 | 30.8802 | 6.9855 | 1.5883 |
| 376.7 | 66.1238 | 276.7538 | 31.3409 | 31.6342 | 7.4408 | 1.5465 |
| 377.4 | 67.1107 | 271.1335 | 32.1053 | 32.3947 | 7.9186 | 1.4985 |
| 378.2 | 68.0977 | 265.6836 | 32.4481 | 32.7326 | 8.4580 | 1.4428 |
| 378.9 | 69.0846 | 260.404 | 33.6216 | 33.9030 | 8.9470 | 1.3783 |
| 379.7 | 70.0715 | 255.2947 | 34.4007 | 34.6779 | 9.4965 | 1.3038 |
| 380.4 | 71.0585 | 250.1854 | 35.2514 | 35.5242 | 10.0615 | 1.25242 |
|  |  |  | 25.8715 | 26.191 | 4.5705 | 1.820 |

# TABLE C-12 I-Pentane

| T(R) | P (psia) | Vexp (ft^3/lb) | DEV SOAVE | DEV PR | DEV VIRIAL/B | DEV VIRIAl/C |
|---|---|---|---|---|---|---|
| 460 | 2.18 | 2236.62 | 0.5603 | 0.2584 | 0.7932 | 0.8073 |
| 470 | 2.87 | 1715.85 | 0.6746 | 0.3035 | 0.8511 | 0.8695 |
| 480 | 3.73 | 1343.05 | 0.7976 | 0.3474 | 0.9106 | 0.9342 |
| 490 | 4.78 | 1065.27 | 0.8827 | 0.3442 | 1.0123 | 1.0418 |
| 500 | 6.05 | 854.779 | 1.0179 | 0.3815 | 1.0733 | 1.1093 |
| 510 | 7.59 | 691.286 | 1.2254 | 0.4793 | 1.0805 | 1.1238 |
| 520 | 9.42 | 564.634 | 1.3879 | 0.5230 | 1.1396 | 1.1903 |
| 530 | 11.57 | 465.5956 | 1.6459 | 0.6528 | 1.1199 | 1.1780 |
| 540 | 14.12 | 386.050 | 1.6024 | 0.4731 | 1.3974 | 1.4623 |
| 550 | 17.06 | 322.975 | 1.9491 | 0.6727 | 1.3300 | 1.4011 |
| 560 | 20.46 | 271.993 | 2.0581 | 0.6297 | 1.4970 | 1.5723 |
| 570 | 24.35 | 230.589 | 2.2757 | 0.6897 | 1.5870 | 1.6638 |
| 580 | 28.79 | 196.548 | 2.6359 | 0.8802 | 1.5808 | 1.6559 |
| 590 | 33.86 | 168.449 | 1.7735 | 0.1346 | 2.6556 | 2.7217 |
| 600 | 39.46 | 145.3154 | 2.7496 | 1.1760 | 2.1770 | 2.2308 |
| 610 | 45.77 | 125.8325 | 3.7728 | 1.3133 | 1.9892 | 2.0215 |
| 620 | 52.84 | 109.4002 | 4.4821 | 1.8283 | 2.1766 | 2.1762 |
| 630 | 60.72 | 95.3860 | 4.2956 | 1.4672 | 2.1185 | 2.0715 |
| 640 | 69.49 | 85.859 | 5.3641 | 2.3240 | 2.8270 | 2.7183 |
| 650 | 79.20 | 75.037 | 5.8596 | 2.6203 | 2.6679 | 2.4724 |
| 660 | 89.92 | 66.1625 | 5.4875 | 5.8596 | 3.0397 | 2.7328 |
|  |  |  | 2.4031 | 1.1422 | 1.6678 | 1.6740 |

# TABLE C-13 Ammonia

| T(k) | P(atm) | Vexp (cm^3/ mole) | DEV SOAVE | DEV PR | DEV VIRIAL /B | DEV VIRIAl /C | DEV This work |
|---|---|---|---|---|---|---|---|
| 357.03 | 44.4115 | 456.260 | 15.283 | 15.4402 | 0.0966 | 2.1485 | 2.1070 |
| 358.06 | 45.398 | 444.679 | 16.1255 | 15.9190 | 0.0023 | 2.1323 | 2.1439 |
| 359.08 | 46.385 | 423.609 | 16.5784 | 16.3762 | 0.1449 | 2.1123 | 2.1426 |
| 360.09 | 47.372 | 422.879 | 16.9818 | 16.8753 | 0.2781 | 2.1081 | 2.1509 |
| 361.09 | 48.359 | 412.661 | 17.4051 | 17.3253 | 0.4474 | 2.0853 | 2.1421 |
| 362.05 | 49.346 | 402.612 | 17.8885 | 17.7953 | 0.6186 | 2.0891 | 2.1306 |
| 363.09 | 50.333 | 393.075 | 18.3275 | 18.3275 | 0.7708 | 2.0730 | 2.1485 |
| 363.95 | 51.3200 | 391.755 | 18.7645 | 18.8145 | 0.9606 | 2.0518 | 2.1323 |
| 365.8 | 53.2938 | 366.507 | 19.2395 | 19.3008 | 1.1605 | 2.0006 | 2.1123 |
| 366.71 | 54.2807 | 358.162 | 19.6919 | 19.8253 | 1.3543 | 1.9907 | 2.1081 |
| 367.6 | 55.2677 | 350.153 | 20.7048 | 20.3279 | 1.5719 | 1.9639 | 2.0891 |
| 368.48 | 56.2546 | 342.493 | 21.2026 | 20.9008 | 1.7770 | 1.9242 | 2.0730 |
| 370.21 | 58.2284 | 327.676 | 21.7061 | 21.4426 | 2.0066 | 1.8751 | 2.0518 |
| 371.05 | 59.2154 | 320.693 | 22.2091 | 21.9919 | 2.2501 | 1.8284 | 2.0286 |
| 371.89 | 60.2023 | 313.818 | 22.7634 | 22.5476 | 2.5041 | 1.7934 | 2.0006 |
| 372.71 | 61.1892 | 307.239 | 23.3023 | 23.10354 | 2.7711 | 1.7542 | 1.9907 |
| 372.71 | 62.1761 | 300.767 | 23.8235 | 23.7117 | 3.0347 | 1.7234 | 1.9639 |
| 373.53 | 63.1630 | 294.636 | 24.3832 | 24.3044 | 3.3229 | 1.6656 | 1.9242 |
| 374.34 | 64.1500 | 288.505 | 24.9790 | 24.8799 | 3.6309 | 1.6250 | 1.8952 |
| 375.13 | 65.1369 | 282.544 | 26.1272 | 25.4947 | 3.9428 | 1.5882 | 1.8751 |
| 375.92 | 66.1238 | 276.753 | 26.7375 | 26.1466 | 4.2612 | 1.5465 | 1.7934 |
| 376.7 | 67.1107 | 271.133 | 27.3747 | 27.4076 | 4.9655 | 1.4984 | 1.7542 |
| 377.47 | 68.0977 | 265.683 | 27.9570 | 28.0756 | 5.3388 | 1.4428 | 1.7234 |
| 378.23 | 70.0715 | 255.294 | 28.6223 | 28.7709 | 5.7195 | 1.3038 | 1.6656 |
| 379.72 | 71.0584 | 2501.18 | 29.3055 | 29.4117 | 5.8325 | 1.2524 | 1.6250 |
| 380.72 | 72.0454 | 245.246 | 29.9982 | 30.1364 | 5.9923 | 1.1889 | 1.5882 |
| 381.19 | 73.0323 | 2403.37 | 30.6969 | 30.8802 | 6.0276 | 1.1380 | 1.5465 |
| 381.0 | 74.0192 | 235.538 | 31.3980 | 31.6342 | 6.4645 | 1.0729 | 1.4984 |
| 382.62 | 75.0061 | 230.940 | 32.0977 | 32.3947 | 6.8023 | 0.9929 | 1.4428 |
| 383.32 | 75.9931 | 226.512 | 32.7922 | 33.1581 | 7.0135 | 0.9056 | 1.3783 |
| 384.02 | 76.9800 | 222.084 | 33.5733 | 33.7251 | 7.2432 | 0.8269 | 1.3038 |
| 384.71 | 77.9669 | 217.656 | 33.8251 | 34.0251 | 7.6758 | 0.7639 | 1.2524 |
| 385.40 | 78.9538 | 213.398 | 34.0221 | 34.3251 | 7.8805 | 0.6744 | 1.6425 |
| AAD% | | | 24.448 | 24.3876 | 3.4504 | 0.929 | 1.875 |

# TABLE C-14 i-Butane

| T(k) | P (atm) | Vexp (cm^3/mole) | DEV SOAVE | DEV PR | DEV VIRIAL /B | DEV VIRIAl/C |
|---|---|---|---|---|---|---|
| 261.32 | 1 | 20682 | 0.7373 | 0.1101 | 0.0023 | 1.69852 |
| 270 | 1.39 | 15202 | 1.0312 | 0.2837 | 0.1449 | 1.7669 |
| 280 | 1.968 | 10921 | 1.8747 | 0.9314 | 0.2781 | 1.4371 |
| 290 | 2.714 | 8032 | 2.7049 | 1.6787 | 0.4474 | 1.2136 |
| 300 | 3.656 | 6031 | 3.5274 | 2.3716 | 0.6186 | 1.1166 |
| 310 | 4.826 | 4615 | 4.2171 | 2.9428 | 0.7708 | 1.2803 |
| 320 | 6.254 | 3577 | 5.2443 | 3.8573 | 0.9606 | 1.3619 |
| 330 | 7.975 | 2801 | 6.6687 | 5.1685 | 1.1605 | 1.3971 |
| 340 | 10.02 | 2209 | 8.7409 | 7.1161 | 1.3543 | 1.3050 |
| 350 | 12.44 | 1750 | 11.4798 | 9.7014 | 1.5719 | 1.2441 |
| 360 | 15.25 | 1387 | 15.5541 | 13.5686 | 1.7770 | 0.9788 |
| 370 | 18.52 | 1094 | 21.3483 | 19.0582 | 2.0066 | 0.7173 |
| 380 | 22.28 | 849.7 | 30.5465 | 27.7788 | 2.2501 | 0.3129 |
| 385 | 24.36 | 745.3 | 36.4548 | 33.3594 | 2.5041 | 0.3541 |
| 390 | 26.59 | 647.6 | 44.2023 | 40.6772 | 2.7711 | 0.5263 |
| 395 | 28.97 | 556.1 | 54.4850 | 50.3904 | 3.0347 | 0.9735 |
| 396 | 29.46 | 539.1 | 56.7822 | 52.5580 | 3.3229 | 1.1187 |
| 397 | 29.96 | 521.6 | 59.4119 | 55.0433 | 3.6309 | 1.2725 |
| 398 | 30.47 | 505.3 | 61.8717 | 57.3570 | 3.9428 | 1.4881 |
| 399 | 30.98 | 488.2 | 64.8632 | 60.1855 | 4.2612 | 1.6767 |
| 400 | 31.51 | 471 | 68.0776 | 63.2189 | 4.9655 | 1.9272 |
|  |  |  | 26.6582 | 24.1598 | 1.9579 | 1.1984 |

# APPENDIX D

## Results of Investigations for Mixtures

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**Table D-1 : Mixture of 0.2143 mole %Propane and 0.7857 mole % n-Octane .**

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 520.55 | 17.001 | 1545.19 | 3.7139 | 0.4361 | 4.7273 |
| 530.15 | 20.402 | 1241.57 | 11.3808 | 2.5615 | 2.0873 |
| 538.85 | 23.809 | 1021.64 | 20.6820 | 4.8847 | 0.1345 |
| 545.65 | 27.211 | 826.678 | 35.1573 | 6.0385 | 1.4639 |
| 550.45 | 30.612 | 623.908 | 162.0557 | 9.1132 | 0.6824 |
| 549.85 | 34.013 | 451.121 | 49.251 | 19.3451 | 3.3896 |
|  |  |  | 50.4982 | 5.10494 | 2.0808 |

**Table D-2 : Mixture of 0.3306 mole %Propane and 0.6694 mole % n-Octane .**

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 516.65 | 20.408 | 1300.63 | 6.1208 | 3.3272 | 3.01707 |
| 524.15 | 23.809 | 1110.29 | 12.9974 | 6.91655 | 0.47478 |
| 530.65 | 27.211 | 911.355 | 20.8161 | 7.7964 | 1.113233 |
| 536.15 | 30.612 | 771.652 | 31.3458 | 8.91726 | 2.64235 |
| 539.65 | 34.031 | 607.367 | 54.7068 | 6.4383 | 1.91642 |
| 539.65 | 37.414 | 535.870 | 76.5719 | 8.78195 | 6.65657 |
| AAD% |  |  | 33.7598 | 7.0295 | 2.6367 |

**Table D-3 : Mixture of 0.5729 mole %Propane and 0.4271 mole % n-Octane .**

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 479.15 | 17.0068 | 1851.249 | 3.36317 | 7.4064 | 1.30037 |
| 487.65 | 20.4081 | 1511.223 | 4.65465 | 8.3314 | 1.46734 |
| 495.15 | 23.8095 | 1276.723 | 6.71127 | 9.5517 | 2.16838 |
| 500.65 | 27.2108 | 1073.188 | 8.4883 | 9.8859 | 1.7977 |
| 505.15 | 30.6123 | 949.3582 | 12.46742 | 12.0986 | 3.8891 |
| 508.65 | 34.0136 | 813.7357 | 15.99074 | 12.3299 | 3.7539 |
| AAD% | | | 8.612588 | 7.3528 | 2.39614 |

**Table D-4 : Mixture of 0.7175 mole %Propane and 0.2825 mole % n-Octane .**

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 450.15 | 13.6054 | 2282.428 | 0.45137 | 4.0015 | 1.26228 |
| 458.75 | 17.0068 | 1831.175 | 1.50452 | 6.17836 | 0.1789 |
| 460.15 | 20.4082 | 1521.619 | 3.2233 | 7.8819 | 1.24178 |
| 472.15 | 23.8095 | 1278.16 | 4.18021 | 8.6533 | 1.26831 |
| 478.15 | 27.2108 | 1139.18 | 7.4886 | 11.3233 | 3.85705 |
| 484.15 | 30.6123 | 1065.133 | 12.17456 | 15.2366 | 8.2063 |
| 488.75 | 34.0136 | 819.333 | 7.12525 | 8.14707 | 0.7484 |
| 491.65 | 37.4149 | 727.0533 | 10.10858 | 9.5234 | 0.14095 |
| 492.75 | 38.2451 | 626.549 | 13.76164 | 9.9875 | 0.92391 |
| AAD% | | | 6.6686 | 8.9925 | 1.98089 |

Table D-5 : Mixture of 0.864 mole %Propane and 0.136 mole % n-Octane .

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 437.65 | 23.8095 | 1250.18 | 4.3497 | 8.78131 | 2.5558 |
| 441.95 | 27.2108 | 1115.026 | 7.6153 | 11.81644 | 5.3489 |
| 445.65 | 30.6122 | 940.925 | 6.5459 | 10.6820 | 3.1209 |
| 448.65 | 34.0136 | 812.617 | 6.8709 | 10.5598 | 2.0196 |
| 450.95 | 37.4144 | 715.1035 | 8.4083 | 11.2754 | 1.8778 |
| 452.45 | 40.8163 | 616.4868 | 9.8079 | 11.1742 | 0.39433 |
| 452.65 | 44.2176 | 511.2752 | 12.6328 | 10.5927 | 2.6992 |
| AAD% | | | 8.03297 | 8.3202 | 2.00186 |

Table D-6 : Mixture of 0.1823 mole %Propane and 0.8177 mole % n-Octane .

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 546.15 | 23.8095 | 945.486 | 10.0756 | 2.62426 | 1.7634 |
| 553.65 | 27.2108 | 693.356 | 14.40127 | 6.6721 | 0.9286 |
| 555.45 | 28.5714 | 581.025 | 18.7638 | 17.8653 | 1.4944 |
| AAD% | | | 14.41355 | 9.0538 | 1.3955 |

**Table D-7 : Mixture 0.4631 mole %Propane and 0.5369 mole % n-Octane**

.

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 527.25 | 30.6122 | 711.6806 | 4.6698 | 2.6892 | 0.17341 |
| 529.45 | 34.0136 | 562.0916 | 8.87988 | 2.7749 | 0.91889 |
| 529.55 | 35.3741 | 504.2765 | 11.9635 | 7.0594 | 1.14948 |
| 528.35 | 36.7347 | 443.4593 | 18.3069 | 12.4208 | 1.13542 |
| AAD% | | | 10.95502 | 6.23607 | 0.84429 |

**Table D-8 : Mixture 0.6709 mole %Propane and 0.3291 mole % n-Octane**

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 500.65 | 40.8163 | 411.7696 | 19.2566 | 1.5325 | 2.0974 |
| 498.95 | 41.4966 | 369.9958 | 23.5627 | 0.3519 | 2.1915 |
| 497.05 | 41.8367 | 331.5547 | 29.9298 | 1.7899 | 0.84651 |
| AAD% | | | 24.2497 | 1.2247 | 1.7179 |

**Table D-9 : Mixture 0.8183 mole %Propane and 0.1817 mole % n-Octane**

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 20.40816 | 456.95 | 1366.376 | 2.93264 | 6.05611 | 1.69247 |
| 23.8095 | 463.55 | 1138.647 | 3.8599 | 6.6378 | 1.49397 |
| 27.21088 | 469.05 | 948.8726 | 6.3869 | 6.16013 | 2.2032 |
| 30.61225 | 473.35 | 803.7509 | 8.9455 | 5.8291 | 2.1751 |
| 34.01361 | 476.35 | 690.0892 | 11.45102 | 5.8787 | 1.2473 |
| AAD% | | | 6.71519 | 6.11716 | 1.76243 |

Table D-10 : Mixture 0.9461 mole %Propane and 0.0539 mole % n-Octane .

| T(K) | P(bar) | Vexp (cm^3/ mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 443.55 | 39.4557 | 384.58 | 34.7854 | 4.7506 | 0.8354 |
| 443.15 | 39.7959 | 427.6099 | 21.9138 | 1.6439 | 2.5982 |
| 440.0 | 39.9524 | 258.0094 | 90.71753 | 11.2561 | 2.8827 |
| AAD% | | | 49.13891 | 5.8835 | 2.1054 |

Table D-11 : Mixture 0.16 mole %N2and 0.84 mole % He .

| T() | P() | Vexp() | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 311.65 | 2543.96 | 1.23573 | 0.03217 | 1.56013 | 0.0479 |
| 311.65 | 1765.79 | 1.471942 | 0.059917 | 1.09838 | 0.00398 |
| 311.65 | 1226.84 | 2.116553 | 0.0449 | 0.75516 | 0.005903 |
| 311.65 | 852.345 | 3.0444 | 0.06195 | 0.55021 | 0.03477 |
| 311.65 | 592.548 | 4.37773 | 0.632208 | 0.3000 | 0.02885 |
| AAD% | | | 0.16623 | 0.85278 | 0.024288 |

Table D-12 Mixture 0.314mole %N2and 0.686 mole % He .

| T() | P() | Vexp() | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 311.65 | 3706.67 | 0.707253 | 0.03357 | 1.5468 | 0.133375 |
| 311.65 | 2566.56 | 1.017025 | 0.053472 | 1.10614 | 0.01662 |
| 311.65 | 1780.17 | 1.4624 | 0.073417 | 0.78258 | 0.02434 |
| 311.65 | 1236.06 | 2.103009 | 0.06021 | 0.54213 | 0.025927 |
| AAD% | | | 0.05516 | 0.9444 | 0.05006 |

### Table D-13: Mixture of 0.564 mole %N2 and 0.436 mole % He

| T() | P() | Vexp() | AAD % Virial truncated to B and Virial mixing rules | AAD % Virial truncated to C with Virial mixing rules with Teja | AAD % Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 311.6 | 4301.34 | 0.61537 | 0.8138 | 0.4149 | 0.7711 |
| 311.6 | 3167.52 | 0.8306 | 0.5512 | 0.3103 | 0.5198 |
| 311.6 | 2337.26 | 1.1212 | 0.4024 | 0.2085 | 0.3794 |
| 311.6 | 1726.18 | 1.5133 | 0.2889 | 0.1484 | 0.2720 |
| 311.6 | 1276.18 | 2.0426 | 0.2096 | 0.1060 | 0.1972 |
| 311.6 | 943.943 | 2.7523 | 0.1516 | 0.0776 | 0.1425 |
| 311.6 | 698.534 | 3.7216 | 0.1156 | 0.0527 | 0.1077 |
| 311.6 | 517.061 | 5.0235 | 0.0845 | 0.0381 | 0.0794 |
| 311.6 | 383.008 | 6.7807 | 0.1115 | 0.0215 | 0.1078 |
| AAD % | | | 0.3032 | 2.6636 | 0.2863 |

### Table D-14 : Mixture of 0.178 mole %N2 and 0.822 mole % He

| T() | P() | Vexp() | AAD % Virial truncated to B and Virial mixing rules | AAD % Virial truncated to C with Virial mixing rules with Teja | AAD % Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 4425.87 | 0.7103 | 0.3421 | 1.4645 | 0.4495 |
| 373.15 | 3265.09 | 0.9585 | 0.1557 | 1.1468 | 0.2359 |
| 373.15 | 2411.94 | 1.2936 | 0.0362 | 0.9087 | 0.0959 |
| 373.15 | 1783.32 | 1.7459 | 0.0421 | 0.7311 | 0.0023 |
| 373.15 | 1319.45 | 2.3561 | 0.0881 | 0.5925 | 0.0551 |
| 373.15 | 976.773 | 3.1800 | 0.0971 | 0.4673 | 0.0726 |
| 373.15 | 723.15 | 4.2915 | 0.0991 | 0.3715 | 0.0899 |
| 373.15 | 535.907 | 5.7911 | 0.0839 | 0.2846 | 0.0704 |
| AAD % | | | 0.1057 | 0.7815 | 0.1328 |

Table D-15 : Mixture of 0.86 mole %N2 and 0.14 mole % He

| T() | P() | Vexp() | AAD % Virial truncated to B and Virial mixing rules | AAD % Virial truncated to C with Virial mixing rules with Teja | AAD % Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 311.65 | 4245.51 | 0.6240 | 1.6753 | 0.4141 | 1.5507 |
| 311.65 | 3127.19 | 0.8373 | 0.6600 | 0.2455 | 0.5663 |
| 311.65 | 2307.27 | 1.1369 | 0.9347 | 0.2944 | 0.8659 |
| 311.65 | 1703.88 | 1.5346 | 0.6921 | 0.2300 | 0.6410 |
| 311.65 | 1259.36 | 2.0713 | 0.5143 | 0.1787 | 0.4764 |
| 311.65 | 931.58 | 2.7959 | 0.4044 | 0.1596 | 0.3763 |
| 311.65 | 689.31 | 3.7740 | 0.3123 | 0.1329 | 0.291 |
| 311.65 | 510.17 | 5.0941 | 0.2357 | 0.1040 | 0.2203 |
| AAD % | | | 0.6786 | 0.2199 | 0.6236 |

Table D-16 : Mixture of 0.513 mole %N2 and 0.487 mole % He

| T() | P() | Vexp() | AAD % Virial truncated to B and Virial mixing rules | AAD % Virial truncated to C with Virial mixing rules with Teja | AAD % Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 4388.58 | 0.7201 | 0.5986 | 0.8859 | 0.3883 |
| 373.15 | 3233.78 | 0.9718 | 0.8095 | 0.6992 | 0.2099 |
| 373.15 | 23869.6 | 1.3116 | 1.0939 | 0.5636 | 0.0905 |
| 373.15 | 1763.35 | 1.7701 | 1.477 | 0.4586 | 0.0153 |
| 373.15 | 1303.74 | 2.3889 | 1.9957 | 0.3958 | 0.0507 |
| 373.15 | 964.816 | 3.2240 | 2.6938 | 0.3168 | 0.0644 |
| 373.15 | 714.239 | 4.3508 | 3.6360 | 0.2612 | 0.0761 |
| 373.15 | 528.916 | 5.8716 | 4.9071 | 0.2121 | 0.0759 |
| AAD % | | | 2.1515 | 0.5007 | 0.1214 |

Table D-17 : Mixture of 0.672 mole %N2 and 0.328 mole % He

| T() | P() | Vexp() | AAD % Virial truncated to B and Virial mixing rules | AAD % Virial truncated to C with Virial mixing rules with Teja | AAD % Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 4488.69 | 0.7042 | 0.7242 | 0.9234 | 0.5580 |
| 373.15 | 3305.93 | 0.9505 | 0.4201 | 0.7656 | 0.2966 |
| 373.15 | 2439.70 | 1.2827 | 0.2348 | 0.6238 | 0.1431 |
| 373.15 | 1802.57 | 1.7311 | 0.1138 | 0.5114 | 0.0457 |
| 373.15 | 1332.82 | 2.3363 | 0.0240 | 0.4331 | 0.0264 |
| 373.15 | 986.196 | 3.1531 | 0.0279 | 0.3632 | 0.0653 |
| 373.15 | 730.046 | 4.2553 | 0.0565 | 0.3031 | 0.0843 |
| 373.15 | 401.044 | 7.7398 | 0.0528 | 0.1870 | 0.0681 |
| AAD % | | | 0.2068 | 0.5372 | 0.1609 |

Table D-18 : Mixture of 0.199 mole %N2 and 0.881 mole % He

| T() | P() | Vexp() | AAD % Virial truncated to B and Virial mixing rules | AAD % Virial truncated to C with Virial mixing rules with Teja | AAD % Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 1989 | 1.4748 | 4.5836 | 0.2249 | 4.5836 |
| 373.15 | 1423.6 | 2.0937 | 3.2769 | 0.2112 | 3.2769 |
| 373.15 | 1014.8 | 2.9728 | 2.2690 | 0.1143 | 2.2690 |
| 373.15 | 720.62 | 4.2203 | 1.6191 | 0.1028 | 1.6191 |
| 373.15 | 510.67 | 5.9916 | 1.1259 | 0.0590 | 1.1259 |
| 373.15 | 361.12 | 8.506 | 0.7979 | 0.0469 | 0.7979 |
| 373.15 | 255.23 | 12.0782 | 0.4994 | 0.0288 | 0.4994 |
| AAD % | | | 2.0245 | 0.1125 | 2.0245 |

**Table D-19 : Mixture of 0.248 mole %CO2 and 0.752 mole % ethylene**

| T(k) | P(kpa) | Vexp(m^3/mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 2045.95 | 1.4279 | 4.0540 | 0.4759 | 4.0540 |
| 373.15 | 1463.44 | 2.0369 | 2.5689 | 0.0646 | 2.5689 |
| 373.15 | 1043.14 | 2.8919 | 1.8165 | 0.0502 | 1.8165 |
| 373.15 | 740.787 | 4.1050 | 1.3058 | 0.0602 | 1.3058 |
| 373.15 | 524.965 | 5.8281 | 0.8993 | 0.0218 | 0.8993 |
| AAD% | | | 2.1289 | 0.1345 | 2.1289 |

**Table D-20 : Mixture of 0.695 mole %CO2 and 0.305 mole % ethylene**

| T(k) | P(kpa) | Vexp(m^3/mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 3143 | 0.9097 | 4.6002 | 0.4603 | 4.6002 |
| 373.15 | 2266.43 | 1.2916 | 3.2973 | 0.3016 | 3.2973 |
| 373.15 | 1262.87 | 1.8339 | 2.1306 | 0.4133 | 2.1306 |
| 373.15 | 1161.18 | 2.6035 | 1.3294 | 0.4668 | 1.3294 |
| 373.15 | 825.292 | 3.6959 | 0.8099 | 0.4580 | 0.8099 |
| AAD% | | | 2.4334 | 0.4200 | 2.4334 |

Table D-21 : Mixture of 0.933 mole %H2S and 0.067mole % CH4

| T(k) | P(kpa) | Vexp(m^3/mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 230.594 | 213.678 | 8.7282 | 2.4389 | 2.4396 | 0.6442 |
| 262.816 | 758.214 | 2.5833 | 6.9098 | 6.9428 | 5.6898 |
| 289.261 | 1702.53 | 1.3016 | 11.1443 | 11.2739 | 0.5913 |
| 323.316 | 3687.67 | 0.6401 | 15.3498 | 16.0095 | 0.9198 |
| 352.983 | 6341.42 | 0.3780 | 16.8320 | 18.3251 | 1.4724 |
| AAD% | | | 10.5349 | 10.9979 | 1.8635 |

Table D-22 : Mixture of 0.771 mole %H2S and 0.229 mole % CH4

| T(k) | P(kpa) | Vexp(m^3/mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 197.816 | 48.25 | 33.4289 | 1.6580 | 1.6584 | 1.1497 |
| 233.15 | 337.75 | 5.8382 | 2.9224 | 2.9107 | 4.6908 |
| 282.761 | 1654.28 | 1.3188 | 3.6850 | 3.9443 | 1.6223 |
| 311.5945 | 3446.42 | 0.6601 | 6.8349 | 7.8399 | 1.7103 |
| AAD% | | | 3.7751 | 4.0883 | 2.2933 |

Table D-23 : Mixture of 0.458 mole %H2S and 0.542 mole % CH4

| T(k) | P(kpa) | Vexp(m^3/mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 198.205 | 117.178 | 13.9745 | 0.1849 | 0.1787 | 1.283 |
| 230.8722 | 544.535 | 3.3943 | 1.2798 | 1.3684 | 1.6995 |
| 254.1722 | 1316.53 | 1.5274 | 0.2994 | 0.7910 | 4.8746 |
| 276.7611 | 3012.17 | 0.63923 | 8.5171 | 11.6032 | 2.27813 |
| AAD% | | | 2.57036 | 3.4853 | 2.5340 |

**Table D-24 : Mixture of 0.15 mole %H2 and 0.85 mole % CH4**

| T(k) | P(kpa) | Vexp(m^3/mole) | AAD% Virial truncated to B and Virial mixing rules | AAD% Virial truncated to C with Virial mixing rules with Teja | AAD% Virial Truncated to C and Virial mixing rules |
|---|---|---|---|---|---|
| 373.15 | 3510.1 | 0.617169 | 4.5891 | 5.4500 | 4.2067 |
| 270 | 3464 | 0.617169 | 4.7373 | 5.6011 | 4.2743 |
| 260 | 3315.2 | 0.617169 | 5.3122 | 6.187 | 4.5767 |
| 250 | 3169.4 | 0.617131 | 5.8466 | 6.7330 | 4.8111 |
| 240 | 3021.8 | 0.617131 | 6.4879 | 7.3880 | 5.1197 |
| 230 | 2869.8 | 0.617131 | 7.3585 | 8.2755 | 5.6170 |
| 220 | 2719.9 | 0.617131 | 8.2415 | 9.1775 | 6.0822 |
| 210 | 2569.7 | 0.617093 | 9.2456 | 10.2038 | 6.6139 |
| 200 | 2418.2 | 0.61709 | 10.4244 | 11.4091 | 7.2538 |
| 190 | 2266.1 | 0.61705 | 11.79512 | 12.8116 | 8.0042 |
| AAD% | | | 7.40386 | 8.3236 | 5.6559 |

# الخلاصة

التنبؤ بالحجم المولي للبخار المشبع يمكن ان يحسب من عدد من معادلات الحالة، البعض من هذه المعادلات يطبق على كلا الطورين السائل والغازي ،والبعض منها يطبق على الطور الغازي فقط . ان دقة هذه المعادلات مختلفة. للمركبات النقية ،الحجم المولي للبخار المشبع يمكن ان يحسب من عدد من المعادلات مثل معادلة لي كسلر التي تعطي انحراف عالي جدا عن الحجم المولي المقاس عمليا ،وقد استعملت لحساب الحجم المولي لثلاث مركبات (72نقطة قطبية وغير قطبية) مع نسبة مئوية لمعدل الخطأ 62.8654 ،وعندما وجد ان انحرافه عالي جدا فلا توجد حاجه لاستخدام هذه المعادلة للمركبات الأخرى. معادلة ريدلك –سواف هي ثاني معادلة حالة استخدمت لحساب الانحراف للحجم المولي في هذا المشروع ،وقد أعطت نسبة مئوية لمعدل الخطأ 15.3125% لأربع عشرة مركب (299نقطة). معادلة الحالة بينغ- روبنسون استخدمت في هذا المشروع وطبقت على 299 نقطة وأعطت نسبة مئوية لمعدل الخطأ 14.3476 % .

واخيرا معادلة الحالة فيريال والتي يمكن ان تستعمل لحساب الحجم المولي (معادلة فيريال المقطوعة للحد الثاني و معادلة فيريال المقطوعة للحد الثالث )،استخدام معادلة فيريال المقطوعة للحد الثاني تعطي نسبة مئوية لمعدل الخطأ 7.5525% ل299نقطة (قطبية وغير قطبية )وهذا الانحراف العالي نسبيا سببه أن حدود بعض المركبات في هذا المشروع عالية نسبيا بينما الحد الثاني يستعمل لضغوط واطئة نسبيا (لا تتجاوز 15 بار) . بينما معادلة فيريال المقطوعة للحد الثالث تعطي نتائج افضل حيث ان النسبة المئوية لمعدل الخطأ هي 1.0955% هذا لانه يمكن استخدامها لضغوط حدودها اكبر من معادلة فيريال المقطوعة للحد الثاني (تصل الى 50 بار).

من المقارنة أعلاه ،يمكن بسهولة أن ندرك ان معادلة فيريال المقطوعة هي أحسن معادلة يمكن استخدامها لحساب الحجم المولي ، ومن الواضح أيضا إن معادلة المقطوعة للحد الثالث هي أحسن من المقطوعة للحد الثاني بالنسبة للظروف الموجودة في هذا المشروع (الضغوط و درجات الحرارة) .

الارتباط يجب أن يتم على هذه المعاملات لمعدلة فيريال لكي تقلل الانحراف للحجم المولي المحسوب من تلك المعادلات. بالنسبة لمعامل فيريال الثاني وباستخدام الطرق الإحصائية فان الارتباط قد طور وهذا التعديل قد حسن نسبة الانحراف من 7.5525 إلى 3.5209 باستخدام 89 نقطة لأربع مركبات وبعدها طبق هذا التطوير على 210 نقاط .

$$B0m = 0.1258 - \frac{0.3017}{Tr} - \frac{0.1258}{Tr^{2.31}} - \frac{0.01325}{Tr^{3.21}} - \frac{0.005748}{Tr^{7.85}}$$

$$B1m = 0.05257 + \frac{0.3575}{Tr^{1.8}} - \frac{0.47155}{Tr^{3}} - \frac{0.002184}{Tr^{7.85}}$$

إن الارتباط طور لتحسين نسبة الانحراف للحجم المولي المحسوب باستخدام معادلة فيريال المقطوعة للحد الثالث تعطي انحراف مقبول نسبيا ويقلل الانحراف من 1.0955 الى0.7899 % هذا الارتباط طور باستخدام 60 نقطة لـ3 مركبات قطبية وغير القطبية وطبقت 239 نقطة (11مركب قطبي وغير قطبي).

$$C1m = 0.022501 + \frac{1.265968}{Tr^{5}} - \frac{0.507}{Tr^{5.5}} - \frac{0.75663}{Tr^{4.4}}$$

بالنسبة للخلائط الثنائية ،حساب الحجم المولي للبخار المشبع تم باستخدام ثلاث طرق.

الطريقة الأولى تتم عن طريق استخدام معادلة فيريال المطورة المقطوعة للحد الثاني مع قانون فيريال للخلائط وقد أعطت نسبة انحراف عالية نسبيا عن الحجم المولي المستحصل من التجارب العملية ،النسبة المئوية لمعدل الخطا هي 8.3919% استخدمت 142 نقطة (6 خلائط).

الطريقة الثانية تمت باستخدام معادلة فيريال المطورة المقطوعة للحد الثالث و معادلة تيجا مع قوانين فيريال للخلائط وهذا يعطي نسبة مئوية لمعدل الخطأ 3.4669 % باستخدام 142 نقطة (6خلائط)،وهذه النسبة هي أفضل نسبيا عن تلك المستحصلة من معادلة فيريال المطورة المقطوعة للحد الثاني .

الطريقة الثالثة تمت باستخدام معادلة فيريال المطورة المقطوعة للحد الثالث مع قوانين فيريال للخلائط وهذه الطريقة أعطت اقل انحراف واحسن دقة من الطريقتين السابقتين المستخدمة لحساب الحجم المولي للبخار المشبع للخلائط الثنائية، نسبة مئوية لمعدل الخطا هي 1.4967% باستخدام 142 نقطة (6خلائط).

## شكر وتقدير

اتقدم بجزيل الشكر و الامتنان الى الاستاذ الدكتور محمود عمر عبدالله المحترم على نصائه القيمة والجهد المبذول م اجل انجاز هذا المشروع . كما واتقدم بالشكر الى السيد عميد كلية الهندسة المحترم والسيد رئيس قسم الهندسة الكيمياوية المحترم على ما قدماه من دعم ومساعدة.

واخيرا اتقدم بجزيل شكري وعظيم امتناني الى اغلى من في هذه الدنيا الى ابي وامي والى زوجي شريك الافراح والاحزان والى جميع افراد عائلتي لدعمهم المتواصل وتشجيعهم الدائم ومساعدتهم في انجاز هذا المشروع .

# التحقق من الارتباطات للتنبؤ بحجم البخار المشبع للمركبات النقية والخلائط

رسالة
مقدمة إلى كلية الهندسة
في جامعة النهرين و هي جزء
من متطلبات نيل درجة
ماجستير علوم
في
الهندسة الكيمياوية

من قبل

ورقاء عبدالرضا كاظم الشمري
بكالوريوس علوم في الهندسة الكيمياوية ٢٠٠٣

ربيع الثاني ١٤٢٧
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