

**PREDICTION AND CORRELATIONS OF
SATURATED LIQUID MOLAR VOLUME
AT ANY TEMPERATURE (INCLUDING
NORMAL BOILING POINT) FOR PURE
COMPONENTS AND MIXTURES**

A Thesis

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Abstract

There are many different correlations available in the literature applied to predict saturated liquid molar volumes for pure compounds. They are Rackett, Spencer and Danner, Yamada and Gunn, Yen Woods, Bradford and Thodos, Reidel, and Hankinson Thomson equations. The investigation of these empirical correlations shows that the best correlation was Hankinson and Thomson equation (HT) for nonpolar and Reidel for Polar components.

There are many methods are available in the literature to predict saturated molar volume of pure liquid compounds at normal boiling point. They are Tyn and Calus, Schroeder, and Le Bas methods. The results show that Tyn and Calus have the highest accuracy among the three correlations. Further more it is simple and easy to use.

The modification of HT equation has been started from the idea that the modification of constants may lead to more accurate results for calculating saturated liquid molar volume.

The value of constants in equation $V_r^{(0)}$ have been estimated using data of Ar for ($\omega=0$), the correlation coefficient of this equation is 0.99998. The second variable of HT equation is $V_r^{(\delta)}$ had constructed for compounds that have a maximum acentric factor like Methane, n-Pentane and Ethanol, and the correlation coefficient of this equation is 0.9896.

The new constants are

$$\begin{array}{llll} a = -1.22916 & b = 0.087280 & c = 1.283902 & d = 0.902008 \\ e = -0.707480 & f = 1.771180 & g = -1.70029 & h = 0.636584 \end{array}$$

The experimental data of the molar volume of saturated liquids, obtained from the literature for the purpose of this investigation consists of 250 data points of six polar pure compounds, and 555 data points of twenty non polar pure compounds. The AAD% of the twenty non polar compounds

for 555 data points is 1.1236% for Rackett, 4.1991% for Yen Wood, 0.9645% for Yamada and Gunn, 1.3593% for Spencer and Danner, 0.9449% for Reidel, 1.2860% for Bradford and Thodos, 0.9141% for Hankinson Thomson, and finally the AAD%. For the modified Hankinson Thomson equation is 0.7888%. The AAD% of the six polar compounds for 250 data points is 2.4863% for Rackett, 4.7266% for Yen Wood, 2.5344% for Yamada and Gunn, 7.1465% for Spencer and Danner, 2.1153% for Reidel, 2.2019% for Bradford and Thodos, 2.2967% for Hankinson Thomson, and finally the AADW%. for the modified Hankinson Thomson equation is 1.7138%.

Another modified correlation was made for Tyn and Calus for changing the slop of data points to another constant, the deviation of data was decreased for nonpolar compounds. So effort was made to modify it to increase its accuracy and to reduce its deviation from experimental value as much as possible using statistical methods. The equation in modified form is:

$$V_b = 0.348V_c^{1.016}$$

The AD% of nonpolar compounds is 3.7716% for Tyne and calus, 4.8210% for Schroeder, 9.5667% for Le Bas and finally the AD% for modified Tyne and calus is 1.1624%, but the results of polar compound were not satisfactory, The AD% of polar compounds is 1.164% for Tyne and calus, 6.2015% for Schroeder, 7.2987% for Le Bas and finally the AD% for modified Tyne and calus is 1.7436%.

On the other hand many other correlations were used to predict molar volumes for mixtures, Hankinson Thomson mixing rule was applied to Hankinson Thomson model and developed Hankinson Thomson. The experimental data of the molar volume of saturated liquids mixtures obtained from the literature for the purpose of this investigation consists of 792 data points of 26 mixtures. The results were obtained for modified HT equation equal to 2.8953 AAD%, while for HT equation is 5.2811 AAD%.

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Nomenclature

Symbol	Description	Units
AAD	Absolute Average Deviation	
EOS	Equation of state	
M.WT	Molecular weight	g/gmol
P	Pressure	Pa
PR	Peng Robinson	
R	Gas constant	J/mole.K
SRK	Sove Redlich Kowing	
T	Temperature	K
x	Mole fraction	
V	Volume	cm ³
V*	characteristic volume	
w	Acentric Factor	
Z	Compressibility factor	
Z _{RA}	unique constant for each compound	
ρ	Density	kg/m ³
α	adjustable parameters	
β	adjustable parameters	

Subscript

Symbol	Description
b	Boiling
c	Critical
cm	Critical for mixture
DB	Double bonds
i	Species
r	Reduced
rs	Reduced in saturation
s	Saturated
sat	Saturated
SC	Scaled
TB	Triple bonds

Superscript

Symbol	Description
(o)	At $\omega = 0$
(δ)	At any ω

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Molar volume is one of the most important thermodynamic properties of a compound. In almost all design calculation, there is a need of the value of molar volume. For saturated liquid or vapor and for gas phase, volume V is important in high pressure processing and particularly in the design and operating high pressure pumps for all liquids in the chemical processing and factories. The volume handling and power characteristics of such pumps are strongly influenced by liquid's isothermal bulk compressibility [1].

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

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

Pure gases are classified as polar and non polar gases. Non polar gases are classified as [1, 2]:

1. Fluids with spherical molecules (simple fluids) as example Argon and Krypton, having a zero acentric factor ($\omega=0$).
2. Quantum gases as example He, H, having negative acentric factor ($\omega<0$).
3. Other nonpolar fluids as example Benzene, n-Butane, having positive acentric factor ($\omega>0$).

Polar gases are classified as:

1. Non hydrogen bonding components such as Ketones, and aldehydes.
2. Hydrogen bonding compounds (a bond forms between the hydrogen atom attached to oxygen in one molecule with the oxygen atom of another molecule) such as alcohols, and water.

1.2 Aim of This Work

- 1- Calculate the molar volume of saturated liquid using many equations and to 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, this modification will be tried by using a statistical methods.
- 2- Calculate the molar volume at normal boiling point using three equations and find the best one, then to modify it using statistical method.
- 3- Applying a suitable mixing rule to the best equation and its modified.

CHAPTER TWO

THEORIES AND LITERATURES

2.1 Introduction.

Liquid densities are needed in many engineering problems such as process calculations, simulations, equipment and pipe design, high pressure vapor-liquid equilibrium studies and liquid metering calculations [3]. Corresponding states theory correlations play an important role in predicting these densities at various conditions [4]. Not infrequently densities and other properties are required at temperatures for which no experimental data exist [5]. A good liquid density correlation should be accurate and reliable over the whole liquid region from the freezing point to the critical point. In most practical cases, the fluids of interest are mixtures [6].

The merit of a complex equation of state lies in its versatility, i. e., the equation may be applicable to all phases, liquid, vapor, and dense phase. However, for the calculation of saturated liquid molar volume alone, simpler equations are often more accurate and easier to use. Numerous accurate corresponding states correlations for the liquid molar volume have been reported in the literature in the past decade [7]. A few of the most widely used correlations are discussed here.

2.2 Density and Molar Volume of Saturated Liquids.

Density shown by d or ρ is defined as mass per unit volume and it is reciprocal of specific volume. Density may also be presented in terms of number of moles per unit volume, which is called *molar density* and it is

reciprocal of molar volume. It can be obtained by dividing absolute density by molecular weight [8].

Density is perhaps one of the most important physical properties of a fluid, since in addition to its direct use in size calculations it is needed to predict other thermodynamic properties, methods to estimate transport properties of dense fluids also require reduced density. Therefore once an accurate value of density is used as an input parameter for a correlation to estimate a physical property, a more reliable value of that property can be calculated. Density may be expressed in the form of absolute density (ρ , g/cm³), molar density (ρ_m , mol/cm³), specific volume (V , cm³/g), molar volume (V_m , cm³/mol), reduced density ($\rho_r = \rho / \rho_c = V_c/V$, dimensionless), or compressibility factor ($Z = PV/RT$ dimensionless) [9].

Density is a state function and for a pure compound depends on both temperature and pressure. Liquid densities decrease as temperature increases but the effect of pressure on liquid densities at moderate pressures is usually negligible. At low and moderate pressures (less than a few bars), saturated liquid density is nearly the same as actual density at the same temperature [10].

Equations of states or generalized correlations predict V_m or Z at a given T and P . Once Z is known, the absolute density can be calculated from:

$$\rho = \frac{MP}{ZRT} \quad (2-1)$$

where M is the molecular weight, R is the gas constant, and T is the absolute temperature. If M is in g/mol, P in bars, T in Kelvin, and $R = 83.14$ bar·cm³/mol·K, then ρ is calculated in g/cm³. Equation (2-1) is valid for gases once their Z values are calculated from an equation of state or a generalized correlation [8].

For high-pressure liquids, density may be estimated from cubic EOS such as PR or SRK equations. However, these equations break at carbon number of about C_{10} for liquid density calculations. They provide reasonable values of liquid density. The error of liquid density calculations from cubic equations of states increases at low and atmospheric pressures. For saturated liquids, special care should be taken to take the right Z value (the lowest root of a cubic equation). The Lee-Kesler correlation is particularly useful for rapid-hand calculations for a single data point. The most accurate method for prediction of saturated liquid densities is through Rackett equation. However, for high-pressure liquids the method of COSTALD correlation may be used combined with the Rackett equation to provide very accurate density values for both pure components and petroleum fractions. These methods are also applicable to nonhydrocarbons as well. At low pressures or when the pressure is near saturation pressure, no correction on the effect of pressure is required and saturated liquid density calculated from Rackett equation may be directly used as the density of compressed (subcooled) liquid at pressure of interest [10].

2.3 Critical Properties.

The critical point is a point on the pressure-volume temperature diagram where the saturated liquid and saturated vapor is identical and indistinguishable. The temperature, pressure, and volume of a pure substance at the critical point are called *critical temperature* (T_c), *critical pressure* (P_c), and *critical volume* (V_c), respectively. In other words, the critical temperature and pressure for a pure compound are the highest temperature and pressure at which the vapor and liquid phase can coexist at equilibrium. In fact, for a pure compound at temperatures above the critical temperature, it is impossible to liquefy a vapor no matter how high the pressure is. A fluid whose temperature

and pressure are above the critical point is called supercritical fluid [11]. For pure compounds, critical temperature and pressure are also called true critical temperature and true critical pressure. *Pseudocritical properties* are defined for mixtures and petroleum fractions, which are different from true critical properties. Pseudocritical properties are important in process calculations for the estimation of thermophysical properties of mixtures [12].

The critical compressibility factor, Z_c , is defined from T_c , P_c , and V_c according to the general definition of compressibility factor [13].

$$Z_c = \frac{P_c V_c}{R T_c} \quad (2-2)$$

where R is the universal gas constant. According to Eq. (2.2), Z_c is dimensionless and V_c must be in terms of molar volume (i.e., cm^3/mol) to be consistent with R values. Critical temperature, pressure, and volume (T_c , P_c , V_c) are called the *critical constants* or *critical properties*. Critical constants are important characteristics of pure compounds and mixtures and are used in corresponding states correlations and equations of state (EOS) to calculate PVT and many other thermodynamic, physical, and transport properties. The results of EOS calculations very much depend on the values of critical properties used. Critical volume may be expressed in terms of specific critical volume (i.e., m^3/kg), molar critical volume (i.e., m^3/kmol), or critical density d_c (i.e., kg/m^3) or critical molar density (i.e., kmol/m^3) [14].

2.4 Reduced Properties.

The most generalized correlation is based on the observation that data for different fluids exhibit a remarkable uniformity when the thermodynamic coordinates are expressed in suitable dimensionless or reduced form. This fact is the experimental basis for the theorem of corresponding states. Thus the reduced conditions are [13, 15].

$$\left. \begin{aligned} Tr &= \frac{T}{T_c} \\ Pr &= \frac{P}{P_c} \\ Vr &= \frac{V}{V_c} \end{aligned} \right\} \quad (2-3)$$

2.5 Acentric Factor (w).

Acentric factor is a parameter that was originally defined by Pitzer to improve accuracy of corresponding state correlations for heavier and more complex compounds [15, 16]. Acentric factor is a defined parameter and not a measurable quantity. It is a dimensionless parameter represented by w and is defined as:

$$w = -1 - \log[\Pr_{sat}]_{Tr=0.7} \quad (2-4)$$

The argument of the logarithm is the reduced vapor pressure (P_{sat}/P_c) evaluated at reduced temperature of 0.7.

Acentric factor is defined in a way that for simple fluids such as argon and xenon it is zero and its value increases as the size and shape of molecule changes. For methane $w = 0.001$ and for decane it is 0.489. Values reported for acentric factor of pure compounds are calculated based on Eq. (2.4), which depends on the values of vapor pressure. For this reason values reported for the acentric factor of a compound may slightly vary from one source to another depending on the relation used to estimate the vapor pressure. In addition, since calculation of the acentric factor requires values of critical temperature and pressure, reported values for w also depend on the values of T_c and P_c used [8]. Values of w for selected substance are given in **Appendix A**.

2.6 Polar Compounds

Polar compounds are characterized by a non-zero dipole moment μ , which expresses the effect of electrostatic forces between molecules. Polar compounds are alcohol, phenol, water, ketones, aldehydes, ether, and alknitriles. The first three are hydrogen bonding compounds (a bond forms between the hydrogen atom attached to oxygen in one molecule), this makes their behavior in the vapor different and more complex than that of non-hydrogen bonding compounds (ketones, etc)[11, 17].

2.7 Boiling Point

The boiling point of a pure compound at a given pressure is the temperature at which vapor and liquid exist together at equilibrium. If the pressure is 1 atm, the boiling point is called the normal boiling point. However, usually the term *boiling point*, T_b , is used instead of normal boiling point and for other pressures the term *saturation temperature* is used. In some cases, especially for heavy hydrocarbons in which thermal cracking may occur at high temperatures, boiling points at pressures other than atmospheric are specified [8]. The boiling point, when available, is one of the most important characterization parameters for hydrocarbons and is frequently used in property estimation methods [18].

2.8 Equation of State.

An EOS is a mathematical equation that relates pressure, volume, and temperature. The simplest form of these equations is the ideal gas law that is only applicable to gases. In 1873, van der Waals proposed the first cubic EOS that was based on the theory of continuity of liquids and gases. Since then

many modifications of cubic equations have been developed and have found great industrial application especially in the petroleum industry because of their mathematical simplicity. More sophisticated equations are also proposed in recent decades that are useful for certain systems [8, 19].

Liquid densities can be calculated from equations of state (EOS). Normally, the accuracy of liquid density predictions with EOS is not sufficient, and therefore special correlations for liquid density are used. Many accurate correlations are available for saturated liquid densities of pure fluids. The accuracy of many models is not good enough for mixtures, mainly due to problems in formulating the mixing rules [6].

2.9 Alternative Analytical Methods.

2.9.1 Guggenheim Equation.

Guggenheim in (1945) suggested a simpler empirical formula for representing saturated liquid argon. The scaling volume was used in the calculation instead of the critical volume. It is of the following form:

$$\begin{aligned} \rho_{rs} &= 1 + \alpha(1 - T_r) + \beta(1 - T_r)^{1/3} \\ \text{where } \alpha &= 3/4 \text{ and } \beta = 7/4 \\ \rho_{rs} &= 1/V_{sc} \\ V_{sc} &= \frac{V_{0.6}}{0.3862 - 0.0866\omega} \end{aligned} \quad (2-5)$$

In this investigation, Eq. 2-5 was used for representing saturated liquid densities for nonpolar and slightly polar compounds, but with the quantities α and β treated as two adjustable parameters. In addition, it was intended to correlate these two parameters in terms of the three parameter corresponding states formulation [21].

The Parameters α and β of the 23 compounds were determined by least squares method. Values of these parameters were also listed in [21] and were further correlated in the following forms linear in the acentric factor:

$$\alpha = 0.73098 + 0.28908\omega \quad (2-6)$$

$$\beta = 1.75238 + 0.74293\omega \quad (2-7)$$

The average deviation of the calculated densities and literature values for a total 595 data points tested was 0.27%. The proposed correlation provide as accurate and simple means of predicting the temperature effect on saturated liquid densities.

2.9.2 Riedel.

Riedel in (1954) proposed an empirical equation for calculating saturated molar volume for liquids depending on two parameters corresponding states method $(1-T_r)$ [22].

$$\rho_s / \rho_C = 1 + (1.69 + 0.984\omega)(1-T_r)^{1/3} + 0.85(1-T_r) \quad (2-8)$$

2.9.3 Alfred W. Francis.

Francis in (1958) presented simple equations which were published [23] for 44 hydrocarbons relating saturated liquid densities with temperature over wide ranges. Another equation showed a simple relation between liquid density and slopes of isochors, $(dP/dt)_V$, for compression of 27 hydrocarbons and hydrogen. The same forms of equations have now been found applicable to non-hydrocarbons over even wider ranges and with deviations hardly greater than uncertainties in observations, or an average of less than 0.0008.

$$\rho_s = A - BT - \frac{C}{E - T} \quad (2-9)$$

Eq. 2-9 has been derived for 81 non-hydrocarbons, including 27 inorganic liquids. The constants were presented for 130 pure substances [23, 24].

2.9.4 Yen and Woods.

Yen and Woods in (1966) proposed a generalized equation for the coefficient in terms of Z_C based on the three parameter corresponding states method [25]

$$V_c/V_s = 1 + A(1-T_r)^{1/3} + B(1-T_r)^{2/3} + (0.93 - B)(1-T_r)^{4/3}$$

where

$$V_s = \text{Saturated liquid molar volume} \tag{2-10}$$

$$A = 17.4425 - 214.578Z_c + 989.625Z_c^2 - 1522.06Z_c^3$$

$$B = -3.28257 + 13.6377Z_c + 107.4844Z_c^2 - 384.211Z_c^3$$

$$B = 60.2091 - 402.063Z_c + 501Z_c^2 + 641Z_c^3$$

This equation was widely used in hydrocarbon industry until the appearance of Rackett equation and its modifications.

2.9.5 Bradford and Thodos.

Bradford and Thodos in (1968) proposed a generalized equation for the coefficient in terms of Z_C based on the three parameter corresponding states method [26].

$$\frac{\rho_s}{\rho_c} = 1 + (2.924 - 7.34Z_c)(1-T_r) - (1.139 - 3.796Z_c)(1-T_r)^2 + (2.785 - 3.544Z_c)(1-T_r)^{(0.16+0.586Z_c)} \tag{2-11}$$

2.9.6 Rackett Equation.

Rackett proposed an unusually simple generalized equation for predicting liquid volumes. The accuracy of this equation is only moderate [27].

$$V_s = V_c Z_c^{(1-T_r)^{2/7}} \tag{2-12}$$

This equation is in fact a generalized correlation for saturated liquids and it is in dimensionless form [8]. Rackett demonstrated the accuracy of equation 2-12 by comparing the actual Z_c with the best values of Z_c back calculated from the equation and experimental volumetric data for a number of substances [27].

2.9.7 Spencer and Danner.

Spencer and Danner in (1972) replaced Z_C in Eq 2-12 with adjustable parameter, Z_{RA} is

$$V_s = \frac{RT_C}{P_C} Z_{RA}^{(1-T_r)^{2/7}} \quad (2-13)$$

Z_{RA} is a unique constant for each compound, and are listed in the literature. If a value of Z_{RA} is not available, it may be estimated from this equation

$$Z_{RA} = 0.29056 - 0.08775w \quad (2-14)$$

Note that Eq. 2-13 does not predict the correct volume at the critical point unless $Z_{RA}=Z_C$ [28, 29]

2.9.8 Bhirud's Method.

Bhirud in [27] has presented the following corresponding states equation for the saturated liquid volume of normal (nonpolar) fluids

$$\ln \frac{P_C V_s}{RT} = \ln V^{(0)} + w \ln V^{(1)} \quad (2-15)$$

$$\ln V^{(0)} = 1.39644 - 24.076T_r + 102.615T_r^2 - 255.719T_r^3 + 355.805T_r^4 - 256.671T_r^5 + 75.1088T_r^6 \quad (2-16)$$

$$\ln V^{(1)} = 13.4412 - 135.7437T_r + 533.38T_r^2 - 1091.453T_r^3 + 1231.43T_r^4 - 728.227T_r^5 + 176.737T_r^6 \quad (2-17)$$

Above $T_r=0.98$, values of $\ln V^{(0)}$ and $\ln V^{(1)}$ from tables in [28] should be used. Eq. 2-15 gave an average percent deviation of 0.76 percent for 752 data points for hydrocarbons for reduced temperatures between 0.3 and 1.0. Bhirud has extended his method to polar compounds, but the extension requires an experimental density [30].

2.9.9 Yamada and Gunn.

Yamada and Gunn in (1973) proposed that Z_c in Equation 2-12 be correlated with the acentric factor.

$$V_s = V_c (0.29056 - 0.08775w)^{(1-T_r)^{2/7}} \quad (2-18)$$

If one experimental density, V_s^R is available at a reference temperature, T^R , Eqs 2-12 and 2-18 can be modified to give

$$V_s = V_s^R (0.29056 - 0.08775w)^\phi \quad (2-19a)$$

$$V_s = V_s^R Z_c^\phi \quad (2-19b)$$

Where

$$\phi = (1 - T/T_c)^{2/7} - (1 - T^R/T_c)^{2/7} \quad (2-20)$$

An often used variation of Eq. 2-18 is

$$V_s = \frac{RT_c}{P_c} (0.29056 - 0.08775w)^{(1-T_r)^{2/7}} \quad (2-21)$$

However, this form dose not predict V_c correctly unless the actual $Z_c = 0.29056 - 0.08775w$, in which case it is identical to Eq 2-12 [28].

2.9.10 Hankinson Thomson Model (HT).

Upon careful examination of Yen-Woods equation, Rackett Equation, as modified by Spencer and Danner, and Gunn Yamada equation, Hankinson and Thomson [31] chose Gunn-Yamada equation to develop more accurate liquid molar volume correlation.

Gunn and Yamada presented a corresponding state correlation for the liquid molar volume in terms of T_r , and "scaled volume", V_{sc}

$$V_s = V_{sc} V_r^{(o)} (1 - w \delta) \quad (2-22)$$

Where $V_r^{(o)}$ and δ are function of T_r and V_{sc} is given by

$$V_{sc} = V_{0.6} / (0.3862 - 0.0866w) \quad (2-23)$$

Where $V_{0.6}$ is the liquid molar volume at $T_r=0.6$ [7].

Hankinson and Thomson modified the Gunn-Yamada equation as follows:

$$V_s = V^* V_r^{(\omega)} (1 - w_{SRK} V_r^{(\delta)}) \quad (2-24)$$

$$\text{where } V_r^{(\omega)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (2-25)$$

when $0.25 \leq T_r \leq 0.95$

$$V_r^{(\delta)} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \text{ when } 0.25 \leq T_r \leq 1.0 \quad (2-26)$$

$$T_r = \frac{T}{T_{C,HT}} \quad (2-27)$$

The pure-component specific parameters are the following: characteristic volume V^* , slightly adjusted critical temperature $T_{C,HBT}$ and the SRK-acentric factor ω_{SRK} .

For Equation 2-25 and 2-26 the general parameters are the following:

$$\begin{aligned} a &= -1.52816 & b &= 1.43907 & c &= -0.81446 & d &= 0.190454 \\ e &= -0.296123 & f &= 0.386914 & g &= -0.0427258 & h &= -0.0480645 \end{aligned}$$

w_{SRK} is the back calculated "acentric factor" that allows the soave R-K equation to best represent the vapor pressure.

V^* is an adjustable parameter called "characteristic volume." The values of this parameter were determined by regression analysis on the liquid molar volume data [31].

2.9.11 Other Equations.

There are many equations to estimate liquid molar volume as shown below [32, 33]:

2.9.11.1 Lyckman et al.

$$\frac{\rho_c}{\rho_s} = V_r = V_r^{(0)} + \omega V_r^{(1)} + \omega^2 V_r^{(2)} \quad (2-27)$$

where $V_r^{(i)}$'s are generalized function of T_r .

2.9.11.2 Halm and Stiel

$$\frac{1}{\rho_s} = V_s = V_r^{(0)} + \omega V^{(1)} + \chi V^{(2)} + \omega^2 V^{(3)} + \chi V^{(4)} + \omega \chi V^{(5)} \quad (2-28)$$

where $V^{(i)}$'s are generalized function of T_r .

$$\text{and } \chi = \log P_r(T_r \rightarrow 0.6) + 1.7\omega + 1.552 \quad (2-29)$$

2.9.11.3 Holmes

$$\frac{\rho_s}{\rho_c} = (1 - \omega) \rho_r^{(0)} + \omega \rho_r^{(1)} \quad (2-30)$$

where $\rho_r^{(i)}$'s are generalized function of T_r and P_r .

2.9.11.4 Harmans

$$\frac{\rho_s}{\rho_c} = (0.43875 - 0.625Z_c) f(T_r) \quad (2-31)$$

where $f(T_r)$ are generalized function, density plot.

2.9.11.5 Harlacher

$$\frac{\rho_s}{\rho_c} = 1 + K(1 - T_r)^{1/3} + L(1 - T_r)^{2/3} \quad (2-32)$$

where K and L are specified constants for each compounds (constants have generalized as function of the preacher and ω)

2.9.11.6 Ehrlich

$$(\rho_s / \rho_c)^{-1} / (\rho_s / \rho_c)(1 - T_r) = A + B(1 - T_r) + C(1 - T_r)^2 \quad (2-33)$$

Where A and B are specified constant for each compound.

2.9.11.7 Narsimham

$$\frac{\rho_s}{\rho_c} = 1 + (0.422 \log P_c + 0.981) / (1 - T_b / T_c)^{0.40} (1 - T_r)^{0.4} \quad (2-34)$$

The detailed information's of these equations are not found in the literatures because of absence of papers [33].

2.10 Methods for Calculating Saturated Liquid Molar Volume at Normal Boiling Points.

Two methods are presented here to estimate the liquid volume at the normal boiling point temperature. In addition, methods will be presented later that give the volume as a function of temperature which may also be used for obtaining V_b at T_b . Equations of state may also be used for estimating volumes.

2.10.1 Additive Methods.

Schroeder (1949) suggested a simple additive method for estimating molar volumes at the normal boiling point. His rule is to count the number of atoms of carbon, hydrogen, oxygen, and nitrogen, add one for each double bond, two for each triple bond and multiply the sum by seven [22]. Schroeder's original rule has been expanded to include halogens, sulfur, and triple bonds. This gives the volume in cubic centimeters per gram mole. This rule is surprisingly accurate, giving results within 3 to 4% error except for highly associated liquids. Table 2-1 gives the contributions to be used. The values in the table may be expressed in equation form as

$$V_b = 7(N_C + N_H + N_O + N_N + N_{DB} + 2N_{TB}) + 31.5N_{Br} + 24.5N_{Cl} + 10.5N_F + 38.5N_I + 21N_S - 7^* \quad (2-35)$$

where subscripts DB and TB stand for double and triple bonds and the last value* is counted once if the compound has one or more rings. V_b for benzene, for example, is $7(6+6+3)-7=98\text{cm}^3\text{mole}^{-1}$ compared to the experimental value of 95.8 or 2.3% error. The average error for the compounds tested is 3.9% with 5 strongly polar and associating substances having errors greater than 10% [22, 23].

The additive volume method of Le Bas (1915) is an alternative to Schroeder's rule. Volume increments from Le Bas are shown in table 2-1 and

calculated values of V_b are compared with experimental values. The average error for the compounds tested is 3.9% with 5 substances having errors greater than 10% [22, 23].

2.10.2 Tyn and Calus Method

In this method, V_b is related to the critical volume by

$$V_b = 0.285V_c^{1.048} \quad (2-36)$$

where both V_b and V_c are expressed in cubic centimeters per gram mole. Comparisons with the substances show that this method is somewhat more accurate and has greater reliability since only 1 substance has an error of more than 10%. The table results are representative of the method where errors exceed 3% only for the low-boiling permanent gases (He, H₂, Ne, Ar, Kr) and some polar nitrogen and phosphorus compounds (HCN, PH₃, BF₃).

Table 2-1: Group/Atom Contribution for Schroeder and Le Bas Methods

	Increment, cm ³ /mol	
	Schroeder	Le Bas
Carbon	7.0	14.8
Hydrogen	7.0	3.7
Oxygen	7.0	7.4
In methyl esters and ethers		9.1
In ethyl esters and ethers		9.9
In higher esters and ethers		11.0
In acids		12.0
Joined to S,P and N		8.3
Nitrogen	7.0	
Doubly bonded		15.6
In primary amines		10.5
In secondary amines		12.0
Bromine	31.5	27.0
Chlorine	24.5	24.6
Flourine	10.5	8.7
Iodine	38.5	37.0
Sulfur	21.0	25.6
Ring,three-membered	-7.0	-6.0
Four-membered	-7.0	-8.5
Five-membered	-7.0	-11.5
Six-membered	-7.0	-15.0
Naphthalene	-7.0	-30.0
Anthracene	-7.0	-47.5
Double bond	7.0	
Triple bond	14.0	

2.11 Methods for Calculating Saturated Liquid Molar Volume for Mixtures.

The methods reviewed above are for pure components calculations. To extend the methods to mixtures, they must be modified to include the additional variable of composition. In essentially all cases, the inclusion is accomplished by averaging pure component constants to obtain constants which hopefully characterize the mixtures. Equations that do this are called mixing rules [16].

2.11.1 Extension of Rackett Equation to Mixture

Rackett in 1971 have reported an extensive evaluation of a form of the Rackett equation for predicting the saturated liquid density of pure compounds (21).

$$V_s = V_c Z_c^{(1-T_r)^{2/7}} \quad (2-12)$$

Spencer and Danner rearranged the Rackett equation by replacing V_c with $Z_c RT_c / P_c$ and then determined the best values of Z_c that would result in least errors for the prediction of saturated liquid molar volume for more than 100 pure fluids. They denoted the Z_c parameter " Z_{RA} " to distinguish it from the actual Z_c . Their modified equation was given in [34]. They recommended the following set of mixing rules for applying Eq. 2-13 to mixtures:

$$RT_c / P_c = R \sum_i^N x_i T_{Ci} / P_{Ci} \quad (2-37)$$

$$Z_{RA} = \sum_i^N x_i Z_{RAi} \quad (2-38)$$

$$T_c = \frac{\sum_i^N x_i V_{Ci} T_{Ci}}{\sum_i^N x_i V_{Ci}} \quad (2-39)$$

2.11.2 Extension of Yen-Woods Equation to Mixture

Eq (2-10) was extended to mixture as follows:

$$T_c = \sum_i^N x_i T_{Ci} \quad (2-40)$$

$$V_c = \sum_i^N x_i V_{Ci} \quad (2-41)$$

$$Z_c = \sum_i^N x_i Z_{Ci} \quad (2-42)$$

2.11.3 Extension of HT Equation to Mixture

The Hankinson-Thomson equation is slightly more accurate than the Spencer-Danner's modified Rackett equation for pure fluids, but it is notably more accurate for mixtures. Hankinson and Thomson recommended the following set of mixing rules:

$$T_{cm} = \sum_i^N x_i (V_{Ci} T_{Ci})^{0.5} \bigg/ V_{cm} \quad (2-43)$$

$$V_{cm} = \frac{1}{4} \sum_i^N x_i V_i^* + 3 \sum_i^N x_i V_i^{*2/3} \sum_i^N x_i V_i^{*1/3} \quad (2-44)$$

$$\omega_{SRK} = \sum_i^N x_i (\omega_{SRK})_i \quad (2-45)$$

Using T_{cm} from Eq. (2-43) to obtain T_r , V^* of Eq. (2-44) is a parameter fit to experimental data and is nearly identical to the pure component V_c , while ω_{SRK} is that value of ω that causes the Soave EOS to be most closely match experimental vapor pressure behavior and it is nearly equal to the true value of ω_i . However, results are only marginally affected if V^* and ω_{SRK} are replaced with the true values of V_c and ω .

CHAPTER THREE

INVESTIGATION AND DEVELOPMENT

3.1 Introduction.

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

In this chapter many different empirical equations were applied to calculate the molar volumes of saturated pure liquids such as Rackett, Spencer and Danner, Yamada and Gunn, Yen Woods, Bradford and Thodos,. Reidel, and Hankinson Thomson equations.

It is a well known fact that the evaluation of any correlations or prediction method is done by comparison of the results with the results of experimental dependable data. The deviation between the experimental results and the results of prediction or correlation method determine the accuracy of the method. The experimental data of the molar volume of saturated liquids, obtained from literature for the purpose of this investigation consists of 250 data points of six polar pure compounds as shown in table 3-1, and 555 data points of twenty non polar pure compounds as shown in table 3-2.

Table 3-1: Experimental Data for Polar Compounds

Compounds	Temp.range(K)	No.of points	Ref.
R-11	203.15-463.15	28	35
R-12	183.15-383.15	38	35
R-22	203.15-368.15	35	35
Water	273.15-638.15	74	35
Ammonia	223.15-403.15	37	35
Ethanol	275.95-508.65	38	36
Total		250	

Table 3-2: Experimental Data for Non-polar Compounds

Compounds	Temp.range(K)	No.of points	Ref.
Argon	83.80-150.00	16	35
1,3-butadiene	273.15-415.38	38	36
Benzene	280.00-555.00	43	36
Carbon Dioxide	216.55-303.00	43	36
Cyclopropane	291.66-397.22	20	37
R-245	233.15-377.59	27	38
R-123	223.15-453.15	38	35
R-134a	203.15-373.15	36	35
Isobutylene	255.37-417.87	31	39
Propane	85.50-360.00	16	35
Isobutane	261.32-407.50	30	40
n-Pentane	309.19-469.50	28	41
Isopentane	301.02-460.39	29	41
Neopentane	282.62-433.75	27	41
Oxygen	54.40-154.60	22	35
Nitrogen	63.10-126.20	16	35
Methane	90.70-180.00	20	35
Ethane	90.40-300.00	23	35
Ethylene	104.00-280.00	20	35
n-Butane	272.67-424.50	32	40
Total		555	

On the other hand many other correlations were used to predict molar volumes for mixtures, Hankinson Thomson mixing rule was applied to Hankinson Thomson model and developed Hankinson Thomson. The experimental data of the molar volume of saturated liquid mixtures obtained from literature for the purpose of this investigation consists of 792 data points of 26 mixtures as shown in table 3-3.

Table 3-3: Experimental Data for Mixtures

Mixtures	No.of points	Ref.
Butane-Octane	65	42
Aniline-Methanol	33	43
Benzene-Methanol	33	43
C₃H₇OH-CCl₄	30	44
C₉H₁₀OH-CCl₄	27	44
C₅H₁₂OH-CCl₄	30	44
C₇H₁₅OH-CCl₄	27	44
C₈H₁₇OH-CCl₄	30	44
CCl₄ -Benzene	8	45
CCl₄ -Hexane	8	45
Hexadecane-Benzene	9	45
Hexadecane-CCl₄	10	45
Hexadecan-Hexane	20	45
Iso C₃H₇OH-CCl₄	42	44
Iso C₄H₁₀OH-CCl₄	30	44
Iso C₅H₁₂OH -CCl₄	27	44
Methane-nDecane	60	46
Methane-3methylpentane	28	47
Methanol-CCl₄	30	44
Phenol-Methanol	22	43
Toluene-Methanol	33	43
Tetradecane-nHexane	10	45
TetraC₅H₁₂OH-CCl₄	27	44
SecC₄H₁₀OH-CCl₄	27	44
R11-R12	48	48
Propane-nOctane	78	42
Total	792	

3.2 Selected Empirical Equations.

3.2.1 Rackett Equation.

Rackett equation (1970) [21] is the simplest in form among all equations considered and requires not arbitrary constants for its evaluation. One simply needs the critical constants T_c , P_c , and Z_c . It is able to predict reasonable results from the triple points to the critical points for most substances. The results of pure non-polar compounds were very good excepted methane, and neopentane and this may be caused by some inaccurate experimental data as shown in table 3-4. Table 3-4 shows the maximum deviation from experimental data which is 3.8530% for neopentane and the minimum deviation is 0.3413% for Cyclopropane, but the results obtained when using this equation to calculate the molar volumes of saturated liquid of pure polar compound were not satisfactory as shown in table 3-5

Table 3-4: Results of Rackett Equation for non polar compounds

Compounds	No.of points	AAD% of Rackett
Argon	16	1.2159
1,3-butadiene	38	0.3881
Benzene	43	1.2541
CarbonDioxide	43	0.8098
Cyclopropane	20	0.3413
R-245	27	0.5815
R-123	38	0.8847
R-134a	36	1.1367
Isobutylene	31	1.4981
propane	16	0.5033
Isobutene	30	2.6388
n-pentane	28	0.3880
Isopentane	29	0.3416
Neopentane	27	3.8530
Oxygen	22	0.7665
Nitrogen	16	0.6281
Methane	20	3.4045
Ethane	23	1.0558
Ethylene	20	0.3515
n-Butane	32	0.4313
Total	555	1.1236

Table 3-5: Results of Rackett Equation for polar compounds

Compounds	No.of points	AAD%of Rackett
R-11	28	3.0047
R-12	38	2.0846
R-22	35	1.9436
water	74	3.8887
Ammonia	37	0.6045
Ethanol	38	3.3921
Total	250	2.4863

3.2.2 Yen-Woods Equation.

Another correlation is Yen-Woods (1966) [24], it was the worst one among all the correlations. Although it worked but it gave inaccurate results for polar and non polar compounds as shown in tables 3-6 and 3-7.

Table 3-6: Results of Yen-Woods Equation for non polar compounds

Compounds	No.of points	AAD%of Yen-Woods
Argon	16	10.2509
1,3-butadiene	38	1.2130
Benzene	43	2.5331
CarbonDioxide	43	3.1900
Cyclopropane	20	2.3417
R-245	27	1.5481
R-123	38	2.4261
R-134a	36	1.6740
Isobutylene	31	3.9476
propane	16	2.5684
Isobutene	30	6.4168
n-pentane	28	1.6426
Isopentane	29	2.2363
Neopentane	27	2.4586
Oxygen	22	8.4013
Nitrogen	16	9.7907
Methane	20	9.5177
Ethane	23	3.2869
Ethylene	20	5.7963
n-Butane	32	2.7421
Total	555	4.1991

Table 3-7: Results of Yen-Woods Equation for polar compounds

Compounds	No.of points	AAD%of Yen-Woods
R-11	28	9.5315
R-12	38	7.0427
R-22	35	4.6206
water	74	2.3345
Ammonia	37	1.0429
Ethanol	38	3.7874
Total	250	4.7266

3.2.3 Yamada and Gunn Equation.

Yamada and Gunn (1973) [22] is another form of Rackett equation but with some corrections in Z_c . It worked very good with non polar compounds except methane, neopentane, and benzene as shown in table 3-8. Table 3-8 shows that the maximum deviation from experimental data is 3.1800% for neopentane and the minimum deviation is 0.1664% for R-123 and the results with polar compounds were not satisfactory except for some slightly polars like R-11, R-12, and R-22 as shown in table 3-9.

Table 3-8: Results of Yamada and Gunn Equation for non polar compounds

Compounds	No.of points	AAD%of Yamada and Gunn
Argon	16	1.3106
1,3-butadiene	38	0.3595
Benzene	43	2.1841
CarbonDioxide	43	0.4661
Cyclopropane	20	0.9185
R-245	27	0.2674
R-123	38	0.1664
R-134a	36	1.1265
Isobutylene	31	1.1540
propane	16	0.2609
Isobutene	30	2.0218
n-pentane	28	0.4364
Isopentane	29	0.2479
Neopentane	27	3.1800
Oxygen	22	0.4452

Nitrogen	16	0.3972
Methane	20	3.1389
Ethane	23	0.3791
Ethylene	20	0.5038
n-Butane	32	0.3276
Total	555	0.9645

Table 3-9: Results of Yamada and Gunn Equation for polar compounds

Compounds	No.of points	AAD% of Yamada and Gunn
R-11	28	0.6621
R-12	38	0.9435
R-22	35	1.3026
water	74	5.0097
Ammonia	37	3.6625
Ethanol	38	3.6262
Total	250	2.5344

3.2.4 Spencer and Danner Equation

Spencer and Danner equation (1972) [22, 23] is a modification of Rackett equation. It is structurally similar to the Rackett equation and requires only the critical constants and the acentric factor for application of pure fluids. It gave acceptable results with nonpolar compounds except methane, benzene, and cyclopropane which may be caused by inaccuracy in experimental data as shown in table 3-10. Table 3-10 shows that the maximum deviation from experimental data is 3.6946% for benzene and the minimum deviation is 0.3289% for n-butane, and it did not give good results with polar compounds as shown in table 3-11.

Table 3-10: Results of Spencer and Danner Equation for non polar compounds

Compounds	No.of points	AAD% of Spencer and Danner
Argon	16	1.5291
1,3-butadiene	38	1.5275
Benzene	43	3.6946
CarbonDioxide	43	1.1958
Cyclopropane	20	2.5920
R-245	27	1.2593
R-123	38	1.0697
R-134a	36	1.1317
Isobutylene	31	0.7932
propane	16	0.5149
Isobutene	30	0.7866
n-pentane	28	0.4528
Isopentane	29	0.7187
Neopentane	27	1.6287
Oxygen	22	1.6196
Nitrogen	16	1.5596
Methane	20	3.2777
Ethane	23	0.6351
Ethylene	20	0.8724
n-Butane	32	0.3289
Total	555	1.3593

Table 3-11: Results of Spencer and Danner Equation for polar compounds

Compounds	No.of points	AAD% of Spencer and Danner
R-11	28	2.8046
R-12	38	0.9698
R-22	35	1.8590
water	74	19.0296
Ammonia	37	13.8138
Ethanol	38	4.4025
Total	250	7.1465

3.2.5 Bradford and Thodos Equation

It is another equation to calculate the molar volume of saturated liquid of pure compounds [27], it gave an ordinary results as the equation mentioned before and the accuracy of the results for polar and non polar were close as shown in tables 3-12 and 3-13. Table 3-12 for non polar compounds shows that the maximum deviation from experimental point is 4.0155% for neopentane and the minimum deviation is 0.2678% for ethylene.

Table 3-12: Results of Bradford and Thodos Equation for non polar compounds

Compounds	No.of points	AAD%of Bradford and Thodos
Argon	16	1.6200
1,3-butadiene	38	0.3867
Benzene	43	1.4733
CarbonDioxide	43	0.8665
Cyclopropane	20	0.5269
R-245	27	0.9930
R-123	38	1.2697
R-134a	36	1.7788
Isobutylene	31	1.6029
propane	16	0.4647
Isobutene	30	2.4290
n-pentane	28	0.4925
Isopentane	29	0.5509
Neopentane	27	4.0155
Oxygen	22	1.3014
Nitrogen	16	0.2569
Methane	20	3.6158
Ethane	23	1.1813
Ethylene	20	0.2678
n-Butane	32	0.6281
Total	555	1.2860

Table 3-13: Results of Bradford and Thodos Equation for polar compounds

Compounds	No.of points	AAD%of Bradford and Thodos
R-11	28	2.7351
R-12	38	1.9797
R-22	35	2.0516
water	74	1.6564
Ammonia	37	1.7515
Ethanol	38	3.0371
Total	250	2.2019

3.2.6 Riedel Equation

Riedel equation (1954) [26] gave a very accurate result for non polar compounds when compared with all the equations mentioned before except for neopentane and methane as shown in table 3-14. Table 3-14 shows that the maximum deviation from experimental data is 3.5877% for methane and the minimum deviation is 0.1986% for n-butane. The results with polar compounds were not satisfactory except for some slightly polars like R-11, R-12, and R-22 as shown in table 3-15.

Table 3-14: Results of Reidel Equation for non polar compounds

Compounds	No.of points	AAD%of Reidel
Argon	16	0.5707
1,3-butadiene	38	0.2424
Benzene	43	1.8917
CarbonDioxide	43	0.4064
Cyclopropane	20	1.0929
R-245	27	0.7530
R-123	38	0.4834
R-134a	36	0.5388
Isobutylene	31	0.9352
propane	16	0.3994
Isobutene	30	2.0769
n-pentane	28	0.2609
Isopentane	29	0.2645
Neopentane	27	3.1909
Oxygen	22	0.6419

Nitrogen	16	0.4763
Methane	20	3.5877
Ethane	23	0.5778
Ethylene	20	0.3087
n-Butane	32	0.1986
Total	555	0.9449

Table 3-15: Results of Reidel Equation for polar compounds

Compounds	No.of points	AAD% of Reidel
R-11	28	0.3053
R-12	38	0.7232
R-22	35	0.9557
water	74	4.3409
Ammonia	37	3.1684
Ethanol	38	3.1984
Total	250	2.1153

3.2.7 Hankinson Thomson Equation (HT)

Hankinson Thomson Equation (1982) [25] is the best one among all the equations mentioned. It gave excellent results with nonpolar compounds except methane, neopentane, and benzene as shown in table 3-16. Table 3-16 shows that the maximum deviation from experimental data is 3.2673% for methane and the minimum deviation is 0.1374% for R-123, but the results of polar compounds were inaccurate except for some slightly polars like R-11, R-12, and R-22 as shown in table 3-17.

Table 3-16: Results of Hankinson Thomson Equation for non polar compounds

Compounds	No.of points	AAD% of Hankinson Thomson
Argon	16	1.2055
1,3-butadiene	38	0.2944
Benzene	43	2.1198
CarbonDioxide	43	0.4638

Cyclopropane	20	0.7948
R-245	27	0.2948
R-123	38	0.1374
R-134a	36	1.1277
Isobutylene	31	1.1234
propane	16	0.1536
Isobutene	30	2.0567
n-pentane	28	0.3463
Isopentane	29	0.3034
Neopentane	27	3.1464
Oxygen	22	0.1990
Nitrogen	16	0.2447
Methane	20	3.2673
Ethane	23	0.4084
Ethylene	20	0.3302
n-Butane	32	0.2651
Total	555	0.9141

Table 3-17: Results of Hankinson Thomson Equation for polar compounds

Compounds	No.of points	AAD% of Hankinson Thomson
R-11	28	0.6208
R-12	38	0.8867
R-22	35	1.2668
water	74	4.9832
Ammonia	37	3.5976
Ethanol	38	2.4252
Total	250	2.2967

3.3 Modification of Hankinson Thomson Equation.

The results indicate clearly that when using HT to predict the saturated liquid molar 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 HT equation, it was applied to polar and nonpolar compounds that listed in tables (3.1) and (3.2).

Appendix B, shows the comparison between the results obtained using the all methods mentioned that predict saturated liquid molar volume and

corresponding counterparts obtained from the HT equation. The comparison indicates that the HT equation is closer to the experimental data. The accuracy of using HT equation was shown when it is applied to all data range.

Therefore, the modification of HT equation has been started from the idea that the modification of constants may lead to more accurate results for calculating saturated liquid molar volume. At the beginning the data were classified and divided into polar and nonpolar components. Equation 2-15 represents the general form of HT equation.

$$V_s = V^* V_r^{(\omega)} (1 - w_{SRK} V_r^{(\delta)}) \quad (2-15)$$

$$\text{where } V_r^{(\omega)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (2-16)$$

when $0.25 \leq T_r \leq 1.0$

$$V_r^{(\delta)} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \text{ when } 0.25 \leq T_r \leq 1.0 \quad (2-17)$$

$$T_r = \frac{T}{T_{C,HT}} \quad (2-18)$$

The constants in Eqs. 2-16 and 17 have been found using the idea of minimizing error of saturated liquid molar volume from experimental data (i. e. $V_s/V^* \cong 0$), this procedure was done best for $V_r^{(0)}$ when acentric factor goes to zero. The simple gases ($\omega = 0$) like Ar, Kr have been used for calculating the constants of equation 2-16 using statistical methods as shown in equation 3-1

$$V_r^{(0)} = \frac{V_s}{V^*} \quad (3-1)$$

Experimental data for Argon was used for evaluating the constants; the number of points that used to fit this equation was 8 points. Numerical experimentation revealed that the most appropriate number of points to fit was 8 points. Fig. 3-1 represents the experimental data of Argon (Experimental V_r vs. T_r). This Figure was constructed by considering the equations above.

STATISTICA package was used for evaluation the constants using Quasi-Newton method, figure 3-1 showed the curve takes exactly the polynomial form like equation 2-16, and the correlation coefficient of this equation is 0.99998.

The coefficients of equation 2-16 had been found as follows:

<i>Constant</i>	<i>Value</i>
a	-1.22916
b	0.087280
c	1.283902
d	0.902008

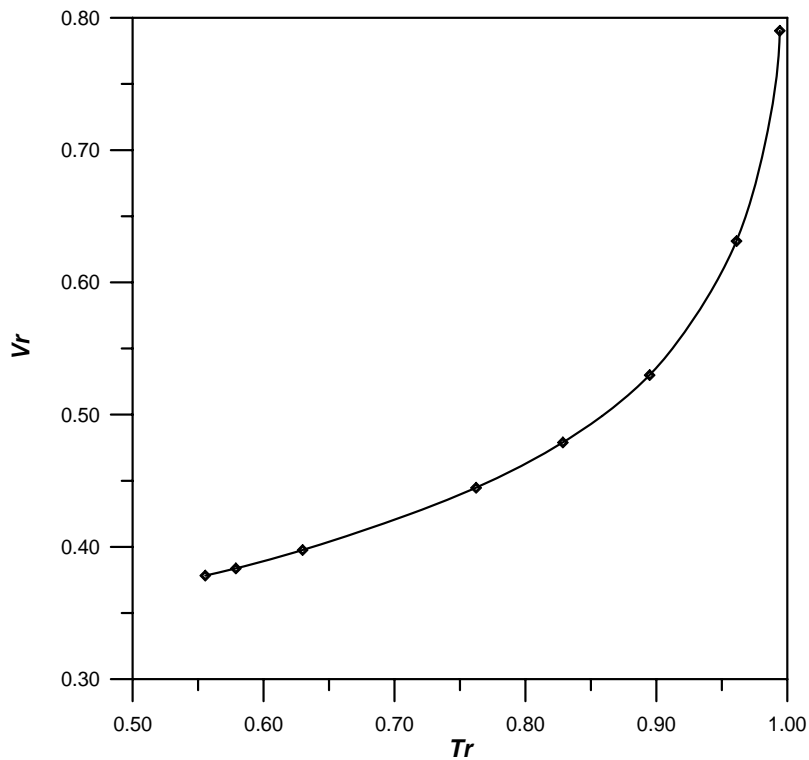


Figure 3-1: Experimental Data for Argon as function of reduced temperature

The second variable of HT equation is $V_r^{(\delta)}$ had constructed for compounds that have a maximum acentric factor in order to control all possible cases in the fit.

Figure 3-2, for Methane, n-Pentane and Ethanol illustrates that the curves of these three compounds are entirely different from those of Simple compounds. The two non-polar compounds above do have approximately maximum and minimum acentric factor. Therefore the end of Methane and Pentane curve is concave down, also for polar compounds the chosen of the best compounds depend on acentric factor as for Ethanol, the experimental data have low $V_r^{(\delta)}$ as shown in figure 3-2 for the points below the curve. This made it possible to construct a model that covers the case of compounds that will have $0.2 \leq Tr \leq 1$.

The experimental data for the three compounds above have been calculated by arranging equation 2-15 in order to evaluate the experimental data for $V_r^{(\delta)}$ using equation 2-16 with new constants for Argon and to minimize the error of V_s from experimental data as shown in equation 3-2:

$$V_r^{(\delta)} = \frac{1}{\omega_{SRK}} \left(1 - \frac{V_s}{V_r^{(0)}} \right) \quad (3-2)$$

The number of points that used was 5 points for Methane, 10 points for n-Pentane and 10 points for Ethanol, this equation has been applied to the rest of compounds in tables 3-1 and 3-2, including the polar compound in spite of the fact it has a high polarity as for water and Ammonia.

STATISTICA package was also used for evaluation of the constants using Quasi-Newton method, figure 3-2 showed the line takes exactly equation 2-17, and the correlation coefficient of this equation is 0.9896.

The coefficients of equation 2-17 had been found as follows:

<i>Constant</i>	<i>Value</i>
e	-0707480
f	1.771180
g	-1.70029
h	0.636584

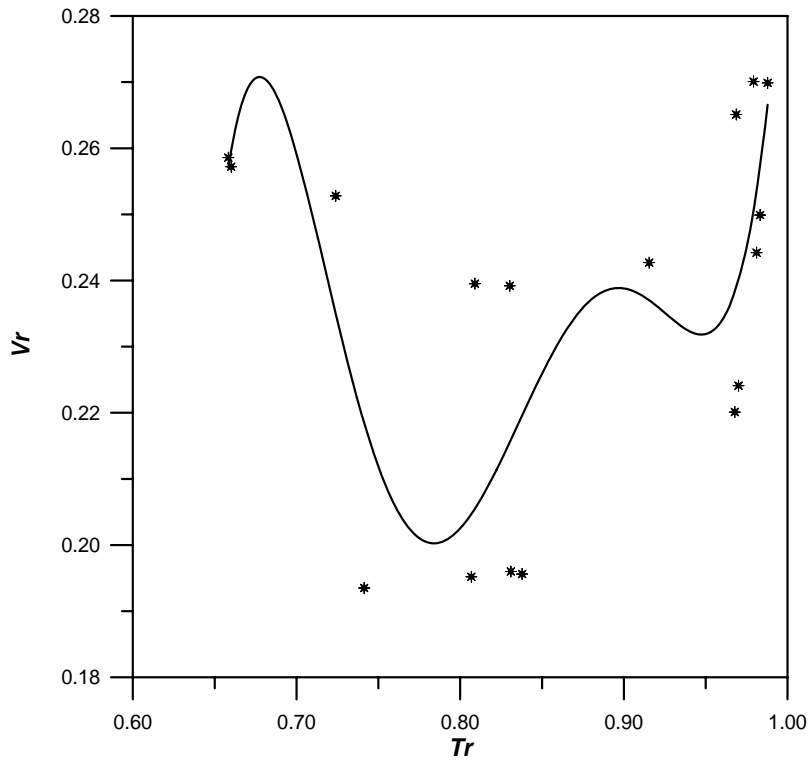


Figure 3-2: Experimental Data for Methane, Pentane and Ethanol as function of reduced temperature

The results of the modified equation are shown in Appendix B.

3.4 Application of the Developed Correlation.

In order to clarify the application of the developed correlation, the detailed calculations are given below for compounds, representative of the polar and nonpolar respectively.

Example 1: Calculation of saturated liquid molar volume for Argon using HT Equation and its Modified.

The properties of Argon are listed below

	M.WT	Tc K	Pc bar	W	Zc	Vc cm ³ /mole
Argon	39.94	150.86	48.98	-0.00	0.291	74.57

Starting from HT equation (i.e. Eqs. 2-15, 16 and 17).

$$V_s = V_r^{(o)} (1 - w_{SRK} V_r^{(\delta)}) \quad (2-15)$$

$$\text{where } V_r^{(o)} = 1 + a(1 - T_r)^{1/3} + b(1 - T_r)^{2/3} + c(1 - T_r) + d(1 - T_r)^{4/3} \quad (2-16)$$

when $0.25 \leq T_r \leq 1.0$

$$V_r^{(\delta)} = \frac{e + fT_r + gT_r^2 + hT_r^3}{T_r - 1.00001} \text{ when } 0.25 \leq T_r \leq 1.0 \quad (2-17)$$

$$T_r = \frac{T}{T_{C,HT}} \quad (2-18)$$

Constants for HT Equation:

$$\begin{aligned} a &= -1.52816 & b &= 1.43907 & c &= -0.81446 & d &= 0.190454 \\ e &= -0.296123 & f &= 0.386914 & g &= -0.0427258 & h &= -0.0480645 \end{aligned}$$

Constants for modified HT Equation:

$$\begin{aligned} a &= -1.22916 & b &= 0.087280 & c &= 1.283902 & d &= 0.902008 \\ e &= -0.707480 & f &= 1.771180 & g &= -1.70029 & h &= 0.636584 \end{aligned}$$

Using HT Equation: T=150K, V_{s,exp}=58.9233cm³/mol

At Tr= 0.9943

$$V_r^{(o)} = 1 - 1.52816(1 - 0.9943)^{1/3} + 1.43907(1 - 0.9943)^{2/3} - 0.81446(1 - 0.9943) + 0.190454(1 - 0.9943)^{4/3}$$

$$V_r^{(o)} = 0.7685$$

$$V_s = 74.57 * 0.7685(1 - 0)$$

$$V_s = 57.3060 \text{ Cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s,exp.} - V_{s,cal.}}{V_{s,exp.}} * 100$$

$$\%Dev. = \frac{58.9233 - 57.3060}{58.9233} * 100$$

$$\%Dev. = 2.7447\%$$

Using modified HT Equation:

At Tr=0.9943

$$V_r^{(\omega)} = 1 - 1.22916(1 - 0.9943)^{1/3} + 0.087280(1 - 0.9943)^{2/3} - 1.283902(1 - 0.9943) + 0.190454(1 - 0.9943)^{4/3}$$

$$V_r^{(\omega)} = 0.7896$$

$$V_s = 74.57 * 0.7896(1 - 0)$$

$$V_s = 58.8813 \text{ Cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s \text{ exp.}} - V_{s \text{ cal.}}}{V_{s \text{ exp.}}} * 100$$

$$\%Dev. = \frac{58.9233 - 58.8813}{58.9233} * 100$$

$$\%Dev. = 0.0713\%$$

The results show that HT equation was extended to work up to Tr=1.

Example 2: Calculation of saturated liquid molar volume for non-Polar compound (as for example 1,3-Butadiene) using HT Equation and its Modified.

The properties of 1,3-Butadiene are listed below

	M.WT	Tc K	Pc bar	W	Zc	Vc cm ³ /mole
1,3-butadiene	54.092	425.00	43.20	0.195	0.270	221.00

By using the same equations and constants in example 1:

Using HT Equation: T=313.1500K, V_{s,exp}=90.8637cm³/mol

At Tr= 0.7368

$$V_r^{(\omega)} = 1 - 1.52816(1 - 0.7368)^{1/3} + 1.43907(1 - 0.7368)^{2/3} - 0.81446(1 - 0.7368) + 0.190454(1 - 0.7368)^{4/3}$$

$$V_r^{(\omega)} = 0.4295$$

$$V_r^{(\delta)} = \frac{-0.296123 + 0.386914 * 0.7368 - 0.0427258(0.7368)^2 - 0.0480645 * (0.7368)^3}{0.7368 - 1.00001}$$

$$V_r^{(\delta)} = 0.2031$$

$$V_s = 221.00 * 0.4295 (1 - 0.195 * 0.2031)$$

$$V_s = 91.1512 \text{ Cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s_{exp.}} - V_{s_{cal.}}}{V_{s_{exp.}}} * 100$$

$$\%Dev. = \frac{90.8637 - 91.1512}{90.8637} * 100$$

$$\%Dev. = 0.3163\%$$

Using modified HT Equation:

At Tr=0.7368

$$V_r^{(\delta)} = 1 - 1.22916(1 - 0.7368)^{1/3} + 0.087280(1 - 0.7368)^{2/3} - 1.283902(1 - 0.7368) + 0.190454(1 - 0.7368)^{4/3}$$

$$V_r^{(\delta)} = 0.4339$$

$$V_r^{(\delta)} = \frac{-0.707480 + 1.771180 * 0.7368 - 1.70029(0.7368)^2 - 0.636584 * (0.7368)^3}{0.7368 - 1.00001}$$

$$V_r^{(\delta)} = 0.2693$$

$$V_s = 221.00 * 0.4339 (1 - 0.195 * 0.2693)$$

$$V_s = 90.8590 \text{ Cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s_{exp.}} - V_{s_{cal.}}}{V_{s_{exp.}}} * 100$$

$$\%Dev. = \frac{90.8637 - 90.8590}{90.8637} * 100$$

$$\%Dev. = 0.0052\%$$

Example 3: Calculation of saturated liquid molar volume for Polar compound (as for example Ammonia) using HT Equation and its Modified.

The properties of Ammonia are listed below

	M.WT	Tc K	Pc bar	W	Zc	Vc cm ³ /mole
Ammonia	17.031	405.40	113.53	0.257	0.255	72.47

By using the same equations and constants in example 1:

**Using HT Equation: T=403.1500K, $V_{s,exp}=53.1708\text{cm}^3/\text{mol}$
At Tr= 0.9944**

$$V_r^{(\circ)} = 1 - 1.52816(1 - 0.9944)^{1/3} + 1.43907(1 - 0.9944)^{2/3} - 0.81446(1 - 0.9944) + 0.190454(1 - 0.9944)^{4/3}$$

$$V_r^{(\circ)} = 0.7702$$

$$V_r^{(\delta)} = \frac{-0.296123 + 0.386914 * 0.9944 - 0.0427258(0.9944)^2 - 0.0480645 * (0.9944)^3}{0.9944 - 1.00001}$$

$$V_r^{(\delta)} = 0.1579$$

$$V_s = 72.47 * 0.7702 (1 - 0.257 * 0.1579)$$

$$V_s = 53.5525 \text{ Cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s,exp.} - V_{s,cal.}}{V_{s,exp.}} * 100$$

$$\%Dev. = \frac{53.1708 - 53.5525}{53.1708} * 100$$

$$\%Dev. = 0.7178\%$$

Using modified HT Equation:

At Tr=0.9944

$$V_r^{(\circ)} = 1 - 1.22916(1 - 0.9944)^{1/3} + 0.087280(1 - 0.9944)^{2/3} - 1.283902(1 - 0.9944) + 0.190454(1 - 0.9944)^{4/3}$$

$$V_r^{(\circ)} = 0.7914$$

$$V_r^{(\delta)} = \frac{-0.707480 + 1.771180 * 0.9944 - 1.70029(0.9944)^2 - 0.636584 * (0.9944)^3}{0.9944 - 1.00001}$$

$$V_r^{(\delta)} = 0.2798$$

$$V_s = 72.47 * 0.7914 (1 - 0.257 * 0.2798)$$

$$V_s = 53.2255 \text{ Cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s,exp.} - V_{s,cal.}}{V_{s,exp.}} * 100$$

$$\%Dev. = \frac{53.1708 - 53.2255}{53.1708} * 100$$

$$\%Dev. = 0.1029\%$$

3.5 Estimation of Liquid Molar Volume at the Normal Boiling Point.

Three methods are available in literature to estimate saturated molar volumes at normal boiling points for polar and non polar compounds. The methods are Tyn and Calus, Schroeder, and Le Bas.

When using Tyn and Calus method, the results for nonpolar compounds were slightly high when it's compared with polar compounds, but this method can be considered the best one among the three methods as shown in tables 3-18 and 3-19.

The results of the two other methods Schroeder and Le Bas were inaccurate in comparison with Tyn and Calus method as shown in tables 3-18 and 3-19.

The development have been made by modifying Tyn and Calus using STATISTICA package for the experimental data in table 3-18, where 10 compounds were used for modifying the constants of Eq. 2-36 to new constants. The correlation coefficient was obtained as 0.998 as shown in modified Eq. 3-3.

$$V_b = 0.348V_c^{1.016} \quad (3-3)$$

Table 3-18: Results for non polar compounds at Normal Boiling Point

Compounds	Tb(K)	V _{exp} (cm ³ /mol)	%Dev. Tyn&Calus	%Dev. Schroeder	%Dev. Le Bas
1,3-butadiene	268.68	83.1643	1.8634	1.0049	2.1214
R-245	255.10	102.3376	2.1074	7.6586	3.2614
R-123	300.81	105.0635	1.1826	3.3918	4.9147
Isobutylene	266.24	89.6382	1.2513	1.5191	0.9351
propane	231.02	75.8349	3.0707	1.5363	2.4196
n-pentane	309.19	118.2	1.2265	0.6768	0.1692
Isopentane	300.99	117.793	1.7868	1.0246	0.5153
Neopentane	282.628	119.6	4.9469	0.5016	1.0033
Oxygen	90.2	28.0311	8.3215	25.0832	47.2015
Nitrogen	77.35	34.7374	8.2514	19.3951	39.5463

Methane	111.66	37.9737	7.7547	7.8311	22.0515
Ethane	184.6	55.2687	4.7102	1.3232	6.2759
Ethylene	169.42	49.4031	4.4263	0.8159	10.1271
n-Butane	272.67	96.66	1.9038	1.3863	0.4758
Total			3.771679	4.8210	9.5667

Table 3-19: Results for polar compounds at Normal Boiling Point

Compounds	Tb(K)	V _{exp} (cm ³ /mol)	%Dev.	%Dev.	%Dev.
			Tyn&Calus	Schroeder	Le Bas
R-11	296.81	92.8398	0.8036	1.9817	4.8041
R-12	243.45	81.2535	1.4600	5.2348	0.1802
R-22	232.14	61.2193	1.2289	2.8084	1.1750
Total			1.164	6.2015	7.2987

3.6 Estimation of Liquid Molar Volume for Mixtures

Mixtures of two compounds have been used to calculate saturated liquid molar volume when using HT equation and its modified form. The modification of mixture was done only for using the same mixing rule of HT equation and applied to modify HT for pure compounds, because the results of pure compounds when using modified HT have been better than from using HT itself. The results of saturated liquid molar volume of mixtures for HT and its modified form with the same mixing rule are shown in appendix C.

Example 4: Calculation of saturated liquid molar volume for Mixtures (as for example 21.43%Propane and n-Octane) using HT Equation and its Modified.

The properties of Propane and n-Octane are listed below

	M.WT	Tc K	Pc bar	W	Zc	Vc cm ³ /mole
propane	44.097	369.83	42.48	0.152	0.275	200.00
Octane	114.231	568.70	24.90	0.399	0.259	492.00

The experimental data for one point is

$$T=447.1500\text{K and } V_{s,\text{exp}}=186.1187 \text{ cm}^3/\text{mole}$$

The mixing rule of HT equation was taken from chapter two as follows

$$T_{cm} = \frac{\sum_i^N x_i (V_{ci} T_{ci})^{0.5}}{V_{cm}} \quad (2-43)$$

$$V_{cm} = \frac{1}{4} \sum_i^N x_i V_i^* + 3 \sum_i^N x_i V_i^{*2/3} \sum_i^N x_i V_i^{*1/3} \quad (2-44)$$

$$\omega_{SRK} = \sum_i^N x_i (\omega_{SRK})_i \quad (2-45)$$

Substitute the properties in the above equations to find the properties for mixture.

$$\begin{aligned} \omega_{SRK} &= (0.2143*0.152+0.7857*0.399) \\ &= 0.3461 \end{aligned}$$

$$\begin{aligned} V_{cm} &= \frac{1}{4} \left[3*(0.2143*200^{2/3}+0.7857*492^{2/3}) \right. \\ &\quad \left. *(0.2143*200^{1/3}+0.7857*492^{1/3}) \right] \\ &= 422.1568\text{cm}^3 / \text{mol} \end{aligned}$$

$$\begin{aligned} T_{cm} &= \left(0.2143*(200*369.83)^{0.5} + 0.7857*(492*568.70)^{0.5} \right)^2 / 422.1568 \\ &= 531.9576\text{K} \end{aligned}$$

$$\begin{aligned} \text{Tr} &= \frac{T}{T_{cm}} = \frac{447.1500}{531.9576} \\ &= 0.84057 \end{aligned}$$

Using HT Equation:

At $Tr=0.8406$

$$V_r^{(o)} = 1 - 1.52816(1 - 0.8406)^{1/3} + 1.43907(1 - 0.8406)^{2/3} - 0.81446(1 - 0.8406) + 0.190454(1 - 0.8406)^{4/3}$$

$$V_r^{(o)} = 0.4811$$

$$V_r^{(\delta)} = \frac{-0.296123 + 0.386914 * 0.8406 - 0.0427258(0.8406)^2 - 0.0480645 * (0.8406)^3}{0.8406 - 1.00001}$$

$$V_r^{(\delta)} = 0.1858$$

$$V_s = 422.1568 * 0.4811(1 - 0.3461 * 0.1858)$$

$$V_s = 190.0422 \text{ cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s \text{ exp.}} - V_{s \text{ cal.}}}{V_{s \text{ exp.}}} * 100$$

$$\%Dev. = \frac{186.1187 - 190.0422}{186.1187} * 100$$

$$\%Dev. = 2.1081\%$$

Using modified HT Equation:

At $Tr=0.8506$

$$V_r^{(o)} = 1 - 1.22916(1 - 0.8506)^{1/3} + 0.087280(1 - 0.8506)^{2/3} - 1.283902(1 - 0.8506) + 0.190454(1 - 0.8506)^{4/3}$$

$$V_r^{(o)} = 0.4859$$

$$V_r^{(\delta)} = \frac{-0.707480 + 1.771180 * 0.8506 - 1.70029(0.8506)^2 - 0.636584 * (0.8506)^3}{0.8506 - 1.00001}$$

$$V_r^{(\delta)} = 0.2632$$

$$V_s = 422.1568 * 0.4859(1 - 0.3461 * 0.2632)$$

$$V_s = 186.4383 \text{ cm}^3 / \text{mol}$$

$$\%Dev. = \frac{V_{s \text{ exp.}} - V_{s \text{ cal.}}}{V_{s \text{ exp.}}} * 100$$

$$\%Dev. = \frac{186.1187 - 186.4383}{186.1187} * 100$$

$$\%Dev. = 0.1717\%$$