Investigation of Correlations for Prediction of Critical Properties of Pure Components

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by

Eba'a Kareem Jassim
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Rabia Al-Awal 1428
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CERTIFICATION

I certify that this thesis entitled "**Investigation of Correlation for Prediction of Critical Properties of pure Component**" was prepared by **Eba'a Kareem Jassim** under my supervision at Nahrain University, College of Engineering, in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering.

Signature: Mahmoud Omar Abdullah
Supervisor: **Prof. Dr. Mahmod Omer Abdullah**
Date: 2 / 10 /2007

Signature:
Name: **Prof. Dr. Qasim J. Slaiman**
(Head of Department)
Date: 19/ 11/2007

CERTIFICATE

We certify, as an examining committee, that we have read this thesis entitled "**Investigation of Correlations for Prediction of Critical Properties of Pure component**" examined the student **Eba'a Kareem Jassim** in its content and found it meets the standard of thesis for the degree of Master of Science in chemical Engineering.

Signature: Mahmoud Omar Abdullah
Name: **Prof. Dr. Mahmod Omer Abdullah**
(Supervisor)
Date: 19/ 11 / **2007**

Signature:
Name: **Ass. Prof. Dr. Aprael S. Yaro**
(Member)
Date: 19 / 11 / **2007**

Signature: K.S. AbDul Masih
Name: **Dr. Kamal S. AbdulMasih**
(Member)
Date:19 / 11 / **2007**

Signature: J. Jamali
Name: **Prof. Dr. Jabir Sh. Jamali**
(Chairman)
Date:19/ 11/ **2007**

Approval of the College of Engineering

Signature: prof Dr. Raad Sami Fyath
for/ Name: **Prof. Dr. Muhsin J. Jweeg**
(Acting Dean)
Date: 11/12/ **2007**

ABSTRACT

Prediction of accurate values of critical properties of any pure component is very important because they are often utilized in estimating the physical properties for chemical process design. Experimental measurements of critical properties for components are very difficult. So, in order to obtain accurate critical property values, attention has been turned to calculate it using mostly a group contribution method which is difficult. To overcome this problem efforts where directed to modify or improve equations to calculate critical properties using relatively simple method.

In this method, critical temperature, critical volume and critical pressure can be estimated solely from data of the normal boiling point and molecular weight of pure substance by means of successive approximations that are repeated until calculation of critical pressure (P_C) converges.

The procedure can be summarized as follows:

1. Calculation of critical temperature.
2. Assuming suitable value of critical pressure and calculating critical volume.
3. Calculation of critical compressibility factor.
4. Calculation of critical pressure from the following equation ;

$$P_c = \frac{Z_c R T_c}{V_c}$$

If $\boldsymbol{P}_C$ obtained is different than $\boldsymbol{P}_C$ assumed , the procedure repeated until $\boldsymbol{P}_C$ obtained is the same as $\boldsymbol{P}_C$ assumed with tolerance of 10^{-4}.

1. A statistical program was used to obtained the following equation to estimate critical temperature for non – polar and polar compounds using the normal boiling point and molecular weight of pure substance ;

$$Tc = -11.5565 - 1.03586Mwt + 2.075167Tb - 0.000281Mwt^2$$
$$- 0.00131Tb^2 + 0.001827MwtTb$$

The AAD% for estimation of critical temperature is 0.9878 % for 114 non-polar compounds and 1.3525 % for 16 polar compounds.

2. Reidel equation for estimation of critical volume was used after assumption of suitable value for critical pressure. The AAD% of estimation critical volume in four steps method is 1.7651 % for 78 compounds of various chemical groups.

3. Pitzer equation for critical compressibility factor was used for non-polar compounds and the following modified equation of Wu and Steil was used for the critical compressibility of polar compounds;

$$Z_c = 0.2901 - 0.879 * \omega - 0.033583\ Y$$

Lee – Keseler method for calculating the acentric factor was used.

4. The results of the values of critical pressures prediction by this four steps procedure proved to be very satisfactory. The AAD% for 114 non-polar compounds is 1.98% and the AAD% for 16 polar compounds is 1.4671%.

5. The above results indicate that the proposed four steps method is more accurate than other methods including group contribution methods; this is in addition to the fact that it is relatively easy method when it is compared to the complicated group contribution method.

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Nomenclature

A	**Molecule surface area**
A_+	**Amount of positively charged surface area**
A_-	**Amount of negatively charged surface area**
A_{HB}	**Amount of charged**
A,B,C	**Constants in Nokay correlation**
a	**Constant in Forman-Thodos correlation (cm^6.atm/ $(gmole)^2$)**
b	**Constant in Forman-Thodos correlation(cm^3/gmole)**
c_1	**Constant in correlation of Mathur et.al.**
f	**Holmholtz free-energy**
Mwt	**Molecular weight**
N_{atoms}	**Number of atoms**
P	**Pressure (bar)**
P_C	**Critical pressure (bar)**
P_r	**Reduced pressure**
P_{CK}	**Group contribution for critical pressure by Joback**
P_{VP}	**Vapor pressure (bar)**
R	**Universal gas constant (cm^3.bar/mole.K)**
S	**Entropy (J/mole.K)**
Sp.Gr	**Specific gravity at 60 °F (15.56)**
T	**Temperature (K)**
T_b	**Normal boiling point (K)**
T_C	**Critical temperature (K)**

T_r	Reduced temperature
t^*	At standard condition
Δ_T	Group contribution for critical temperature
U	Internal energy (J/mole)
V	Volume (cm^3/mole)
V_C	Critical volume (cm^3/mole)
V_r	Reduced volume
V_{lb}	Volume of liquid at boiling point (cm^3/gmole)
$\Delta\nu$	Group contribution for critical volume
V_{CK}	Group contribution for critical volume by Jobock
ω	Acentric factor
Y	Polarity factor
Z_C	Critical compressibility factor
Z	Compressibility factor
ρ_l	Density of liquid (g/ cm^3)
α	Riedel factor
θ_r	T_b/T_C

CHAPTER ONE

Introduction

Thermodynamic properties correlation developed in the past 50 years and based on the principle of corresponding states.

Critical properties are related to chemical process design. Having said that the vapor-liquid critical point is at best weakly defined in comparison with say the triple point. In fact it is best to think of it not a point but a region of undefined boundaries where the stability of the system breaks down and the response to a small turbulence is massive in comparison to the size of the disturbance. The practical need is for knowledge of the critical properties of as much substance as possible. Then, corresponding states correlations can be devised and applied to estimate properties away from critical point. However, the number of substance that is stable at their critical point is limited.

Critical properties are essential in estimating thermodynamic and volumetric properties by the theorem of corresponding states. They are also of importance in determining the existing phase conditions in or the permissible operating ranges of both reactors and mass transfer equipment. As critical properties are often difficult to measure experimentally, reliable method for correlating and predicting them are necessary.

The principle aim of this work is to study the existing methods for calculating the critical properties (critical volume, critical temperature, critical pressure and critical compessibility factor), and to present the results of these methods for critical properties that will show which of these methods are more suitable and rliable than others. Efforts will also be directed to modify or improve the best method if possible in order to come out with a method, or methods, that may predict the critical properties for pure components with high accuracy.

CHAPTER TWO

Theories and Definitions

2.1 Thermodynamic of the Critical Point

The critical state of a fluid is represented by the point on P, V, T surface where the volume of the gas and liquid phases become identical.

Such a point may be said to lie on the border separating the stable and unstable parts of a continuous P, V, T surface[8].

A discussion of the behavior of thermodynamic functions at and near this point may, therefore, be based on either of the two surfaces U,S,V or F,V,T.

Liquid and gas can exist together at equilibrium if the temperature, pressures and chemical potential of the two phases are equal. These qualities may be written in terms of the molar Helmhohz Free – energy of a one component system, as follows

:

$$T^l = T^g \qquad (2.1)$$

$$\left(\frac{\partial f}{\partial \upsilon}\right)_T^l = \left(\frac{\partial f}{\partial \upsilon}\right)_T^g \qquad (2.2)$$

$$f^l - \upsilon^l \left(\frac{\partial f}{\partial \upsilon}\right)_T^l = f^g - \upsilon^g \left(\frac{\partial f}{\partial \upsilon}\right)_T^g \qquad (2.3)$$

Thus, a graph of f as a function of $\boldsymbol{v}$ at constant temperature is represented by the full – line in Fig 2.1.

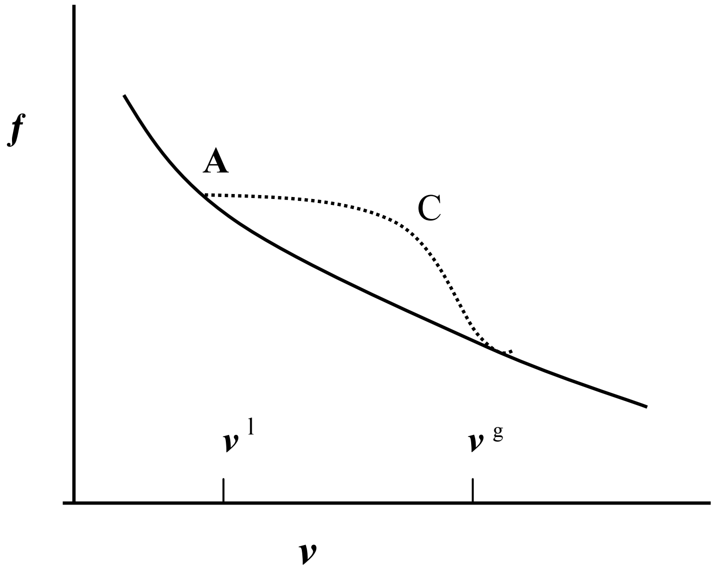

Fig. 2.1 The Holmholtz free-energy as a function of volume[33]

The curve on the P,V,T surface which corresponds to the dashed curve in Fig 2.1 is shown in Fig 2.2 .

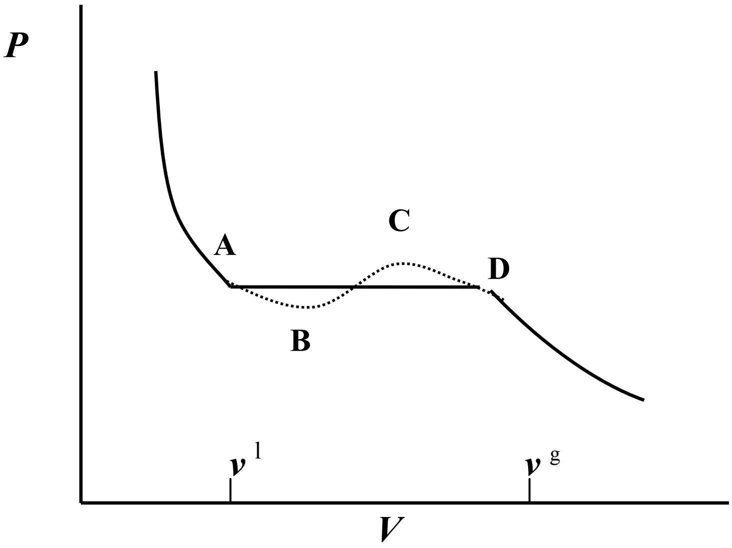

Fig. 2.2 the pressure as a function of volume[33]

The equality of the chemical potential of the two phases requires that [26],

$$\int_{ABCD} \upsilon \,\partial P = 0 \qquad (2.4)$$

Thus, the straight line AD cuts the continuous curve to form two equal areas above and below the transition pressure.

A critical point occurs on a free – energy surface if the tangent AD becomes vanishingly small, so that the four points A,B,C and D coincide .

At such a point,

$$(\frac{\partial f}{\partial \upsilon})_T < 0 \quad , \quad (\frac{\partial^2 f}{\partial \upsilon^2}) = 0 \quad , \quad (\frac{\partial^3 f}{\partial \upsilon^3}) = 0 \qquad (2.5)$$

That is

$$P>0 \; , \; (\frac{\partial f}{\partial \upsilon})_T = 0 \quad , \quad (\frac{\partial^2 p}{\partial \upsilon^2}) = 0 \quad , \quad (\frac{\partial^3 p}{\partial \upsilon^3}) < 0 \qquad (2.6)$$

The second derivative and third derivative expressed in eq. (2.5) are necessary if B and C are to coincide, and the fourth is the condition that the fluid should be stable at volumes immediately above and below the critical point. The fluid is stable at this point as the pressure falls with increasing volume, but the stability is of lower order than that of other states of the fluid.

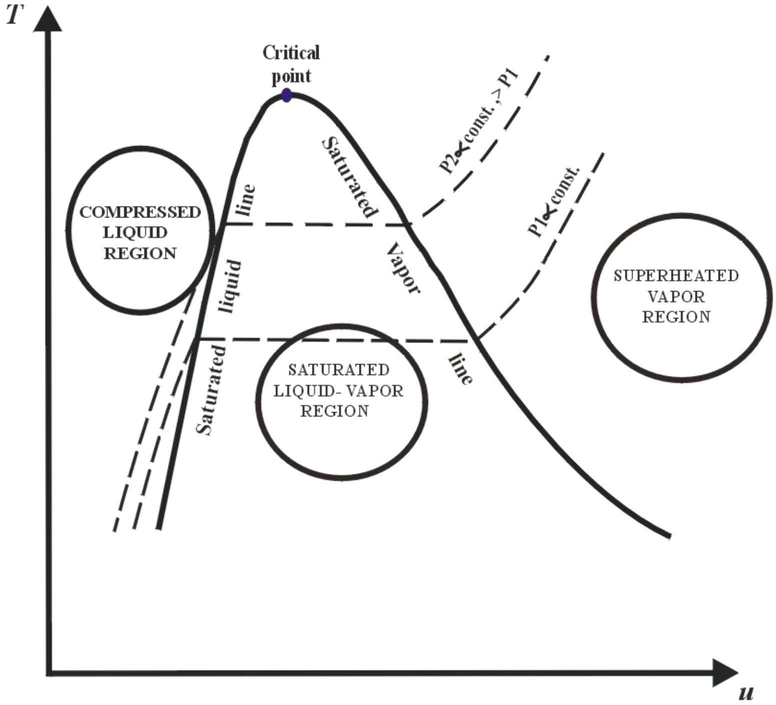

Fig. 2.3 The P-V behavior of the fluid[33]

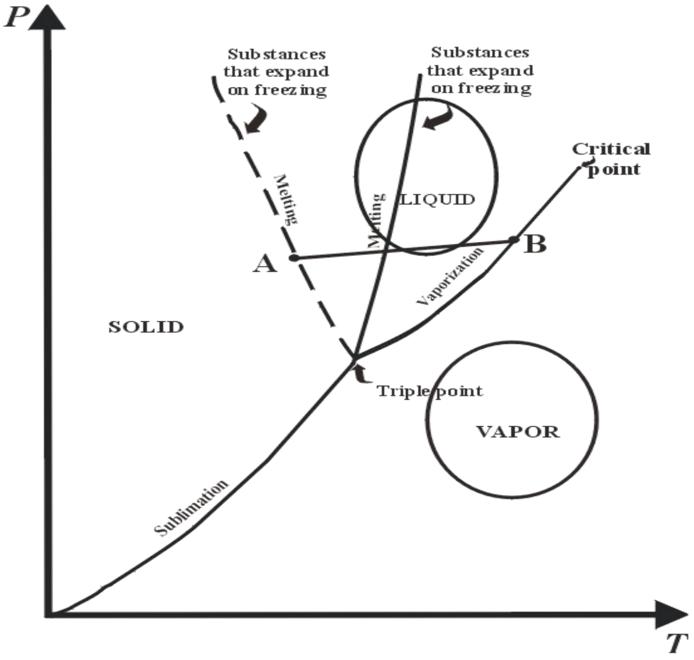

Fig. 2.4 The P-T behavior of the fluid[33]

2.2 Critical Phenomena in Liquids

If a liquid, such as water, is sealed in an evacuated tube, a certain amount will evaporate to form vapor. This vapor will exert a pressure just as any gas does, and provided the temperature is maintained constant, and equilibrium will be established between the liquid and vapor phases. The vapor pressure established is characteristic for each liquid and is constant at any given temperature; it is known as the saturated vapor pressure of the liquid. The saturated vapor pressure increases continuously with temperature. Thus, at 25 ºC the vapor pressure of water is 23.76 mmHg, while at 100 ºC it is 760 mmHg. As the water in the sealed tube is heated further, more and more water evaporates and the pressure continues to increase. At all times there is a definite line of demarcation, or meniscus, between the liquid and vapor phases. When the temperature of 374 ºC is reached, however, the meniscus becomes indefinite, fades into the vapor, and disappears. At this temperature the physical properties of liquid and vapor become identical, and no designated can be observed between the two. A liquid in this condition is said to be at the critical point. The temperature, saturated vapor pressure, and molar volume corresponding to this point are designated the critical temperature, critical pressure, and critical volume respectively. Their values, which are constant and characteristic for each substance, are known as the critical constants. On heating the sealed tube even slightly above the critical temperature, no evidence can be found of the presence of liquid. The whole mass is gaseous and remains in that state no matter how high it is heated, or how large an external pressure is applied. Since the phenomena described for water is exhibited by all liquids, it must be concluded that no liquid can exist at such temperature above the critical under any applied pressure.

The critical phenomena is reversible, when the gas in the tube is cooled below the critical temperature, if the pressure is sufficiently high, the meniscus reappears, and again we have the two phases, liquid and vapor[26].

2.3 The Boiling Point of Liquids

The normal boiling point of a liquid is the temperature at which the vapor pressure of the liquid equal 760 mm Hg pressure, or 1 atm. However, a liquid can be made to boil at any temperature between its freezing point and the critical temperature by merely raising or lowering, as the case may be, the external pressure on the liquid. Therefore, it may be stated in general that boiling point of a liquid is the temperature at which the vapor pressure of a liquid becomes equal to the external pressure acting upon the surface of the liquid. Boiling is characterized by the formation within the liquid of bubbles of vapor, which rise and escape into the vapor phase[28].

2.4 Critical Temperature

The critical temperature is that temperature above which unique liquid and gas phases do not exist. As approach the critical temperature, the properties of the gas and liquid phases become the same, so above the critical temperature there is only one phase. The critical pressure refers to the vapor pressure at the critical temperature. The critical molar volume is the volume of one mole of material at the critical temperature and pressure[30].

2.5 Three Parameter Correlations (non-spherical molecules)

In general, successful equations of state 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, 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 Z_C (Lyderson 1955) and the acentic factor ω (Pitzer and Curl 1955)[18] .

Lyderson and later revision by Hougan, et al., (1959) tabulated Z (and reduced thermodynamic properties) at increment of T_r and P_r for different values of Z_C 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[28].

2.5.1Critical Compressibility Factor

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

$$Z_c = \frac{P_c V}{R T_c} \qquad (2.7)$$

The value of Zc varies from about 1.23 for water to 0.3 for low hydrocarbons[33].

The compressibility factor of a polar fluid can expressed as a linear relationship in the ω and polarity factor Y as following equation[36],

$$Z_c = 0.2901 - 0.0879\,\omega - 0.00266\ \mathrm{Y} \qquad (2.8)$$

Most polar compounds have polarity factor in the range of 0.24 to 0.26, while hydrocarbons are normally in the 0.26 to 0.28 range.

Table 2.1 shows the values of w and Y for polar fluids.

Table 2.1 Values of ω and Y for polar fluids

Substance	ω	Y
Ammonia	**0.252**	**0.739**
Acetone	**0.305**	**0.652**
Ethylene Oxide	**0.202**	**0.565**
Hydrogen Chloride	**0.126**	**0.565**
Methyl Floride	**0.191**	**0.739**
Methyle Chloride	**0.152**	**0.304**
CH_2F_2(R-32)	**0.278**	**0.696**
Water	**0.344**	**1.00**
Ethanol	**0.641**	**0.213**
Methanol	**0.559**	**0.652**
Iso-Propanol	**0.663**	**0.0521**
n-Propanol	**0.626**	**-0.0521**

2.5.2 A centric Factor

Pitzer in 1955[18] postulated that the slope of the reduced vapor pressure against reciprocal of reduced temperature curve is the most sensitive property for a third parameter base. Since vapor pressure can be measured with grater accuracy than critical properties, this approach should be superior to the critical compressibility factor .Thus he defined his acentric factor ω, as:

$$\omega = -\log(P_r^{sat})_{Tr=0.7} - 1 \qquad (2.9)$$

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

This latter estimation would normally be made by using one of the reduced vapor pressure correlations, for example

$$\log P_{vp} = A + \frac{B}{T} \qquad (2.10)$$

With A and B found , from the sets (T_C , P_C ,T_b , P=1), then

$$\omega = \frac{3}{7} * \frac{\theta}{1-\theta} \ \log P_C - 1 \qquad (2.11)$$

Similarly , if the Lee- Kesler vapor pressure relations are used

$$\omega = \frac{\alpha}{\beta} \qquad (2.12)$$

Where

$$\alpha = -\ln P_C - 5.97214 + 6.09648\,\theta^{-1} + 1.28862\ \ln\ \theta - 0.169347\,\theta^6 \qquad (2.13)$$

$$\beta = 15.2518 - 15.6875\theta^{-1} - 13.472\ln\theta + 0.43577\theta^{6} \tag{2.14}$$

2.6 Reduced Properties

The most generalized correlations are based on the observation that data for different fluids exhibited a remarkable uniformity when the thermodynamic coordinates are expressed in suitable dimensionless or reduced form. This fact is experimental basis of the theorem of corresponding states[40]. Thus the reduced conditions are

$$T_r = \frac{T}{T_C} \tag{2.15}$$

$$P_r = \frac{P}{P_C} \tag{2.16}$$

$$V_r = \frac{V}{V_C} \tag{2.17}$$

2.7 Universal gas constant

As the pressure approaches zero, the molecules was separated by the infinite distances. Their volumes become negligible compared with the total volume of the gas, and the intermolecular forces approach to zero. At the conditions all gases was said to be ideal, the proportionality constant is called universal gas constant. Its numerical value is determined by means of the following equation:

$$R = \frac{(P\ V)_{t^*}}{273\ .15\ K} \tag{2.18}$$

Since PVT data are not in fact be taken at zero pressure, data are taken at infinite pressure are extrapolated to the zero pressure state[40]. The accepted value of (PV)t* is 22,7118 cm^3.bar.mole^{-1}, leading to the following value of R:

$$R = \frac{22{,}711.8\,\mathrm{cm}^3.\mathrm{bar.mole}^{-1}}{273.15K} \tag{2.19}$$

CHAPTER THREE

Literature Survey

Correlation attempts on the critical properties of pure liquids are numerous and have been reviewed by several authors

3.1 Reidel Method

Reidel [3] proposed the following correlation for V_c ;

$$V_c = \frac{RT_c}{P_c}[3.72 + 0.26(\alpha - 0.7)]^{-1} \tag{3.1}$$

where

$$\alpha = 0.9076\ [1.0 + \frac{(T_b / T_c)\ln P_c'}{1.0 - (T_b / T_c)}] \tag{3.2}$$

$$P_c' = P_c / 1.01325(10^5) \tag{3.3}$$

3.2 Method of Lyderesn

Lydersen [23]described a group-contribution method for estimating critical temperature, critical pressure, and critical volume utilizing atomic and structural increments for each multivalent atom or group in the molecule, his final equations are:

$$T_b / T_c = 0.567 + \sum\Delta_T - (\sum\Delta_T)^2 \tag{3.4}$$

$$P_c = 0.101325M / (\sum\Delta_{\mathrm{P}} + 0.34)^2 \tag{3.5}$$

$$V_c = (2.497 + 0.06243\sum\Delta_\upsilon) / M \tag{3.6}$$

3.3 Forman and Thodos

Forman and Thodos [9] devised a group contribution method which depends on structure and estimated suitable Van der Waals' constants (a and b) which were correlated with molecular structure.

Then their equations are;

$$T_c = 8a / 27\ bR \tag{3.7}$$

$$P_c = 0.101325 * a/27b^2 \tag{3.8}$$

3.4 Nokay Method

Nokay [27] had correlated critical temperature by

$$\log T_c = A + B\log(Sp.Gr.) - C\log T_b \tag{3.9}$$

Table 3.1 Summery of revised constants for use in Nokay's equation for predicting critical temperature

Family of compounds	A	B	C
Alkanes (Paraffine)	1.359397	0.436843	0.562244
Cycloalkanes (naphthenes)	0.568122	-0.071646	0.811961
Alkenes (Olefins)	1.095340	0.277495	0.655628
Alkynes (acetylenes)	0.746733	0.303809	0.799872
Alkadienes (diolefins)	0.147578	-0.396178	0.994809
Aromatics	1.057019	0.227320	0.669286

3.5 Viswanash Method

Viswanash [36] estimated V_c from T_c and P_c by the simple equation

$$V_c=(0.6243+0.259RT_c/P_c)/M \tag{3.10}$$

3.6 Mathur et al. Method

Mathur et al., developed a simple relationship for critical temperature which for hydrocarbons is:

$$T_c = n_1(\log M) + C_1 \tag{3.11}$$

Results of the evaluations are summarized in table 3.2. The method of Mathur et al. was the poorest of the correlations for estimating critical temperature, Lydersen and Forman-Thodos were almost equivalent in the first evaluation.

Table 3.2 Comparison of the methods for prediction of critical temperature

	Mathur et al.		Forman-Thodos		Lydersen	
Chem.famialy	**Avg.dev.(K)**	**Data point**	**Avg.dev.(K)**	**Data point**	**Avg.dev.(K)**	**Data point**
Paraffins	**4.77**	**20**	**7.55**	**78**	**3.12**	**86**
Naphthenes	**11.0**	**27**	**8.24**	**35**	**8.32**	**36**
Olefins	**4.73**	**9**	**3.74**	**34**	**6.62**	**34**
Diolefins	**-----**	**-----**	**12.08**	**9**	**8.20**	**9**
Acetylenes	**18.07**	**7**	**9.18**	**14**	**8.10**	**14**
Aromatics	**5.56**	**5**	**7.01**	**24**	**5.20**	**26**
Overall Avg.dev	**8.66**	**68**	**7.27**	**194**	**5.44**	**205**

Results of the evaluations of critical pressure are summarized in table 3.3.for saturated compounds and aromatics, the methods are essentially equivalent with Lydersen. However Forman-Thodos method is appreciably better for all classes of unsaturated compounds.

Table 3.3 Comparison of the methods for prediction critical pressure

Lydersen			Forman-Thodos	
Avg.dev.(MN/m^2)		Data point	Avg.dev.(MN/m^2)	Data point
Chem. Family				
Paraffins	0.0949	86	0.0945	78
Naphthenes	0.1089	35	0.1401	35
Olefins	0.1159	34	0.0866	34
Diolefins	0.3233	9	0.0931	9
Acetylenes	0.2044	14	0.1435	14
Aromatics	0.1176	24	0.1326	24
Overall Avg.dev	0.1213	202	0.1096	194

Results of the evaluations of critical volume are summarized in table 3.4.With the correlation of Reidel showing the greatest accuracy for saturated and aromatics with the correlation of Lydersen having a slight advantage for unsaturated hydrocarbons.

Table 3.4 Results of the evaluating of methods for predicting the critical volume of pure hydrocarbon

Avg. Deviation , m^3/Kg. * 10^3					
No. of data points		Lydersen	Viswanath	Riedel	Hall-Yarborough
Chem. family					
Paraffins	78	0.1205	0.1617	0.0868	0.1636
Naphthenes	6	0.0306	0.0606	0.0266	0.0643
Olefins	13	0.1673	0.1654	0.1785	0.2260
Diolefins	2	0.0537	0.0387	0.0581	0.1779
Acetylenes	5	0.0325	0.0755	0.0624	0.2628
Aromatics	22	0.0925	0.0874	0.0661	0.1105
Overall Avg.dev	126	0.1120	0.1386	0.0888	0.1607

3.7 Leonard I.Stiel and George Thodos Method

Frost and Kalkwarf[5] developed the following equation for the vapor pressure of pure substance which is applicable between the triple and critical point:

$$\log p = A + \frac{R}{T} + C\log T + D\frac{p}{T^2} \qquad (3.12)$$

Where A,B,C and D are constants specific to the individual substances.

Reynes and Thodos had expressed equation (3.12) in the following reduced form:

$$\log p_R = a + \frac{\beta}{T_R} + \gamma \log T_R + 0.1832\frac{p_R}{T_R^2} \qquad (3.13)$$

They applied Eq.(3.13) to 54 hydrocarbons of all types and they found the following relationship to exist between the constants ***β*** and γ for these substances:

$$\beta = \frac{5}{9}(\gamma - \frac{8}{3}) \qquad (3.14)$$

These constants can be determined for any substances from its vapor pressure data using the procedure suggested by Frost and Kalkwarf. They showed that the constant C is the slope, and the constant B, is the intercept of the equation (3.15)

$$Y = CX + B \qquad (3.15)$$

The resulting relationship is presented in figure 3.1 and can be expressed analytically as follows:

$$T_c = \frac{B}{0.5643 * C - 1.452} \qquad (3.16)$$

Thus, equation (3.5) permits the establishment of the critical temperature of any pure substance from its available vapor pressure data.

At critical point, the Frost – Kalkwarf equation becomes,

$$\log P_c = A + \frac{B}{T_c} + C\log T_c + D\frac{P_c}{T_c^2} \tag{3.17}$$

from Van der Waal's constant

$$D = \frac{a}{2.303\ R^2} \tag{3.18}$$

where R is the universal gas constant. Therefore, the following expression results for critical pressure:

$$\log P_c = A + \frac{B}{T_c} + C\log T_c + 0.1832 \tag{3.19}$$

critical temperatures and pressures for 64 non-hydrogen bonding substance including saturated and unsaturated aliphatics, naphthenes, aromatics, alkyl halids, monatomic and diatomic gases, sulphur dioxide, and nitrous oxide were calculated by the approach outlined above using experimental vapor pressure data obtained from literatures. The resulting average deviations were 0.59% for critical temperature and 3.18 % for critical pressure.

3.8 New Simple Correlation Pridicts Critical Temperature

They showed how several transport and thermodynamic properties of organic liquids can be correlated with the molecular weight to within an average error of 5% from experimental values. They also presented a similar method for predicting the critical temperature within an overall average error of 0.78%. They used two equations for hydrocarbons and related compounds [25],

$$T_c = n_1(\log M) + C_1 \tag{3.20}$$

For other organic liquids ,

$$T_c = C_2(M)^{n2} \tag{3.21}$$

For hydrocarbons and related compounds, the linear relationship was obtained in semilogarithmic coordinates; for other organics, in logarithmic ones. Data for 219 organic liquids –with molecular weights between 30 and 590 and with critical temperatures between 190 and 905 °K –were used.

The values of the constants for both equations are given in table (3.5), as well as average percent error and the number of compounds considered in their study. Table (3.6) shows only a small section of the much larger complete tabulation.

Table 3.5 Values of constants n_1,C_1 for Eq.(3.20),and n_2,C_2 for Eq.(3.21)

Mathur-Ibrahim-Kuloor method				
series	**No.Compounds Considered**	**Value of constants** **n_1**	**c_1**	**Avg. % error**
hydrocarbons and related compounds,Eq.(1)				
paraffins	**20**	**497.5**	**-453.0**	**0.68**
noco-oiefins	**19**	**490.0**	**-441.0**	**0.78**
alkynes	**10**	**465.4**	**-370.8**	**0.82**
aikyibenzenes				
up to C_{25}	**20**	**454.5**	**-309**	**0.67**
aboveC_{25}	**14**	**227.4**	**+255.7**	**0.33**
Cyclohexanes				
up to C_{25}	**20**	**500**	**-428**	**0.47**
aboveC_{25}	**17**	**304.1**	**+63.9**	**0.27**
Cyclopentanes				
up to C_{25}	**21**	**454**	**-333**	**0.54**
aboveC_{25}	**13**	**278.4**	**+112.7**	**0.24**
Other organic liquids , Eq. (2)		**n_2**	**C_2**	
alcohols	**8**	**0.2525**	**191.4**	**1.22**
isoalcohols	**4**	**0.2820**	**161**	**0.76**
ketones	**4**	**0.2251**	**205.5**	**0.59**
Acids	**4**	**0.1876**	**274.4**	**0.58**
Esters	**19**	**0.3259**	**123**	**1.06**

Semesters	15	0.3048	133.7	0.91
Ethers	11	0.5469	46.3	2.55
total No = 219			overall avg . = 0.78	

Table 3.6 Comparison of experimental and calculated values of critical temperatures by Mathur method

		Tc, °K		
Compound	Mwt	Experimental	calculated	Avg. % error
Normal paraffins				
Methane	16.04	190.6	46.4	-75.6
Ethane	30.07	305.4	282.3	7.6
Propane	44.09	369.8	365.0	1.29
Butane	58.12	425.1	424.9	0.047
Pentane	72.15	469.4	471.4	0.420
Hexene	86.17	507.3	510.1	0.550
Normal Mono-Olefins				
Ethene(ethylene)	28.05	282.9	268.5	-5.000
Propene(propylene)	42.07	364.9	354.7	-2.800
Butene	56.10	419.0	416.0	-0.710
Pentene	70.13	461.0	463.4	0.520
Hexene	84.15	501.0	502.2	0.230
Alkynes				
Ethyne (acetylene)	26.03	309.3	287.9	-6.910
Propyne (methyl Acetylene)	40.06	394.6	375.0	-4.96
n-Hexyne	82.14	521.0	520.2	-0.0153

n-Heptyne	**96.16**	**553.0**	**522.0**	**-0.180**

3.9 Toshikatsu Hakuta and Mitsuho Hirata

Normal boiling points and liquid densities for very large numbers of compounds are given in the literature, and with rare exceptions these data are very accurate[12]. The proposed method used only these accurate data, and the critical temperature was calculated from normal boiling point by using the following equations proposed by Sato.

To estimate Tc, Sato divided substances in to five classes as follows:-

(A) Inorganic compounds [halogenated and sulfur compounds except elements and hydrogen compounds were classified in to B_1 and B_2. carbon compounds were included in C_1 and C_2].

$$T_c\ [°k]=1075\ T_b\ [°C]+473 \tag{3.22}$$

For B1: Halogenide and sulfur compounds.

$$T_c=1.38\ T_b+450-11F \tag{3.23}$$

Where F is the number of flucrine atoms per molecule.

For B2: Cylices, aromatics, naphthalenes and heterocyclic free of halogens and sulfur.

$$T_c=1.38\ T_b+450-r^{0.6}\ (0.3\ T_b-10) \tag{3.24}$$

Where r is the ratio of noncyclic carbon atoms to total number of carbon atoms in the molecule.

For C1: Noncyclic carbon compounds of which Tb is below 30 °C.

$$Tc = 1045\ T_b + 430 \tag{3.25}$$

For C2: Noncyclic carbon compounds of which Tb is equal to or greater than 30°C .

$$T_c = 1.08\ Tb + 446 \tag{3.26}$$

By using the critical temperature obtained above and a liquid density (ρ_L) at or below the normal boiling point (T_b), molar volume of liquid (V_{lb}) at normal boiling point (T_b) calculated from the following modified Goldhamer equation , which was also .

Used by Fishtine;

$$V_{lb} = \frac{M}{\rho_l^t}\left(\frac{T_c - T^l}{T_c - T_b}\right)^n \tag{3.27}$$

The values of n are listed in table (3.7) for different group of compounds.

where values of exponent n are given in table (3.7), critical volume was estimated from modified Benson equation by using T_c , V_{lb} and an assumed p_c;

$$V_c = V_{Lb}(1.981 + 0.422 * \log P_c) \tag{3.28}$$

Acentric factor ω was calculated from equation proposed by demister .

$$\omega = \frac{3}{7}\left(\frac{\log P_c}{(T_c/T_b) - 1}\right) - 1 \tag{3.29}$$

where T_c and P_c are the values used in previous steps. The correlation between critical compressibility factor Z_c and acentric factor w is given as the following equation ;

$$Z_c = 0.291 - 0.08\,\omega \tag{3.30}$$

Eq.3.30) had been proposed by Pitzer.

Critical pressure was estimated by using the critical temperature, critical volume and critical compressibility factor in previous steps;

$$P_c = \frac{Z_c R T_c}{V_c} \tag{3. 31}$$

Table (3.8) shows a summary of statistical data

Table (3.7) Recommended exponent for the Goldhammer equation(eq.3.27)

compound group	n
Alcohols and water	0.25
Hydrocarbons and ethers	0.29
All other organic compounds	0.31
All inorganic compounds except water	0.333

Table (3.8) Summary of statistical data

Average deviation%				
No.ofsubstances	T_c	P_c	V_c	Remarks
240 for T_c and P_c 228 for V_c	1.39	2.61	2.04	All substances
153 for T_c,P_c and V_c	1.34	2.39	1.91	hydrocarbons
68 for T_c and P_c,	1.27	2.86	2.54	organic ompounds excepthydrocarbons
19 for T_c and P_c, compounds14 for Vc	2.28	3.58	3.02	Inorganic

3.10 Method of Joback

Joback [17] reevaluated Lydersen's group contribution scheme, added several new functional groups, and determined new contribution, these relations for the critical properties are;

$$T_C\,(K) = T_b\,[\,0.584 + 0.965\,\{\,\sum_k N_k(tck)\} - \{\sum_k N_K\,(pck)\}^2\,]^{-1} \qquad (3.32)$$

$$P_C\,(bar) = [\,0.113 + 0.0032\,N_{atoms} - \sum_k N_k\,(pck)\,]^{-2} \qquad (3.33)$$

$$V_C(\,cm^3\,mol^{-1}) = 17.5 + \sum_k N_k(vck\,) \qquad (3.34)$$

Where the contributions are indicated as tck, pck and vck. The group identities and Joback's values for contributions to the critical properties were given in tables. For T_b , a value of the normal boiling point , was needed, this may be taken from experiment or by estimation from the following equation;

$$T_b = M^{-0.404} \sum_k N_k (tbbk) + 156.00 \tag{3.35}$$

Where M is the molecular weight and N_k is the number of atoms of type k with contributions $tbbk$.

3.11 Method of Constantionu & Gani (GC)

Constantinonu & Gani [28] developed an advanced group contribution method based on the UNIFAC groups, but they allowed for more sophisticated functions of the desired properties and also for contributions at a "second order" level. The functions give more flexibility to the correlation while the second order partially overcomes the limitation of UNIFAC which cannot distinguish special configurations such as isomers, multiple groups located close together, resonance structures, etc., at the "first order" the general (CG) formnlation of a function f(F) of aproperty F is:

$$F = f\,[\, \sum_k (F_{1i}) + W \sum_j M_j (F_{2j})\,] \tag{3.36}$$

Where f can be alinear or non linear functiun, N_K is the number of first - order groups of type k in the molecule; F_{1k} is the contribution for the first - order group labeled 1k be the specified property, F; N_J is the number of second – order groups of type j in the molecule; and F_{2J} is the contribution for the second – order group label 2j to the specified property, F. The value of W is set bo zero for first - order calculations and Set to unity for second – order calculations for the critical properties, the CG formulations are:

$$T_c(k) = 181.128 \ln [\sum_k N_k(tc1k) + W \sum_j M_j (tc2j)] \quad (3.37)$$

$$P_c(bar) = [\sum_k N_k (pc1k) + W \sum_k M_j(pc2j) + 0.10022]^{-2} + 1.3705 \quad (3.38)$$

$$V_c(cm^3mol^{-1}) = -0.00435 + [\sum_k(vc1k) + W \sum_k M_j(vc2j)] \quad (3.39)$$

3.12 Method of Marrero and Pardillo

Marrero –Marejon and Pardillo –Fontdevila[28] described a method for T_c, P_c and V_c they called it a group interaction contribution technique or what is effectively a ***bond contribution method*** .They gave equations that use values from pairs of atoms alone, such as > C. and - N , or with hydrogen attached , such as CH_3 – and -NH_2 .

Their basic equations are:

$$T_c = T_b [0.5851- 0.9286(\sum_k N_k \, tcbk) + (\sum_k N_k \, tcbj)^2] \quad (3.40)$$

$$P_c = [0.1285 + 0.0059 N_{atoms} - \sum_k N_k \, pcbk]^{-2} \quad (3.41)$$

$$V_c = 25.1 + \sum_k N_k \, vcbk \quad (3.42)$$

Where N_{atoms} is the number of atoms compound, N_k is the number of atoms of type *k* contribulions *tcbk*, *tpcbk* and *vcbk*. Marrero and Pardillo provided estimation method for T_b,

$$T_b = M^{-0.404} \sum_k N_k (tbbk) + 156.00 \quad (3.43)$$

3.13 Method of Grigoras

An early molecular structural approach to physical properties of pure organic substance was proposed by Grigoras[28]. The concept was to relate several properities to the molecular surface areas and electrostatics as generated by combining quantum mechanical results with data to determine the proper form of the correlation. Grigoras related the critical properties to molecular properties via relations such as:

$$\boldsymbol{V_c = 2.217\, A - 93.0} \qquad (3.44)$$

$$\boldsymbol{T_c = 0.633A - 1.562\, A + 0.427\, A_+ + 9.914\, A_{HB} + 263.4} \qquad (3.45)$$

Where A is the molecular surface area, A_- and A_+ are the a mount of negatively and positively charged surface area on the molecule and A_{HB} is the amount of charged. Surface area involved hydrogen bonding.

These relationships can be used to obtain other properties such as P_c by correlations such as:

$$\boldsymbol{P_c = 2.9 + 25.2\, (T_c / v_c)} \qquad (3.46)$$

CHAPTER FOUR

Investigation and Development

4.1 Investigation of the Equations

Critical properties can be calculated using many equations. Usually the accuracy of some equations to calculate the critical properties of pure components is not satisfactory.

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.

There are several equations of state that are used to describe the critical properties of pure components, such as Lydesen , Nokay , Thodos , Viswanath , Mathur Fetal and many other equations. These equations are the most important and accurate equations that are used to determine the critical properties of pure component.

4.1.1 Viswanath Equation

Viswanath[36] proposed equation to estimate the critical volume for hydrocarbons by using the critical temperature (T_c) and critical pressure (P_c), which is simply :-

$$V_c = 0.6243 + 0.259 \frac{RT_c}{P_c} \qquad (3.10)$$

The absolute average deviation obtained from above equation is shown in table 4.1

Table 4.1 The AAD% of Viswanath from the experimental Data

Chemical family	No. of Data point	AAD%
Paraffins	**52**	**3.366**
Olefins	**14**	**5.0903**
Dioelefins	**2**	**5.2822**
Acetylenes	**2**	**4.5415**
Aromatics	**8**	**2.8025**
Over all AAD%	**78**	**3.8881%**

4.1.2 Reidel Equation

Reidel [3] has proposed an equation for evaluating the critical volume (Vc) for hydrocarbons by the following equation:

$$V_c = \frac{RT_c}{P_c}\left[3.72 + 0.26(\alpha - 7.0)\right]^{-1} \qquad (3.1)$$

Where

$$\alpha = 0.9076\left[1.0 + \frac{\left(T_b / T_c\right)\ln P_c}{1.0 - \left(T_b / T_c\right)}\right] \qquad (3.2)$$

The results obtained in using this equation to calculate the critical volume of hydrocarbons compound are not very satisfactory, however, they are better than when using Viswanath equation. The absolute average deviation obtained from above equation is shown in table 4.2

Table 4.2 The AAD% of Reidel from the experimental Data

Chemical family	No. of Data point	AAD %
Paraffins	**52**	**1.7647**
Olefins	**14**	**1.7638**
Diolefins	**2**	**0.995621**
Acetylenes	**2**	**1.8204305**
Aromatics	**8**	**1.3764**
Over all AAD%	**78**	**1.7651%**

4.1.3 Sato Method

Sato [12] divided substances into five classes: Inorganic compounds, Halogenide and Sulfur compounds, Cylices – Aromatics – Naphthalenes and Heterocyclic, Non cyclic carbon compound of which T_b is below 30 ºC, Non cyclic carbon compounds which T_b is equal to or greater than 30ºC. This method is not satisfactory because it is not one general method for all compounds, in addition to the fact that its accuracy is rather high .Some of the results obtained from this method are listed in table 4.3 for 2 classes only because the percentage absolute average deviation obtained from this method is very high as shown in table 4.3

Table 4.3 The AAD% of Sato from experimental data

Chemical family	No. of Data point	AAD %
Sulfur compounds	**7**	**5.337**
Non cyclic carbons (below 30ºC)	**33**	**2.5323**
Over all AAD%	**40**	**3.93465**

4.2 Experimental Data

The experimental data of the critical properties, obtained from literature for the purpose of this investigation consist of 108 values of pure components as shown in table 4-4. Table 4.5 shows the critical properties of polar components.

Table 4-4 The pure component critical properties data

Chemical family	No. of compound	Data Reference
Organic		
Paraffins	**70**	**21,22,25,28**
Olefins	**14**	**21,22,25,28**
Diolefins	**2**	**21,22,25,28**
Acetylenes	**2**	**21,22,25,28**
Aromatics	**8**	**21,22,25,28**
Inorganic	**12**	**21,22,25,28**
$\sum$	**108**	

4.3 Selection of the Correlations

Based on the findings of past investigators, of more recent correlations and on the criterion that a useful method must have input parameters which are available and accurate, the selection of correlations for each critical property was made. Several methods are available in the literatures for prediction of critical properties of pure substances. Most of these methods require the use of group contribution to determine the critical constants from molecular structures. It would be desirable to have an alternative easy method rather than the relatively complex method of group contribution and also to permit the estimation of the critical properties of substances for which group contribution are not available.

Certain methods were eliminated from evaluation because of their limited applicability or because they require input parameters which are not available or which are difficult to measure or predict accurately on their own right.

4.4 Development of the Correlation

The results indicate clearly that when evaluating critical volume (V_C), and critical temperature (T_C) there is no suitable equation that gives little deviation without using group contribution method. So in this work a simple equation was used for predicting critical temperature as a function of normal boiling point (T_b) and molecular weight (Mwt) which are available for very large number of compounds in the literature, and with rare exception these data are very accurate. The proposed method uses only these accurate data.

The critical temperature generally can be estimated more accurately than other critical properties such as critical pressure and critical volume. So it is advisable to estimate critical temperature first.

4.5 Steps of Development

Step One

Since the critical temperature can be estimated more accurately than other critical properties (critical pressure and critical volume), so a new equation was proposed for prediction of critical temperature as a function of normal boiling point (T_b) and molecular weight (Mwt) as follows ;

$$Tc = -11.5565 - 1.03586Mwt + 2.075167Tb - 0.000281Mwt^2 - 0.00131Tb^2 + 0.001827MwtTb \tag{4.1}$$

This equation was obtained by fitting 30 point data of 30 components.
The coefficient of correlation value of this fitting was 0.99999.

Step Two

A suitable value of critical pressure (P_C) was assumed for a component and used in the following equations together with the critical temperature obtained in step one, to calculate critical volume (V_C)as in the following equations ;

$$Vc = \frac{R\ Tc}{R}\left[3.72 + 0.26\left(\alpha - 7\right)\right]^{-1} \tag{3.1}$$

Where R is gas constant.
And

$$\alpha = 0.9076\left[1 + \frac{(Tb/Tc)\ln Pc}{1-(Tb/Tc)}\right] \qquad (3.2)$$

Step Three

Critical pressure (P_C) assumed in step two and critical temperature (T_C) obtained in step one were used to calculate the acentric factor (ω). Using two methods:

Method one

Using the following equation of vapor pressure;

$$\text{Log } P_{VP} = A + \frac{B}{T} \qquad (2.10)$$

By applying the value of vapor pressure and temperature at T_r= 0.7 in equation (4.7), the acentric factor was calculated;

$$\omega = \frac{3}{7}\left[\frac{\phi}{1-\phi} LOG\ p_c\right] - 1 \qquad (2.11)$$

Where

$$\phi = \frac{T_b}{T_C}$$

Method two

Using equation of Lee-Kesler to calculate the acentric factor (ω)

$$\omega = \frac{\alpha}{\beta} \qquad (2.12)$$

Where

$$\alpha = -\ln P_C - 5.97214 + 6.09648\phi^{-1} + 1.28862\ln\phi - 0.169347\phi^{6} \qquad (2.13)$$

And

$$\beta = 15.2518 - 15.6875\phi^{-1} - 13.4721\ln\phi + 0.43577\phi^{6} \quad (2.14)$$

Step Four

To calculate critical pressure (P_C) by

$$P_c = \frac{Z_c R T_c}{V_c} \qquad (4.2)$$

Using critical compressibility factor (Z_C) obtained for non – polar components from the following equation by Pitzer;

$$Z_c = 0291 - 0.08\omega \qquad (3.30)$$

Or using critical compressibility factor (Z_C) of polar compounds by employing the equation of Wu and Stiel

$$Z_c = 0.2901 - 0.0879\ w - 0.00266\ Y \qquad (2.8)$$

This equation was modificated by statistical fitting and the following equation was obtained

$$Z_c = 0.2901 - 0.879 * \omega - 0.033583\ Y \qquad (4.3)$$

Step Five

If the value of critical pressure (P_C) calculated in step four is the same value as critical pressure (P_C) assumed in step two, then this the correct critical pressure (P_C) for the compound otherwise the value critical pressure (P_C) obtained in step four would be assumed again in step two and the steps repeated until the value of critical pressure (P_C) obtained in step four is the same as the value of critical pressure (P_C) assumed with the tolerance of 10^{-4}.

4.6 Application of the Developed Correlation

1. In order to clarify the application of the developed correlation an example is given below for Isobutane which was not included in statistical fitting:

Table 4.5 Properties of Isobutane

comp	Mwt	T_b(K)	T_C (K)	P_C (bar)	V_C (cm^3 / mol)	Z_C	ω
Isobutane	**58.123**	**261.43**	**407.85**	**36.4**	**262.7**	**0.278**	**0.186**

Assume P_C = 40 bar

Table 4.6

Iteration No.	T_C (K)	V_C (cm^3 / mol)	ω	Z_C	P_C (bar)
1	407.867	229.83	0.1903	0.2721	39.998
2	407.867	240.82	0.189	0.2254	38.103
3	407.867	255.815	0.1885	0.2601	37.56
4	407.867	261.927	0.1865	0.2689	36.499
% dev.	0.00416	0.291	0.2688	0.327	0.0618

Trial 2

1. By using the value of P_c estimated in step four, the new value of V_c is calculated in step two. These procedures are continued in the same way, and the new values of V_c, Z_c and P_c are estimated.

In this fashion successive approximations are continued till P_c converges.

2. In order to clarify the application of the developed correlation an example for polar component is given below for Ammonia.

Table 4.7 properties of Ammonia

Comp.	Mwt	T_b (K)	T_C (K)	P_C (bar)	V_C (cm ^{3}/ mol)	Z_C	ω
Ammonia	17.031	239.82	405.4	113.53	72.47	0.278	0.25

Assume P_C = 40 bar

Table 4.8

Iteration No.	T_C (K)	V_C (cm ^{3} / mol)	ω	Z_C	P_C (bar)
1	390.6	86.45	0.21	0.22	101.4
2	390.6	85.14	0.215	0.224	103
3	390.6	83.34	0.22	0.231	105.16
4	390.6	81.82	0.23	0.236	107.12
5	390.6	80.2	0.235	0.24	109.3013
6	390.6	78.45	0.237	0.2409	111.7327
7	390.6	76.586	0.24	0.243	114.45

4.7 Further Attempt to Improve The Method of Correlation for Prediction of Critical Properties

1. Changing the constants of equation for acentric factor by fitting 30 data points to improve the values of acentric factor for the components

$$Z_c = 0.2901 - 0.879 * \omega - 0.033583$$

2. As more accurate values of acentric factor predicted, the more accurate values of critical compressibility factor (Z_C) and critical pressure predicted as shown in table 4.6.
3. Changing the constants of Wu and Stiel equation for critical compressibility factor (Z_C) calculated by fitting 16 data point .The equation obtained is as follows;

$$Z_c = 0.2901 - 0.879 * \omega - 0.033583$$

Note that all the compounds that are predicted by this work are not included in statistical fitting of the developed equations of acentric factor and critical compressibility factor.

CHAPTER FIVE

Discussions

5.1 Introduction

This chapter is indented to deal with the discussion of the results presented in chapter four. Many excellent estimation methods have been proposed in literature and mentioned in chapter three, For instance, Lydesen, Thodos, constantionu and Gani, Joback, Toshikatsu Hakuta and Mitsuho Hirata and others. However, these authors used group contribution estimation of critical properties of compounds. This method, that is group contribution method, is rather complicated and difficult because it deals with chemical structures and concerned with number of atoms and bonds between them. So for this reason a new and relatively simple, accurate and generalized method is proposed in this research which does not use group contribution technique.

In this work critical temperature, critical pressure, and critical volume can be estimated solely from data of normal boiling point and molecular weight of pure substance by means of successive approximations that are repeated until the calculated critical pressure converges.

As a result of this study the method discussed below was proposed as the best available generalized techniques for estimating the critical properties of pure components.

5.2 Experimental Data

Appendix A shows the experimental values of critical properties of various compounds including Hydrocarbons, Aromatics, Amines, Alcohols and other polar compounds. These data were taken from Ref (20).

Table 5.1 Typical experimental critical properties of some polar and non-polar components

components	$T_{Cexp.}$	$V_{Cexp.}$	P_{Cexp}	$Z_{Cexp.}$
Organic CompoundsHydrocarbons				
Isobutane	**407.85**	**259**	**36.4**	**0.278**
2,2,4-Trimethylpentane	**544.1**	**470.1**	**25.4**	**0.253**
Cyclohexane	**553**	**307.8**	**40.0**	**0.234**
Benzene	**562**	**260.3**	**48.6**	**0.26**
Dimethylamine	**456.4**	**182**	**56.4**	**0.27**
Triethylamine	**535**	**389**	**30.3**	**0.265**
Methyl alcohol	**512.6**	**118**	**80.9**	**0.224**
Ethyl alcohol	**513.9**	**176.1**	**61.4**	**0.24**
n. Propyl alcohol	**536.8**	**219**	**51.7**	**0.253**
Aromatic				
C_6H_6	**562.05**	**256**	**48.95**	**0.271**
C_8H_{10}	**630.3**	**370**	**37.32**	**0.262**
Organic Compounds				
Ammonia	**405.5**	**72.5**	**113.5**	**0.244**
Water	**647.3**	**57.1**	**221.2**	**0.235**
Chlorine	**324.7**	**80.9**	**83.1**	**0.249**

5.3 Method of Proposed Correlation of Critical Properties

5.3.1 Step One: Estimation of Critical Temperature

A statistical program was used to obtain a general equation to calculate the critical temperature by using normal boiling point and molecular weight. This equation is then used to calculate the critical temperatures of various compounds which were not used in the fitting. The results of estimation of various groups of compounds are shown in table 5.2

Table 5.2 shows The AAD% of various group of compounds

Group of comp.	No. of data point	AAD%
Paraffine	**114**	**1.8703**
olefine	**14**	**0.3422**
Diolefine	**2**	**2.2515**
Aromatic	**8**	**2.57**

The detail deviation of individual components is shown in appendix B.

Comparison between the above proposed method for estimating critical temperature and Klincewicz equation used also the normal boiling point and molecular weight in deriving his equation below;

$$T_C = 50.2 - 0.16\, Mwt + 1.41\, T_b$$

Table 5.3 shows the results of predicting critical temperature T_C for some none – polar compounds using the proposed method and Klincewicz method.

Table 5.3 shows the results of comparison of predicting critical temperature (T_C) for 15 polar compounds using the proposed method and Klincewicz method.

Table 5.3 The results of using the proposed equation in this work and that of Klincewicz for some non-polar compounds

Comp.	Tc exp.	Tc Klincewicz.(K)	AAD%	Tc this work(K)	AAD%
CH_4	19056	180.506	5.27	190.5799	$1.04*10^{-2}$
C_2H_6	305.32	310.4	1.66	305.04	$8.8*10^{-2}$
C_3H_8	369.8	361.059	2.147	370.09	$7.15*10^{-2}$
C_4H_{10}	425	420.58	1.04	425.35	$5.5*10^{-2}$
C_4H_{10}	407.85	410.9	0.747	408.203	$8.664*10^{-2}$
C_5H_{10}	452.7	449.03	0.8106	452.5329	$3.691*10^{-2}$
C_5H_{12}	469.7	465	1.0006	469.535	$3.5*10^{-2}$
C_5H_{12}	433.75	430.2	0.818	437.6675	0.90317
C_6H_{12}	504	509.71	1.132	503.12	0.173
C_6H_{12}	495	489.7	1.07	493.334	0.336
C_6H_{14}	497.5	491.2	1.266	498.887	0.278
C_7H_{14}	572.19	565	1.256	568.19	0.697
C_7H_{14}	569.5	553.4	2.82	561.03	1.486
C_7H_{16}	520.4	515	1.037	526.05	1.087
C_8H_{16}	567	560.8	1.0934	564.017	0.526
C_8H_{18}	559.6	550	1.715	562.714	0.556
C_9H_{20}	577.8	590.08	2.12	586.95	1.584
$C_{10}H_{14}$	652	660.71	1.335	633.156	2.89
$C_{10}H_{18}$	703.6	710.02	0.912	691.445	1.727
$C_{11}H_{24}$	639	631.34	1.198	638.59	$6.2*10^{-2}$
$C_{14}H_{22}$	708	699.59	1.187	771.668	0.518
Overall AAD%			1.4702%		0.6599%

As shown in table 5.3 the overall average deviation for 20 non-polar compounds by Klincewicz is 1.4702 % while in this work is 0.6599 % , and for 114 non-polar compounds shown in appendix B is 0.9878 %.

Table 5.4 shows the results of comparison of predicting critical temperature for 16 polar compounds using the method of Klincewicz and the proposed method in this work.

Table 5.4 shows the comparison of results of using the proposed equation in this work and that of Klincewicz for 15 polar compounds

Polar compound	Tc exp.	Tc Klincewicz.(K)	AAD%	Tc this work(K)	AAD%
H2O	647.3	573.45	11.408	621.563	3.976
NH3	405.5	386.6	4.66	399.014	1.599
HCL	324.7	375.916	1.577	320.89	1.1733
CH3OH	512.6	522.517	1.9346	514.029	0.278
C2H5OH	513.9	539.594	4.99	520.645	1.3125
Ethylene Oxide	469	421.325	10.23	452.305	3.559
Acetone	508.1	505.7105	0.4702	509.57	0.2893
I- Propanol	508.3	515.412	1.399	510.66	0.4642
N -Propanol	536.8	524.9	2.21	531.97	0.899
CH3CL	416.3	409.15	1.71775	417.76	0.35
CH3F	315	310.78	1.3396	317.15	0.68
R_{12}	385	379.61	1.3999	383.72	0.332
R_{11}	471.2	450.97	4.2932	460.029	2.3707
R_{22}	369.3	361.85	2.017	371.603	0.623
R_{32}	351.6	340.03	3.2906	349.016	0.736

R_{124}	**399.9**	**380.51**	**4.8487**	**387.908**	**2.998**
Overall AAD%			**3.523%**		**1.3525%**

As shown in table 5.4 the overall average deviation for 16 polar compounds is 3.523 % using Klincewicz method and 1.3525 % for predicting the critical temperatures for these compounds.

It is clear from tables 5.3 and 5.4 that the proposed method for estimating the critical temperature for non-polar and polar compounds is more accurate than that of Klincewicz method.

Comparing this method with group contribution method for predicting critical temperature is as follows. Ambarose (19) stated that AAD%for his method of group contribution for 400 pure non - polar compounds was 4.3% and Jobake (19) stated that AAD% for his method of group contribution for 400 non-polar pure compounds was 3.6%, the AAD % for prediction of critical temperature (T_C) for 114 non-polar compounds in this work was 0.9878%. It is clear that the prediction method in this work is better than that are mentioned above.

5.3.2 Step Two: Estimation of Critical Volume

The following equations of Reidel (2) were used to estimate the critical volume after assumption of suitable value for critical pressure;

$$V_c = \frac{RT_c}{P_c}\left[3.72 + 0.26(\alpha - 7.0)\right]^{-1}$$

Where

$$\alpha = 0.9076\left[1.0+\frac{\left(T_b/T_c\right)\ln P_c}{1.0-\left(T_b/T_c\right)}\right]$$

Reidel pointed out that the above equations can be used only for hydrocarbons. However, in this work the above equations used for various groups of compounds including polar compounds.

After obtaining the most accurate value of critical pressure (P_C), the results of the values of critical volumes (V_C) using the above equations are shown in table 5.5 for various groups of compounds. Table 5.5 also includes the values of critical volumes for some compounds estimated by Viswanth.

Table 5.5The AAD% of critical volume estimated by Reidel method and Viswanath method

Chemical family	No. of Data point	AAD % Reidel method	AAD % Viswanath method
Paraffins	52	1.7647	3.359
Olefins	14	1.7638	5.09029
Diolefins	2	0.995621	5.2822
Acetylenes	2	1.8204305	4.51556
Aromatics	8	1.3764	2.802511
Over all AAD%	78	1.7651%	3.8881%

The overall AAD% for predicting critical volumes by Reidel method which is used in this work is 1.7651% and the AAD% for predicting critical volumes by Viswanath method for the same compounds is 3.8881 %.
Comparing this method with group contribution method for critical volume is as follows: Amabrose stated that AAD% for his method of group contribution for 400 pure compounds was 8.5% and Jobake stated that AAD% that AAD% for his method of group contribution was 7.5%.It is clear that prediction method used in this work for critical volume (V_C) is better than those mentioned above.

5.3.3 Step Three: Estimation of Acentric Factor

The following equations of vapor pressure equation (19,20), and that of Lee-Kesler(19,20) were used to estimate acentric factor after applying the assumption of suitable value for critical pressure;

$$\omega = \frac{3}{7}\left[\frac{\phi}{1-\phi} LOG\, p_c\right] - 1$$

Where

$$\phi = \frac{T_b}{T_C}$$

Or using Lee-Kesler equation

$$\omega = \frac{\alpha}{\beta}$$

Where

$$\alpha = -\ln P_C - 5.97214 + 6.09648\phi^{-1} + 1.28862\ln\phi - 0.169347\phi^6$$

$$\beta = 15.2518 - 15.6875\phi^{-1} - 13.4721\ln\phi + 0.43577\phi^6$$

Acentric factor is very widely used as a parameter which in some manner is supposed to measure the complexity of a molecule with respect to both the geometry and polarity.

5.3.4 Step Four: Estimation of Critical Compressibility Factor

For non-polar compounds, critical compressibility factor (Z_C) was obtained by Pitzer equation;

$$Z_c = 0.0291 - 0.08 \quad \omega \qquad (5.1)$$

Wu and Stiel (26) modified the Lee-Kesler scheme by incorporating the polar substance water as a third reference fluid. The compression factor is given in this extended schemes is given by;

$$Z = Z_\circ + \omega Z_1 + YZ_2 \qquad (5.2)$$

Where Y is a forth parameter characteristic for polar compounds. When the above equation was applied at the critical point, the following equation was obtained;

$$Z_C = 0.2901 - 0.0879\ \omega - 0.0226\ Y \qquad (5.3)$$

Where the first two terms on the right hand side of the above equation is for non-polar compounds (Pitzer equation for Z_C). When using equation (5.3) for estimating critical compressibility factor (Z_C) for 16 polar compounds it is found that the deviation of the values of Z_C from the values of Z_C obtained from literature were rather high. The Wu and Steil equation was modified by statistical method based on values of Z_C obtained from literature. The following modified equation was obtained;

$$Z_C = 0.2901 - 0.879 * \omega - 0.033583 * Y \qquad (5.4)$$

The fourth parameter (Y) of equation (5.4) is determined from PVT data for the fluid.Tables 5.6 indicate the results of estimating Z_C by Wu and Steil equation and modified form of this equation that is done in this work. It is obvious that using the modified Wu and Steil equation gives more accurate values of Z_C which is the original equation.

Table 5.6 The Comparison of the results of estimating Z_c by Wu and Steil equation and modified form

Polar compound	**$Z_C$lit.**	**$Z_{CWu\ \&steil}$**	**ΔZ_C**	**$Z_C$in this work**	**ΔZ_C**
H2O	**0.235**	**0.267**	**0.032**	**0.256**	**0.021**
NH3	**0.244**	**0.273**	**0.029**	**0.265**	**0.021**
HCL	**0.249**	**0.277**	**0.028**	**0.271**	**0.022**
CH3OH	**0.224**	**0.275**	**0.051**	**0.268**	**0.044**
C2H5OH	**0.24**	**0.285**	**0.045**	**0.0282**	**0.042**
Ethylene Oxide	**0.259**	**0.277**	**0.018**	**0.271**	**0.012**
Acetone	**0.232**	**0.275**	**0.043**	**0.268**	**0.036**
I- Propanol	**0.248**	**0.2889**	**0.0409**	**0.2883**	**0.0403**
N - Propanol	**0.253**	**0.2912**	**0.0382**	**0.2918**	**0.0388**
CH3CL	**0.259**	**0.283**	**0.014**	**0.279**	**0.01**
CH3F	**0.24**	**0.273**	**0.033**	**0.265**	**0.025**
R_{12}	**0.28**	**0.2896**	**9.6E-3**	**0.2893**	**9.3E-3**
R_{11}	**0.279**	**0.2897**	**0.0107**	**0.2895**	**0.0105**
R_{22}	**0.268**	**0.2863**	**0.0187**	**0.2845**	**0.0165**
R_{32}	**0.241**	**0.274**	**0.033**	**0.266**	**0.025**
R_{124}	**0.273**	**0.29012**	**0.01712**	**0.29013**	**0.01713**

5.3.5 Step Five: Estimation of Critical Pressure

The results of the values of critical pressure prediction by this four steps procedure proved to be satisfactory. For 11 non-polar compounds (in Appendix C) the overall percent deviation is 1.98%. Table 5.7 shows typical results of 20 non-polar compounds.

Table 5.7 Typical results of 16 non-polar compounds

Comp.	Pc exp.(bar)	Pc cal.(bar)	Dev.%
CH_4	45.99	45.1	0.6305
C_2H_6	48.72	48.09	1.29
C_3H_8	42.48	42.3	0.423
C_4H_{10}	37.96	37.6	0.9483
C_4H_{10}	36.4	36.05	0.961
C_5H_{12}	33.7	33.1	1.7
C_5H_{12}	31.96	31.8	0.5
C_6H_{14}	30.1	29.98	0.398
C_7H_{16}	27.4	27.12	1.02
C_8H_{18}	24.9	24.35	2.208
C_9H_{20}	25.3	25.1	0.79
$C_{10}H_{22}$	21.1	20.89	0.99
$C_{11}H_{24}$	19.8	19.45	0.38

$C_{12}H_{26}$	**18.2**	**18**	**1.09**
$C_{13}H_{28}$	**16.8**	**16.02**	**4.6**
$C_{14}H_{30}$	**15.7**	**15.25**	**2.86**
OverallAAD%			**1.2349%**

Table 5.8 shows the results of predicted critical pressure of 16 polar compounds.The overall average deviation is 1.4671% which are regarded very satisfactory.

Table 5.8 Results of 16 polar compounds

Comp.	Pc exp.(bar)	Pc cal.(bar)	Dev.%
H_2O	**221.2**	**220.1**	**0.497**
NH_3	**113.5**	**111.73**	**0.835**
HCl	**83.1**	**80.9**	**2.64**
CH_3OH	**80.9**	**78.98**	**2.37**
C_2H_5OH	**61.4**	**60.5**	**1.46**
Ethyl oxide	**71.9**	**70.76**	**1.58**
Acetone	**47**	**45.9**	**2.2**
I-propanol	**42.5**	**41.8**	**1.66**
n-propanol	**51.7**	**50.87**	**1.5**
CH_3Cl	**67**	**66.65**	**0.522**

CH_3F	**56**	**55.46**	**0.964**
R_{12}	**41.4**	**40.3**	**2.65**
R_{11}	**44.1**	**43.7**	**0.907**
R_{22}	**49.7**	**48.45**	**2.51**
R_{32}	**58.3**	**57.91**	**0.668**
R_{124}	**37.2**	**37.01**	**0.5107**
Overall AAD%			**1.4671%**

It is important to mention that the group contribution method to estimate critical pressure indicate the AAD% is 4.6 for 400 compounds by Ambarose and 5.2 by Jobake for 400 compounds also.

So, these four steps method to predict critical properties seems to be better than those of group contribution method.

5.2 Conclusions

1- A fairly accurate and easy method for estimation of critical temperature, critical volume and critical pressure from data of normal boiling point and molecular weight of pure substance only. This method consists of four steps and by means of successive approximation that are repeated until calculation of the critical pressure converges. This method proved to be more accurate than group contribution method.

2- A new general equation has been obtained to predict critical temperature. This equation is a relation of normal boiling point and molecular weight;

$$Tc = -11.5565 - 1.03586 Mwt + 2.075167 Tb - 0.000281 Mwt^2 \\ - 0.00131 Tb^2 + 0.001827 MwtTb$$

The AAD% for 114 pure compounds obtained from the above equation is 0.9878% and for 16 polar compounds is 1.3525 %.

3- Reidel equation for critical volume was used successfully for non-polar and polar compounds. The AAD% for critical volume in these four steps of successive approximation using Reidel equation is 1.7651 % for 78 data point.

4. Modification of Wu and Steil equation in the following form;

$$Z_c = 0.2901 - 0.879 * \omega - 0.033583 \ \mathrm{Y}$$

Proved to be more successful than their original equation for critical compressibility factor (Z_C) for polar compounds.

5. The results of the values of critical pressure predicted by these four steps of successive approximation proved to be satisfactory.

The AAD % for 114 non-polar compounds is 1.89% and the AAD % for 16 polar compounds is 1.4671 %.

5.3 Recommendations

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

1. Applying the developed correlation for further available experimental data – polar and non polar.

2. Studying the possibility of applying this correlation for binary mixture with an acceptable accuracy.

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Appendix A
The Critical Properties of non-polar Components

Critical Properties of Paraffin Components

Component	Mwt	T_C (K)	P_C (bar)	T_b (K)	ω	V_C (cm^3/mol)
CH_4	16.043	190.56	45.99	111.66	0.011	98.6
C_2H_6	30.07	305.32	48.72	184.55	0.099	145.5
C_3H_8	44.097	369.83	42.48	231.02	0.152	200
C_4H_{10}	58.123	425.12	37.96	272.66	0.2	255
C_4H_{10}	58.123	407.85	36.4	261.34	0.186	259
C_5H_{12}	72.15	469.7	33.7	309.22	0.252	311
C_5H_{12}	72.15	460.4	33.81	300.99	0.229	306
C_5H_{12}	72.15	433.8	31.96	282.65	0.197	307
C_6H_{14}	86.177	507.6	30.25	341.88	0.3	368
C_6H_{14}	86.177	497.5	30.1	333.4	0.278	366.7
C_6H_{14}	86.177	504.4	31.2	336.4	0.273	366.7
C_6H_{14}	86.177	488.7	30.8	322.87	0.233	359.1
C_6H_{14}	86.177	4999.9	31.3	331.12	0.248	357
C_7H_{16}	100.204	540.2	27.4	371.57	0.35	428
C_7H_{16}	100.204	520.4	27.7	352.32	0.287	415.8
C_7H_{16}	100.204	519.7	27.4	353.62	0.304	417.5
C_7H_{16}	100.204	536.3	29.5	359.19	0.269	414.1
C_7H_{16}	100.204	537.3	29.1	362.91	0.297	393
C_7H_{16}	100.204	530.1	27.3	363.18	0.331	421
C_7H_{16}	100.204	535.2	28.1	365.0	0.323	404
C_7H_{16}	100.204	540.5	28.9	366.63	0.311	415.8
C_7H_{16}	100.204	531.1	29.5	354.01	0.25	398
C_8H_{18}	114.231	568.7	24.9	398.82	0.399	492
C_8H_{18}	114.231	567.8	28.7	379.44	0.248	488
C_8H_{18}	114.231	559.6	24.8	390.8	0.378	464
C_8H_{18}	114.231	563.6	25.5	392.08	0.378	471.1
C_8H_{18}	114.231	561.7	25.4	390.66	0.372	476
C_9H_{20}	128.258	577.8	23.5	405.97	0.383	525
C_8H_{18}	114.231	563.4	26.3	388.76	0.347	468.2
C_8H_{18}	114.231	553.5	25.6	382.58	0.344	472
C_8H_{18}	114.231	550	24.9	382.26	0.357	482

C_8H_{18}	**114.231**	**568.8**	**26.9**	**390.88**	**0.338**	**458.8**
C_8H_{18}	**114.231**	**563.4**	**72.3**	**382.99**	**0.298**	**436**
C_8H_{18}	**114.231**	**573.5**	**28.2**	**387.92**	**0.291**	**455.1**
C_8H_{18}	**114.231**	**566.3**	**27.3**	**386.62**	**0.316**	**456.2**
C_9H_{20}	**128.258**	**594.6**	**22.9**	**423.97**	**0.445**	**555**
C_9H_{20}	**128.258**	**587**	**23.1**	**416.44**	**0.423**	**529**
C_9H_{20}	**128.258**	**592.7**	**25.3**	**406.18**	**0.301**	**490**
C_9H_{20}	**128.258**	**574.6**	**24.9**	**395.44**	**0.314**	**504.0**
$C_{10}H_{22}$	**142.285**	**617.7**	**21.1**	**447.3**	**0.490**	**624**
$C_{10}H_{22}$	**142.285**	**609.6**	**23.2**	**428.83**	**0.383**	**564**
$C_{11}H_{24}$	**156.312**	**639.0**	**19.8**	**469.08**	**0.537**	**689.0**
$C_{12}H_{26}$	**170.338**	**658**	**18.2**	**489.48**	**0.576**	**754.0**
$C_{13}H_{28}$	**184.365**	**675.0**	**16.8**	**508.63**	**0.618**	**823**
$C_{14}H_{30}$	**198.392**	**693**	**15.7**	**526.76**	**0.644**	**894**
$C_{15}H_{32}$	**212.419**	**708**	**14.8**	**543.83**	**0.685**	**966**
$C_{16}H_{34}$	**226.446**	**723**	**14.0**	**559.98**	**0.718**	**1034**
$C_{17}H_{36}$	**240.473**	**736**	**13.4**	**574.56**	**0.753**	**1103**

Critical Properties of Olefins Components

Component	Mwt	T_C (K)	P_C (bar)	T_b (K)	ω	V_C (cm^3/mol)
C_3H_4	**42.081**	**398.25**	**55.75**	**240.34**	**0.13**	**162.8**
C_4H_8	**56.108**	**419.5**	**40.2**	**266.92**	**0.194**	**240.8**
C_4H_8	**56.108**	**435.5**	**42.1**	**276.87**	**0.203**	**233.8**
C_4H_8	**56.108**	**428.6**	**41.0**	**274.03**	**0.218**	**237.7**
C_5H_{10}	**70.143**	**464.8**	**35.6**	**303.11**	**0.237**	**298.4**
C_5H_{10}	**70.134**	**475.0**	**36.9**	**310.07**	**0.253**	**302.1**
C_5H_{10}	**70.134**	**470**	**38.6**	**311.7**	**0.336**	**292**
C_6H_{12}	**84.161**	**504**	**31.43**	**336.63**	**0.281**	**355.1**
C_7H_{14}	**98.188**	**537.3**	**29.2**	**366.79**	**0.343**	**409**
C_7H_{16}	**100.204**	**537.3**	**29.1**	**362.91**	**0.297**	**393**
C_8H_{16}	**112.215**	**567**	**26.8**	**394.44**	**0.266**	**468**
C_9H_{18}	**126.242**	**594**	**23.3**	**420**	**0.411**	**526**

Critical Properties of Diolefins Components

Component	Mwt	T_C (K)	P_C (bar)	T_b (K)	ω	V_C (cm^3/mol)
C_3H_4	40.065	394	52.5	238.77	0.122	173.9
C_4H_6	54.092	425	43.2	268.62	0.195	221

Critical Properties of Acetylenes Components

Component	Mwt	T_C (K)	P_C (bar)	T_b (K)	ω	V_C (cm^3/mol)
C_2H_2	26.038	308.3	61.14	188.4	0.189	112.2
C_4H_8	56.108	419.5	40.2	266.92	0.194	240.8

Critical Properties of Aromatics Components

Component	Mwt	T_C (K)	P_C (bar)	T_b (K)	ω	V_C (cm^3/mol)
C_6H_6	78.114	562.05	48.95	353.24	0.21	256
C_7H_8	92.141	591.75	41.08	383.79	0.264	316
C_8H_{10}	106.167	630.3	37.32	417.59	0.312	370
C_8H_{10}	106.167	617	35.41	412.34	0.327	375
C_8H_{10}	106.167	616.2	35.11	411.53	0.322	378
C_9H_{12}	120.194	664.5	34.54	449.23	0.367	435
C_9H_{12}	120.194	649.1	32.32	442.49	0.377	435
C_9H_{12}	120.194	637.3	31.27	437.9	0.399	430

The Critical Properties of Polar Components

Critical Properties of Polar Components

Polar compound	T_b (K)	T_C (K)	P_C (bar)	V_C (cm^3/mol)	Z_C	ω	Y
H2O	373.2	647.3	221.2	57.1	0.235	0.344	1.0
NH3	239.8	405.5	113.5	72.5	0.244	0.25	0.739
HCL	188.1	324.7	83.1	80.9	0.249	0.133	0.565
CH3OH	337.7	512.6	80.9	118.0	0.224	0.556	0.652
C2H5OH	351.4	513.9	61.4	167.1	0.24	0.644	0.213
Ethylene Oxide	283.7	469	71.9	140.0	0.259	0.202	0.565
Acetone	329.2	508.1	47.0	209	0.232	0.304	0.652
I- Propanol	355.4	508.3	42.5	220	0.248	0.248	0.052
N - Propanol	370.3	536.8	51.7	219	0.253	0.254	-0.052
CH3CL	249.1	416.3	67.0	138.9	0.259	0.153	0.304
CH3F	194.7	315	56	113.2	0.24	0.187	0.739
R_{12}	245.2	385	41.4	216.7	0.28	0.204	0.021
R_{11}	296.9	471.2	44.1	247.8	0.279	0.189	0.015
R_{22}	232.4	369.3	49.7	165.6	0.268	0.221	0.164
R_{32}	221.5	351.6	58.3	120.8	0.241	0.271	0.704
R_{124}	263	399.9	37.2	244	0.273	0.281	-0.001

Appendix B
Results of Investigation for Critical Temperatures

Critical Temperatures for Organic Components

Component	T_C (K)	T_C cal. (K)	Dev. %
CH_4	190.56	190.5799	$1.043357*10^{-2}$
C_2H_4	282.38	278.4239	1.4009
C_2H_6	305.32	305.0491	$8.872807*10^{-2}$
C_3H_4	394	397.6411	0.9241482
C_3H_6	364.9	363.7002	0.3288104
C_3H_8	369.81	370.0946	$7.154299*10^{-2}$
C_4H_6	440	435.8007	0.9543957
C_4H_6	425	422.0742	0.6884191
C_4H_8	460	452.8507	1.554187
C_4H_8	419.5	415.7707	0.412231
C_4H_8	435.5	433.5311	0.4521016
C_4H_8	417.9	415.4891	0.5768983
C_4H_{10}	425.12	425.3574	$5.583499*10^{-2}$
C_4H_{10}	407.85	408.2034	$8.664044*10^{-2}$
C_5H_8	470	473.1609	0.6725425
C_5H_{10}	464.8	463.2576	0.3318458
C_5H_{10}	475	471.5228	0.7320428
C_5H_{10}	470	466.5704	0.7297078
C_5H_{10}	452.7	452.5329	$3.691501*10^{-2}$
C_5H_{12}	469.7	469.5349	$3.515661*10^{-2}$
C_5H_{12}	460.39	460.751	$7.841676*10^{-2}$
C_5H_{12}	433.75	437.6675	0.9031726
C_6H_{12}	504	503.1235	0.1739078
C_6H_{12}	495	493.3348	0.3364085
C_6H_{14}	507.6	507.357	$4.788061*10^{-2}$
C_6H_{14}	497.5	498.887	0.2787988
C_6H_{14}	504.4	504.1355	$5.243167*10^{-2}$
C_6H_{14}	488.7	493.0939	0.8990977
C_6H_{14}	499.9	501.7596	0.371986
C_7H_{14}	572.19	568.1995	0.6974044
C_7H_{14}	553	549.2634	0.6757022

C_7H_{14}	537.3	534.6062	0.5013562
C_7H_{16}	540.2	539.8822	$5.88392*10^{-2}$
C_7H_{16}	530.1	532.0615	0.3700336
C_7H_{16}	535.2	535.5968	$7.413855*10^{-2}$
C_7H_{16}	540.5	539.7595	0.1370101
C_7H_{16}	537.3	537.7984	$9.276254*10^{-2}$
C_7H_{16}	519.7	524.3073	0.8865189
C_7H_{16}	536.3	539.5013	0.5969222
C_8H_{16}	567	564.0172	0.5260649
C_8H_{18}	568.7	568.6844	$2.747494*10^{-3}$
C_8H_{18}	559.6	562.7146	0.5565804
C_8H_{18}	563.6	565.0589	0.2588579
C_8H_{18}	565.4	566.0217	0.1099475
C_8H_{18}	563.4	565.4199	0.3585192
C_8H_{18}	553.5	559.0392	1.000767
C_8H_{18}	550	556.4148	1.166326
C_8H_{18}	562	566.9741	0.8850749
C_8H_{18}	568.8	569.5404	0.1301719
C_8H_{18}	567	568.701	0.299992
C_8H_{18}	576.5	577.945	0.2506517
C_8H_{18}	563.4	570.0463	1.179666
C_8H_{18}	573.5	577.7971	0.7492797
C_8H_{18}	566.3	569.6481	0.5912316
C_9H_{18}	594	593.8601	$2.35509*10^{-2}$
C_9H_{20}	594.6	594.579	$3.520864*10^{-3}$
C_9H_{20}	587	590.4653	0.5903462
C_9H_{20}	577.8	586.956	1.584632
C_9H_{20}	607.6	615.1904	1.249252
C_9H_{20}	607.1	614.8072	1.269513
$C_{10}H_{18}$	703.6	691.4445	1.727618
$C_{10}H_{22}$	617.7	617.8368	0.0221434
$C_{10}H_{22}$	609.6	622.8995	2.181677
$C_{11}H_{24}$	639	638.5988	$6.278311*10^{-2}$
$C_{12}H_{26}$	658	658.0058	$8.812067*10^{-4}$
$C_{13}H_{28}$	675	675.3093	0.0458261
$C_{14}H_{22}$	708	771.6688	0.5181867
$C_{14}H_{30}$	693	693.1696	$2.447571*10^{-2}$
$C_{15}H_{32}$	708	707.6653	$4.727639*10^{-2}$

$C_{16}H_{34}$	723	722	$8.887664*10^{-2}$
$C_{17}H_{36}$	736	736.2701	$3.670402*10^{-2}$
$C_{18}H_{38}$	747	746.485	$6.893623*10^{-2}$

For Paraffin

Component	V_C cm^3/mol	Dev. %
CH_4	98.6	2.328188
C_2H_6	145.5	1.238974
C_3H_8	200	0.3022537
C_4H_{10}	255	0.5210727
C_4H_{10}	259	1.428069
C_5H_{12}	311	0.2459363
C_5H_{12}	306	0.1267477
C_5H_{12}	307	0.3065376
C_6H_{14}	368	0.1200634
C_6H_{14}	366.7	0.548376
C_6H_{14}	359.1	0.9970265
C_6H_{14}	357	0.2827535
C_7H_{16}	428	0.7105319
C_7H_{16}	415.8	0.5877606
C_7H_{16}	417.5	0.5811424
C_7H_{16}	393	3.033773
C_7H_{16}	421	$2.553763*10^{-2}$
C_7H_{16}	404	2.502222
C_7H_{16}	415.8	1.837983
C_7H_{16}	398	0.7638289
C_8H_{18}	492	1.463305
C_8H_{18}	471.1	0.4575564
C_8H_{18}	476	0.4303107
C_9H_{20}	525	$5.66638*10^{-2}$
C_8H_{18}	468.2	1.274307
C_8H_{18}	472	1.041865
C_8H_{18}	482	1.413116
C_8H_{18}	458.8	0.2808775

C_8H_{18}	455.1	1.78992
C_8H_{18}	456.2	0.9034728
C_9H_{20}	529	1.239948
C_9H_{20}	504.0	$9.349035*10^{-2}$
$C_{10}H_{22}$	564	0.577529

For Olefins

Component	V_C cm^3/mol	Dev. %
C_3H_4	162.8	1.90419
C_4H_8	240.8	1.576471
C_4H_8	233.8	$6.257539*10^{-2}$
C_4H_8	237.7	0.8948185
C_5H_{10}	298.4	2.109456
C_6H_{12}	355.1	0.4697008
C_7H_{14}	409	2.810162
C_7H_{16}	393	3.033773
C_8H_{16}	468	2.55518
C_9H_{18}	526	1.318129

For Diolefins

Component	V_C cm^3/mol	Dev. %
C_3H_4	173.9	0.405582
C_4H_6	221	1.058566

For Acetylenes

Component	V_C cm^3/mol	Dev. %
C_2H_2	112.2	2.06439
C_4H_8	240.8	1.576471

For Aromatics

Component	V_C cm^3/mol	Dev. %
C_6H_6	256	1.08453
C_7H_8	316	0.9602124
C_8H_{10}	370	0.4610216
C_8H_{10}	375	0.8209473
C_8H_{10}	378	0.9408941
C_9H_{12}	435	5.233695
C_9H_{12}	435	1.383323
C_9H_{12}	430	0.5280889

Appendix C
Results of Investigation for Critical Pressure
Critical Pressures for Organic Components

For Paraffine compounds

Component	$P_{Cexp.}$ (bar)	$P_{Ccal.}$ (bar)	Dev. %
CH_4	45.99	44.01	4.305
C_2H_6	48.72	47.9	1.683
C_3H_8	42.48	42.01	1.106
C_4H_{10}	37.96	37.1	2.265
C_4H_{10}	36.4	37.03	1.730
C_5H_{12}	33.7	33.056	1.910
C_5H_{12}	33.81	34.02	0.621
C_5H_{12}	31.96	31.6	1.126
C_6H_{14}	30.25	30.1	0.495
C_6H_{14}	30.1	29.89	0.697
C_6H_{14}	31.2	31.05	0.4807
C_6H_{14}	30.8	30.3	1.623
C_6H_{14}	31.3	30.99	0.9904
C_7H_{16}	27.4	27.012	1.416
C_7H_{16}	27.7	27.4	1.083
C_7H_{16}	27.4	27.06	1.240
C_7H_{16}	29.5	28.97	1.796
C_7H_{16}	29.1	28.95	0.515
C_7H_{16}	27.3	26.91	1.428
C_7H_{16}	28.1	29.99	6.725
C_7H_{16}	28.9	28.7	0.692
C_7H_{16}	29.5	29.2	1.016
C_8H_{18}	24.9	24.5	1.606
C_8H_{18}	28.7	28.6	0.3484
C_8H_{18}	24.8	24.7	0.4032
C_8H_{18}	25.5	25.035	1.823
C_8H_{18}	25.4	25.35	0.196
C_9H_{20}	23.5	23.43	0.297
C_8H_{18}	26.3	26.05	0.9505
C_8H_{18}	25.6	25.54	0.3243
C_8H_{18}	24.9	24.87	0.1204

C_8H_{18}	26.9	26.92	0.0743
C_8H_{18}	72.3	72.12	0.2489
C_8H_{18}	28.2	28.045	0.5496
C_8H_{18}	27.3	27.4	0.366
C_9H_{20}	22.9	23.01	0.4803
C_9H_{20}	23.1	22.96	0.6060
C_9H_{20}	25.3	25.04	1.027
C_9H_{20}	24.9	24.81	0.3614
$C_{10}H_{22}$	21.1	20.94	0.758
$C_{10}H_{22}$	23.2	23.4	0.862
$C_{11}H_{24}$	19.8	20.03	1.16
$C_{12}H_{26}$	18.2	18.5	1.64
$C_{13}H_{28}$	16.8	16.7	0.595
$C_{14}H_{30}$	15.7	15.65	0.3184
$C_{15}H_{32}$	14.8	14.57	1.55
$C_{16}H_{34}$	14.0	14.3	2.14
$C_{17}H_{36}$	13.4	13.6	1.49

for Olefins Compounds

Component	$P_{Cexp.}$ (bar)	$P_{Ccal.}$ (bar)	Dev. %
C_3H_4	55.75	55.67	0.143
C_4H_8	40.2	40.3	0.248
C_4H_8	42.1	42.4	0.712
C_4H_8	41.0	40.99	0.024
C_5H_{10}	35.6	35.4	0.5617
C_5H_{10}	36.9	36.84	0.162
C_5H_{10}	38.6	38.45	0.388
C_6H_{12}	31.43	31.41	0.0636
C_7H_{14}	29.2	28.89	1.06
C_7H_{16}	29.1	28.78	1.09
C_8H_{16}	26.8	26.48	1.19
C_9H_{18}	23.3	23.01	1.24

for Diolefins Compounds

Component	$P_{Cexp.}$ (bar)	$P_{Ccal.}$ (bar)	Dev. %
C_3H_4	52.5	51.987	0.977
C_4H_6	43.2	43.1	0.2314

for Acetylenes Compounds

Component	$P_{Cexp.}$ (bar)	$P_{Ccal.}$ (bar)	Dev. %
C_2H_2	61.14	61.03	0.1799
C_4H_8	40.2	41.05	2.11

for Aromatics Compounds

Component	$P_{Cexp.}$ (bar)	$P_{Ccal.}$ (bar)	Dev. %
C_6H_6	48.95	48.82	0.2655
C_7H_8	41.08	41.1	0.0486
C_8H_{10}	37.32	37.4	0.214
C_8H_{10}	35.41	35.1	1.94
C_8H_{10}	35.11	34.97	0.398
C_9H_{12}	34.54	34.35	0.55
C_9H_{12}	32.32	32.2	0.43
C_9H_{12}	31.27	31.4	0.415

for Polar Compounds

Polar compound	$P_{Cexp.}$ (bar)	$P_{Ccal.}$ (bar)	Dev. %
H2O	221.2	220.1	0.497
NH_3	113.5	114.45	0.837
HCL	83.1	82.9	0.24
CH_3OH	80.9	81.6	0.865
C2H5OH	61.4	60.99	1.279
Ethylene Oxide	71.9	70.98	1.279
Acetone	47.0	46.89	0.234
I- Propanol	42.5	42.9	0.9411
N - Propanol	51.7	52.01	0.599
CH3CL	67.0	67.5	0.746
CH3F	56	56.9	1.607
R_{12}	41.4	41.89	1.183
R_{11}	44.1	45.03	2.108
R_{22}	49.7	48.85	1.71
R_{32}	58.3	57.78	0.891
R_{124}	37.2	37.94	1.98

الخلاصة

التنبؤ بالقيم الدقيقة للخواص الحرجة لأي مركب نقي مهم جداً لأنها تدخل غالباً في حساب الخواص الفيزيائية المستعملة في عمليات التصميم الكيمياوية .القياس المختبري للخواص الحرجة لأي مركب هي عملية صعبة ومعقدة ومكلفة في نفس الوقت , لهذا السبب ولقياس الخواص الحرجة بصورة دقيقة فإن الاهتمام قد وجه لقياس هذه الخواص , وغالباً ما تقاس بطريقة المجموعات المساهمة , والتي تعتبر طريقة صعبة ومعقدة.

ولتفادي هذه المشكلة فإن الجهود قد بذلت من اجل تحسين أو تعديل المعدلات المتوفرة لحساب الخواص الحرجة للمركبات النقية من دون اللجوء إلى استعمال طريقة المجموعات المساهمة باستعمال طريقة سهلة نسبياً.

الطريقة المقترحة في هذا البحث , درجة الحرارة الحرجة ,الحجم الحرج والضغط الحرج يمكن أن تحسب من بيانات درجة الغليان الطبيعية والوزن الجزيئي للمركب وذلك عن طريق التكرار حتى تتلاقى أو تقل نسبة الخطأ بالنسبة للضغط الحرج.

الطريقة المتبعة في هذا البحث يمكن أن تلخص بالخطوات التالية:

1. حساب درجة الحرارة الحرجة .
2. افتراض قيمة مناسبة للضغط الحرج وحساب الحجم الحرج .
3. حساب عامل الانضغاطية الحرج .
4. حساب الضغط الحرج باستعمال المعادلة التالية :

$$P_c = \frac{Z_c R T_c}{V_c}$$

اذا كان الضغط الحرج الناتج من المعادلة أعلاه يختلف عن الضغط الحرج المفروض في الخطوة الثانية فإن الخطوات تكرر إلى أن تثبت قيمة الضغط الحرج وبنسبة خطأ تصل إلى 10^{-4} .

1. استعمل برنامج إحصائي لإيجاد معادلة مناسبة وسهلة لقياس درجة الحرارة الحرجة للمركبات القطبية وغير القطبية باستعمال درجة الغليان الطبيعية والوزن الجزيئي للمركبات النقية ، والمعادلة هي كالتالي :

$$Tc = -11.5565 - 1.03586Mwt + 2.075167Tb - 0.000281Mwt^{2} - 0.00131Tb^{2} + 0.001827MwtTb$$

النسبة المئوية لمعدل الخطأ لحساب درجة الحرارة الحرجة هي 1.9878% لـ 114 مركب نقي.

2. **معادلة رايدل لحساب الحجم الحرج استعملت بعد فرض قيمة مناسبة للضغط الحرج. النسبة المئوية لمعدل الخطأ لحساب الحجم الحرج بطريقة الأربع خطوات هي 1.7651% لـ 78 مركب نقي من مجموعات كيميائية مختلفة .**
3. **معادلة بيتزر لحساب عامل الانضغاطية الحرج قد استعملت للمركبات الغير قطبية ، أما بالنسبة للمركبات القطبية فقد استعملت معادلة وو و ستيل بعد تحسينها وهي كالتالي :**

$$Z_c = 0.2901 - 0.879 * \omega - 0.033583\,Y$$

طريقة لي – كيسلر استعملت لحساب عامل اللامركزية .

4. **قيم نتائج الضغط الحرج المحسوب بطريقة الاربع خطوات هي قيم مرضية. النسبة المئوية لمعدل الخطأ لحساب الضغط الحرج لـ 114 مركب غير قطبي هي 1.98% و النسبة المئوية لمعدل الخطأ لحساب الضغط الحرج لـ 16 مركب قطبي هي 1.4671% .**
5. **النتائج أعلاه تشير بأن طريقة الأربع خطوات المقترحة لهذا البحث هي طريقة أكثر دقة من الطرق الاخرى المتوفرة لحساب الخواص الحرجة بضمنها طريقة المجموعات المساهمة ، هذا بالإضافة إلى حقيقة بأنها طريقة سهلة نسبيا إذا ما قورنت بطريقة المجموعات المساهمة.**

شكر وتقدير

أتقدم بشكري وإمتناني الكبيرين إلى أساتذتي الأعزاء في قسم الهندسة الكيمياوية وخصوصا الأب الأول أستاذي الفاضل د.محمود عمر عبد الله الذي أسدى لي النصيحة ومد يد العون في إعداد هذا البحث والى قسم الهندسة الكيمياوية لما قدمه لي من تسهيلات ومصادر علمية متمنية دوام الموفقية والنجاح للمسيرة العلمية في وطننا العزيز.

التحقق من الارتباطات للتنبؤ بالخواص الحرجة للمركبات النقية

رسالة

مقدمة إلى كلية الهندسة في جامعة النهرين

وهي جزء من متطلبات نيل درجة ماجستير علوم

في الهندسة الكيمياوية

من قبل

إباء كريم جاسم

بكالوريوس علوم في الهندسة الكيمياوية ٢٠٠٣

ربيع الأول ١٤٢٨

تشرين الثاني ٢٠٠٧