Correlation of Viscosity of Dense Gases with an Equation of State

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Abstract

This research was undertaken with the objective of calculating the viscosity of pure gases and their mixtures using the Enskog theory together with a volume translated Peng-Robinson (TPR) equation of state. The TPR equation was used to predict the density which is an independent variable of the radial distribution function (χ) involved in the Enskog equation. In the original Enskog equation,

$$\eta = \eta_0 b_0 \rho (1/b_0 \rho \chi + 0.800 + 0.7614(b_0 \rho \chi))$$

the radial distribution function χ was added to the $\eta_0 b_0 \rho$ term and the constant 0.8 was treated as substance and temperature dependent in this research. The modified Enskog equation

$$\eta = \eta_0 (b_0 \rho \chi)(\frac{1.000}{(b_0 \rho \chi)} + H_{(T)} + 0.7614(b_0 \rho \chi))$$

was found to be satisfactory for the representation of the viscosity for real gases.

Extensive comparisons of calculated viscosities with experimental data for pure gases were undertaken over a temperature range from 200 to 1000 K and a pressure range from 1 to 980 atm. The overall average absolute deviations for the viscosity of gas mixtures such as carbon dioxide-methane, argon-neon, carbon dioxide-krypton and hydrogen-nitrogen were less than one percent. The procedure for the prediction of the viscosities for mixtures is simple and straightforward. Only the critical

parameters, the accentric factor, and the viscosity at low pressure for the gases are required.

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Notation

Various symbols, superscripts, subscripts and abbreviations used frequently in this work are summarized below. All notation is fully defined where it first arises in the text.

Symbols

a, b	Parameters of Peng-Robinsion equation of state
A, B, C	dimensionless form of the parameters a,b and c.
c	parameters of Translated Peng-Robinsion equation of state
B	Second virial coefficient.
c	parameters of Translated Peng-Robinsion equation of state
f	velocity coefficient, defined in Equaton 2.25
k	Boltzman constant.
k_{ij}	binary interaction coefficient.
L, M, N	coefficients of the dimensionless general cubic equation of state, (Equation 2.45) as defined in Equations 2.46-2.48.
m	constant in the α expression.

P pressure, Pa

R gas constant. $kg.m^2./mol.K.sec^2$

T absolute temperature, K

u, w coefficients in the Schmidt-Wenzel general form for cubic equation of state, Equation 2.44.

v molar volume, m^3/mol

Z compressibility factor.

Greek Letters

α temperature dependent portion of a.

γ orientation parameter.

ϵ characteristic energy

ζ inverse collision frequency.

η shear viscosity, $Pa.s$

η_0 shear viscosity at low pressure, $Pa.s$

μ_r dimensionless dipole moment.

ρ molar density. kg/m^3

σ molecular diameter.

χ radial distribution function.

ω	Pitzer's accentric factor.
Ω_v	collision intrgral.

Subscripts

c	critical point property.
i, j, k	Property of components i, j and k in mixture calculations.
m	mixing property, defined in Equation 2.64
r	reduced property.

Superscripts

$*$	dimensionless quantity.

Abbreviations

AAPD	average absolute percentage deviations.
PR	Peng-Robinsion equation of state.
R-K	Redlich-Kwong equation of state.
S-R-K	Soave-Redlich-Kwong equation of state.
TPR	Volume Translated Peng-Robinsiong equation of state.
VLE	vapor-liquid equilibrium.

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Chapter 1

Introduction

Transport and equilibrium properties are useful in chemical process design. Our understanding of equilibrium properties is much better than that of transport properties. The lack of a satisfactorily developed prediction method for calculating transport properties in real dense gases is due to the difficulties involved in accurate measurements and the complexity involved in theoretical treatment. The calculation of transport properties is either theoretically or empirically based. In practice the theoretically based correlation is preferred as more confidence can be obtained outside the range of correlation.

Viscosity is a measure of internal fluid friction, which is a function of the state of the fluid. When a shearing stress is applied to any portion of a confined fluid, it will move and a velocity gradient will be created within the fluid with a maximum velocity at the point where the stress is applied. If the shear stress per-unit area at any point is divided by the velocity gradient (a driving force), the ratio obtained (proportionality constant) is defined as the viscosity of the medium which tends to oppose any dynamic change in the fluid motion.

For the viscosity of gases, when a gas is undergoing a shearing stress, a bulk

motion is produced. The molecules at any point have the bulk velocity vector added to their random velocity vector, and this bulk motion velocity (or momentum) becomes distributed throughout the fluid. Near the source of the applied stress, the bulk velocity is greater than further away from the source. Molecular collisions cause an interchange of momentum. These velocity gradients cause the other sections of the fluid to move in that direction. This random, molecular momentum interchange is the predominant cause of gaseous viscosity. Enskog developed a theory that assumes all molecules are non-interacting rigid spheres moving randomly at a mean velocity.

The Enskog equation for viscosity η is given as follows:

$$\eta = \eta_0 b_0 \rho (1/b_0 \rho \chi + 0.800 + 0.7614(b_0 \rho \chi)) \tag{1.1}$$

where ρ is the molar density, η_0 is the low-pressure gas viscosity, b_0 is the associated volume where the radial is the distance between two oncoming molecular centers and χ is the radial distribution function which is density dependent. For real dense gases, interacting multiple molecular forces are significant. Cohen and Sandler, (1980) correlated the density dependence of viscosity for simple gases at constant temperature in order to modify the Enskog equation to calculate the viscosity of real gases.

Equations of state (EOS) are able to provide the equilibrium properties accurately, such as density, enthalpy, vapor pressure, fugacity, fugacity coefficient and vapor liquid equilibrium properties; they can also be extended to calculate transport properties. The prediction of viscosities for gases is very important, when experimental data are scarce. Cubic equations of state are preferred because fewer

adjustable parameters are needed. The popular cubic equations of state which are used to calculate the density in the Enskog equation, are of the van der Waal type. This gives a consideration to the intermolecular forces. The Peng-Robinsion equation of state is one of the most popular cubic equations of state. The equation is widely used in chemical engineering process simulation, design and optimization. It is intended in this work to predict viscosities of gas mixtures by combining the modified Enskog theory with a volume translated Peng-Robinsion EOS.

Chapter 2

Literature Review

Many industrial processes require viscosity data for design and process control. For example, they are needed in petroleum engineering in order to predict the stability front separating the displaced and displacing phases (Homsy, 1987). The use of the Enskog theory for the prediction of viscosity has been improved through the utilization of cubic equations of state. This chapter presents a review of the Enskog theory for gas viscosity and cubic equations of state that may be useful for the correlation of viscosity for pure gases. The corresponding states methods for the calculation of gas viscosity are discussed.

2.1 Corresponding States Methods for Calculation of Viscosity and Their Limitations

Essentially all gas viscosity estimation techniques are based on either the Enksog theory or the law of corresponding states, both of which require a low pressure viscosity. For the multiparameter correlation, the method of Chung et al. (1984) yielded the best calculated viscosities for pure gases. This method is then selected to estimate the gas viscosity at low pressures. Several multiparameter correlation methods which are based on the concept of corresponding states, provide better

calculated viscosities than other empirical methods. Such methods are discussed below.

2.1.1 Estimation of Viscosity of Pure Gases at Low Pressure

In general the Chapman-Enskog viscosity equation is given as follow:

$$\eta = \frac{26.09(MT)^{\frac{1}{2}}}{\sigma^2 \Omega_v} \tag{2.1}$$

where

$$\sigma = 0.809 V_c^{\frac{1}{3}}$$

and Ω_v , the collision integral which takes into account the dynamics of binary collisions, is obtained as a complex function of dimensionless temperature T^*.

$$\Omega_v = [A(T^*)^{-B}] + C[exp(-DT^*)] + E[exp(-FT^*)] \tag{2.2}$$

$$A = 1.1645 \tag{2.3}$$

$$B = 0.14874 \tag{2.4}$$

$$C = 0.52487 \tag{2.5}$$

$$D = 0.77320 \tag{2.6}$$

$$E = 2.16178 \tag{2.7}$$

$$F = 2.43787 \tag{2.8}$$

Chung et al. (1984) proposed that a correction term F_c be added to the right side of the equation (2.1).

$$\eta = 40.785 \frac{F_c (MT)^{\frac{1}{2}}}{V_c^{\frac{2}{3}} \Omega_v} \tag{2.9}$$

For polar fluids

$$F_c = 1 - 0.276\omega + 0.59035\mu_r{}^4 + \kappa$$

where ω is the accentric factor, κ is a special correction term for highly polar substance and μ_r is a dimensionless dipole moment.

For non-polar fluids

$$F_c = 1$$

The functionality depends on the chosen intermolecular potential. The dimensionless temperature T^* is related to ϵ by

$$T^* = \frac{kT}{\epsilon} \tag{2.10}$$

where ϵ is the characteristic energy defined as follows

$$\frac{\epsilon}{k} = \frac{T_c}{1.2593} \tag{2.11}$$

then

$$T^* = 1.2593T_r \tag{2.12}$$

The deviations in calculated viscosities by means of this method are only 1% for most non-polar substances.

2.1.2 The Reichenberg Method for Calculating Dense Gas Viscosities

Reichenberg (1975) employed a multiparameter correlation technique for calculating the viscosities of dense gases. He suggested that the term $log\Omega_v$ is a linear function of $logT^*$. The dense gas viscosity is correlated as a function of T_r and P_r. The viscosity ratio η/η_0 is given by the following equation:

$$\frac{\eta}{\eta_0} = 1 + Q\frac{AP_r^{1.5}}{BP_r + (1 + CP_r^D)^{-1}} \tag{2.13}$$

The parameters A, B, C, and D are functions of reduced temperature,

where

$$Q = 1 - 5.655\mu_r$$

For nonpolar materials Q is equal to 1.

Larger deviations in the calculated viscosities obtained from this method occur at high pressures. For example the deviations of calculated viscosities of carbon dioxide are from 1% to 10% (Reichenberg, 1975) over a temperature range from 360 to 500 K and a pressure range from 50 to 800 bar.

2.1.3 The Lucas Method for Calculating Dense Gas Viscosities

Lucas (1981) employed a method which is similar to that proposed by Reichenberg (1981) in some aspects. This method also employed temperature and pressure as state variables. The specific form is based on the assumption that V_c is proportional to $\frac{RT_c}{P_c}$.

$$\eta = \frac{Z_2 F_P F_Q}{\xi} \tag{2.14}$$

where Z_2 is a temperature and pressure dependent parameter. F_P and F_Q are the correction factors for polarity and quantum factor, which are respectively described by

$$F_p = \frac{1 + (F_P^\circ - 1)Y^{-3}}{F_P^\circ}$$

$$F_Q = \frac{1 + (F_Q^\circ - 1)[Y^{-1} - (0.007)(lnY)^4]}{F_Q^\circ}$$

The quantity ξ is described by

$$\xi = 0.176(\frac{T_c}{M^3 P_c^4})^{\frac{1}{6}}$$

The Lucas method requires the critical temperature, critical pressure, critical compressibility factor and the dipole moment. Volumetric data are not required in both cases. The error in the calculated viscosities is less than 10% (Reid et al., 1987). For example the deviations of calculated viscosities of carbon dioxide vary from 1.1% to 9.6% over a temperature range from 360 to 500 K and a pressure range from 50 to 800 bar(Reid et al., 1987). However, the deviations are normally up to 8% for dense gases.

2.1.4 The Chung et al. Method for Calculating Dense Gas Viscosities

Chung et al. (1988) extended their multiparameter correlation for low-pressure gas viscosities to account for high-pressure gas viscosities by employing an empirical correction factor. This method employs temperature and volume as the state variables.

The proposed equation is:

$$\eta = \eta^* \frac{36.344(MT_c)^{0.5}}{V_c^{\frac{2}{3}}} \tag{2.15}$$

Where η^* is given by

$$\eta^* = \frac{(T^*)^{0.5}[F_c(G_2^{-1} + E_6 Y)]}{\Omega_v} + \eta^{**}$$

The quantity η^{**} is given by

$$\eta^{**} = E_7 Y^2 G_2 EXP(E_8 + E_9(T^*)^{-1} + E_{10}(T^*)^{-2})$$

and

$$Y = \frac{\rho V_c}{6}$$

the parameters E_1 to E_{10} are linear functions of ω, μ_r and κ. The values of F_c, Ω_v and T^* are defined as in §2.1.1 The deviations in the calculated viscosities are usually less than 5% (Reid et al., 1987). At high pressures, larger deviations in the calculated viscosities occurr, for example at a pressure of 140 bar and at a temperature of 680 K, the deviation in the calculated viscosity of n-butane is more than 10%.

2.1.5 The Brule and Starling Method for Calculating Dense Gas Viscosities

Brule and Starling, (1984) developed a method similar in form to that of Chung et al.. The correlation was modified to make its characterization parameters compatible with those of the Benedict-Webb-Rubin EOS. In this work no polarity terms are included and the orientation parameter γ has replaced the accentric factor ω. The parameter γ represents the intermolecular energy which acts to favor alignment. If the value of γ is not available, the accentric factor may be substituted. The correlation is

$$\eta = \left[\frac{26.693\sqrt{M(\epsilon/k)}}{\sigma^2}\right]\eta^* \tag{2.16}$$

$$\eta^* = \eta^*_\kappa + \eta^*_\phi \tag{2.17}$$

$$\eta^*_\kappa = \eta^*_0[E_6 y + 1/G_n(y)] \tag{2.18}$$

$$\eta^*_\phi = E_7 y^2 [G_n(y)] e^{E_8 + E_9/T^* + E_{10}/T^{*2}} \tag{2.19}$$

$$\eta^*_0 = E_0 \eta^*_{CE} \tag{2.20}$$

$$\eta^*_{CE} = \sqrt{T^*}/\Omega^{(2,2)*} \tag{2.21}$$

where the parameter E_1 to E_{10} are function of γ. Larger deviations in the calculated viscosities for pure gases occur at high pressure . For an example, at a pressure of 200 bars the highest deviation in the calculated results of methane is 16% (Reid et al.,1987). However, this technique was developed to be more applicable for heavy hydrocarbons rather than for simple molecules.

2.1.6 The Limitation in Corresponding States Methods

The multiparameter correlations are completely empirical with no further resource to theory and are limited to a specific state or region. The accuracy of the calculated results is not particularly reliable especially when it is outside the range of correlation, and the accuracy of calculated viscosities for gas mixtures may hardly be obtained with mixing rules because of the involvement of multiple parameters.

2.2 The Extension of Enskog Method for Calculating Viscosities for Pure Gases

Applications of theoretical developments in the generalized Boltzman equation method (Chapman and Cowling, 1952) has only been possible for simple gases. By the modification of the collision term in the Boltzmann equation, Enskog developed a hard spherical model for dense gases. With the use of an EOS to calculate the thermal pressure to account for the intermolecular forces, the Enskog equation is able to apply for simple dense gases.

2.2.1 The Enskog Theory

From the macroscopic point of view, transport properties are those coefficients, or characteristics of a fluid, which measure its trend to produce entropy when perturbed from an equilibrium state. From the microscopic point of view, the entropy production, and therefore the values of the transport coefficients, are a manifestation of the departures of the motion of the molecules which make up the fluid from their equilibrium distribution. For this reason, transport coefficients are closely related to molecular motion, to the mechanism of molecular encounters and thereby to the intermolecular force field. The molecular theory of fluids seeks to establish the formal connection between these microscopic events and the observable transport coefficients. First such a connection enables a knowledge of the details of the molecular encounters to be employed to evaluate the transport coefficients. Secondly, a precise knowledge of transport coefficients from experiment can be applied to the verification of the molecular theory itself and of hypothesis and statements made

about the intermolecular potential. Finally, the molecular theory may reveal relationships among different transport coefficients, or between transport coefficients and the parameters of the thermodynamic state of the fluid.

The Enskog theory is one of the most theoretical methods to predict the effect of pressure on the viscosity of gases. It assumes that the gas consists of hard spheres and behaves like a low density hard-sphere system except all events occur at a fast rate due to the higher rate of collision.

For dilute gases, it is assumed that there are only two body collisions and the molecular diameter σ is small compared with the average distance between molecules. By considering only two body collisions and by taking into account the finite size of the molecules, Enskog took advantage of the kinetic model for dilute gases to develop a kinetic theory for dense gases. The transport properties are regarded solely based on the free motion of the molecules between collisions.

For dense gases, additional effects must be considered. First, it becomes necessary to account for the finite size of the molecules, because this significantly reduces the free volume available for molecular centers at high densities. Secondly, one must consider a new mechanism of transport, known as collisional transfer, which becomes important as the density increases. This mechanism allows energy or momentum to be transferred instantaneously upon the collision of two molecules across a distance equal to the separation of their centers, and is, therefore, distinct from the kinetic mechanism of transport which involves free molecular motion. Finally, it is necessary to re-examine the hypothesis of molecular force at elevated densities, because the possibilities of multi-body collisions, and correlations among molecular velocities can no longer be discounted.

Multiple and repeated encounters must be accounted for the dense gases. Some correction between the velocities of neighboring molecules might be done for a gas. Thus, an equilibrium radial distribution function (χ) must be employed. The increase in collision rate is proportional to the radial distribution function χ. The quantity χ is a function of density, and it becomes infinite when the molecules are packed so closely that motion is impossible. The radial distribution is dominated by two factors (Hirsch et al., 1964) which are the increase of the probability of molecular collisions due to the reduction of volume where the molecules can occupy and the decrease of the probability of molecular collision due to the shielding effect on the center of molecules at high densities. The correction (Chapman and Cowling, 1970) for dense gases is defined by

$$\chi = (1 - \frac{11}{8} b_0\rho)/(1 - 2b_0\rho) \tag{2.22}$$

where the denominator represents the reduction of the volume and the numerator represents the shielding effect. This equation can be expanded to give

$$\chi = 1 + 0.6250 b_0\rho + 0.2869(b_0\rho)^2 + 0.115(b_0\rho)^3 + 0.109(b_0\rho)^4 + ... \tag{2.23}$$

where the associated volume b_0 is given by

$$b_0 = \frac{2}{3}\pi\sigma^3 \tag{2.24}$$

where σ is the molecular diameter

A velocity distribution function $f(r, c, t)$ is introduced to describe the molecular motion in term of the velocity c, the distance r and the time t. Since the time scale for the observation of most macroscopic processes in the gas is insignificant comparing to the time between molecular collision, it is postulated that the eliminating of

the explicit dependence of $f(r,c,t)$ on time can always be accepted. To account for the fact that the collision frequency in a dilute gas is not high enough to ensure the local equilibrium. A solution was sought for $f(r,c,t)$ in the form of an expansion using the inverse collision frequency, ξ, as a parameter. The following equation is the expansion form of the velocity distributioin function (f).

$$f = f^0 + \zeta f^1 + \zeta f^2 + ... \tag{2.25}$$

where ζ is the inverse collision frequency. The Boltzmann equation expressed in terms of f is as follow:

$$\frac{\partial f}{\partial t} + c \cdot \frac{\partial f}{\partial r} = J(ff) \tag{2.26}$$

Where $J(ff)$ is the difference between gain and loss of molecules in the gas which takes place in the three-dimensional volume *dcdr* in an infinitesimal interval of time due to molecular collisions. In dense gases, by considering that the center of two colliding molecules can not be simultaneously at the same point and that free volume which the molecules may occupy is reduced, the collision term of the Boltzman equation has been modified. Thus if the center of one molecule is located at r, the second molecule must lie at $(r-\sigma h)$ and the collision frequency is increased by a factor of χ.The quantity h is a unit vector along the direction of the line between centers at contact. By means of an expansion of f and χ about the point r, the modified Boltzmann equation may be solved by a method similar to that employed for dilute gases to yield the function for the equilibrium and non-equilibrium states.

The viscosity of a gas of rigid spheres may be derived from the first-order solution of the modified Boltzmann equation (Chapman and Cowling, 1970) for non-equilibrium states.

$$\eta = \eta_0(\chi)^{-1}(1 + \frac{2}{5}b_0\rho\chi)^2 + \frac{3}{5}\varpi \tag{2.27}$$

where η_0 is the shear viscosity for dilute gas and ϖ is the bulk viscosity,

$$\varpi = 1.002\eta_0\chi\rho^2 b_0^2 \tag{2.28}$$

The viscosity in a dense gas is given in terms of the viscosity for dilute gases in the Enskog equation (Chapman and Cowling,1970):

$$\eta = \eta_0 b_0\rho(1/b_0\rho\chi + 0.800 + 0.7614(b_0\rho\chi)) \tag{2.29}$$

The equation is based on the assumption that the intermolecular potential function is spherical symmetric, thus it is more suitable to apply for simple gases.

2.2.2 The Modified Enskog Theory

The Enskog theory does not calculate the viscosity accurately because it completely neglects the effects of the correlated molecular motion in the gas, especially at high densities where the intermolecular effects become important. The difference between the hard-sphere model and real fluid behavour lies in the consideration of intermolecular forces. The influence of the intermolecular force can be taken into account by introducing the thermal pressure $[T(\frac{\partial P}{\partial T})_V]$, which is the sum of external and internal pressures.

For a closed system of constant composition that only does pressure-volume work, the first and second laws for a reversible process may be combined by inserting the definition of entropy into the differential form of the first law of thermodynamic in order to obtain the following equation:

$$dU = TdS - PdV$$

The fundamental equation expressed in terms of the internal energy U can be written in the form:

$$(\frac{\partial U}{\partial V})_T = T(\frac{\partial S}{\partial V})_T \; - \; P$$

The sum of external and internal pressures is related to the thermal pressure by a thermodynamic relation. The procedure most commonly used is the one introduced by Michels and Gibson (1931).

$$T(\frac{\partial P}{\partial T})_V \; = \; P + (\frac{\partial U}{\partial V})_T \tag{2.30}$$

where external pressure (P) is due to the walls of the container and the internal pressure which is due to the intermolecular forces is expressed by:

$$(\frac{\partial U}{\partial V})_T = a\rho^2$$

The term $a\rho^2$ which represents the force of cohesion of the molecules, is the van der Waal's correction for the attraction field of force.

Since the calculated viscosities in the original Enskog equation (Eq 2.29) is not reliable for dense gases. Enskog preferred a different procedure based on the relation between $b_0\rho\chi$ and compressibility of the hard sphere equation of state. The hard sphere model is represented by (Hill, 1956):

$$P \; = \; nkT(1 \; + \; b_0\rho\chi) \tag{2.31}$$

He observed that, if the (spherical) molecules were surrounded by the weak attractive field of force, the EOS would be modified to the following equation:

$$P \; + \; a\rho^2 = \; nkT(1 \; + \; b\rho\chi) \tag{2.32}$$

After replacing the system pressure by the thermal pressure $[T(\frac{\partial P}{\partial T})_V]$ the equation becomes:

$$b_0\rho\chi = \frac{V}{R}(\frac{\partial P}{\partial T})_V - 1 \tag{2.33}$$

The value of $b_0\rho\chi$ can be obtained directly from EOS. The radial distribution function in Equation (2.23) at low pressure leads to:

$$\lim_{\rho \to 0} \chi = 1 \tag{2.34}$$

By means of an EOS to calculate the thermal pressure for considering the intermolecular effects, the Enskog theory has been modified for real dense gases.

2.2.3 Equations of State for Determining the Thermal Pressure

Hanley and Cohen (1972) used the modified Enskog theory to predict the viscosity of simple dense gases by the viral equation of state. Hanley et al. (1976) used the modified Benedict-Webb-Rubin equation of state to get better results for calculating gas viscosities. By introducing the thermal pressure to account for the influence of attraction force between molecules, the modified Enskog theory can give smaller deviations (less than 10%) in viscosity for dense gases. Dipippo et al. (1977) used the modified Enskog theory formula for calculating the viscosity of gas mixtures, and the deviations were found to be less than 5 percent for simple gases. By using the second virial equation of state, Cohen and Sandler (1980) explored the use of the Enskog dense gas theory as a basis for correlating the density dependence of viscosity of simple gases. The term b_0 were considered as a function of temperature. The average deviation in b_0 between the calculated value and experimental value was reported to be 3.56%. With the aid of a cubic equation of state, Sheng

et al. (1989) correlated the Modified Enskog equation by taking the constant 0.8 in Equation (1.1) as substance dependent at a given temperature. After the correlation, the equation could reduce the deviation to 3 percent for dense gases over temperatures ranging from 220 to 500 K and pressures ranging from 1 to 740 atm.

2.3 Equations of State

The ideal gas law is approached only by gases at low pressures, and where the intermolecular forces are totally ignored. Since the ideal gas law is only a rough approximation of true behavior, modification is required for practical and theoretical development. Van der Waals (1873) adjusted the deviation of the ideal gas law by introducing two parameters which describe the attractive force and the repulsive force. In this work a cubic EOS is used to provide the equilibrium properties for calculating the thermal pressure.

2.3.1 The Virial Equation

The virial equation of state may be described by a power series expansion in density,

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + ... \tag{2.35}$$

or pressure,

$$Z = 1 + B'P + C'P^2 + D'P^3 + ... \tag{2.36}$$

where B, C, D... and B', C', D'.... are the second, third, fourth, etc. virial coefficients respectively, and ρ is the molar density. The virial coefficients are functions of temperature, and are equal to zero for an ideal gas. Virial coefficients can be related to molecular interactions. The second, third, fourth, etc. virial coefficients

correspond to two-body, three-body and four-body molecular interactions.

Because of its theoretical correctness at low densities, the virial coefficients is a good reference for the purpose of evaluation of equatioins of state. The virial equation has been used in the development of other EOS. The higher order coefficients become important when multiple collisions occur at high densities.

2.3.2 The van der Waals Equation

The van der Waals equation of state is described as follow:

$$P = \frac{RT}{v-b} - \frac{a}{v^2} \tag{2.37}$$

The first term on the right hand side of the equation accounts for the repulsive effects due to the co-volume occupied by the molecules. The second term on the right hand side of the equation indicates the effect of the attractive forces. When a and b are zero, the equation is the same as the ideal gas equation. Van der Waals accounted for repulsive and attractive forces with the constants a and b without considering the temperature dependence of these constants.

2.3.3 The Redlich-Kwong Equation

The Redlich-Kwong equation (Redlich and Kwong 1949) was a considerable improvement over other EOS of relatively simple forms at that time. The van der Waals EOS did not represent the attraction term as temperature dependent. By adding the term ($T^{-0.5}$) in the attraction term of VDW EOS. The Redlich-Kwong equation is

$$P = \frac{RT}{v-b} - \frac{a}{T^{0.5}v(v+b)} \tag{2.38}$$

The predictions of vapor pressure and vapor liquid equilibria (VLE) was improved by considering the attraction force as a temperature dependent.

2.3.4 The Soave form of the Redlich-Kwong Equation

The temperature-dependent term $a_c/T^{0.5}$ of the R-K equation was replaced by a more general term $a(T,\omega)$ involving the temperature and acentric factor by Soave(1972), so that the equation becomes

$$P = \frac{RT}{(v-b)} - \frac{a(T,\omega)}{v(v+b)} \tag{2.39}$$

The parameter $a(T,\omega)$ was formulated primarily to force the equation to fit the vapor pressure data of hydrocarbons based on equal fugacities of the saturated vapor and the saturated liquid, the term $a(T,\omega)$ is defined

$$a(T,\omega) = \alpha(T)a_c \tag{2.40}$$

$$\alpha^{0.5} = 1 + m(1-\sqrt{T_r}) \tag{2.41}$$

where m is represented a function of the acentric factor.

$$m = 0.480 + 1.574\omega - 0.176\omega^2 \tag{2.42}$$

The equation was a highly successful form for describing vapor liquid equilibrium.

2.3.5 The Peng-Robinsion Equation

Peng and Robinsion (1976) developed one of the most popular two-parameter equations of state. Following the same approach of Soave they modified the form of the attraction term to get better volumetric results than S-R-K EOS.

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

where

$$a(T) = a(T_c)\alpha(T)$$

$$a(T_c) = 0.45724\frac{R^2T_c^2}{P_c}$$

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2$$

$$m = 0.37464 + 1.54226\omega - 0.26997\omega^2$$

$$b = 0.07780\frac{RT_c}{P_c}$$

$$Z_c = 0.307 \tag{2.43}$$

For accurate calculation of saturated liquid volumes, the PR equation is only suitable for molecules whose sizes are close to that of n-hexane. However, it gives a more realistic value in the compressibility factor at critical point.

2.3.6 General Expression of Cubic Equation of State

In a general expression of cubic equation of state, the quadratic expression for volume ($v^2 + ubv + wb^2$) replaces the v^2 term in the denominator of the VDW equation:

$$P = \frac{RT}{v - b} - \frac{a}{v^2 + ubv + wb^2} \tag{2.44}$$

Most of the popular EOS can be represented by fitting certain values for the parameters u and w. Multiplying the equation by ($\frac{P^2V^3}{R^3T^3}$), and rearranging yields a cubic equation in z,

$$z^3 + Lz^2 + Mz + N = 0 \tag{2.45}$$

where

$$L = (uB - B) - 1 \tag{2.46}$$

$$M = (w-u)B^2 - uB + A \tag{2.47}$$

$$N = -[wB^3 + wB^2 + AB] \tag{2.48}$$

The dimensionless constants A,B,C are defined as follows:

$$A = \frac{aP}{R^2T^2} \tag{2.49}$$

$$B = \frac{bP}{RT} \tag{2.50}$$

$$C = \frac{cP}{RT} \tag{2.51}$$

The general expression of cubic EOS is recommended on calculation due to its limited range of values. Effects of the form of the equation of state are therefor easier to be observed.

2.3.7 The Volume Translated Peng-Robinsion Equation

Yu and Lu (1987) developed a volume translated PR equation which improves the prediction of volumetric values. Using the expression:

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + ubv + wb^2} \tag{2.52}$$

with

$$v' = v - c \tag{2.53}$$

$$b' = b - c \tag{2.54}$$

where

$$u = 1.5251 + 1.1146\omega + 1.1538\omega^2 \tag{2.55}$$

Equation (2.52) was transformed to

$$P = \frac{RT}{v'-b'} - \frac{a}{v'^2 + u'b'v' + w'b'^2} \tag{2.56}$$

where

$$u' = u - \frac{2c}{b} - \frac{uc}{b} \tag{2.57}$$

$$w' = w + \frac{(u+2w)c}{b} + \frac{(1+u+w)c^2}{b^2} \tag{2.58}$$

Substituting Equation 2.57 to 2.58 yields the following equation.

$$w' = w + [\frac{4w-u^2}{(2+u)^2}]u' + [\frac{1+u+w}{(2+u)^2}](u')^2 - [\frac{(u+2w)}{2+u}]u + [\frac{1+u+w}{(2+u)^2}](u)^2 \tag{2.59}$$

The volume translated Peng-Robinsion E.O.S. can be obtained by letting $u = 2$ and $w = -1$. Hence:

$$u' = (2.0 - \frac{4c}{b}) \tag{2.60}$$

$$w' = (\frac{2c^2}{b^2} - 1) \tag{2.61}$$

$$w' = \frac{(u')^2 - 4u' - 4}{8} \tag{2.62}$$

$$P = \frac{RT}{v-b} - \frac{a}{v^2 + (2-4c/b)bv + (2c^2/b^2 - 1)b^2} \tag{2.63}$$

The application of volume transformation technique of the TPR EOS has significantly improved the prediction of saturation liquid volume.

2.3.8 Mixing Rules

Since either a mixture of constant composition or pure fluid has only one critical point on the P-V diagram, van der Waals assumed that a mixture of constant composition can be treated as a single pure fluid. The description of mixtures for the EOS is the same as that of pure fluids. By replacing the pure fluid parameters with the mixture parameters, then E.O.S can be represented in the following equation.

$$P = \frac{RT}{v_m - b_m} - \frac{a_m}{v_m^2 + u_m b_m v_m + w_m b_m^2} \tag{2.64}$$

where the subscript (m) denotes a mixture property.

Mixing rules are function of compositions and pure fluid parameters. The conventional mixing rules where the molecules are randomly mixed at low densities are mainly for non-polar components.

Most of the popular mixing rules which were proposed by adopting the mixture parameters a and b, are quadratic functions of composition,

$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{2.65}$$

$$b = \sum_i \sum_j x_i x_j b_{ij} \tag{2.66}$$

A geometric mean is used to describe the cross coefficient a_{ij}, and an arithmetic mean to calculate b_{ij}

$$a_{ij} = (a_i a_j)^{\frac{1}{2}} \tag{2.67}$$

$$b_{ij} = (b_i + b_j)/2 \tag{2.68}$$

where a_i and b_i are the constants for pure substances. These simple mixing rules are useful for non-polar and slightly polar fluids. However, the addition of a binary interaction coefficient (k_{ij}) to the mixing rules,

$$a_{ij} = (a_i aj)^{\frac{1}{2}}(1 - k_{ij}) \tag{2.69}$$

is required in order to obtain better results. The value of k_{ij} is generally determined by fitting the binary VLE data of the mixture under consideration. It is considered as an empirical parameter.

For the calculation of viscosities for gas mixtures, the simple mixing rule is applied to estimate the mixture parameters.

2.4 Possible Improvements

Hanley (1976) improved the accuracy of the calculation for pure substances by selecting the Benedict-Webb-Rubin EOS in terms of the virial EOS to calculate the thermal pressure. Sheng et al. (1989) selected the PR EOS to obtain better results for his correlation. But cubic EOS with fixed values of u and w (see §2.3.6) such as the R-K, S-R-K and PR EOS cannot give good volumetric representation for many substances (Yu et al., 1986), leading to the conclusion that one of the prospects which could be modified would be the calculation of the thermal pressure by means of a more suitable TPR EOS.The parameters u and w of the TPR EOS are treated to be substance dependent.

Even though the modified Enskog theory accounts for intermolecular forces, the Enskog equation for calculating gaseous viscosity is based on the model of the simple gases. Thus a modification is required. As viscosity is a function of temperature and pressure, Sheng et al. (1989) treated the constant (0.8) in the Enskog equation as substance dependent to improve the accuracy of calculated viscosities. However the deviations in calculated viscosities are increased for dense gases using the method of Sheng et al. (1989).

In this work an addition of the radial distribution function to the modified Enskog equation is proposed:

$$\eta = \eta_0(b_0\rho\chi)(\frac{1.000}{(b_0\rho\chi)} + H_{(T)} + 0.7614(b_0\rho\chi)) \tag{2.70}$$

An extension of the calculation of viscosities from pure gases to their mixtures is also undertaken in this work.

Chapter 3

The Proposed Approach

In this chapter, some relationships for further developments are presented. Some of the computational methods and the prediction of the viscosity for gas mixtures are also discussed.

3.1 Modification of the Enskog Theory

The viscosity of a dense gas is given in terms of the viscosity for a dilute gas in the Enskog equation as discussed in §2.2.1. The original Enskog equation (Eq 2.1) ignored the intermolecular forces, and assumes that the gas is sufficiently dilute for only binary collision to occur. Enskog selected the hard sphere equation of state

$$P = nkT(1 + b\rho\chi) \tag{3.1}$$

and modified the equation to form

$$P + a\rho^2 = nkT(1 + b\rho\chi) \tag{3.2}$$

After replacing the system pressure by the thermal pressure (Eq 2.30) for real gases, the value of $b_0\rho\chi$ is obtained as follow:

$$b_0\rho\chi = \frac{1}{R}(\frac{\partial vP}{\partial T})_v - 1 \tag{3.3}$$

The quantity $b_0\rho\chi$ can be calculated directly by means of EOS. The introduction of thermal pressure in the Enskog equation to account for the intermolecular forces in real gases has improved the calculated viscosities of pure gases over wide ranges of temperature and pressure. The Enskog theory for dense gases was used as a basis to correlate the variation of viscosities with pressures. A correlation where the constant (0.8) in the original Enskog equation was treated as a substance-dependent parameter H for minimizing the deviations in the calculated viscosities for pure gases has been proposed by Sheng et al. (1989). However, further modifications are considered in this work.

3.2 Prediction of Viscosities for Gases

The correlation between calculated and experimental viscosities is performed at given temperatures.The values of the parameter H are found to be sensitive to the variation of temperature. Selection of an appropriated value of H at a given temperature will lead to a good prediction of the viscosities for pure gases and their mixtures.

3.2.1 Selection of Equation

The application of the modified Enskog theory with the general cubic equation of state for calculating the thermal pressure is described in this section

The generalized van der Waal type equation of state considered in this work is given by:

$$P = \frac{RT}{v-b} - \frac{a}{v^2+ubv+wb^2} \tag{3.4}$$

The temperature dependent parameter a is given by:

$$a(T) = \Omega_a c \frac{R^2 T_c^2}{P_c} \alpha(T) \tag{3.5}$$

$$\alpha(T) = [1 + m(1 - T_r^{0.5})]^2 \tag{3.6}$$

$$m = 0.37464 + 1.54226\omega - 0.26997\omega^2 \tag{3.7}$$

The parameter b is obtained as follow:

$$b = (\frac{.3112}{2+u}) \frac{RT_c}{P_c} \tag{3.8}$$

The thermal pressure $T[\frac{\partial P}{\partial T}]_v$ is calculated by means of the generalized equation of state in the following manner:

$$[\frac{\partial P}{\partial T}]_v = \frac{R}{v-b} - \frac{1}{v^2 + ubv + wb^2} (\frac{\partial a(T)}{\partial T}) \tag{3.9}$$

where

$$\frac{\partial [a(T)]}{\partial T} = a(T_c) \frac{\partial \alpha(T)}{\partial T} = -a(T_c) \frac{[1 + m(1 - T_r^{0.5})]m}{\sqrt{T T_c}} \tag{3.10}$$

then

$$[\frac{\partial P}{\partial T}]_v = \frac{R}{v-b} + \frac{a(T_c)}{v^2 + ubv + wb^2} \frac{[1 + m(1 - T_r^{0.5})]m}{\sqrt{T T_c}} \tag{3.11}$$

By substituting the expression of the thermal presure into Equation (3.3), the following result is obtained:

$$b_0 \rho \chi = \frac{v}{R} [\frac{R}{v-b} + \frac{a(T_c)[m + m^2(1 - T_r^{0.5})]}{v^2 + ubv + wb^2} \frac{1}{\sqrt{T T_c}}] - 1 \tag{3.12}$$

At low densities

$$\lim_{\rho \to 0} \chi = 1 \tag{3.13}$$

then

$$b_0 = \lim_{\rho \to 0} b_0 \chi \tag{3.14}$$

$$b_0 = \lim_{\rho \to 0}[\frac{v^2}{v-b} - v + \frac{a(T_c)[m + m^2(1-\sqrt{T_r})]}{R\sqrt{TT_c}} \frac{v^2}{v^2 + ubv + wb^2}] \tag{3.15}$$

$$= b + \frac{a(T_c)[m + m^2(1-\sqrt{Tr})]}{R\sqrt{TT_c}} \tag{3.16}$$

$$b_0\rho = \frac{1}{v}(b + \frac{a(T_c)[m + m^2(1-\sqrt{T_r})]}{R\sqrt{TT_c}}) \tag{3.17}$$

For the Peng-Robinsion E.O.S.

$$\Omega_{ac} = 0.45724$$

$$u = 2 \tag{3.18}$$

$$w = -1 \tag{3.19}$$

For the volume translated Peng-Robinsion E.O.S

$$\frac{c}{b} = \frac{2.0 - u}{4} \tag{3.20}$$

$$w = \frac{u^2 - 4u - 4}{8} \tag{3.21}$$

where

$$u = 1.5251 + 1.1146\omega + 1.1538\omega^2 \tag{3.22}$$

Once the values of η_0, $b_0\rho$ and $b_0\rho\chi$ have been obtained, the minimization of deviations between the calculated and the experimental viscosities is performed by means of the Gauss-Newton method. This minimization routine gives the value of the parameter H over a wide range of pressures at a given temperature. The parameter H in the following equation is therefor treated as a function of temperature

$$\eta = \eta_0(b_0\rho)(\frac{1.000}{(b_0\rho\chi)} + H_{(T)} + 0.7614(b_0\rho\chi)) \tag{3.23}$$

By determining the values of H over a wide range of temperatures using this correlation, the accuracy of the gas viscosity could be significantly improved.

The value of $b_0\rho$ is obtained using the assumption expressed in Equation (3.14). Modification for the probability of multiple intermolecular collisions is required at high pressures. Equation 3.23 can be rearranged with the additional of the radial distribution function χ as follow:

$$\eta = \eta_0(b_0\rho\chi)(\frac{1.000}{(b_0\rho\chi)} + H_{(T)} + 0.7614(b_0\rho\chi)) \tag{3.24}$$

Equation 3.24 is adopted in this work to reduce deviations in the calculated viscosities, especially for dense gases.

3.2.2 Prediction of Viscosity for Gas Mixtures

The conventional mixing rules (Equation 2.65 to 2.69) are adopted for computing mixture parameters in the calculation of the viscosity of gas mixtures. The mixing rules used in the calculation are as follow:

$$a = \sum_i \sum_j x_i x_j (a_{ij}) \tag{3.25}$$

$$b = \sum_i x_i b_i \tag{3.26}$$

$$c = \sum_i x_i c_i \tag{3.27}$$

A geometric mean is used to describe the cross coefficient a_{ij} with the addition of k_{ij}:

$$a_{ij} = (a_i a_j)^{\frac{1}{2}}(1 - k_{ij}) \tag{3.28}$$

Applying these mixing rules to the quantity $\partial a(T)$ for mixtures in Equation 3.10 gives:

$$\partial(a) = \partial \sum_i \sum_j x_i x_j (a_i a_j)^{\frac{1}{2}}(1 - k_{ij}) \tag{3.29}$$

The value of $b_0\rho\chi$ for gas mixture can be determined by using the parameters of mixtures in the above equations in terms of pure gases.

The variation of the parameter H with temperature indicates a smooth trend (see Appendices A). It has been found that a second order function in terms of temperature is adequate to represent the H values:

$$H_(T) = k_0 + k_1 T + k_2 T^2 \tag{3.30}$$

where the values of the parameters k_0, k_1 and k_2 are determined by means of the least squares method. The values of H for gas mixtures at a given temperature can be obtained by the following linear mixing rule:

$$H = \sum_i x_i H_i \tag{3.31}$$

Having determined all the relevant parameters such as a, b, c and H for a given composition, the viscosity of the gas mixture can be calculated with the aid of the TPR-EOS.

Chapter 4

Results and Discussion

In this work the viscosity for gas mixtures were predicted using the Enskog equation together with an equation of state. The TPR equation of state described in §2.3.7 was used to determine the density value required for the radial distribution function in the Enskog equation (see §2.2.1). A modified Enskog equation was used to correlate the viscosity of pure gases. Extensive comparisons between calculated and literature results have been carried out over a wide range of fluid states with temperatures ranging from 180 to 1200 K and with pressures ranging from 1 to 980 atm.

The calculated results are summarized in Table 4.1. The dependence of the viscosity on pressure at different temperatures is illustrated in Figures 4.1 to 4.13.

Table 4.1: The Calculated Values of Viscosities for Pure Gases

fluid	NDP	Temperture K	Pressure $1.0133 \times 10^5\ Pa$	AAPD	H	ref
Methane	270	200-500	1-740	1.83	0.34-0.63	Burua et al., 1964
Ethane	180	320-500	1-740	1.90	0.37-0.66	Hanley, 1977
Propane	106	380-500	1-394	1.07	0.26-0.32	Hanley et al., 1979
n-butane	305	450-850	1-197	1.69	0.016-0.18	Stephan and Lucas, 1979
n-pentane	264	490-900	1-148	1.72	0.36-0.60	Stephan and Lucas, 1979
n-hexane	275	400-1000	1-149	1.78	(-.52)-0.79	Stephan and Lucas, 1979
n-heptane	69	550-620	1-500	1.66	0.33-0.60	Stephan and Lucas, 1979
n-octane	128	320-500	9.8-493	2.62	0.3-(-1.44)	Stephan and Lucas, 1979
i-butane	440	424-850	1-197	3.71	0.27-0.63	Stephan and Lucas, 1979
i-pentane	200	470-750	1-197	2.60	(-.11)-0.28	Stephan and Lucas, 1979
Ethylene	336	300-700	1-400	2.15	0.25-0.41	Stephan and Lucas, 1979
CO	145	220-500	1-148	1.95	0.10-0.34	Stephan and Lucas, 1979
CO2	359	315-900	1-986	0.79	0.08-0.32	Stephan and Lucas, 1979
Nitrogen	46	183-298	1-263	0.40	0.31-0.36	Flynn, 1963
Oxygen	441	180-1200	1-986	0.36	0.31-0.41	Stephan and Lucas, 1979
Fluorine	238	160-300	1-197	1.17	0.65-0.90	Stephan and Lucas, 1979
Krypton	240	270-600	1-296	0.76	0.48-0.83	Stephan and Lucas, 1979
Argon	155	200-500	1-149	0.18	0.42-0.64	Gracki, 1969

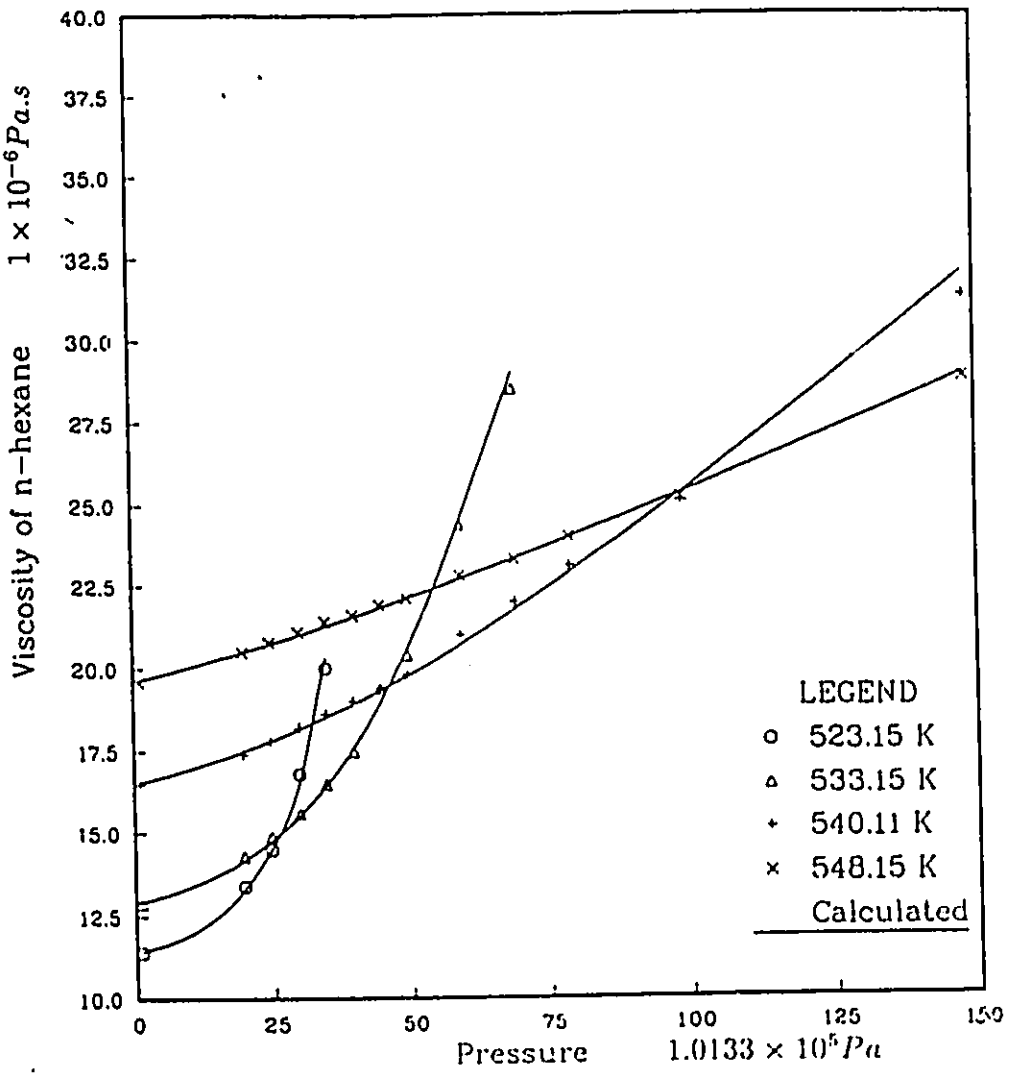

Figure 4.1: Comparison of Calculated and Literature Viscosities for n-Hexane at Four Isothermal Conditions.

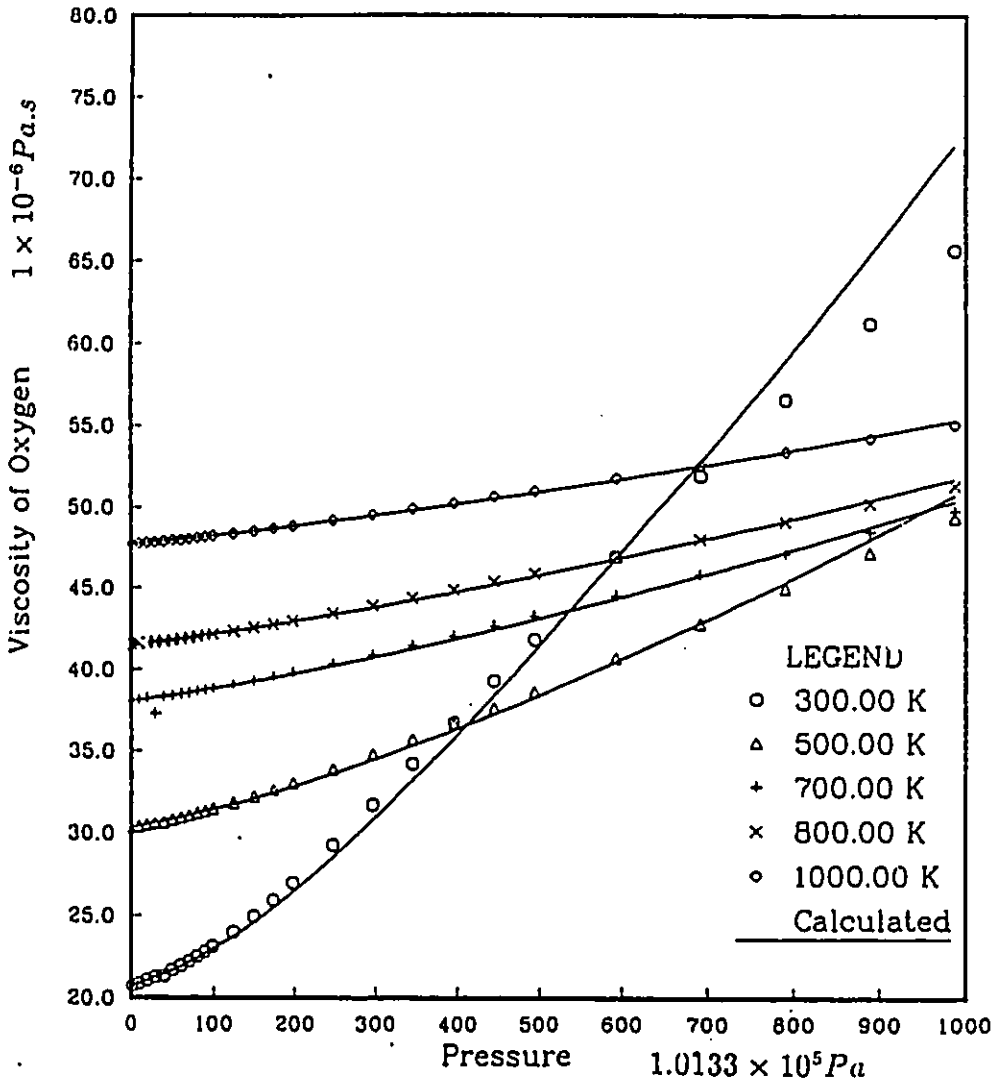

Figure 4.2: Comparison of Calculated and Literature Viscosities for Oxygen at Five Isothermal Conditions.

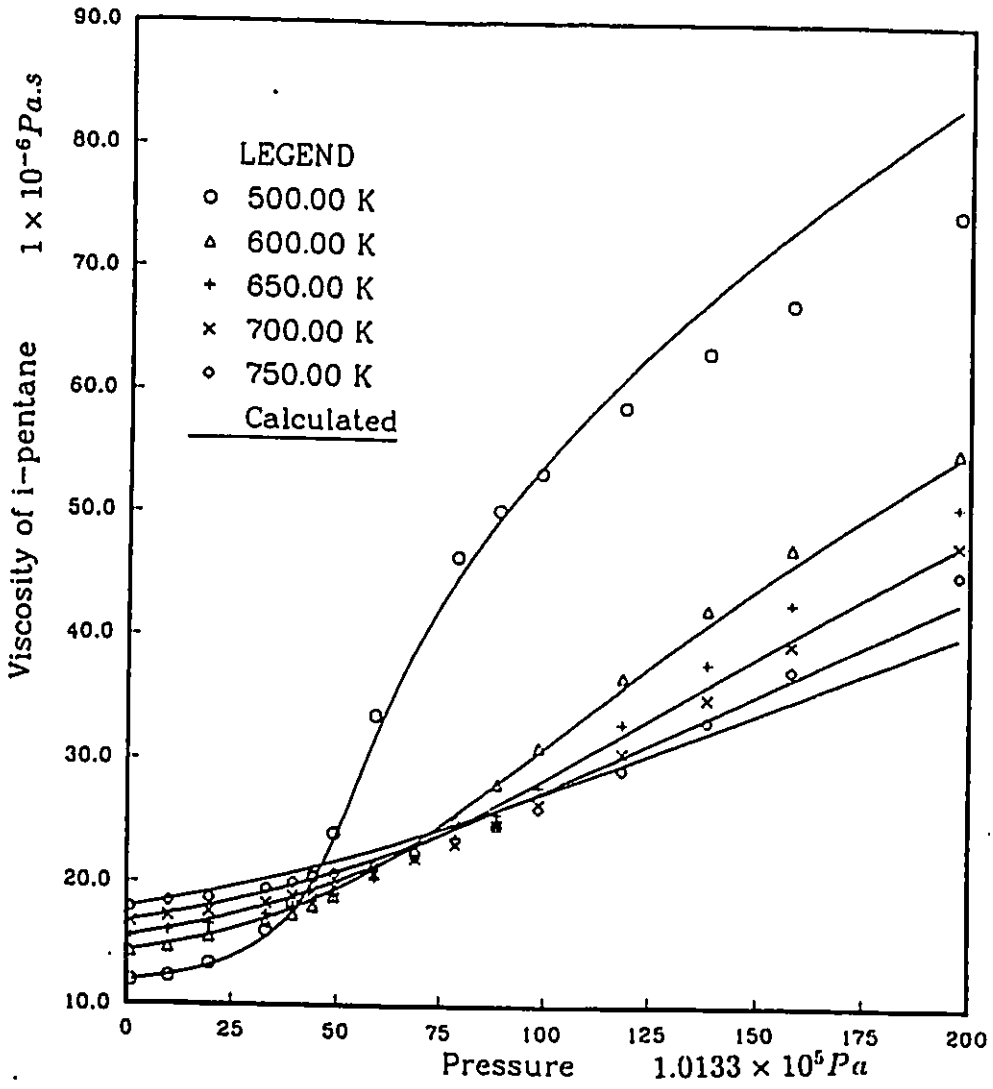

Figure 4.3: Comparison of Calculated and Literature Viscosities for i-Pentane at Five Isothermal Conditions.

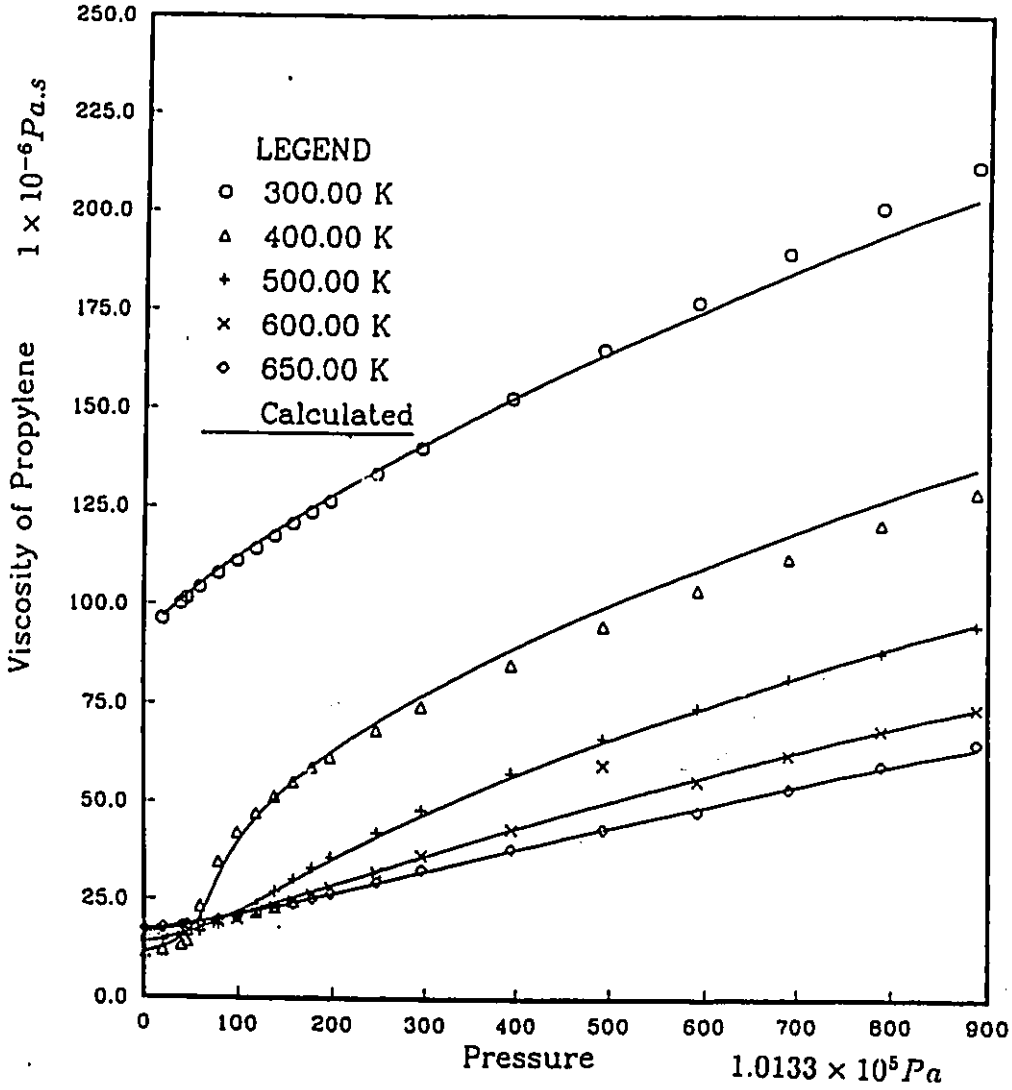

Figure 4.4: Comparison of Calculated and Literature Viscosities for Propylene at Five Isothermal Conditions.

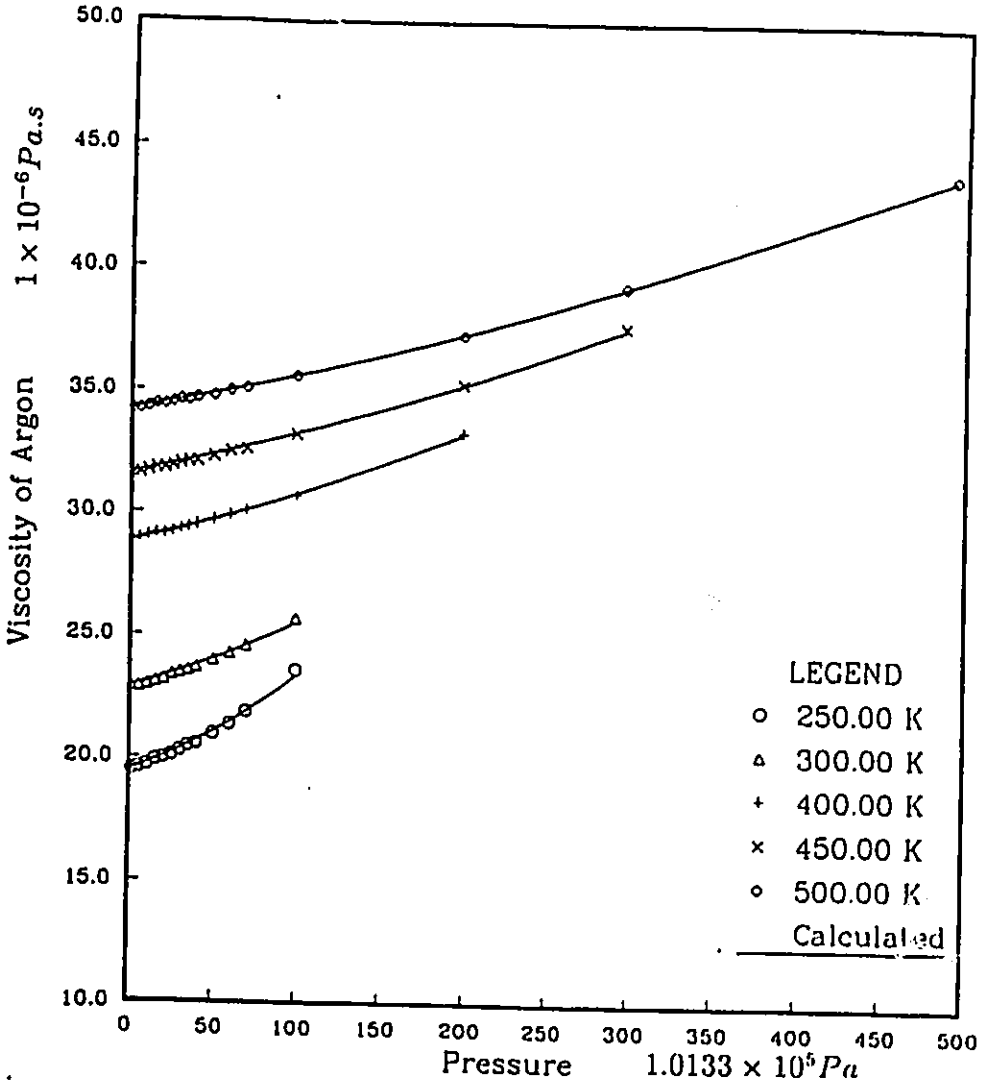

Figure 4.5: Comparison of Calculated and Literature Viscosities for Argon at Five Isothermal Conditions.

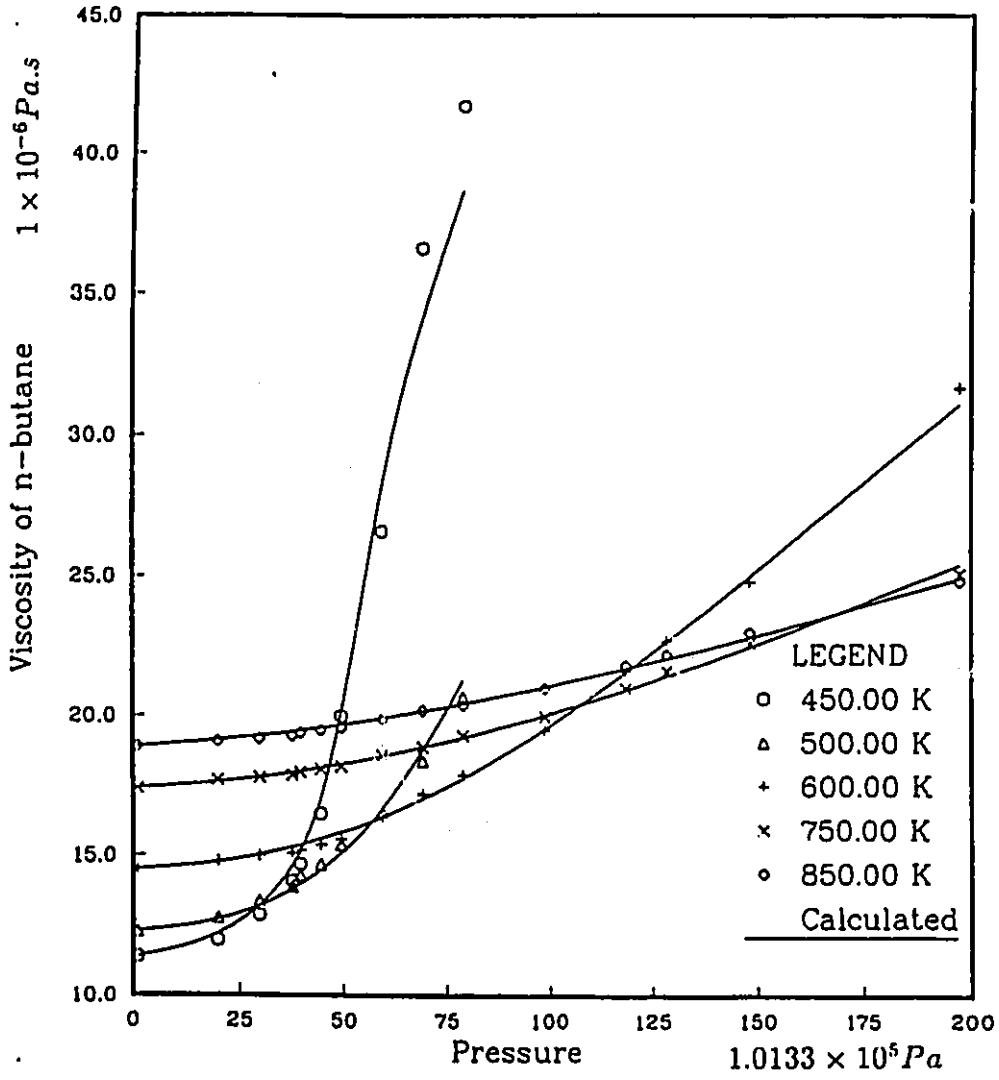

Figure 4.6: Comparison of Calculated and Literature Viscosities for n-Butane at Five Isothermal Conditions.

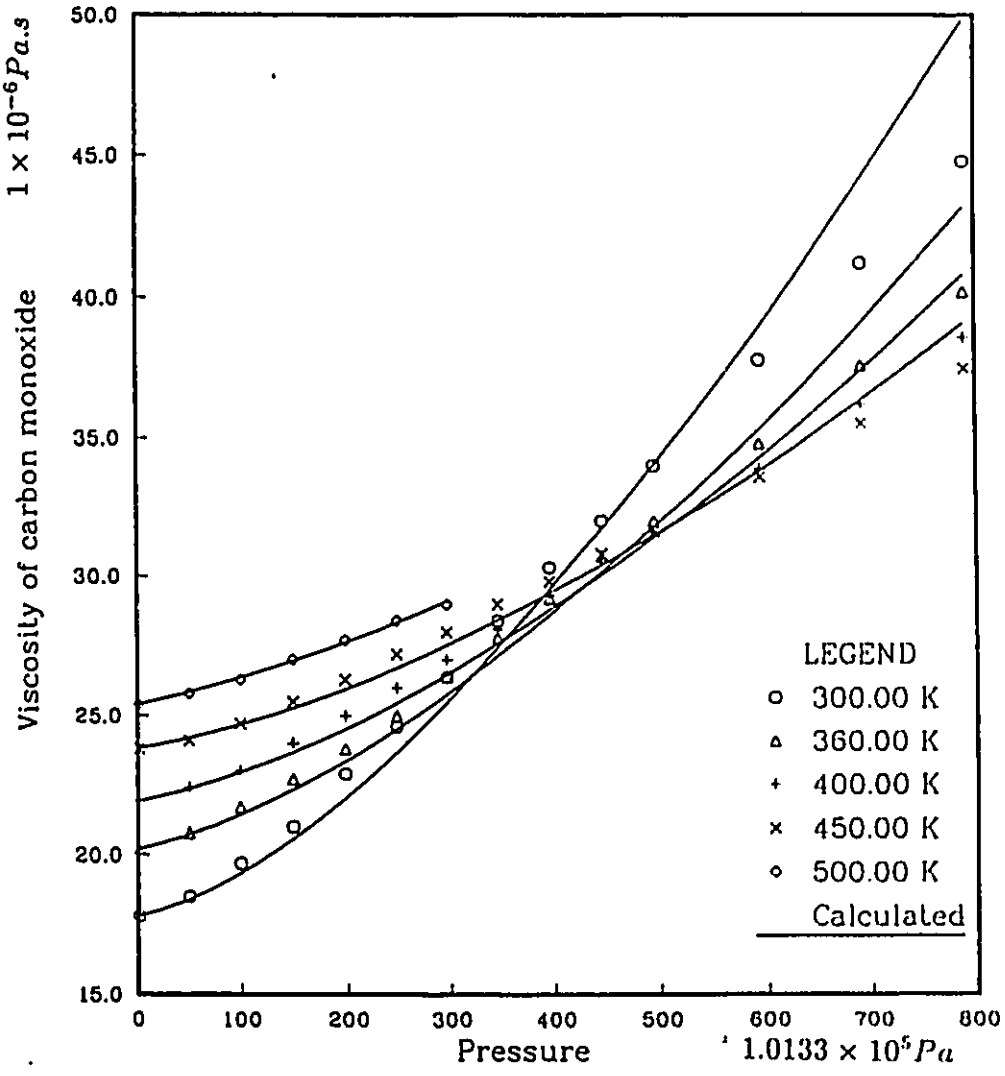

Figure 4.7: Comparison of Calculated and Literature Viscosities for Carbon-Monoxide at Five Isothermal Conditions.

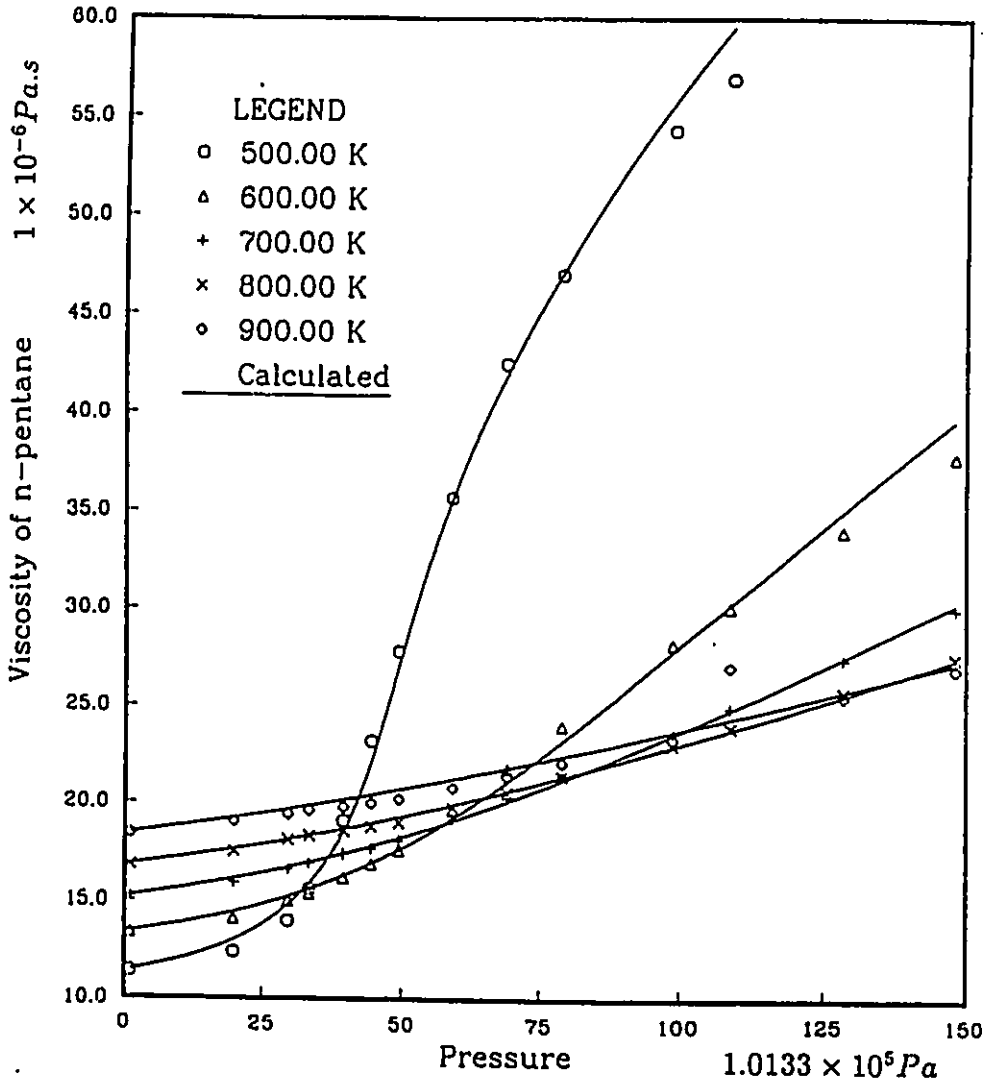

Figure 4.8: Comparison of Calculated and Literature Viscosities for n-Pentane at Five Isothermal Conditions.

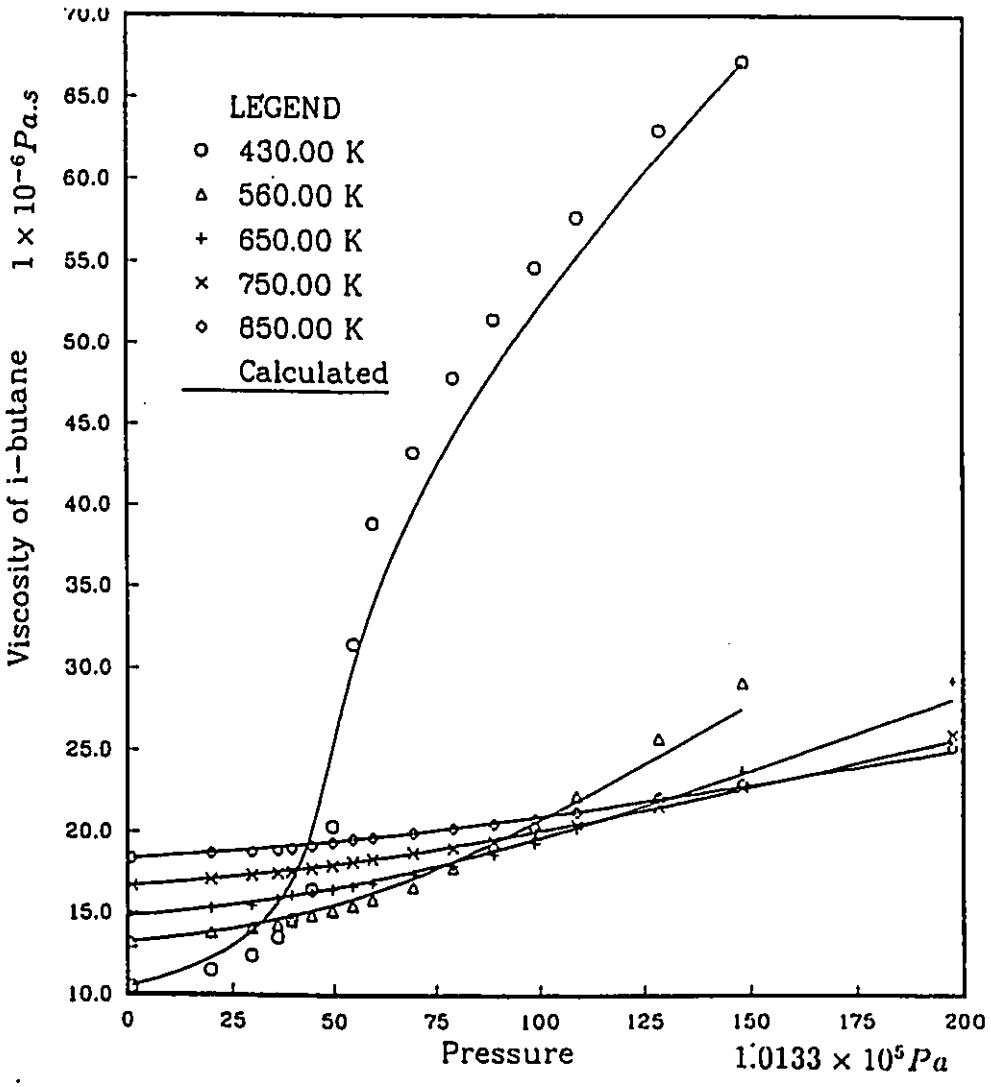

Figure 4.9: Comparison of Calculated and Literature Viscosities for i-Butane at Five Isothermal Conditions.

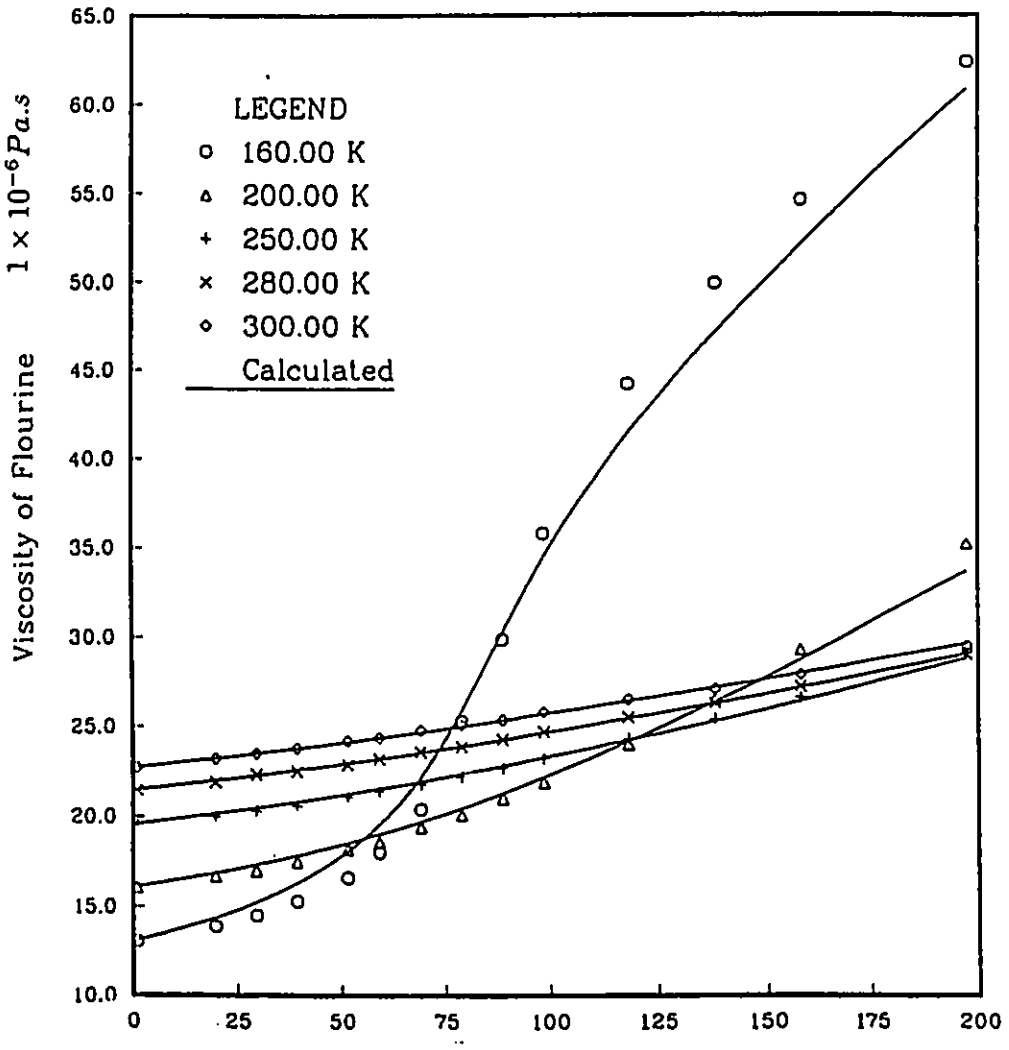

Figure 4.10: Comparison of Calculated and Literature Viscosities for Fluorine at Five Isothermal Conditions.

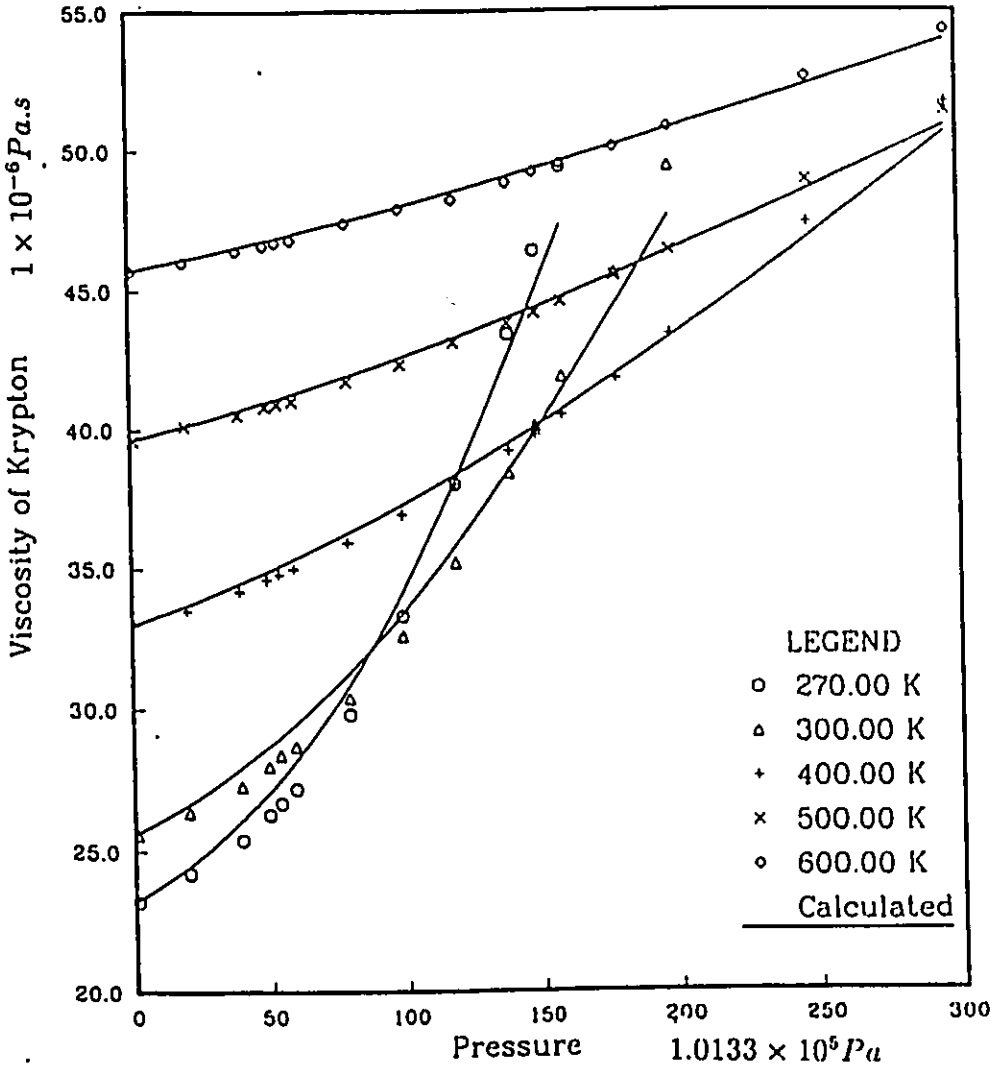

Figure 4.11: Comparison of Calculated and Literature Viscosities for Krypton at Five Isothermal Conditions.

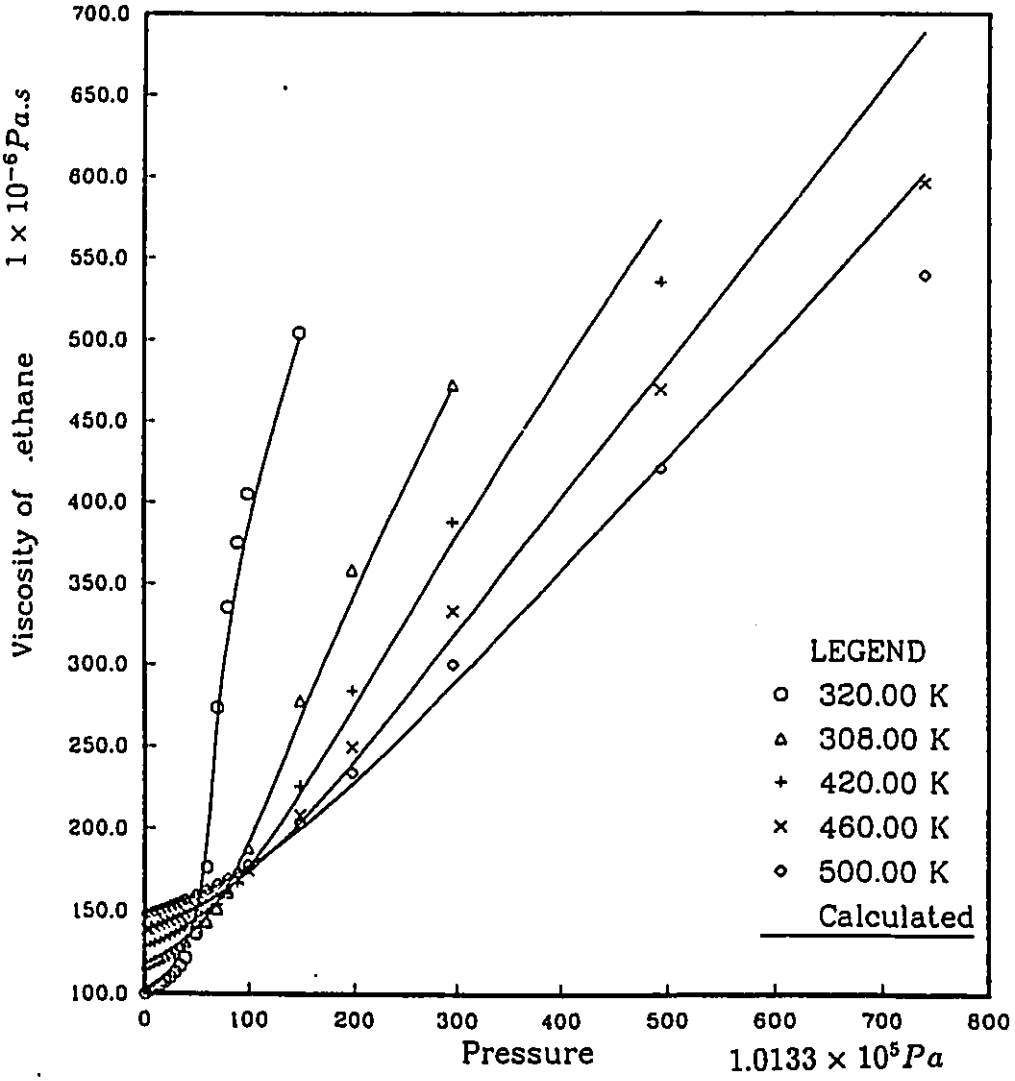

Figure 4.12: Comparison of Calculated and Literature Viscosities for Ethane at Five Isothermal Conditions.

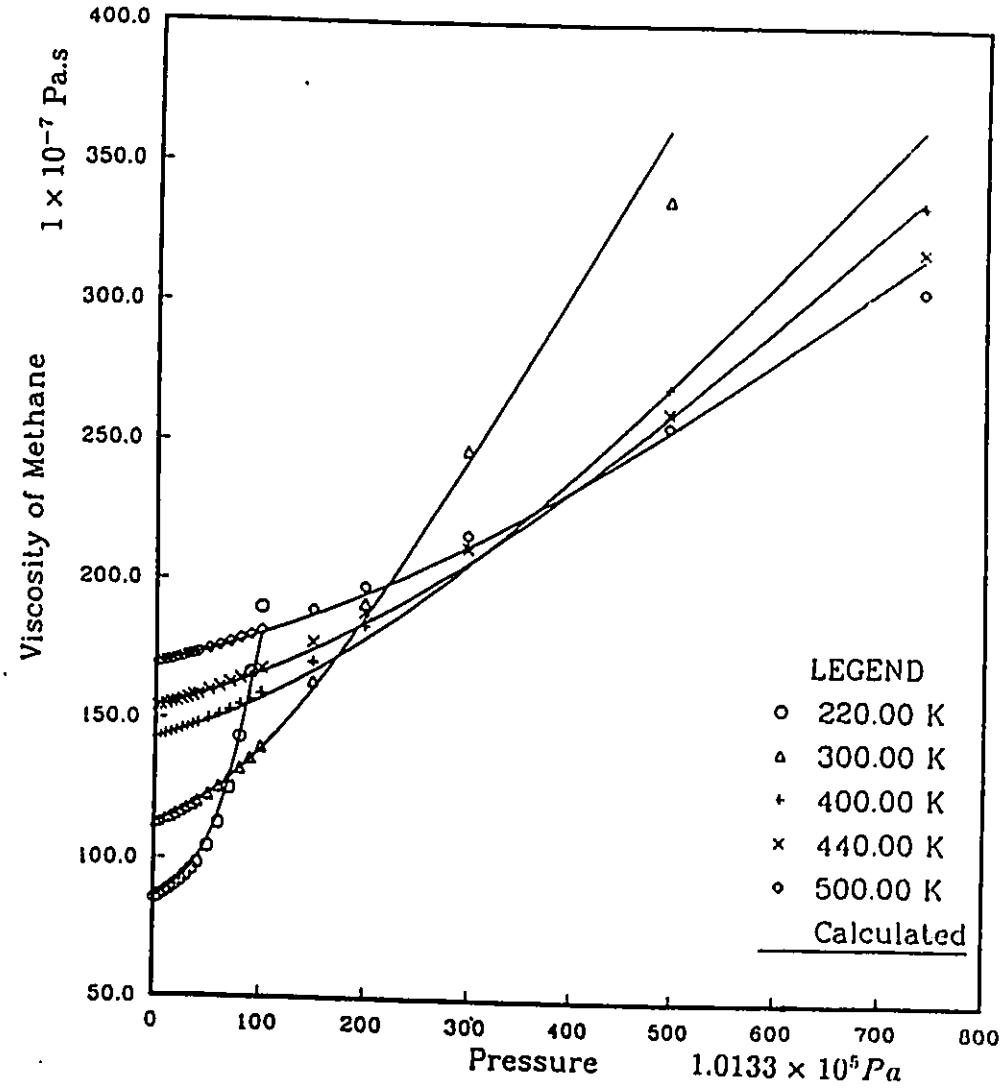

Figure 4.13: Comparison of Calculated and Literature Viscosities for Methane at Five Isothermal Conditions.

For simple gases such as argon, krypton, and nitrogen, the average absolute percentage deviation (AAPD) of viscosity for pure gases is less than 1% over a wide range of temperature and pressure. For hydrocarbons such as methane, ethane, propane, n-butane, n-pentane, n-hexane, n-heptane, i-pentane, n-octane and ehtylene, the deviation of the calculated viscosity is less than 2%.

A comparison of the calculated viscosities obtained from this work with those obtained from the multiparameter correlation reported by Chung et al. (1988) is presented in Table 4.2.

Table 4.2: Comparison of Calculated Viscosities for Pure Gases Obtained from Equation 2.15 with Multiparameter Correlation of Chung et al. (1988)

fluid	NDP	Temperature K	Pressure $1.0133 \times 10^5\ Pa$	AAPD This work	AAPD (Chung)
Methane	270	200-500	1-740	1.83	2.25
Ethane	180	320-500	1-740	1.90	2.01
Propane	106	380-500	1-394	1.07	1.81
n-butane	305	450-850	1-197	1.69	6.29
n-pentane	264	490-900	1-148	1.72	5.12
n-hexane	275	400-1000	1-149	1.78	6.80
n-heptane	69	550-620	1-500	1.66	4.57
i-butane	440	424-850	1-197	3.71	7.35
i-pentane	200	470-750	1-197	2.60	11.0
Ethylene	336	300-700	1-400	2.15	3.23
CO	145	220-500	1-148	1.95	3.59
CO2	359	315-900	1-986	0.79	3.40
Nitrogen	46	183-298	1-263	0.40	1.30
Oxygen	441	180-1200	1-400	0.36	2.45
Fluorine	238	160-300	1-197	1.17	3.44
Argon	155	200-500	1-149	0.18	0.88
Krypton	240	270-600	1-296	0.76	0.88

For hydrocarbons such as n-butane, n-hexane, i-butane and i-pentane the AAPD is higher than 6%. Clearly the results obtained from this work are closer to the literature values than those obtained from Chung et al. (1988). The modified Enskog equation was found to be more reliable in correlating gas viscosities than the multiparameter correlation used by Chung et al.. In addition, the Enskog equation is based on the kinetic theory of gases. Better calculated viscosities can be obtained when higher pressures are encountered. The results obtained from n-butane are presented as an example in Table 4.3. The deviations in calculated viscosities obtained from Chung's method increase rapidly when the pressure is more than 60 atm.

Table 4.3: Comparison of Calculated Viscosities for n-Butane Obtained from Equation 2.15 with Multiparameter Correlation of Chung et al. (1988)

N	Temperature K	Pressure $1.0133 \times 10^5\ Pa$	ERR % (Chung)	ERR % This work
1	680.00	0.99	1.54	0.04
2	680.00	19.74	1.53	-0.95
3	680.00	29.61	3.06	-0.31
4	680.00	37.50	3.90	-0.28
5	680.00	39.48	3.85	-0.53
6	680.00	44.41	4.72	-0.22
7	680.00	49.35	5.07	-0.42
8	680.00	59.22	5.44	-1.13
9	680.00	69.08	6.12	-1.50
10	680.00	78.95	7.59	-1.03
11	680.00	98.69	9.76	-0.41
12	680.00	118.43	10.50	-0.43
13	680.00	128.30	10.64	-0.39
14	680.00	148.04	11.41	0.55

In addition, the viscosity values obtained from the PR and the TPR equations of state are compare in Table 4-4.

Table 4.4: Comparison of Calculated Results Obtained from Equation 2.24 by Means of the PR and the TPR Equations

fluid	NDP	Temperature K	Pressure $1.0133 \times 10^5\ Pa$	AAPD TPR	AAPD PR
Methane	270	200-500	1-740	1.83	1.05
Ethane	180	320-500	1-740	1.90	1.81
Propane	106	380-500	1-394	1.07	1.59
n-butane	305	450-850	1-197	1.69	1.59
n-pentane	264	490-900	1-148	1.72	1.61
n-hexane	275	400-1000	1-149	1.78	1.81
n-heptane	69	550-620	1-500	1.66	1.71
i-butane	440	424-850	1-197	3.71	4.59
i-pentane	200	470-750	1-197	2.60	2.65
Ethylene	336	300-700	1-400	2.15	2.36
CO	145	220-500	1-148	1.95	1.26
CO2	359	315-900	1-986	0.79	0.72
Nitrogen	46	183-298	1-263	0.40	1.60
Oxygen	441	180-1200	1-986	0.36	0.40
Fluorine	238	160-300	1-197	1.17	1.94
Argon	155	200-500	1-149	0.18	0.24
Krypton	240	270-600	1-296	0.76	1.19

For simple gases, the TPR-EOS yields better results than the PR-EOS, but for hydrocarbons the deviations in the calculated viscosity values between these two equations of state vary with substances. This is perhaps due to the over correction of the vapor volume by the volume transformation technique for these gases. However, the TPR equation of state gives better results over a wide range of temperature and pressure.

The values of $b\rho$ and $b\rho\chi$ in Equations 3.23 and 3.24 were calculated by the use of Equations 3.17 and 3.12 respectively. The calculated results are presented in Tables 4.5 and 4.6.

Table 4.5: Comparison of the Calculated Viscosities Obtained from Equation 3.23 and Equation 3.24 (with the additional term χ) by Means of the TPR EOS

fluid	NDP	Temperature K	Pressure 1.0133×10^5 Pa	AAPD Eq(3.24)	AAPD Eq(3.23)
Methane	270	200-500	1-740	1.83	1.56
Ethane	180	320-500	1-740	1.92	2.33
Propane	106	380-500	1-394	1.07	1.74
n-butane	305	450-850	1-197	1.69	1.75
n-pentane	264	490-900	1-148	1.72	1.66
n-hexane	275	400-1000	1-149	1.78	1.80
i-butane	440	424-850	1-197	3.71	4.50
i-pentane	200	470-750	1-197	2.60	2.85
Ethylene	336	300-700	1-400	2.15	2.95
CO	145	220-500	1-148	1.95	0.82
CO2	359	315-900	1-986	0.79	0.86
Nitrogen	46	183-298	1-263	0.40	1.60
Oxygen	441	180-1200	1-986	0.36	0.49
Fluorine	238	160-300	1-197	1.17	2.54
Argon	155	200-500	1-149	0.18	0.47
Krypton	240	270-600	1-296	0.76	1.75

Table 4.6: Comparison of the Calculated Viscosities Obtained from Equation 3.23 with Equation 3.24 (with the additional term χ) by Means of the PR EOS

fluid	NDP	Temperature K	Pressure 1.0133×10^5 Pa	AAPD Eq(3.23)	AAPD Eq(3.24)
Methane	270	200-500	1-740	2.16	1.05
Ethane	180	320-500	1-740	2.87	1.81
Propane	106	380-500	1-394	2.08	1.59
n-butane	305	450-850	1-197	1.74	1.59
n-pentane	264	490-900	1-148	1.59	1.61
n-hexane	275	400-1000	1-149	1.78	1.81
i-butane	440	424-850	1-197	4.82	4.59
i-pentane	200	470-750	1-197	2.60	2.65
Ethylene	420	300-700	1-810	3.53	2.36
CO	145	220-500	1-148	1.21	1.26
CO2	359	315-900	1-986	0.90	0.72
Nitrogen	46	183-298	1-263	1.88	1.60
Oxygen	441	180-1200	1-986	0.59	0.40
Fluorine	238	160-300	1-197	2.81	1.94
Argon	155	200-500	1-149	0.54	0.24
Krypton	240	270-600	1-296	1.96	1.19

Better results are obtained by means of Equation 3.24. This is due to the additional of the term χ, which considers the increase of collision rates at high densities.

The variation of viscosity for pure gases is shown as a function of pressure at isothermal conditions in Figure 4.14, where carbon dioxide is used as an example.

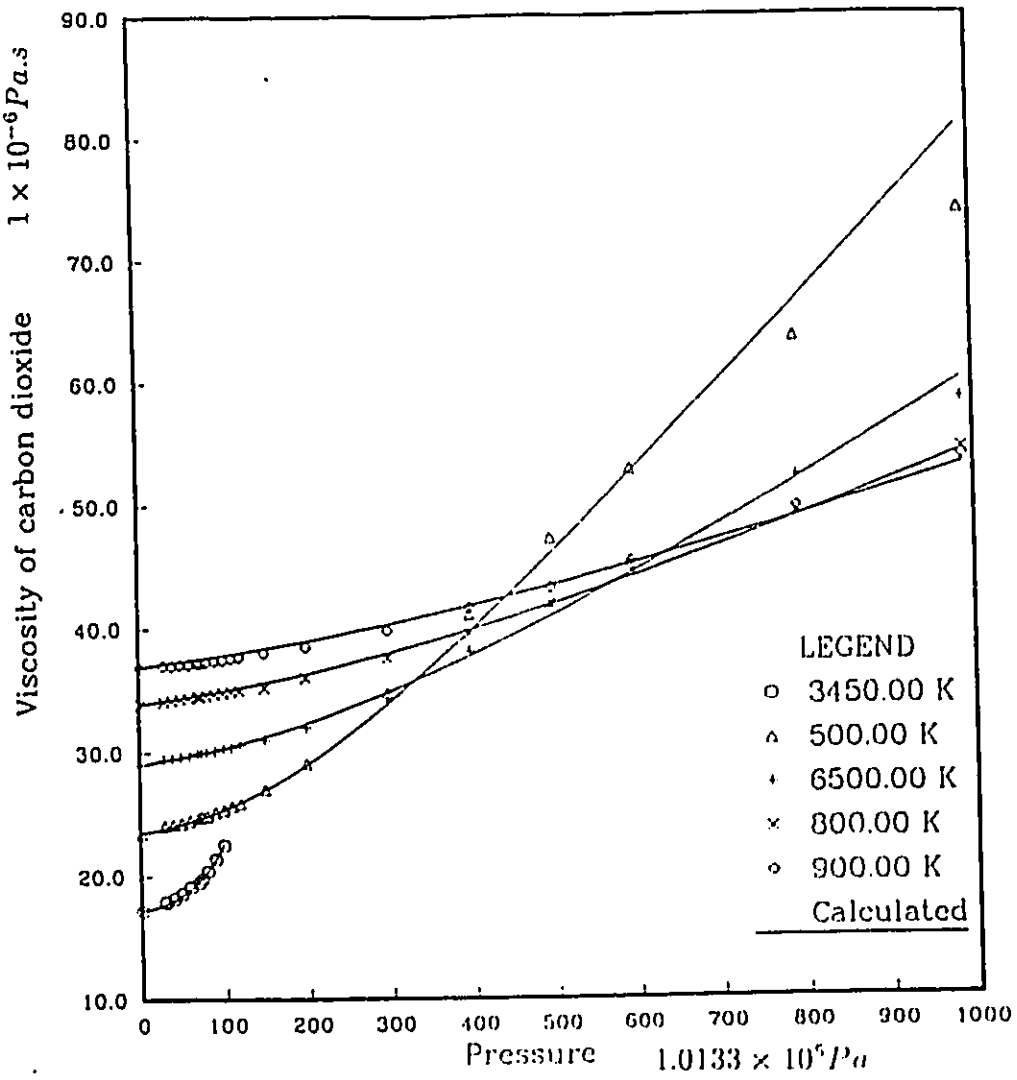

Figure 4.14: Comparison of Calculated and Literature Viscosities for Carbon-Dioxide at Five Isothermal Conditions.

For a dilute system, the momentum of the fluids is transferred by the free kinetic motion of the molecules. As the temperature increases, the mean velocity increases and this produces an associated transport of momentum. Since gas viscosity is a measurement of internal friction and is proportional to the momentum flux, the viscosity should increase as the temperature increases at constant pressure. In dense gases, the transport of momentum is due to the intermolecular forces when the molecules move in their mutual interaction fields. The viscosity is mainly depended on density. An increase in temperature at constant pressure corresponds to a decrease in density and consequently a decrease in viscosity.

Finally, the predicted viscosities for three binary systems (carbon dioxide-methane, argon-neon and hydrogen-nitrogen systems) are listed in Tables 4.7 to 4.9. The predicted viscosities for the carbon dioxide-methane gas mixtures with a temperature independent parameter k_{ij} are listed in Table C.3. The deviations of the calculated viscosities for the carbon dioxide-methane mixtures are somewhat reduced. Since the average percentage deviations are low, the calculated viscosities for simple gas mixtures can be obtained without the parameter k_{ij}. The dependence of the viscosities of gas mixtures on pressure at isothermal conditions is illustrated in Figures 4.15 to 4.18.

Table 4.7: Comparison of The Predicted and Experimental Viscosities for the Carbon Dioxide(1)-Methane(2) Gas Mixtures (Kestin and Nagashima, 1964)

Mole Fraction y_1	Temperature K	Pressure 1.0133×10^5 Pa	η (Expt) 1×10^{-6} $Pa.s$	η(Cald)	APD
0.8565	293.15	1.06	144.33	144.44	0.08
	293.15	5.02	144.69	144.94	0.17
	293.15	15.03	145.69	146.81	0.77
	293.15	25.23	148.19	149.85	1.12
	303.15	1.05	149.20	149.31	0.07
	303.15	5.02	149.57	149.80	0.15
	303.15	15.09	150.88	151.60	0.48
	303.15	25.09	153.08	154.34	0.82
0.6624	293.15	1.03	140.03	140.17	0.10
	293.15	4.99	140.36	140.79	0.31
	293.15	15.01	141.77	142.82	0.74
	293.15	25.39	144.06	145.77	1.18
	303.15	1.05	144.66	144.80	0.10
	303.15	5.02	145.07	145.40	0.23
	303.15	15.02	146.49	147.31	0.56
	303.15	25.09	148.66	149.95	0.87
0.4806	293.15	1.05	134.48	134.65	0.12
	293.15	5.01	134.84	135.32	0.36
	293.15	15.02	136.36	137.38	0.75
	293.15	25.22	138.51	140.08	1.13
	303.15	1.05	138.81	138.97	0.11
	303.15	5.01	139.25	139.61	0.26
	303.15	15.02	140.72	141.55	0.59
	303.15	25.22	142.82	144.05	0.86
0.3257	293.15	1.05	128.26	128.43	0.13
	293.15	5.02	128.73	129.12	0.30
	293.15	15.02	130.26	131.12	0.66
	293.15	22.92	131.83	133.01	0.89
	303.15	1.04	132.37	132.53	0.12
	303.15	5.01	132.81	133.18	0.28
	303.15	14.98	134.34	135.06	0.54
	303.15	25.02	136.28	137.33	0.77

Table 4.8: Comparison of The Predicted and Experimental Viscosities for the Argon(1)-Neon(2) Gas Mixtures (Kestin and Yata 1968)

Mole Fraction y_1	Temperature K	Pressure 1.0133×10^5 Pa	η (Expt) 1×10^{-6} $Pa.s$	η(Cald)	APD
0.4020	293.15	1.02	271.63	271.86	0.08
	293.15	7.87	272.15	273.40	0.46
	293.15	14.75	272.96	274.97	0.74
	293.15	21.55	273.56	276.54	1.09
	293.15	28.63	274.34	278.18	1.40
	293.15	35.43	275.27	279.78	1.64
	303.15	1.01	278.56	278.80	0.09
	303.15	7.83	279.23	280.44	0.43
	303.15	14.27	279.74	282.00	0.81
	303.15	21.55	280.30	283.79	1.24
	303.15	28.29	280.94	285.45	1.60
	303.15	34.34	282.03	286.95	1.75
0.5130	303.15	1.05	210.40	210.77	0.18
	303.15	5.01	211.34	212.24	0.43
	303.15	15.02	213.91	216.51	1.21
	303.15	21.10	215.90	219.52	1.68
	293.15	1.06	203.79	204.18	0.19
	293.15	5.03	204.63	205.71	0.53
	293.15	15.03	207.23	210.18	1.42
	293.15	21.01	209.40	213.33	1.88
0.6680	293.15	1.03	230.03	230.26	0.10
	293.15	5.06	230.62	231.17	0.24
	293.15	9.88	231.55	232.28	0.31
	293.15	15.02	232.51	233.47	0.41
	293.15	20.12	233.51	234.68	0.50
	293.15	25.02	234.58	235.85	0.54
	293.15	31.01	236.10	237.31	0.51
	303.15	1.03	254.75	255.01	0.10
	303.15	7.70	255.81	256.69	0.34
	303.15	15.02	256.71	258.57	0.72
	303.15	21.62	257.75	260.29	0.99
	303.15	28.49	258.65	262.12	1.34
	303.15	33.66	259.66	263.51	1.48
0.7383	303.15	1.05	184.72	184.96	0.13
	303.15	5.02	185.48	185.96	0.26
	303.15	15.10	187.40	189.11	0.92
	303.15	21.02	189.14	191.45	1.22
	293.15	1.05	178.99	179.24	0.14
	293.15	5.02	179.56	180.26	0.39
	293.15	15.17	181.64	183.60	1.08
	293.15	21.16	183.33	186.14	1.53
1.000	303.15	1.04	151.69	151.77	0.05
	303.15	5.00	151.94	152.14	0.13
	303.15	15.05	153.26	153.76	0.32
	303.15	21.04	154.49	155.26	0.50
	293.15	1.04	146.74	146.81	0.05
	293.15	5.01	146.93	147.19	0.17
	293.15	15.08	148.15	148.87	0.48
	293.15	21.08	149.34	150.49	0.77

Table 4.9: Comparison of the Predicted and Experimental Viscosities for the Hydrogen(1)-Nitrogen(2) Gas Mixtures (Kestin and Yata 1968)

Mole Fraction y_1	Temperature K	Pressure 1.0133×10^5 Pa	η (Expt) 1×10^{-6} $Pa.s$	η(Cald)	APD
0.1593	293.15	1.05	173.10	173.36	0.15
	293.15	5.01	173.65	174.36	0.41
	293.15	15.00	174.88	176.93	1.17
	293.15	23.91	176.00	179.29	1.87
0.3279	293.15	1.06	168.88	169.16	0.17
	293.15	5.01	169.26	170.23	0.57
	293.15	15.06	170.19	172.98	1.64
	293.15	25.30	171.21	175.84	2.70
0.5121	293.15	1.04	160.71	160.98	0.17
	293.15	5.01	161.00	162.02	0.63
	293.15	15.05	161.59	164.68	1.91
	293.15	25.15	162.34	167.40	3.11
0.7250	293.15	1.05	143.32	143.55	0.16
	293.15	4.99	143.48	144.43	0.66
	293.15	15.01	143.91	146.68	1.93
	293.15	24.47	144.20	148.83	3.21
0.8373	293.15	1.05	127.44	127.64	0.15
	293.15	5.01	127.59	128.38	0.62
	293.15	14.95	127.81	130.27	1.93
	293.15	23.96	128.02	132.00	3.11
0.9039	293.15	1.07	114.38	114.55	0.15
	293.15	5.01	114.45	115.20	0.65
	293.15	14.89	114.65	116.82	1.89
	293.15	23.78	114.73	118.29	3.11
1.000	293.15	1.05	88.27	88.39	0.14
	293.15	4.95	88.29	88.86	0.64
	293.15	10.01	88.34	89.46	1.27
	293.15	14.95	88.25	90.05	2.04
	293.15	19.10	88.26	90.55	2.59
	293.15	23.14	88.31	91.04	3.09
	293.15	23.43	88.29	91.07	3.15

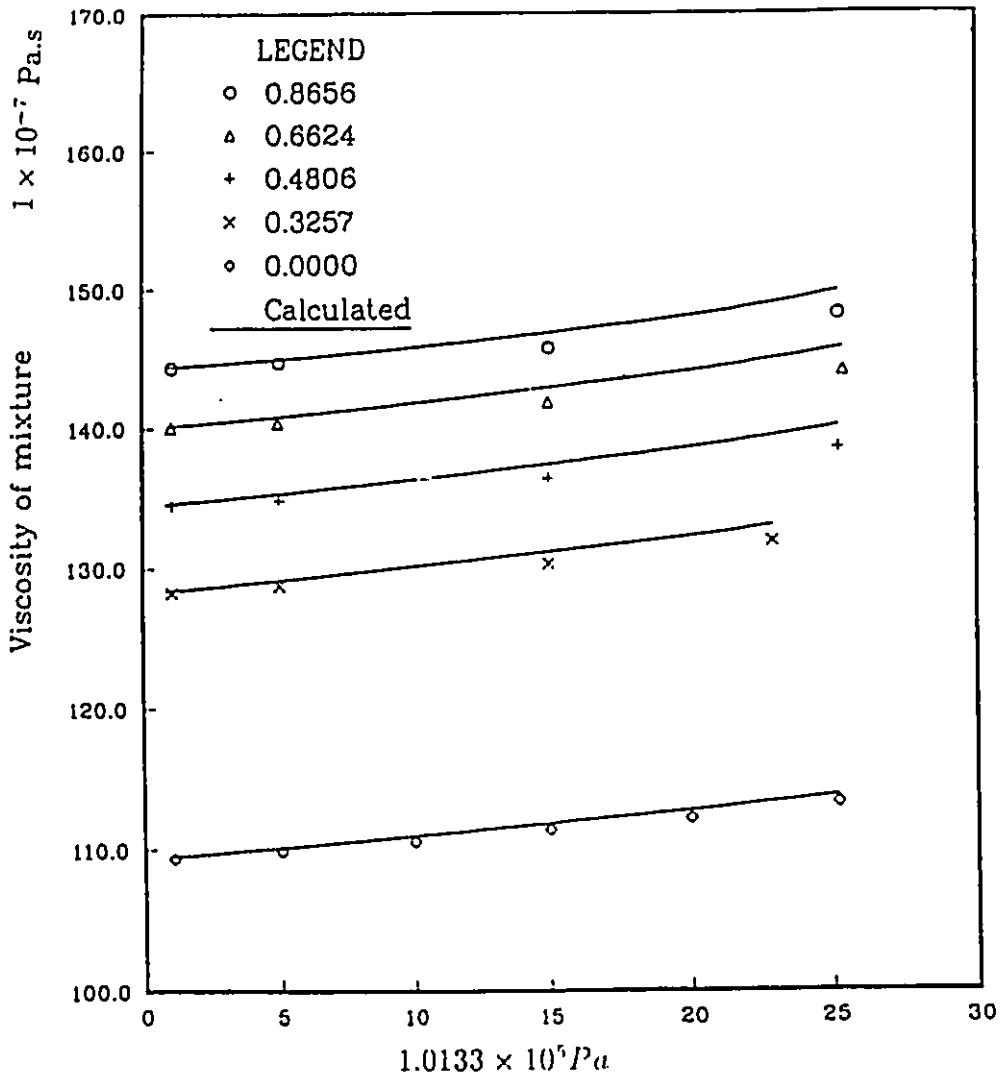

Figure 4.15: Comparison of Calculated and Literature Viscosity Values for the Carbon Dioxide-Methane Mixture.

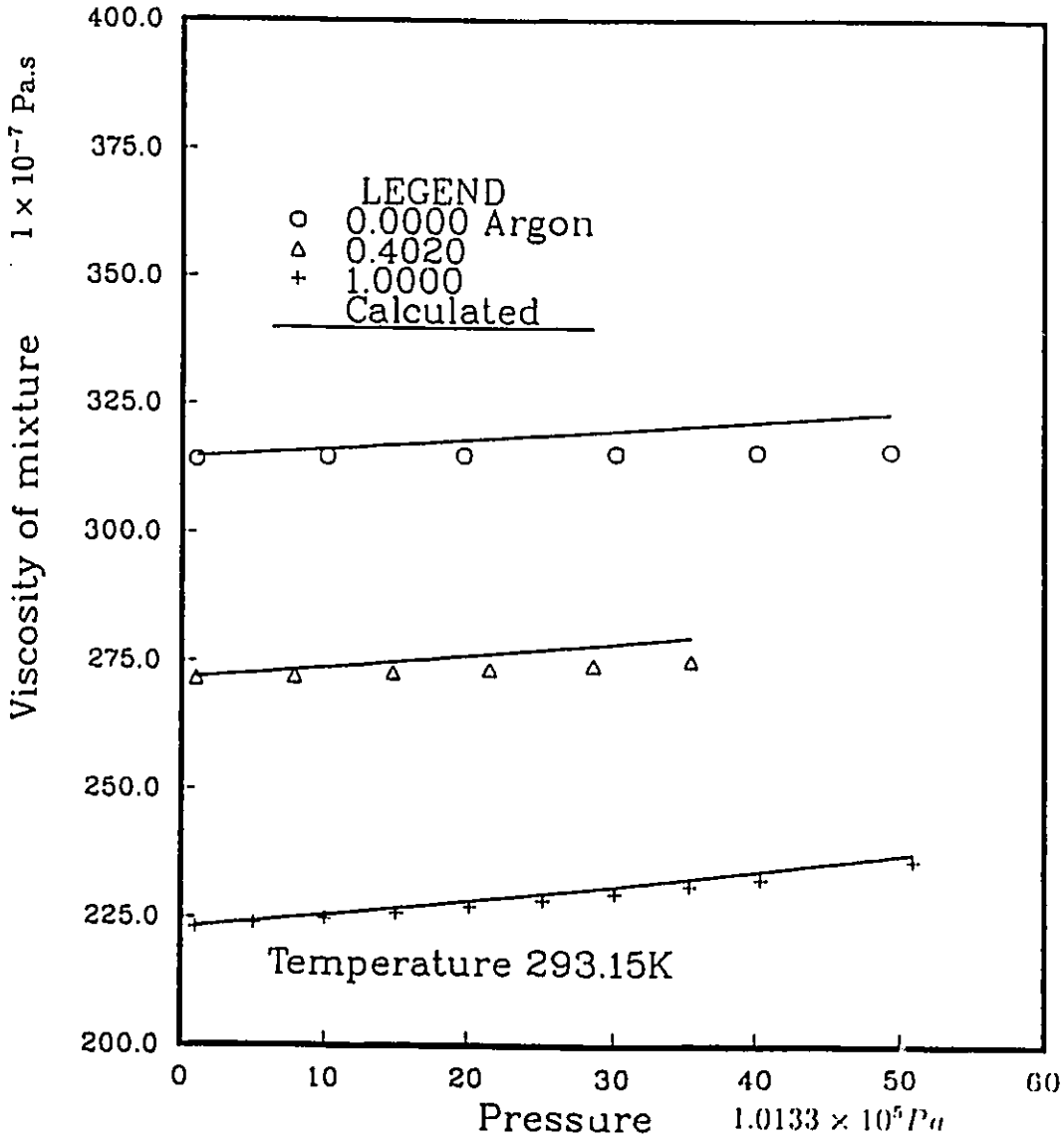

Figure 4.16: Comparison of Calculated and Literature Viscosity Values for the Argon-Neon Mixture.

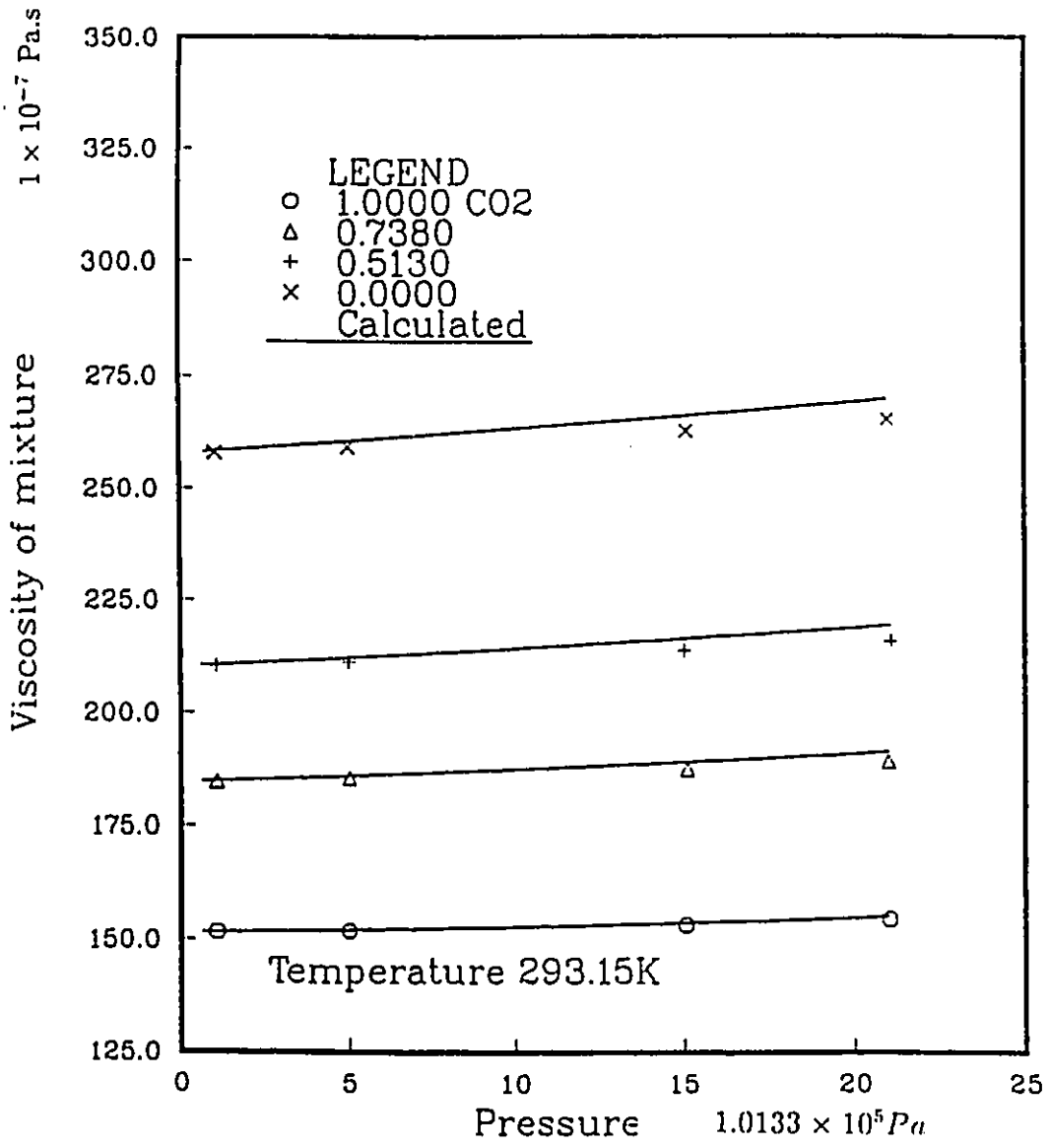

Figure 4.17: Comparison of Calculated and Literature Viscosity Values for the Carbon Dioxide-Krypton Mixture.

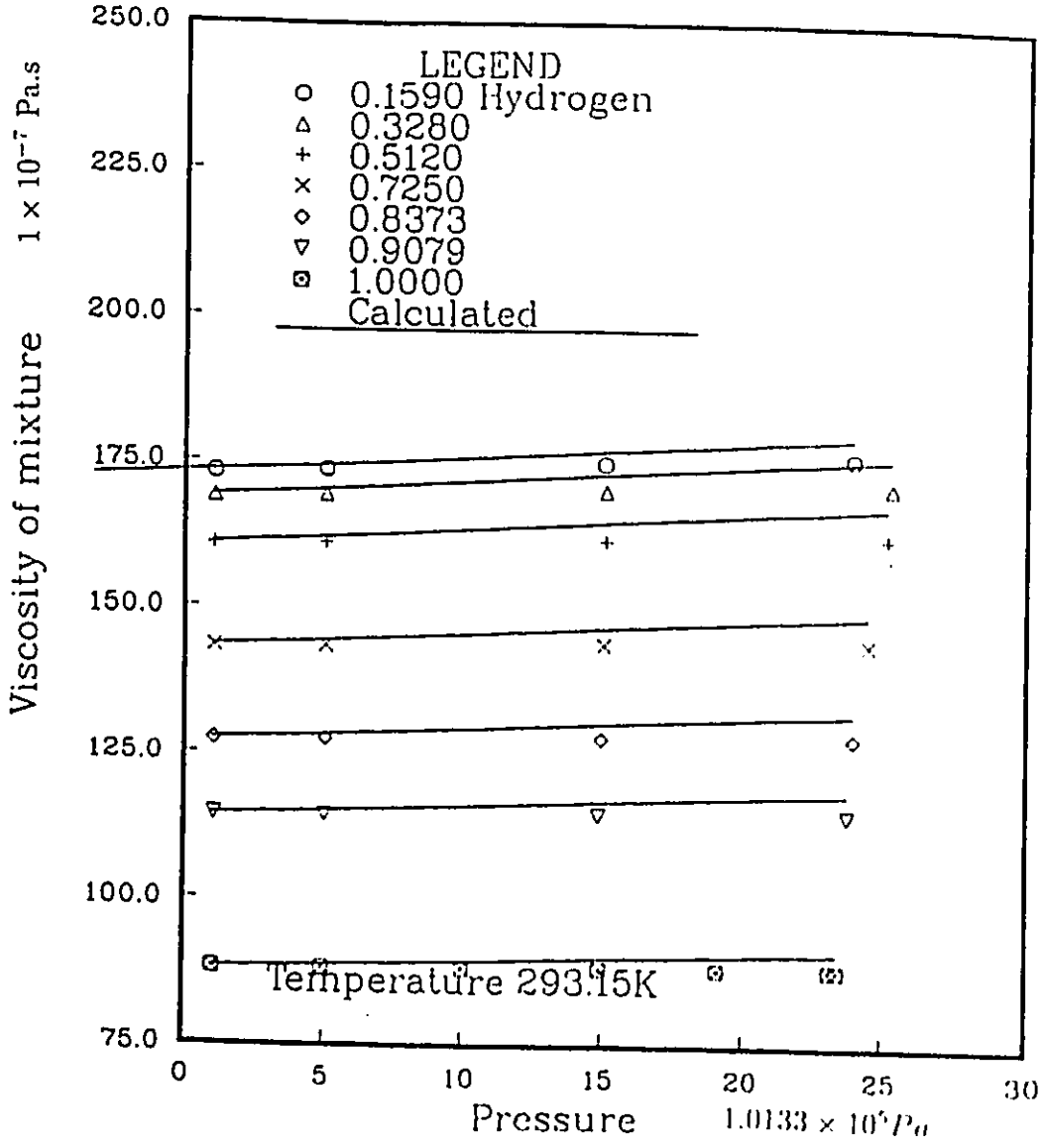

Figure 4.18: Comparison of Calculated and Literature Viscosity Values for the Hydrogen-Nitrogen Mixture

The highest absolute percentage deviations in the calculated viscosity values for the carbon dioxide-methane, argon-neon, and hydrogen-nitrogen systems are 1.18%, 1.88%, and 3.21% respectively. The absolute average deviation in the calculated viscosity values for all gas mixtures is less than 1%.

The Enskog theory is based on the kinetic theory for simple gases. Introducing the thermal pressure with cubic equations of state yields better calculated results for pure gas viscosity. Fitting of the temperature dependent parameter H to a generalized polynomial for pure gases cannot be reached. The H values obtained from fluorine, propane and i-pentane are shown in Figures 4.19 to 4.21 respectively as examples.

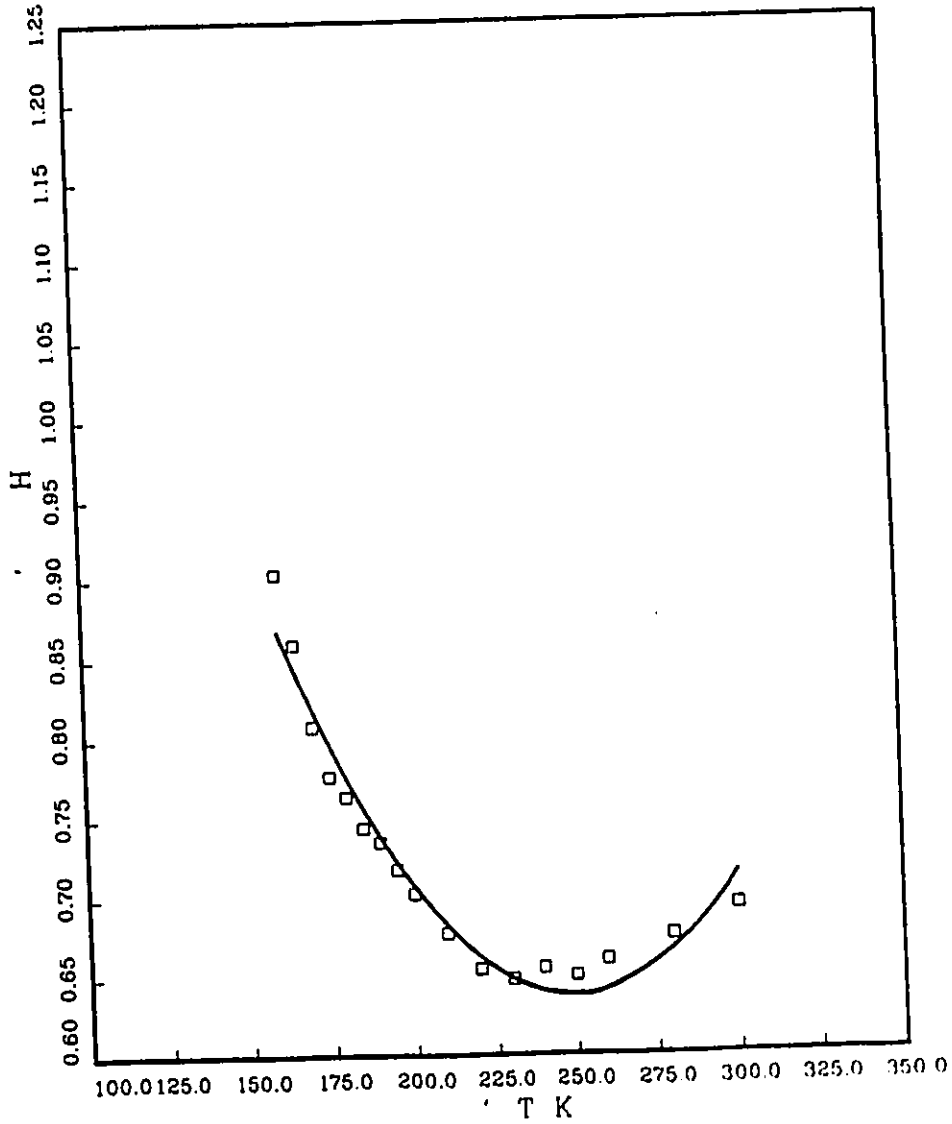

Figure 4.19: Values of Parameter (H) for Fluorine at Different Temperatures.

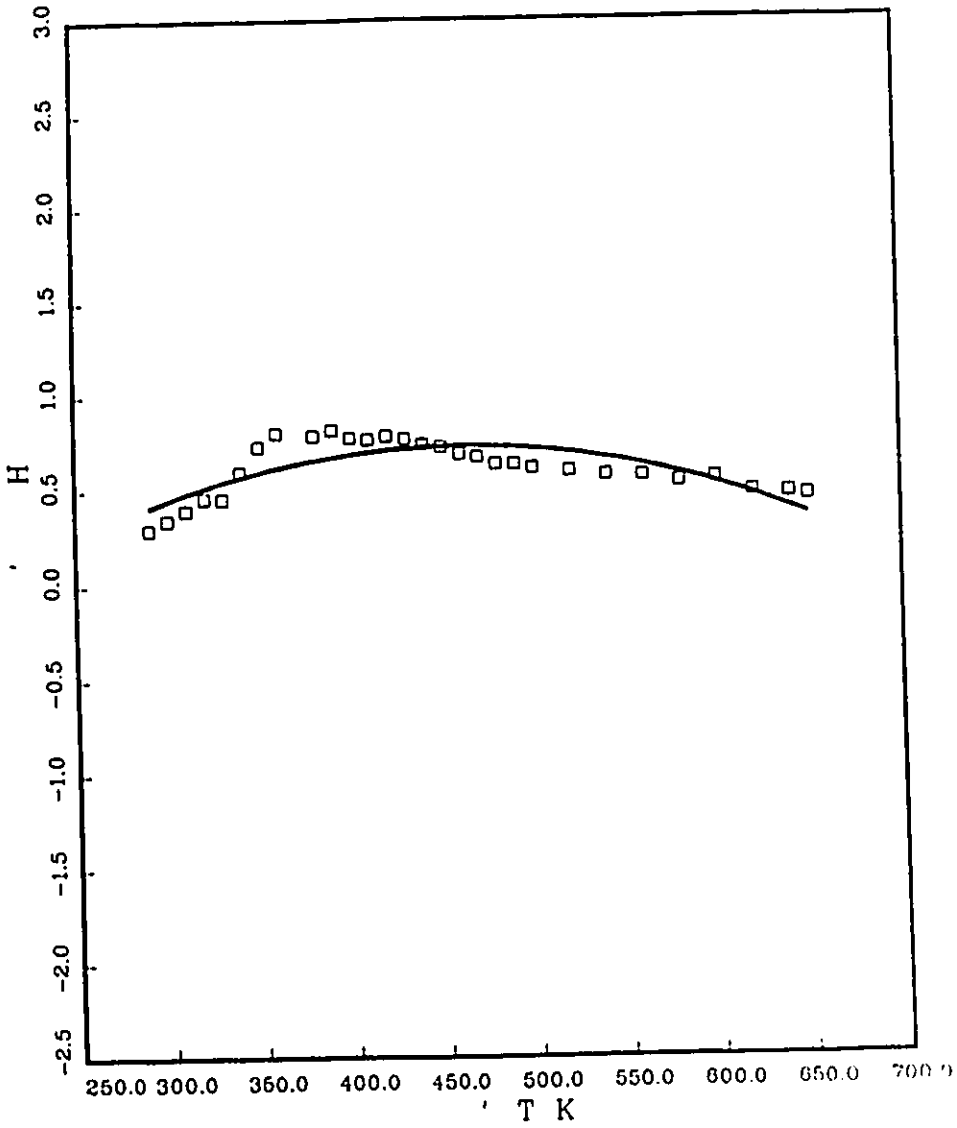

Figure 4.20: Values of Parameter (H) for Propylene at Different Temperatures.

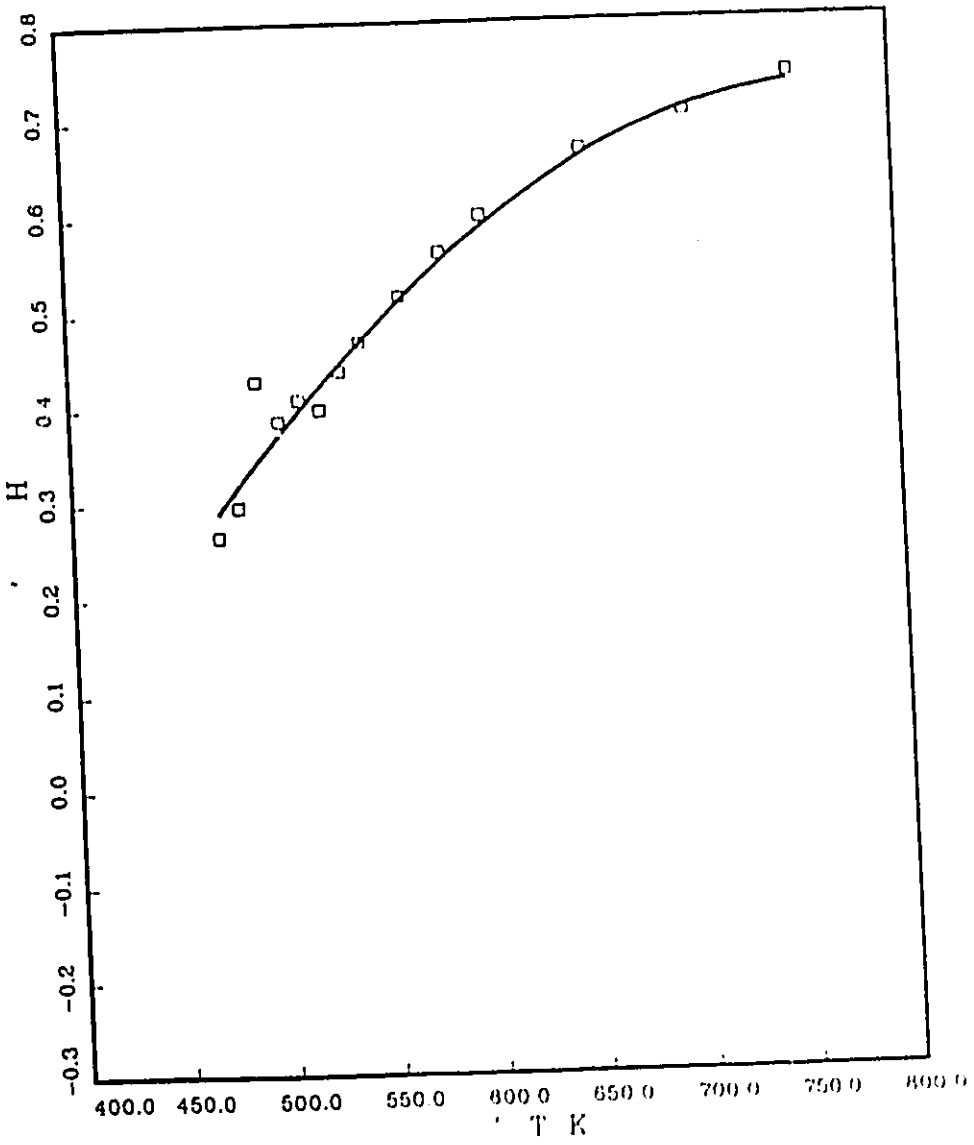

Figure 4.21: Values of Parameter (H) for i-Pentane at Different Temperatures.

Chapter 5

Conclusion

The influence of temperature on the collisional transfer in the Enskog equation is the predominant factor affecting the accuracy of the calculated viscosity for pure gases. In this work the least-squares method is suitable to use as a tool to correlate the parameter H in terms of temperatures.

The calculated viscosities are sensitive to the selection of EOS which provides the volumetric data required in the Enskog equation. In general the three-parameter TPR EOS provides better volumetric calculation than the two-parameter PR EOS. The addition of the radial distribution function in the Enskog equation is to consider the multimolecular collisions for dense gases. Clearly the deviations in the calculated viscosities for dense gases are reduced with the application of the TPR EOS and the addition of the radial distribution function.

A simple mixing rule adopted in this work for the calculation of H is found to be adequate for the prediction of gas mixtures. Because of the unique parameter H in the Enskog equation, the extension of viscosity calculation from pure gases to their mixtures is much simpler than that of other methods.

Chapter 6

Recommendations

A more appropriate selection of the cubic equation of state may get better result for the calculation. For polar fluid and their mixtures, the calculated viscosities might be plausible with the utilization of the Iwai-Margerun-Lu EOS (Iwai et al. 1988) The thermal conductivity can also be calculated by the same approach. Furthermore the accuracy of the calculated results will depend on the future development of EOS for describing the multiple molecular encounters.

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Appendix A

Correlation of Parameter H in Terms of Temperature

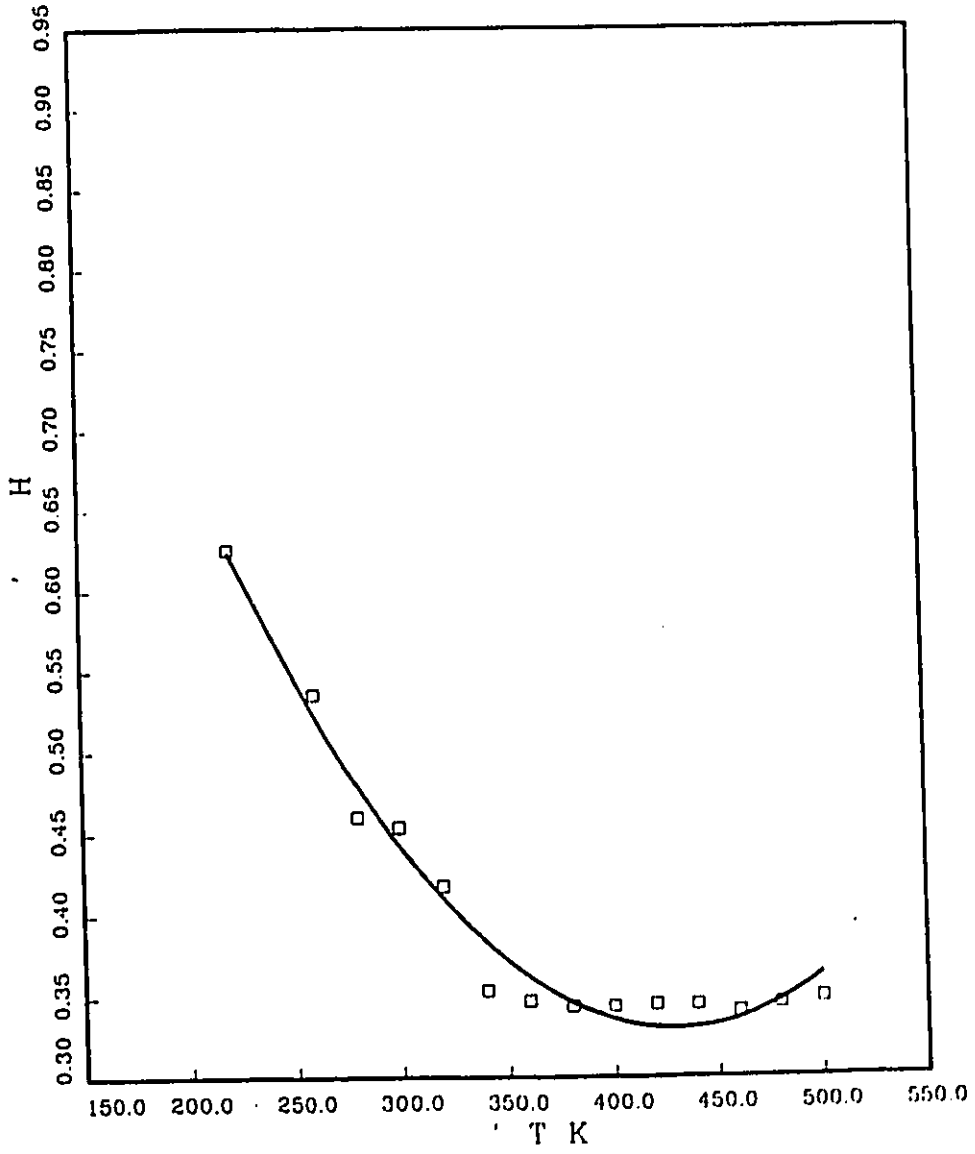

Figure A.1: Values of Parai .eter H for Methane at Different Temperatures.

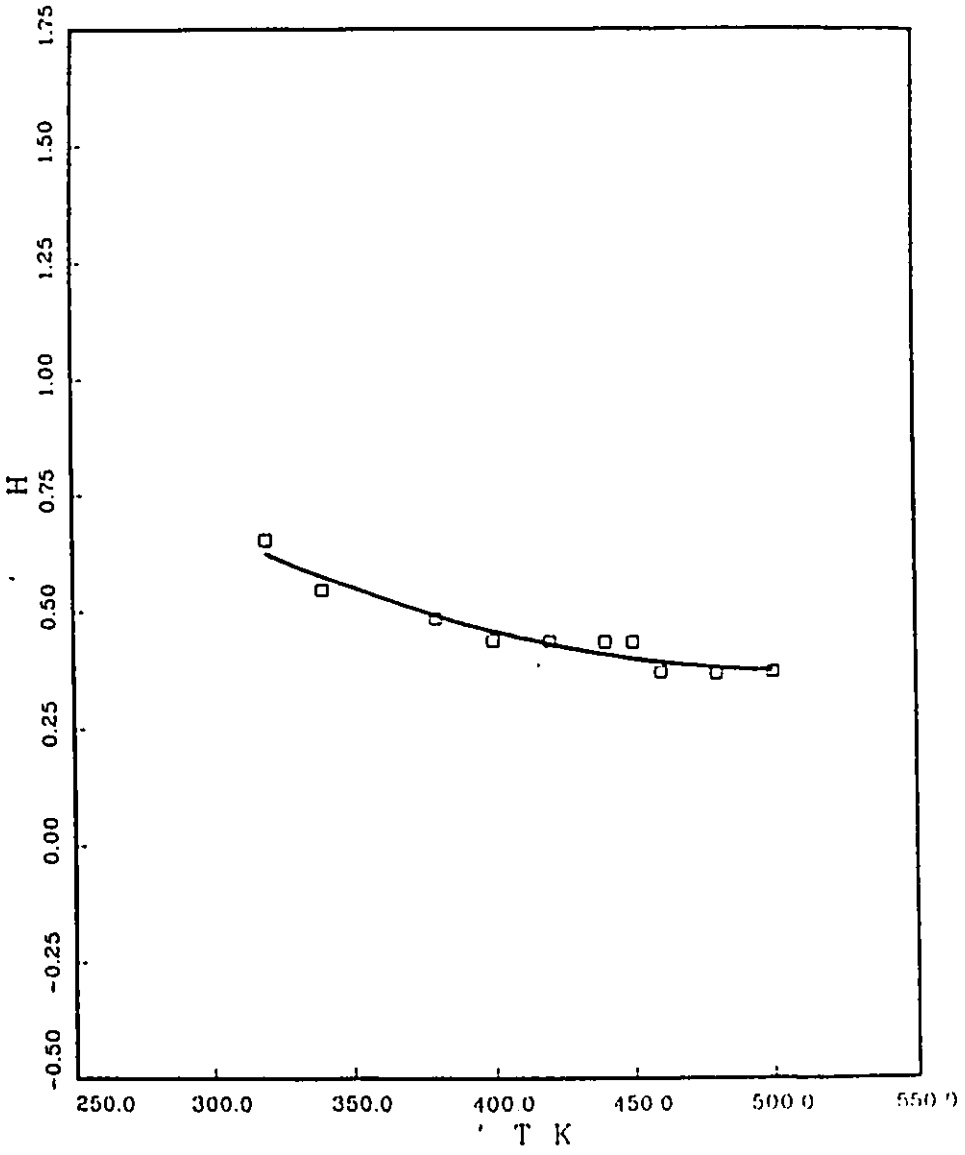

Figure A.2: Values of Parameter H for Ethane at Different Temperatures.

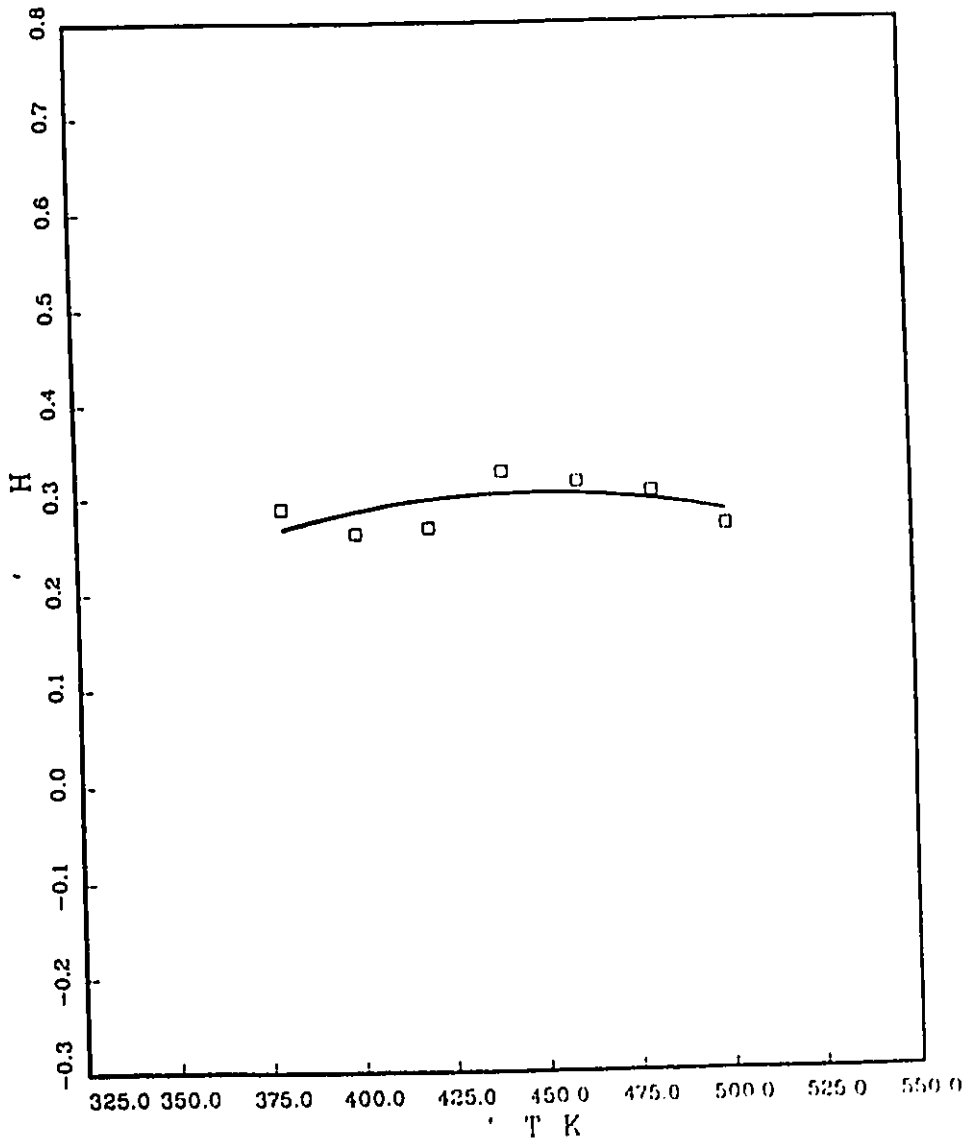

Figure A.3: Values of Parameter H for Propane at Different Temperatures.

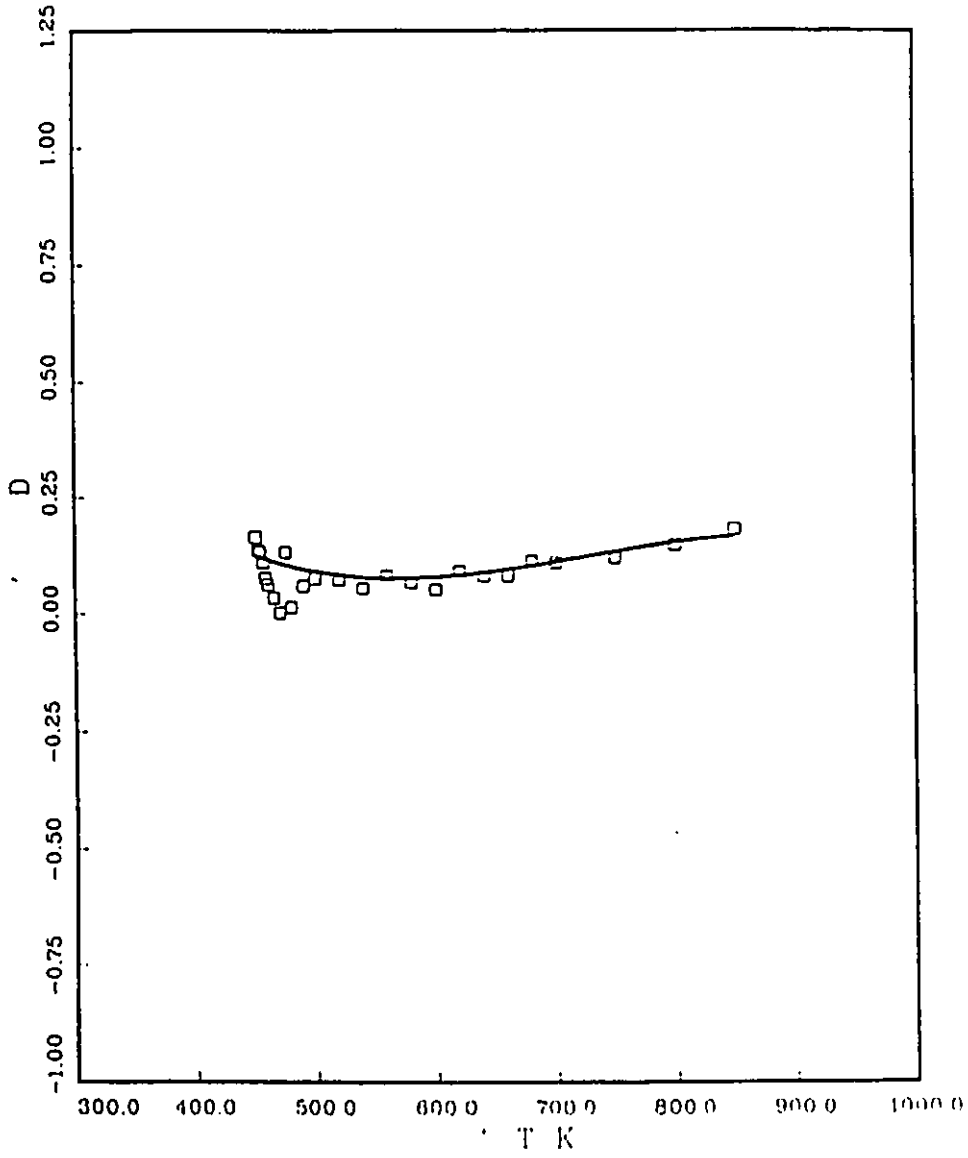

Figure A.4: Values of Parameter H for n-Butane at Different Temperatures.

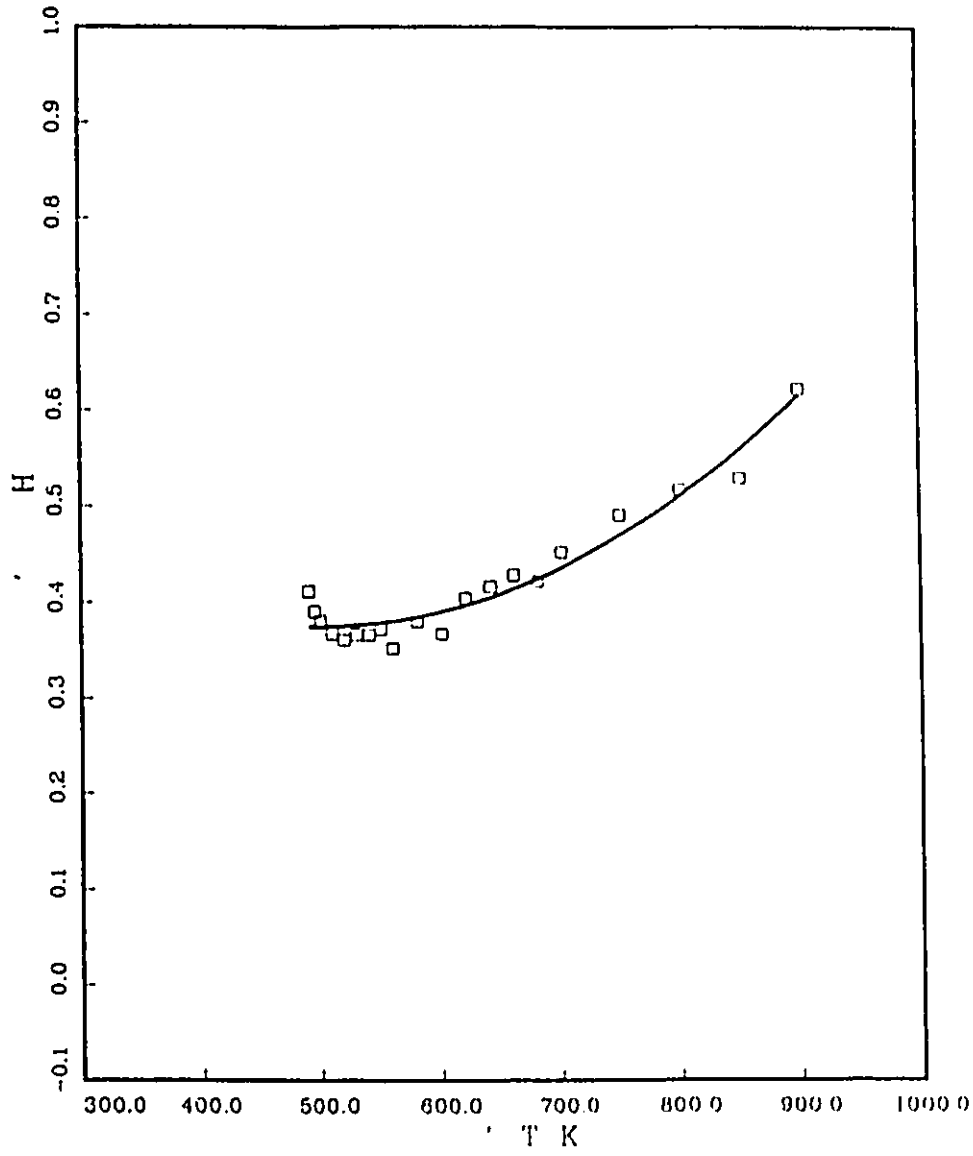

Figure A.5: Values of Parameter H for n-Pentane at Different Temperatures.

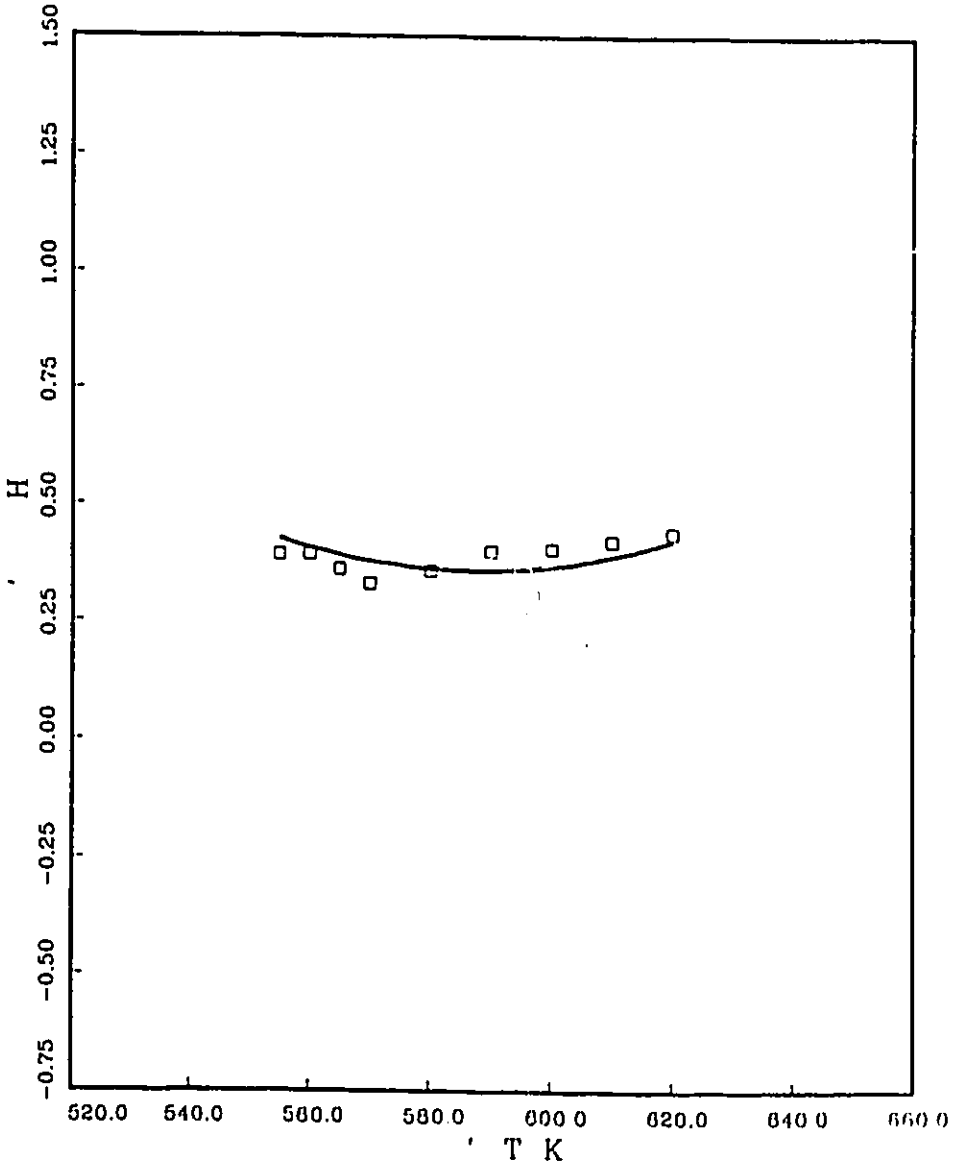

Figure A.6: Values of Parameter H for n-Heptane at Different Temperatures.

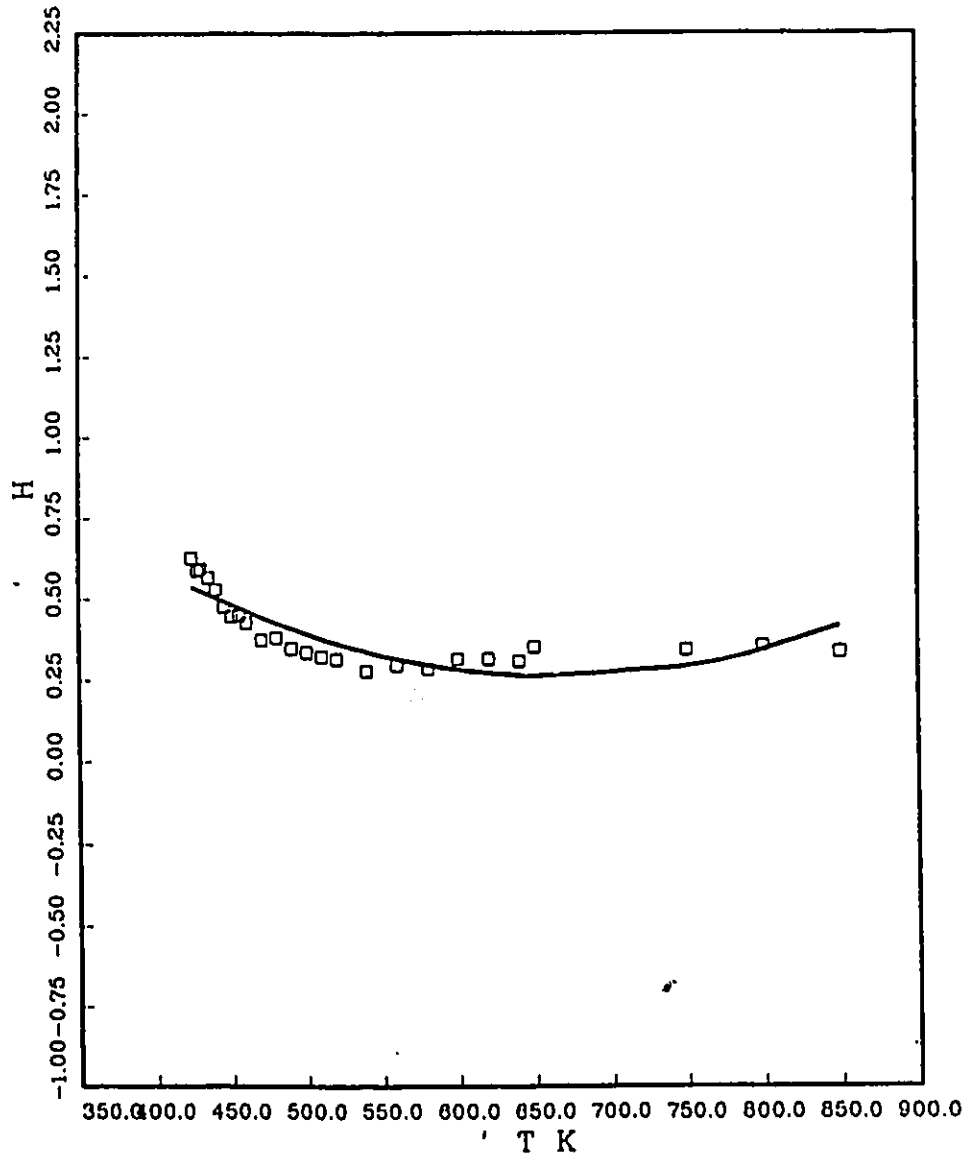

Figure A.7: Values of Parameter H for i-Butane at Different Temperatures.

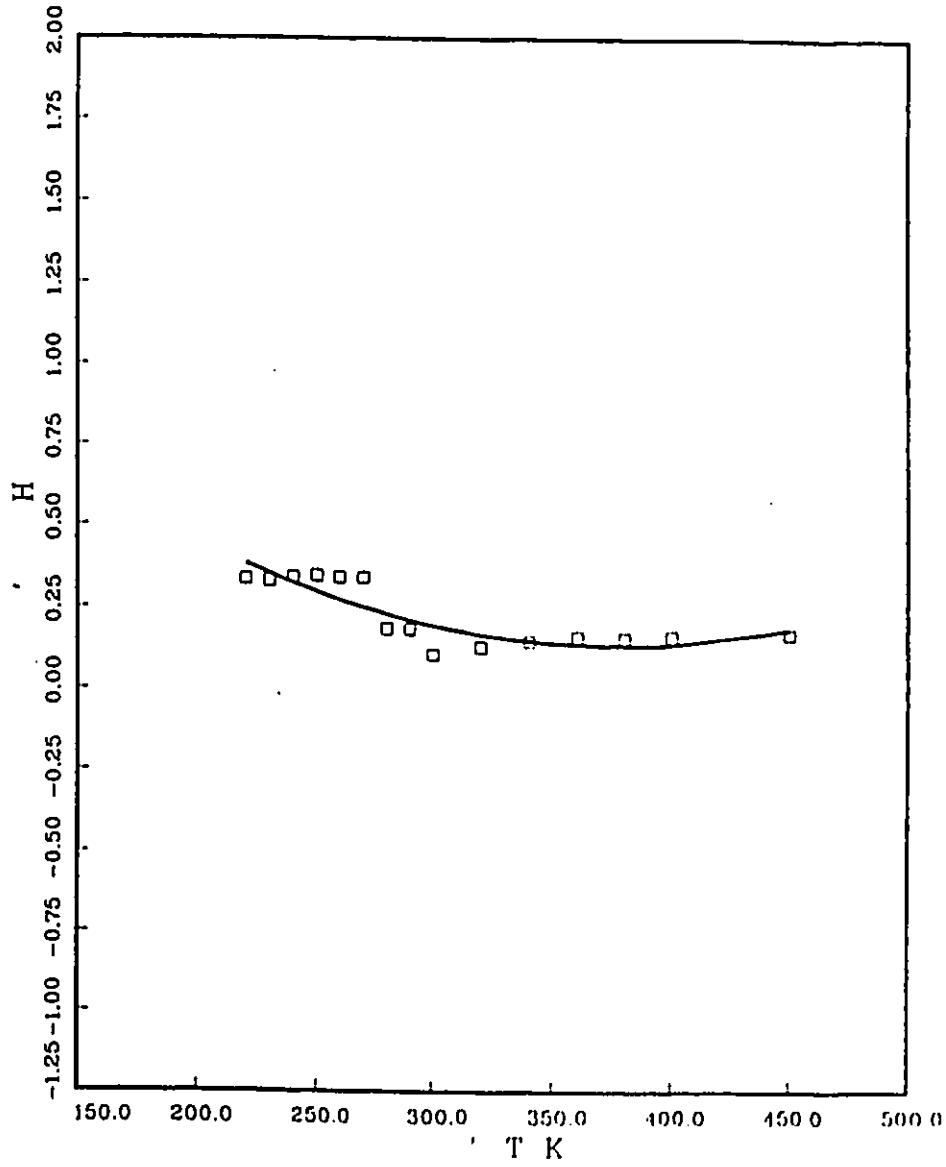

Figure A.8: Values of Parameter H for Carbon Monoxide at Different Temperatures.

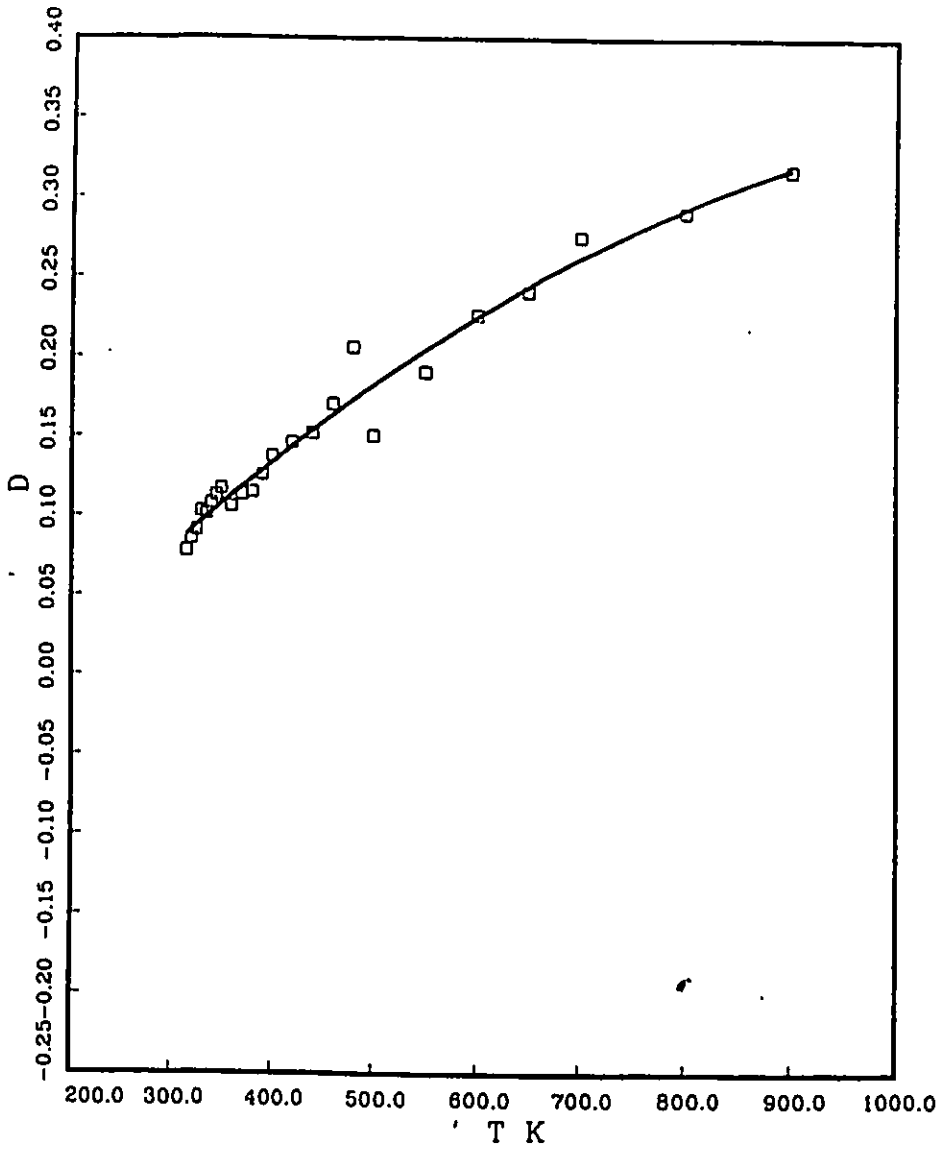

Figure A.9: Values of Parameter H for Carbon Dioxide at Different Temperatures.

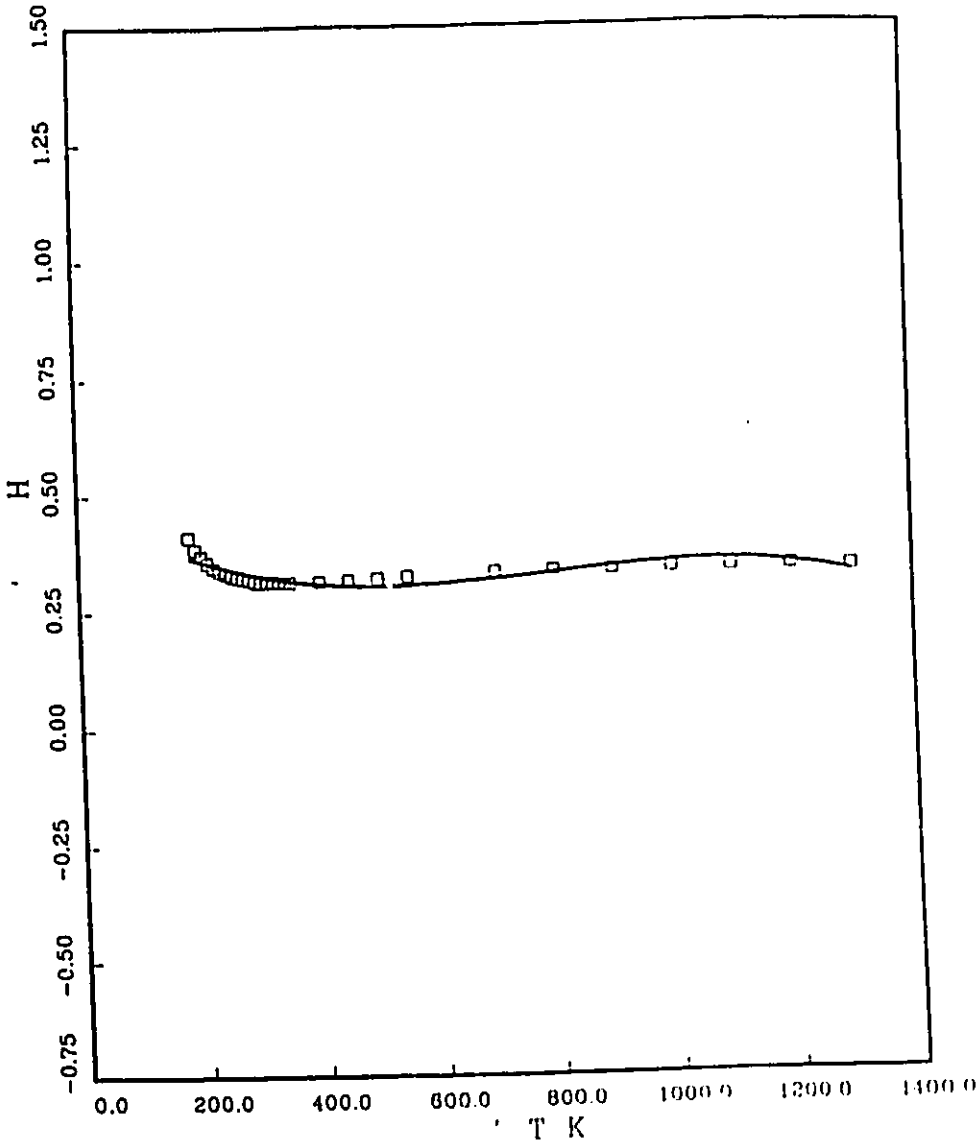

Figure A.10: Values of Parameter H for Oxygen at Different Temperatures.

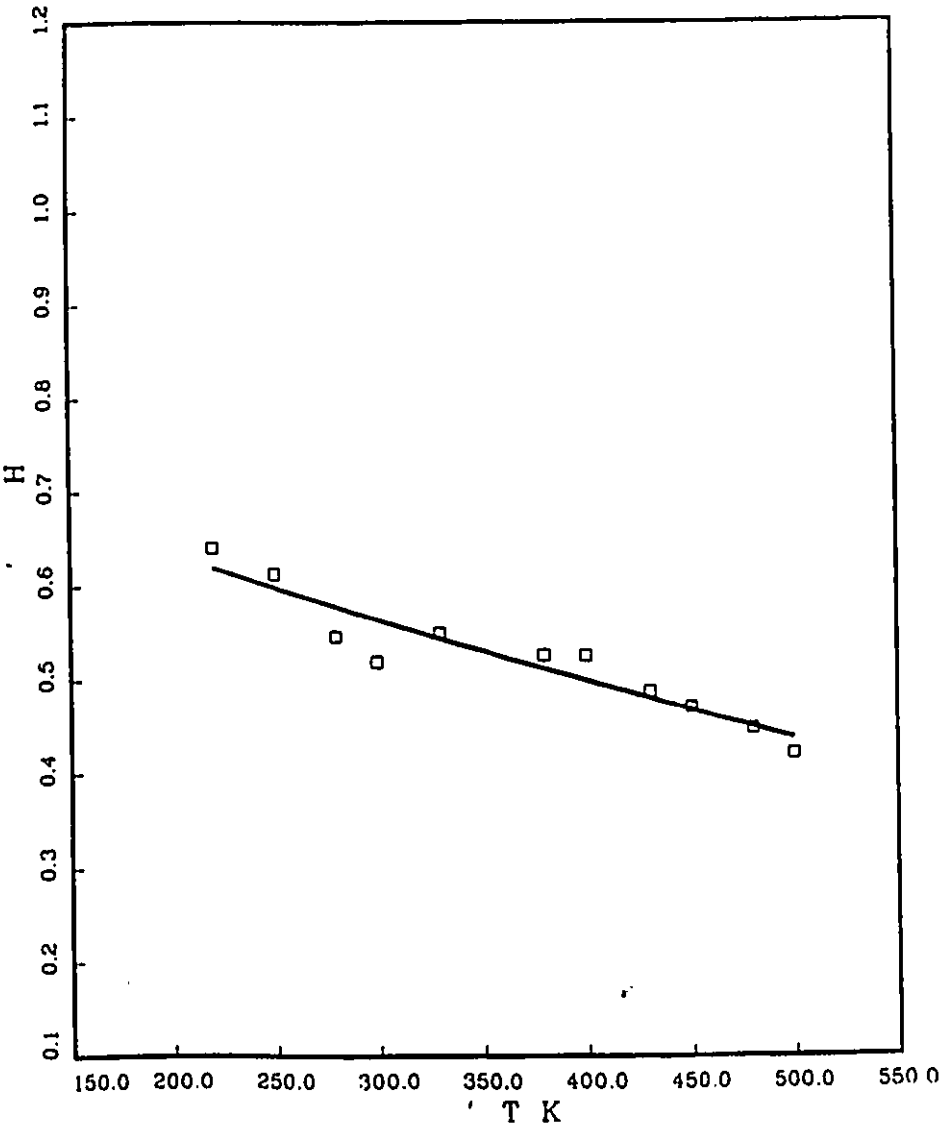

Figure A.11: Values of Parameter H for Argon at Different Temperatures.

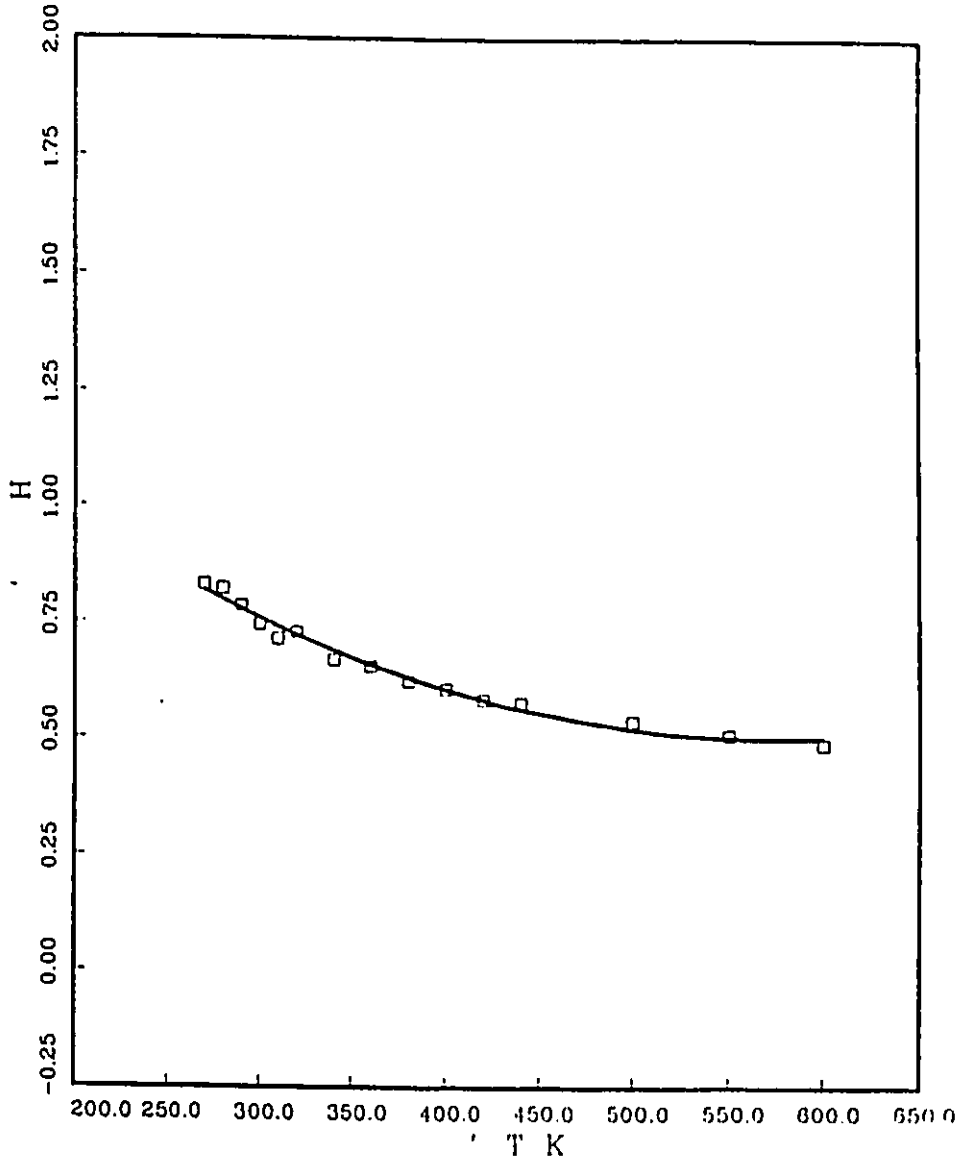

Figure A.12: Values of Parameter H for Krypton at Different Temperatures.

Appendix B

Program

```
c=======================================================
C     PROGRAM TRANS
C-------------------------------------------------------
C  CALCULATE VISCOSITY BY  USING TPR EQUAITON OF STATE
C  COMBINE THE ENSKOG'S THEORY
       IMPLICIT REAL*8 (A-H,O-Z)
       REAL*8 T(200),P(200),XX(1), WOR(3),H(1),G(1),IS,M
       CHARACTER*80 REF
       CHARACTER*30 NAME,NAMEN,PNAME,TNAME
       COMMON /PROP/ TC,PC,AC,AX,BX,CX,VISO,M,VC
       COMMON /DAT/T,P,VIS(200),VISC(200),VV(200),IS(200),N
       EXTERNAL FUN
       ISYS=0
  211  ISYS=ISYS+1
            NSUM=0
       SNER=0.
```

```
      READ(5,*) REF
      WRITE(9,*) REF
      READ(5,*) NAME
      READ(5,*) PNAME
      READ(5,*) TNAME
      WRITE(6,*) REF
1     READ(4,*) NAMEN
       IF (NAMEN.EQ.NAME) THEN
      READ(4,*) TC,PC,AC,M,VC
        GOTO 6
       ENDIF
      READ(4,*)
      GOTO 1
6     REWIND 4
      IF(ISYS.GE.2) GOTO 5
     WRITE(7,*) 'INPUT IREG AND XI'
      READ(7,*) IREG,XX
5    READ(5,*) L
     READ(5,*) (P(I),I=1,L)
      DO 51 I=1,L
      IF(PNAME.EQ.'MPA') P(I)=P(I)/1.01325*10.00
      IF(PNAME.EQ.'BAR') P(I)=P(I)/1.01325
      IF(PNAME.EQ.'KPA') P(I)=P(I)/101.1325
      IF(PNAME.EQ.'PSIA') P(I)=P(I)/14.696
```

```
      IF(PNAME.EQ.'MMHG') P(I)=P(I)/760.0
   51   CONTINUE
        NER=0
    2   NER= NER+1
      READ(5,*) N

      IF(N.LE.0)  THEN
C      WRITE(9,'(10HDATA POINT,I6)') NSUM
       WRITE(9,23) SNER/FLOAT(NER-1),NER-1,SNER,NSUM
   23  FORMAT(F7.2, I4, F7.3, I4)
       GO TO 211
       ENDIF
      IF(N.GT.500) GO TO 1000
       NSUM=NSUM+N
  322  READ(5,*) (T(I),I=1,N)
      READ(5,*) (VIS(I),I=1,N)
       DO 10 I=1,N
       IF(TNAME.EQ.'C') T(I)=T(I)+273.15
       IF(TNAME.EQ.'F') T(I)=(T(I)-32.)/1.8+273.15
   10  CONTINUE
       IF (P(1).GT.0.8)    THEN
       CALL LOWP (VISOO )
       ELSE
       VISO=VIS(1)
```

```
      END IF
       WRITE(6,*) VISO
       IF(IREG.EQ.1) THEN
       CALL FUN(1,XX,FF)
       ELSE
       CALL ZXMIN(FUN,1,2,100,3,XX,H,G,F,WOR,IER)
       ENDIF
C       CALL OPTIM(2)
       SERV=0.
       SSS=0.
       WRITE(6,*)
      WRITE(6,90)
       WRITE(6,*)
      WRITE(6,*) N
       DO 100 I=1,N
       ERV=100.D0*(VISC(I)-VIS(I))/VIS(I)
      SERV=SERV+DABS(ERV)
      SER=(IS(I)-VIS(I))/VIS(I)*100
      SSS=SSS+DABS(SER)
C      WRITE(9,*)'V',T(I),P(I),VV(I)
       WRITE(6,50) I,T(I),P(I),VIS(I),VISC(I),ERV,1/VV(I),IS(I),SER
 100  CONTINUE
      SNER=SNER+SERV/FLOAT(N)
```

```
C     WRITE(6,70) SERV/FLOAT(N)
       WRITE(9,'(7G12.5)') T(1),P(1),P(N),N,SERV/FLOAT(N),XX
C     WRITE 9,'(6G12.5)') T(1),XX
C     WRITE(9,'(6G12.5)') T(1),SERV/FLOAT(N) ,XX
C70    FORMAT(39X,F7.2,F7.2,F12.2)
  50    FORMAT(I4,2F8.2,2F9.2,F8.2,F12.5,2F9.2)
C     WRITE(6,*) N
C      DO 345 I=1,N
C       WRITE(6,505) I,T(I),P(I),VISC(I),ERV,VV(I),IS(I),SER
C 505   FORMAT(I4,2F8.2,F9.2,F8.2,F12.5,2F9.2)
C345   CONTINUE
 90     FORMAT('  NO','   T  K',2X,' P ATM',4X,' VIS EXP',2X,'VIS CAL',
     # 3X,'ERR %','  V CM3/MOL')
C      WRITE(6,200) AX,CX
      GOTO 2

1000  CONTINUE

C      WRITE(9,'(10HDATA POINT,I6)') NSUM
       WRITE(9,24) SNER/FLOAT(NER-1),NER-1,SNER , NSUM
  24   FORMAT(F7.2, I4, F7.3, I4)
C      WRITE(9,'(10HERRORPOINT,F6.3)') SNER/FLOAT(NER)
C200   FORMAT(//' COEFFICIENTS : AX =',F8.4,'  CX=',F9.4)
       END
```

```
      SUBROUTINE MODEL
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 T(200),P(200)
      COMMON /PROP/ TC,PC,AC,AX,BX,CX,VISO/DAT/T,P,VIS(200),VISCC(200)
        F=0.
      DO 100 I=1,N
      CALL VISC(T(I),P(I),VISCC(I))
100   CONTINUE
      F=F*10000D0
      RETURN
           END
      SUBROUTINE FUN(M,XX,F)
      IMPLICIT REAL*8 (A-H,O-Z)
      REAL*8 T(200),P(200),XX(M),IS
      COMMON /PROP/ TC,PC,AC,AX,BX,CX,VISO
      COMMON /DAT/T,P,VIS(200),VISCC(200),VV(200),IS(200),N
        F=0.
      WRITE(7,*) 'X',XX
      AX=XX(1)
      CX=XX(2)
      DO 100 I=1,N
      CALL VISC(T(I),P(I),VI,VI2,V)
      VISCC(I)=VI
      VV(I)=V
```

```
        IS(I)=VI2
        F=F+((VI-VIS(I))/VI)**2
100     CONTINUE
        F=F*10000D0
      WRITE(7,'(5H XI F,3G15.5)') XX,F
      RETURN
           END
C
      SUBROUTINE ESPR(TR,PR,AC,A,B,U,W)
      IMPLICIT DOUBLE PRECISION (A-Z)
      COMMON /PAR/OMEGAC,OMA,OMEGBC,SM
C-----------------------------------------------------------------
C SET CRITICAL POINT VALUES.
C-----------------------------------------------------------------
      OMEGAC=0.45724D0
      U=2
      OMEGBC=.3112D0/(2D0+U)
C-----------------------------------------------------------------
C CALCULATE ALPHA.
C-----------------------------------------------------------------
      IF (AC.LT..2D0) THEN
         SM=.37464D0+1.54226D0*AC-.26992D0*AC**2
      ELSE
         SM=.37964D0+1.48503D0*AC-.16442D0*AC**2+.01667D0*AC**3
```

```
      END IF
      ALPHA=(1D0+SM*(1D0-DSQRT(TR)))**2
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      W=2D0*((2D0-U)/4D0)**2-1D0
C      WRITE(9,*) 'A',A,'B',B
      RETURN
      END
C
      SUBROUTINE ESTPR(TR,PR,AC,A,B,U,W)
      IMPLICIT DOUBLE PRECISION (A-Z)
      COMMON /PAR/OMEGAC,OMA,OMEGBC,SM
      OMEGAC=0.45724D0
      U=1.5251D0+1.1146D0*AC+1.1538D0*AC**2
      OMEGBC=.3112D0/(2D0+U)
C-----------------------------------------------------------------------
C CALCULATE ALPHA.
C-----------------------------------------------------------------------
      IF (AC.LT..2D0) THEN
         SM=.37464D0+1.54226D0*AC-.26992D0*AC**2
      ELSE
         SM=.37964D0+1.48503D0*AC-.16442D0*AC**2+.01667D0*AC**3
      END IF
      ALPHA=(1D0+SM*(1D0-DSQRT(TR)))**2
```

```
      A=ALPHA*OMEGAC*PR/TR**2
      B=OMEGBC*PR/TR
      W=2D0*((2D0-U)/4D0)**2-1D0
C      WRITE(9,*)'A',A,'B',B
      RETURN
      END
C
      SUBROUTINE VISC(T,P,VIS,VIS2,V)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
      REAL*8 Z(2)
      COMMON /PROP/ TC,PC,AC,AX,BX,CX,VISO
      COMMON /PAR/OMEGAC,OMA,OMEGBC,SM
C/AX,BX,CX,VI/AX,BX,CX,VI/* *
C---- CALCULATE PURE COMPONENT EOS PARAMETERS.
C
         TR=T/TC
         PR=P/PC
         CALL ESTPR(TR,PR,AC,A,B,U,W)

        CALL ESPR(TR,PR,AC,A,B,U,W)
         C=(2D0-U)/4D0*B
       OMA=OMEGAC*82.0535*82.0535*TC*TC/PC
C       WRITE(7,*) 'U',U
C
```

```
C---- CALCULATE MIXTURE PARAMETERS
C     WRITE(7,'(4HB BL,4G15.5)') B,BL
      UL=2D0-4D0*C/B
      WL=2D0*(C/B)**2-1D0
C
C---- CALCULATE MIXTURE COMPRESSIBILITY FACTOR.
      CALL ZGEOS(A,B,UL,WL,Z,IST)
       IF(IST.EQ.1) ZL=Z(1)
       IF(IST.EQ.2) ZL=Z(2)
      V=ZL*82.0535/P*T
C     WRITE(9,*) 'V',V
      XIAOB=B*82.0535*T/P
      XIAOC=XIAOB*(2D0-U)/4D0
      DPDT=82.0535/(V-XIAOB)+OMA*(1D0+SM*(1D0-DSQRT(TR)))*SM
     #/(V*V+(2D0-4D0*XIAOC/XIAOB)*XIAOB*V+(2D0*XIAOC**2/XIAOB**2-1D0)
     #*XIAOB**2)/DSQRT(T*TC)
       BRO=(XIAOB+SM*OMA*(1.+SM*(1.-DSQRT(TR)))/82.0535/DSQRT(TC*T))/V
       BX=V/82.0535*DPDT-1D0
C     VIS=VIS0*BRO*(1./BX+AX+.7614*BX)
      VIS=VIS0*BRO*(1./BX+AX+.7614*BX)
      VIS=VIS0*BX*(1./BX+AX+.7614*BX)
C     VIS=VIS0*BRO*(1D0/BX+AX+.755*AX*BX)    (BX=HIGH)4324
      VIS2=VIS0*BRO*(1D0/BX+0.8+.7614*BX)
C     VIS2=VIS0*BRO*(1D0/BX+1.2+.7550*BX)
```

```
C       WRITE(9,*)'BX',BX
        RETURN
        END
C
        SUBROUTINE ZGEOS(A,B,U,W,Z,ISTATE)
        IMPLICIT DOUBLE PRECISION (A-Z)
        INTEGER ISTATE,NRT,NNEG
        DIMENSION RT(3),Z(2)
        CALL RTCUB(U*B-B-1D0,
     1            (W-U)*B**2-U*B+A,-W*B**3-W*B**2-A*B,RT,NRT,NNEG)
        IF (NRT.EQ.1) THEN
           ISTATE=1
           Z(1)=RT(1)
           Z(2)=RT(1)
        ELSE IF (NNEG.NE.0) THEN
           ISTATE=1
           Z(1)=RT(3)
           Z(2)=RT(3)
        ELSE
           ISTATE=2
           Z(1)=RT(1)
           Z(2)=RT(3)
        END IF
C
```

```
      RETURN
      END
      SUBROUTINE RTCUB (B,C,D,X,NROOT,NNEG)
      IMPLICIT DOUBLE PRECISION (A-Z)
      INTEGER I,J,NNEG,NROOT
      DIMENSION X(3)
C-----------------------------------------------------------------------
C INITIALIZE QUANTITIES.
C-----------------------------------------------------------------------
      NNEG=0
      P=(3D0*C-B**2)/3D0
      Q=(27D0*D-9D0*B*C+2D0*B**3)/27D0
      R=(P/3D0)**3+(Q/2D0)**2
C-----------------------------------------------------------------------
C CALCULATE ROOTS (SORTED), NUMBER OF ROOTS, NUMBER OF NEGATIVE ROOTS.
C-----------------------------------------------------------------------
      IF (R.GE.0D0) THEN
         NROOT=1
         AU=DSIGN(DABS(-Q/2D0+DSQRT(R))**(1D0/3D0),-Q/2D0+DSQRT(R))
         BU=DSIGN(DABS(-Q/2D0-DSQRT(R))**(1D0/3D0),-Q/2D0-DSQRT(R))
         X(1)=AU+BU-B/3D0
         IF (X(1).LT.0D0) NNEG=1
      ELSE
         NROOT=3
```

```
          P1=DACOS(DSQRT(-Q**2/P**3*27D0/4D0))/3D0
          P2=DACOS(-1D0)*2D0/3D0
          DO 1000 I=1,3
             X(I)=-DSIGN(2D0,Q)*DSQRT(-P/3D0)*DCOS(P1+P2*DFLOAT(I))-B/3D0
             IF (X(I).LT.0D0) NNEG=NNEG+1
 1000     CONTINUE
          DO 1001 J=1,NROOT-1
          DO 1001 I=J+1,NROOT
             IF (X(J).GT.X(I)) THEN
                TEMP=X(I)
                X(I)=X(J)
                X(J)=TEMP
             END IF
 1001     CONTINUE
       END IF
C
       RETURN
       END
       SUBROUTINE LOWP(VISOO)
        IMPLICIT REAL*8     (A-H,O-Z)
        REAL*8 T(200),P(200),M
       COMMON /PROP/ TC,PC,AC,AX,BX,CX,VISO,M,VC
       COMMON /DAT/T,P,VIS(200),VISC(200),VV(200),IS(200),N
```

```
      DATA  A,B,C,D,E,F/1.16145,0.14874,0.52487,0.77320,2.16178,2.43783/

      FC=1.0-0.2756*AC
      TR=T(1)/TC
      TST=1.2593*TR
      OMAGAV =(A*TST**(-B))+C*(EXP(-D*TST))+E*(EXP(-F*TST))
      VISO =40.785*FC*((M*T(1))**0.5)/(VC**(2.0/3.0)*OMAGAV)
      VISO =40.785*FC*((M*T(1))**0.5)/(VC**(2.0/3.0)*OMAGAV)*.1
       VISOO=   VISO
C      WRITE (6,*)VISOO
      RETURN
      END

      IF (R.GE.0D0) THEN
         NROOT=1
         AU=DSIGN(DABS(-Q/2D0+DSQRT(R))**(1D0/3D0),-Q/2D0+DSQRT(R))
         BU=DSIGN(DABS(-Q/2D0-DSQRT(R))**(1D0/3D0),-Q/2D0-DSQRT(R))
         X(1)=AU+BU-B/3D0
         IF (X(1).LT.0D0) NNEG=1
      ELSE
         NROOT=3
         P1=DACOS(DSQRT(-Q**2/P**3*27D0/4D0))/3D0
         P2=DACOS(-1D0)*2D0/3D0
         DO 1000 I=1,3
```

```
            X(I)=-DSIGN(2D0,Q)*DSQRT(-P/3D0)*DCOS(P1+P2*DFLOAT(I))-B/3D0
            IF (X(I).LT.0D0) NNEG=NNEG+1
 1000    CONTINUE
C--------BUBBLE SORT.
         DO 1001 J=1,NROOT-1
         DO 1001 I=J+1,NROOT
            IF (X(J).GT.X(I)) THEN
               TEMP=X(I)
               X(I)=X(J)
               X(J)=TEMP
            END IF
 1001    CONTINUE
      END IF
C
      RETURN
      END
      SUBROUTINE LOWP(VISOO)
       IMPLICIT REAL*8     (A-H,O-Z)
       REAL*8 T(200),P(200),M
      COMMON /PROP/ TC,PC,AC,AX,BX,CX,VISO,M,VC
      COMMON /DAT/T,P,VIS(200),VISC(200),VV(200),IS(200),N

      DATA  A,B,C,D,E,F/1.16145,0.14874,0.52487,0.77320,2.16178,2.43783/
```

```
C        READ (5,*)N
C      READ (5,*)(P(I),I=1,N)
C      READ (5,*)(T(I),I=1,N)
C      READ (5,*)(VIS(I),I=1,N)
C      WRITE (6,*)(VIS(I),I=1,N)
       FC=1.0-0.2756*AC
       TR=T(1)/TC
       TST=1.2593*TR
       OMAGAV =(A*TST**(-B))+C*(EXP(-D*TST))+E*(EXP(-F*TST))
       VIS0 =40.785*FC*((M*T(1))**0.5)/(VC**(.6667)*OMAGAV)
       VIS0 =40.785*FC*((M*T(1))**0.5)/(VC**(.6667)*OMAGAV)*.1
        VIS00=   VIS0
       WRITE (6,*)VIS
       RETURN
```

Appendix C

Sample Calculation

The viscosity of krypton at temperature 270K and pressure 118.43×10^5 Pa is 38.0×10^{-6} Pa.s. The value of η_0 is 23.32×10^{-6}Pa.s. (Stephan and Lucas, 1979)

The parameters u and w of the Peng-Robinsion EOS are equal to 2 and -1 respectively.

Hence

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

in which

$$a(T) = 0.45724\frac{R^2T_c^2}{P_c}[1+m(1-T_r^{0.5})]^2$$

$$m = 0.37464 + 1.54226\omega - 0.26997\omega^2$$

$$b = 0.07780\frac{RT_c}{P_c}$$

The accentric factor,ω, for krypton is 0.005, and the values T_c, P_c and V_c are listed in Table C.1. The volume v is then calculated to be .12378 m^3/mol (see §2.3), the value of $b_0\rho\chi$ is calculated by Eq 3.12 and is equal to 0.57912. The parameter H in the Enskog equation is correlated by means of the Gauss-Newton method. At 270K, $H = 0.664928$. Hence,

$$\eta = \eta_0(b_0\rho\chi)(\frac{1.000}{(b_0\rho\chi)} + H_{(T)} + 0.7614(b_0\rho\chi)) \quad (C.1)$$
$$= 23.20(0.57912)[\frac{1.000}{0.57912} + 0.664928 + 0.7614(0.57912)]$$

The calculated viscosity is equal to 38.058×10^{-6} Pa.s. This value is 0.15% higher than the experimental value.

Table C.1: Physical Properties of Pure Components

fluid	M	T_c	P_c	V_c	Accentric
Methane	16.04	190.5	45.34	99.0	.011
Ethane	30.07	305.4	48.20	148.	.099
Propane	44.09	369.8	41.94	203.	.153
n-butane	58.12	25.2	37.50	255.	.201
n-pentane	72.13	469.6	33.26	304.	.251
n-hexane	86.18	507.4	29.71	370.	.299
n-heptane	100.	540.1	87.04	432	.349
i-butane	58.12	408.1	36.02	263	.183
i-pentane	72.15	460.4	33.46	306	.271
Ethylene	28.05	282.4	49.74	129	.085
Propylene	42.08	365.0	45.60	181	0.14
CO	28.0	132.9	34.5	93.1	.066
CO_2	44.0	304.2	72.86	94.0	0.239
Nitrogen	28.01	126.2	33.45	8.5	.039
Oxygen	32.0	154.8	50.20	73.4	.025
Fluorine	37.99	144.3	51.51	66.2	.054
Helium	4.0	5.201	.2452	57.3	-.387
Neon	20.18	44.4	26.19	41.7	-0.03
Krypton	83.8	209.4	54.28	91.2	.005
Argon	39.95	150.8	48.33	74.9	.001

Reference: Reid et al. 1987.

Table C.2: Coefficients k_2, k_1 and k_0 of Equation 3.30

fluid	k_2	k_1	k_0
Methane	.67e-05	-.57e-02	1.57
Ethane	.70e-05	-.71e-02	2.20
Propane	-.078e-05	.7e-02	-1.26
n-butane	.155e-05	-.17e-02	.57
n-pentane	.148e-05	-.146e-02	.74
n-hexane	-.376	.6e-02	-1.90
n-heptane	.64e-04	-.75e-02	22.3
i-butane	.42e-05	-.56e-02	2.15
i-pentane	-.46e-05	.607e-02	-2.09
Ethylene	.58e-06	.38e-03	.438
Propylene	-.106e-04	.98e-02	-1.5
CO	-.000008	.0078	-1.28
CO_2	-.29e-06	.75e-03	-.1
Nitrogen	.667e-05	-.44e-02	1.2
Oxygen	.82e-06	-.49e-03	.27
Fluorine	.29e-04	-.15e-01	2.4
Helium	.58e-04	-.11e-01	2.15
Neon	-.21e-04	.47e-01	-4.56
Krypton	.34e-05	.39e-02	1.632
Argon	.22e-06	-.81e-03	.787

The Gauss-Newton Method

The Gauss-Newton method is based on the first order Tailor expansion:

$$f(X, b_1, b_2 \cdots b_m) \approx f^0 + \frac{\partial f^0}{\partial b_1}\Delta_1 + \cdots \frac{\partial f^0}{\partial b_m}\Delta_m$$

with

$$f^0 \;=\; f(X, b_1^{(0)}, b_2^{(0)}, \cdots b_m^{(0)})$$

where X is a vector respond involving P variables:

$$X \;=\; (x_1, x_2 \cdots x_p)$$

The quantities $b_1 \cdots b_m$ are parameters which are required in the least squares method.

Initial values of $b_i^{(0)}$ are estimated and the better approximated values of b_i are obtained as follow:

$$b_i = b_i^{(0)} + \Delta_i \quad i = 1, 2 \cdots, m$$

After applying the least squares method, the Hessian matrix is formed in the following manner:

$$\begin{cases} a_{11}\Delta_1 & +a_{12}\Delta_2 & \cdots & +a_{1m}\Delta_m & = a_{1y} \\ a_{21}\Delta_2 & +a_{22}\Delta_2 & \cdots & +a_{12}\Delta_m & = a_{2y} \\ \cdots & & & & \\ a_{m1}\Delta_1 & +a_{m2}\Delta_2 & \cdots & +a_{mm}\Delta_m & = a_{my} \end{cases}$$

where

$$\begin{cases} a_{ij} = & \sum_{k=1}^{n} \frac{\partial f_k^0}{\partial b_i} \cdot \frac{\partial f_k^0}{\partial b_j} & i = 1, 2, \cdots, m \\ a_{iy} = & \sum_{k=1}^{n} (y_k - f_k^0) & i = 1, 2, \cdots, m \end{cases}$$

The values of Δ_i can be obtained by solving the linear matrix. Then the values of b_i are treated as the intial values ($b_i^{(0)}$) again until the predetermined tolerance of Δ_i is reached.

Table C.3: Comparison of the Experimental and the Predicted Viscosities for the Carbon Dioxide(1)-Methane(2) Gas Mixtures ($k_{12} = 0.10471$) (Kestin and Nagashima, 1964)

Mole Fraction y_1	Temperature K	Pressure 1.0133×10^5 Pa	η (Expt) 1×10^{-6} $Pa.s$	η(Cald)	APD
0.8565	293.15	1.06	144.33	144.44	0.08
	293.15	5.02	144.69	144.94	0.17
	293.15	15.03	145.69	146.81	0.77
	293.15	25.23	148.19	149.84	1.11
	303.15	1.05	149.20	149.31	0.07
	303.15	5.02	149.57	149.80	0.15
	303.15	15.09	150.88	151.59	0.47
	303.15	25.09	153.08	154.33	0.82
0.6624	293.15	1.03	140.03	140.17	0.10
	293.15	4.99	140.36	140.78	0.30
	293.15	15.01	141.77	142.78	0.71
	293.15	25.39	144.06	145.69	1.13
	303.15	1.05	144.66	144.80	0.10
	303.15	5.02	145.07	145.39	0.22
	303.15	15.02	146.49	147.28	0.54
	303.15	25.09	148.66	149.88	0.82
0.4806	293.15	1.05	134.48	134.64	0.12
	293.15	5.01	134.84	135.31	0.35
	293.15	15.02	136.36	137.34	0.72
	293.15	25.22	138.51	140.00	1.08
	303.15	1.05	138.81	138.97	0.11
	303.15	5.01	139.25	139.60	0.25
	303.15	15.02	140.72	141.51	0.56
	303.15	25.22	142.82	143.99	0.82
0.3257	293.15	1.05	128.26	128.43	0.13
	293.15	5.02	128.73	129.11	0.30
	293.15	15.02	130.26	131.11	0.65
	293.15	22.92	131.83	132.99	0.88
	303.15	1.04	132.37	132.53	0.12
	303.15	5.01	132.81	133.18	0.28
	303.15	14.98	134.34	135.05	0.53
	303.15	25.02	136.28	137.32	0.77