UNIVERSITY MICROFILMS, ANN ARBOR, MICH.

L. C. Card no. Mic 58-901

DE ROCCO, Andrew Gabriel. THE INTERMOLECULAR POTENTIALS OF ARGON METHANE AND ETHANE

University of Michigan
Ph. D., 1957
Chemistry, Physical

THE INTERMOLECULAR POTENTIALS OF ARGON METHANE AND ETHANE

by
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A dissertation submitted in partial fulfullment
of the requirements for the degree of
Doctor of Philosophy in the
University of Michigan
1956

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Abstract

THE INTERMOLECULAR POTENTIALS
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by Andrew Gabriel De Rocco

The Chapman-Enskog theory gives the transport properties of a dilute non-polar gas in terms of a set of integrals which involve the intermolecular force law. Since direct calculation of the force law is impossible at the present time, the usual procedure has been to compare experimentally derived collision integrals with those computed for an assumed force law having several adjustable parameters. The Exp-Six potential differs from the usual Lennard-Jones potential in two significant ways: 1) it represents the short range repulsive forces by an exponential term rather than the term in r^{-12} employed by Lennard Jones, 2) it contains an additional parameter, α, related to the steepness of the repulsive part of the potential.

The objectives of this research were to measure the viscosities of argon, methane and ethane from ca. 200-500° K, and from these data to derive the potential parameters for the three gases from the temperature variation of the viscosity.

The viscosities of argon, methane, and ethane have been determined from 210°K to 473°K using a capillary viscometer. The viscometer was calibrated using oxygen, and a secondary calibration with helium confirmed the reliability of the primary calibration. The estimated accuracy of the method was 0.5 per cent.

The results for argon were in substantial agreement with previous investigations, while those for methane and ethane were a few per cent higher than previously reported values.

The potential parameters for an Exp-Six potential were determined from the viscosity data. For argon and methane the agreement between calculated and experimental values for the transport coefficients and second virial coefficients was very good. For ethane, however, a single set of parameters was unable to fit both the transport and equilibrium properties. It was concluded that the Enskog-Chapman theory failed for the slightly non-spherical ethane molecule. It was suggested that proper modification of the Enskog-Chapman theory would probably resolve the non-spherical problem and permit a detailed comparison of the Exp-Six and Lennard-Jones potentials.

The potential parameters determined for the three gases are summarized below:

1) Argon $r_m = 3.867\text{Å}$; $(\epsilon/k) = 123.0$; $\alpha = 14$

2) Methane $r_m = 4.209\text{Å}$; $(\epsilon/k) = 152.4$; $\alpha = 14$

3) Ethane $r_m = 4.905\text{Å}$; $(\epsilon/k) = 229.1$; $\gamma = 16$ (viscosity)

$r_m = 5.226\text{Å}$; $(\epsilon/k) = 249.5$; $\gamma = 16$ (2nd virial)

The results reported above for argon and methane are in good agreement with previously reported values, while for ethane no previous results have been reported.

ACKNOWLEDGEMENTS

The author is pleased to acknowledge the guidance and patience given by Professor J. O. Halford throughout the course of this research. In his many discussions with Professor Halford, the author was offered the opportunity to develop an independent attitude towards the spirit of scientific inquiry.

Appreciation is also given to the E. I. du Pont de Nemours and Company for generous support awarded during the year 1954- 1955 and during the summers of 1955 and 1956.

Finally, the author offers his gratitude to his wife, Sussanne Beardsley De Rocco, who typed and edited the entire manuscript.

TABLE OF CONTENTS

PART I

page

INTRODUCTION.....1

A. General Introduction.....1

B. Statement of the Problem.....6

PART II

THEORETICAL.....8

A. Summary of Kinetic Theory Formulae for Pure Gases and the Equation of State.....8

B. The Computation of Collision Integrals.....14

C. Determination of the Potential Parameters.....15

PART III

EXPERIMENTAL DESIGN AND PROCEDURE.....22

A. The Choice and Theory of the Method.....22

B. Apparatus Design.....26

C. The Procedure and Standardization of the Method.....33

PART IV

RESULTS.....39

A. Argon.....39

B. Methane.....44

C. Ethane.....47

PART V

CONCLUSIONS AND SUMMARY.....56

APPENDIX I

A REVIEW OF THE KINETIC THEORY OF DILUTE GASES.....58

page

A. Outline of the Problem and Method of Approach.....58

B. The Description of Non-Equilibrium Systems.....59

C. The Boltzmann Equation.....60

D. The Flux Vectors and the Equations of Change.....65

E. Enskog's Solution of the Boltzmann Equation.....73

F. The Sonine Polynomial Expansion.....78

APPENDIX II

THE COLLISION INTEGRALS $\Omega^{(l,s)*}(\alpha, T^*)$ FOR CALCULATING THE TRANSPORT COEFFICIENTS FOR THE MODIFIED BUCKINGHAM POTENTIAL.....83

APPENDIX III

A RELATION BETWEEN THE CHARACTERISTIC DISTANCE PARAMETERS OF THE LENNARD-JONES AND EXPONENTIAL-SIX POTENTIAL FUNCTIONS.....85

APPENDIX IV

SOURCE AND PURITY OF THE GASES.....92

BIBLIOGRAPHY.....93

LIST OF TABLES

page

Table 1. The Quantity $\Delta V/\Delta P$ for Argon and Oxygen at 273.16° K.....37

Table 2. Comparison of Observed Viscosity of Argon with those Calculated for the Exp-Six Potential.....40

Table 3. Thermal Conductivity for Argon Using Potential Parameters from Viscosity.....42

Table 4. Coefficient of Self-Diffusion for Argon Using Potential Parameters from Viscosity.....42

Table 5. Comparison of Observed Viscosities of Methane with those Calculated for the Exp-Six Potential.....45

Table 6. Coefficient of Self-Diffusion for Methane Using Potential Parameters from Viscosity.....49

Table 7. Comparison of Observed Viscosities of Ethane with those Calculated for the Exp-Six Potential.....50

Table 8. Comparison of Values of the Potential Parameters by Different Methods.....55

Table IIIA
(σ/r_m) for Selected Values of ϵ^* and Alpha.....87

Table IIIB
A Comparison of Experimental and Calculated Values for (σ/r_m).....90

LIST OF FIGURES

page

Fig. 1 The Buckingham Potential as a Function of Intermolecular Separation. (The Magnitude of $\phi(R_{max})$ Relative to ϵ Is Much Reduced in the Figure).....4

Fig. 2 A Plot of the Reduced Quantities log $[-B^*(\alpha, T^*)]$ vs log T* for Selected Values of the Parameter 17

Fig. 3 A Plot of the Reduced Quantities for Viscosity vs log T* for Selected α 19

Fig. 4 The Capillary System.....28

Fig. 5 The Constant Temperature Bath.....32

Fig. 6 A Plot of ΔV vs ΔP for Argon at 300.16°K.....38

Fig. 7 The Viscosity of Argon vs Temperature.....41

Fig. 8 The Second Virial Coefficient of Argon.....43

Fig. 9 The Viscosity of Methane vs Temperature.....46

Fig. 10 The Second Virial Coefficient of Methane.....48

Fig. 11 The Viscosity of Ethane.....52

Fig. 12 The Second Virial Coefficient of Ethane.....54

PART ONE

INTRODUCTION.

A. General Introduction The influence of intermolecular forces on the transport properties of gases is well known, and information concerning intermolecular forces may be obtained from the temperature variation of gaseous transport coefficients by means of the theory developed by Enskog[1] and Chapman[2]. Such information is useful in correlating other properties of gases, as well as properties of the liquid and solid states. The general subject of intermolecular forces and the properties of matter has recently received an admirable review by Rowlinson[3].

The theory of Enskog and Chapman depends on the following assumptions: 1) only binary collisions between molecules are important; 2) the binary collisions are elastic; 3) the intermolecular force field is spherically symmetric; 4) molecular collisions are adequately described by classical mechanics. The theory, therefore, strictly applies only to monatomic gases at moderate pressures and temperatures high enough that quantum effects are negligible. It is not completely understood to what degree the theoretical relations still apply when conditions (2) and (3) are not met. The many successful applications of the theory to polyatomic molecules, however, indicates that these restrictions may not be too severe. It is known, however, that when the form of the force field is non-spherical, energy may be exchanged among the internal degrees of freedom.

This phenomenon seems to affect seriously the thermal conductivity; while the coefficient of viscosity appears to measure an energy averaged over all orientations, yielding, as a result, information about the variation of the energy with distance[3].

In order to learn the detail of the intermolecular forces from transport phenomena, it is necessary to assume some analytical form for the intermolecular potential, and then compare the experimentally derived "collision integrals" with those calculated from the Enskog-Chapman theory. If the theory is correct and the assumed potential form adequate, a single set of potential parameters should be sufficient to describe all the transport properties of the gas, as well as other properties, such as the equation of state. Except for very simple and physically unrealistic potential forms, the calculation of the collision integrals requires extensive numerical integrations.

Prior to the appearance of a paper by Mason[4], the most extensive calculations of collision integrals had been made for a potential form due to Lennard-Jones, which approximated attractive energies with a term varying as the inverse sixth power of the distance separating the centers of the two molecules, and required the repulsive energies to be represented by a term varying as the inverse twelfth power of the separation distance. Independent computations for the Lennard-Jones (12-6) potential had been made by several workers[5-8], and comparisons with experiment were numerous[9-12].

The results obtained, however, were not entirely satisfactory, and the question naturally arose as to whether the discrepancies were primarily the fault of the theory or of an inadequate potential form. The lack of complete agreement between theory and experiment even for the rare gases indicated that the Lennard-Jones potential was not entirely satisfactory.

In the paper of Mason (cf. ref. 4), computations of the collision integrals (or more exactly, functions related to the collision integrals) for a more realistic potential form were presented.

A considerable body of evidence was available to indicate that the form for the repulsive term of an intermolecular potential was more suitably described by an exponential term[13-18] rather than the term in r^{-12} employed by Lennard-Jones. Mason, therefore, computed the "collision-integral-functions" for a potential form which was a modification of the form used extensively by Buckingham[19]. The potential function, usually called the modified Buckingham or "Exp-Six", is illustrated in Figure 1; it has the following analytical properties;

$$\varphi(r) = \frac{\epsilon}{1 - 6/\alpha}\left[\frac{6}{\alpha} e^{\alpha(1 - r/r_m)} - \left(\frac{r_m}{r}\right)^6\right], \quad r > r_{max}$$

$$\varphi(r) = \infty \quad , \quad r < r_{max} \qquad (1)$$

where $\varphi(r)$ is the potential energy of the molecules at separation distance r, $-\epsilon$ is the minimum potential energy for the value of $r = r_m$, and α is an additional parameter which may be considered a measure of the steepness of the

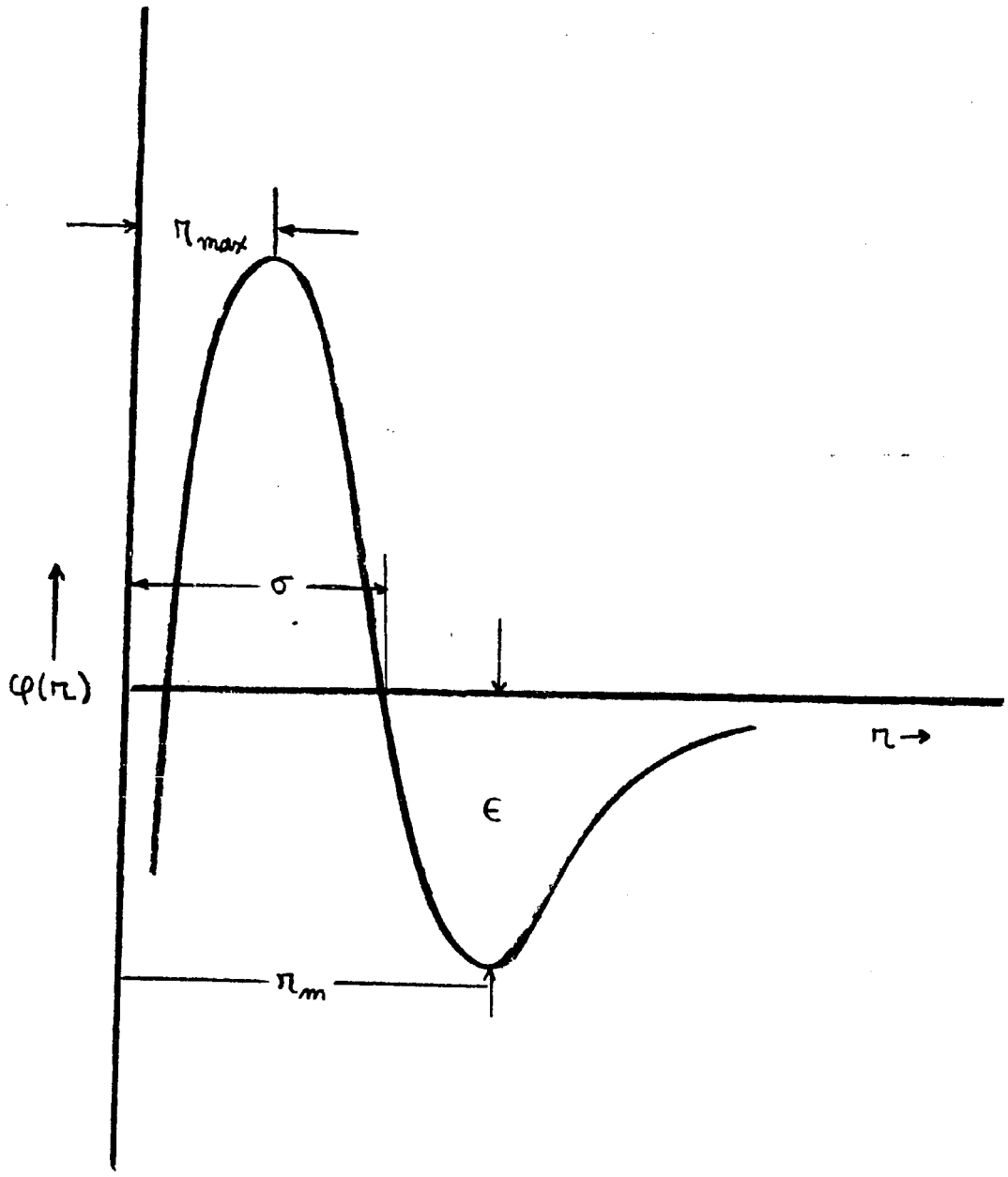

Fig. 1 The Buckingham Potential as a Function of Intermolecular Separation

repulsion energy. The next higher term, varying as r^{-8} and representing the dipole-quadrupole energy, in the dispersion energy, was not included since the same effect could be achieved to a good approximation by a variation of the parameter α .

A somewhat more easily visualized measure of the steepness of the repulsion energy than α is the ratio (σ/r_m) where σ is the value of r for which $\varphi(r) = 0$, (cf. Fig.1). Mason[4] includes a table of the values of (σ/r_m) for α ranging from 12-15, and includes, for comparison, the fixed value of (σ/r_m) for a Lennard-Jones potential which, having a value of 0.8909, lies near the mean of the values calculated for varying values of α . An interesting property of the value of (σ/r_m), where σ is measured for a (12-6) potential and r_m for a corresponding Exp-Six potential, was uncovered during the research to be described herein and will be discussed later (cf. p.20).

A potential of the form of Eq. (1) was derived theoretically by Slater and Kirkwood[20] for the special case of helium and, as cited earlier[19] , had been employed in great detail by Buckingham. The potential described by Eq. (1) is defective in that at a small separation distance, r_{max} , it has a spurious maximum and approaches minus infinity as r approaches zero. Buckingham sought to relieve this difficulty for $r < r_{max}$ by multiplying the inverse sixth-power term of Eq. (1) with another exponential term to prevent the potential from having a maximum. However, the location of r_{max} is at such high energies that it has

little effect on ordinary thermal collisions, (for example, with argon $r_{max} = 0.78\text{Å}$, $\varphi(r_{max}) = 7490$ Kcal/mole) and Mason found that it was adequate to define $\varphi(r) = \infty$ for $r < r_{max}$; in this form, Eq. (1) has been called the "modified-Buckingham" or "Exp-Six" potential.

In a later paper[21] Mason and Rice discussed the application of Eq. (1) and the Enskog-Chapman theory to several simple nonpolar molecules. They found, for example, that the measured values for the viscosity of argon deviated greatly from the calculated values at high temperatures ($T > 600^{\circ}K$). In addition, the deviations at low temperature ($T < 200^{\circ}K$) for argon and methane were greater than the estimated experimental error.

B. Statement of the Problem The principal objectives of this problem were to measure the viscosities of argon, methane, and ethane from ca. 200-500°K., and from these data to redetermine the potential parameters for argon and methane, and determine a set of potential parameters for ethane.

In the temperature range from 300-500°K., only scanty or questionable viscosity data were available for the three gases cited and construction of an apparatus designed to measure the viscosities in this region was considered justified over and above the usefulness of the data in providing a basis for deduction of the potential parameters.

In addition to the hope that a re-evaluation of the potential parameters for argon and methane might help resolve

the discrepancies mentioned earlier for these two gases, the gases were chosen for the following reasons: (a) argon presumably violated none of the assumptions of the Enskog-Chapman theory, (b) methane violated condition (2) and no others, (c) ethane represented the extreme case for which the theory might be expected to hold, since it violated conditions (2) and (3) but, presumably, no others.

PART TWO

THEORETICAL

A. Summary of Kinetic Theory Formulae for Pure Gases and the Equation of State In Appendix I it is shown that the transport coefficients, as defined by Eq. (I.21a), may be expressed in terms of a set of integrals $\Omega^{(l,s)}$ (the collision integrals), the molecular masses, and the number densities of the various components. Before any calculations of transport coefficients can be made for an arbitrary potential $\varphi(r)$, the angle of deflection in a collision, χ, must be calculated according to Eq. (I.50). For any realistic potential function it is not possible to express χ analytically, but numerical methods may be used to evaluate χ for a large number of values of g and b from which the integrals $\Omega^{(l,s)}$ may be evaluated numerically. In this connection, it is convenient to define a set of quantities, $Q^{(l)}$, called the cross-sections, as follows:

$$Q^{(l)}(g) = 2\pi \int_0^\infty (1-\cos^l\chi)\, b\, db \,, \qquad (2)$$

where the quantities g, b and χ have the meanings indicated in Appendix I. The collision integrals can now be expressed as

$$\Omega^{(l,s)}(T) = \sqrt{\frac{kT}{2\pi\mu}} \int_0^\infty e^{-\gamma^2} \gamma^{2s+3}\, Q^{(l)}(g)\, d\gamma \,, \qquad (3)$$

in accordance with Eq. (I.49). The quantities $Q^{(\ell)}$ and $\Omega^{(\ell,s)}$ can be evaluated analytically for a rigid sphere molecular model: and if the following definitions are employed for the "reduced variables",

$r^* = r/r_m$	reduced intermolecular distance
$b^* = b/r_m$	reduced impact parameter
$\varphi^* = \varphi/\epsilon$	reduced intermolecular potential
$T^* = kT/\epsilon$	reduced temperature
$g^{*2} = \frac{1}{2}\mu g^2/\epsilon$	reduced relative kinetic energy

then the reduced quantities $Q^{(\ell)\star}(g^*)$ and $\Omega^{(\ell,s)\star}(T^*)$ have the following form:

$$Q^{(\ell)\star}(g^*) = \frac{2}{\left[1 - \frac{1}{2}\,\frac{1+(-1)^\ell}{1+\ell}\right]} \int_0^\infty (1-\cos^\ell\chi)\, b^*\, db^* \tag{4}$$

$$\Omega^{(\ell,s)\star}(T^*) = \frac{2}{(s+1)!\,T^{*s-2}} \int_0^\infty e^{-g^{*2}/T^*}\, g^{*2s+3}\, Q^{(\ell)\star}(g^*)\, dg^* \tag{5}$$

where the quantities $Q^{(\ell)\star}(g^*)$ and $\Omega^{(\ell,s)\star}(T^*)$ are defined as

$$Q^{(\ell)\star} \equiv \frac{[Q^{(\ell)}]}{[Q^{(\ell)}]_{\text{rig sphere}}} = \frac{Q^{(\ell)}}{\left[1 - \frac{1}{2}\,\frac{1+(-1)^\ell}{1+\ell}\right]\pi r_m^2} \tag{6}$$

and

$$\Omega^{(\ell,s)^*} \equiv \frac{[\Omega^{(\ell,s)}]}{[\Omega^{(\ell,s)}]_{\text{rig sphere}}} = \frac{\Omega^{(\ell,s)}\sqrt{2\pi\mu/kT}}{\frac{1}{2}(s+1)!\left[1-\frac{1}{2}\,\frac{1+(-1)^\ell}{1+\ell}\right]\pi\eta_m^2} \qquad (7)$$

a. The coefficient of viscosity To a first approximation the viscosity of a pure gas is given in practical units as

$$[\eta]_1 \times 10^7 = 266.93\,\frac{\sqrt{MT}}{\eta_m^2\,\Omega^{(2,2)^*}(T^*)} \qquad (8)$$

where η has the units g-cm^{-1}-sec^{-1}, T is in $^\circ$K., M is the molecular weight and η_m is the collision diameter in angstroms. Higher order approximations to the viscosity are given by the equation

$$[\eta]_k = [\eta]_1 f_\eta^k \qquad (9)$$

where f_η^k is a slowly varying function of integrals $\Omega^{(\ell,s)^*}(T^*)$ and, therefore, T*; it differs only slightly from unity. This function as far as the third approximation ($k = 3$) has been tabulated by Mason[4], where the functions f_λ^k and f_D^k, to be defined below, may also be found.

b. The coefficient of thermal conductivity The coefficient of thermal conductivity, λ, in cal-cm^{-1}-sec^{-1}-$^\circ$K^{-1} is given in the first approximation by

$$[\lambda]_1 \times 10^7 = 1989.1 \frac{\sqrt{T/M}}{\pi_m^2 \Omega^{(2,2)*}(T^*)}$$

$$= \frac{15}{4}\frac{R}{M}[\eta]_1 \times 10^7 \qquad (10)$$

The second equation describes the well-known relationship between λ and η in which R is the gas constant. As with Eq. (9), higher order approximations are given by

$$[\lambda]_k = [\lambda]_1 f_\lambda^k = \frac{15}{4}\frac{R}{M}[\eta]_1 \frac{f_\lambda^k}{f_\eta^k} \qquad (11)$$

For polyatomic gases, where energy transfer may occur between translational and internal degrees of freedom, Eq. (11), should be modified to read

$$[\lambda]_1^{\text{Eucken}} = \frac{15}{4}\frac{R}{M}[\eta]_1 \left(\frac{4}{15}\frac{\tilde{C}_v}{R} + \frac{3}{5}\right) \qquad (12)$$

in which $\tilde{C}_v$ is the heat capacity per mole. For a monatomic gas, $\tilde{C}_v = \frac{3}{2}R$ and Eq. (12) reduces to Eq. (11).

The presence of internal degrees of freedom does not affect the expressions for η and D in terms of the distribution functions and flux vectors. The heat flux vector, $\vec{q}$, (cf. Appendix I, Eq. (I.21)) on the other hand, is altered by a term representing the internal energy. In addition, the time lag in the transfer of energy from the translational to the internal degrees of freedom presents a second modification for the coefficient of thermal conductivity of a polyatomic molecule. The exact expression for λ depends upon the

transition probabilities for energy transfer among the various degrees of freedom of the molecule, but the simpler expression due to Eucken[23] has very often been used to estimate the effect of internal degrees of freedom on the thermal conductivity. A fuller discussion of this point may be found in Hirschfelder[24] where it is pointed out that the Eucken correction is applicable at sufficiently high temperatures that the transfer from translational to internal degrees of freedom is a relatively easy and rapid process.

c. The coefficient of self-diffusion For a gas with but a single component the coefficient of "self-diffusion" in cm^2-sec^{-1} may be written as

$$[D]_1 \times 10^7 = 26280 \frac{\sqrt{T^3/M}}{p\, \sigma_m^2\, \Omega^{(1,1)*}(T^*)} \qquad (13)$$

in which p represents the pressure in atmospheres. In the usual manner, higher order approximations have the form

$$[D]_k = [D]_1 f_D^k \qquad (14)$$

If all the molecules of a gas are physically indistinguishable, then measurement of their interdiffusion is not possible and D is meaningless. If, however, two isotopic forms of a gas are available or if ortho and para forms exist, then D can be measured and provides still another source of information concerning intermolecular forces.

d. The equation of state and the second virial coefficient A formal development of the equation of state may be made by

the standard techniques of statistical mechanics. The results may be represented in several fashions, one of which leads to an expression for the pressure in terms of the <u>configurational integral</u> Q, defined as

$$Q(T) = \int \cdots \int e^{-\varphi(r_1, r_2, \cdots r_N)/kT} \, dr_1 \cdots dr_N \quad . \qquad (15)$$

If thereare N molecules in a gas and the total potential energy can be written as a sum over <u>pairs</u> of molecules, then Eq. (15) has the form

$$Q_N(T) = \int \cdots \int e^{-\frac{1}{2}\sum_i \sum_j \varphi(r_{ij})/kT} \, dr_1 \, dr_2 \cdots dr_N \quad . \qquad (16)$$

In terms of Eq. (16), the equation of state may be derived from the expression

$$pV = kT \left(\frac{\partial \ln Q_N(T)}{\partial \ln V} \right)_T \qquad (17)$$

It is possible to develop ln Q_N (T) as a power series in the number density N/V leading to the "virial expansion" form of the equation of state:

$$\frac{pV}{nRT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2} + \cdots \qquad (18)$$

in which B(T), C(T), ... are the second, third, ... virial coefficients. The virial coefficients are functions only of

the temperature and it may be shown that they are given as integrals which contain the intermolecular potential[25]. If the quantity $f_{12} \equiv (e^{-\varphi(r_{12})/kT} - 1)$ is employed and only spherically symmetric potentials considered, then B(T) becomes

$$B(T) = -2\pi \tilde{N} \int_0^\infty f_{12} r_{12}^2 \, dr_{12} \tag{19}$$

where $\tilde{N}$ is the Avogadro number.

Rice and Hirschfelder[26] have calculated the second virial coefficients of a gas obeying the Exp-Six potential (Eq. (1)), and the results may be expressed in the very simple form:

$$B(T) = b_0 B^*(\alpha, T^*) \tag{20}$$

where $B^*(T^*)$ is a tabulated function of T* defined in a manner similar to the $\Omega^{(l)*}$ and $\Omega^{(l,s)*}$ of the previous sections, and $b_0 = (2\pi \tilde{N} r_m^3)/3$. The quantity b_0 is just the second virial coefficient for a rigid sphere model.

B. <u>The Computation of Collision Integrals $\Omega^{(l,s)*}(\alpha, T^*)$</u>

The details of the technique for numerical evaluation of the reduced collision integrals $\Omega^{(l,s)*}(T^*)$ are discussed by Mason[4]. For an Exp-Six potential the functions $\Omega^{(l,s)*}$ become dependent on the parameter α in addition to the reduced temperature T*. The functions $\Omega^{(l,s)*}(\alpha, T^*)$ vary quite rapidly for small values of T* and unless

tabulations are made for very small intervals in T* interpolation becomes quite difficult. For this reason, Mason found it more convenient to tabulate the function $\Omega^{(\ell,s)*}(\alpha,T^*)$ multiplied by a function of both T* and α in such a way that the product varied only relatively slowly with T* and was finite and independent of α for $T^* = 0$. However, in order to use Eqs. (8), (10) and (13) for calculations of η, λ and D, it became necessary to compute the integrals $\Omega^{(\ell,s)*}(\alpha,T^*)$ explicitly. The results are tabulated in Appendix II, where $\Omega^{(2,2)*}(\alpha,T^*)$ is given for a variation of α from 12 to 17 and for T* from 0.1 to 200. The computations cover all the practical cases for T* and for all realistic values of α. The inherent error of the entries, based on the tabulations of Mason, is estimated to be of the order of 0.2 percent, except for small T* where it may be as large as one percent. The computations are tedious and since relatively little data are available for self-diffusion, which requires $\Omega^{(1,1)*}$, the latter functions were calculated only when needed and at widely separated points: no tabulation for $\Omega^{(1,1)*}$ is included.

C. Determination of the Potential Parameters Several different methods have been used for the determination of the potential parameters from experimental results on transport coefficients[9] and second virial coefficients[27]. The method employed in this research was based on the technique described by Mason and Rice[28], and was simple, accurate and permitted the simultaneous fit of several different gas properties with

relatively little calculation.

The method employed was as follows:

The second virial coefficient of a pure gas is given by Eq.(20) as $B(T) = b_o B^*(\alpha, T^*)$, where $T^* = \frac{kT}{\epsilon}$, and $b_o = \frac{2}{3}(\pi r_m^3 \tilde{N})$, and the parameters α, r_m, and ϵ are defined in connection with the Exp-Six potential, Eq. (1). Taking the logarithms of B(T) and T* one obtains

$$\log B(T) = \log B^*(\alpha, T^*) + \log b_o \qquad \text{a.}$$

$$\log T = \log T^* + \log(\epsilon/k) \qquad \text{b.} \qquad (21)$$

A plot of the tabulated quantities $\log B^*(\alpha, T^*)$, vs $\log T^*$ yields a family of curves, one for each value of α. From Eqs. (21) it is clear that a plot of the experimental quantities log B(T) vs log T should be superposable by parallel translation of axes on one of the theoretical curves. From the ammount of translation parallel to the B(T) axis, it is evident that $\log b_o$ may be directly determined, and the quantity $\log(\epsilon/k)$ is determined by the ammount of translation parallel to the T axis. The parameter r_m is directly obtainable from b_o, and the third parameter α has, of course, already been determined by the decision to superpose the experimental plot on a particular member of the family of theoretical curves. A plot of the reduced quantities $\log B^*(\alpha, T^*)$ and $\log T^*$ was made and is illustrated in Figure 2. The decision to calculate and plot $\log[-B^*(\alpha, T^*)]$ rather than a positive $B^*(\alpha, T^*)$ was governed by the fact

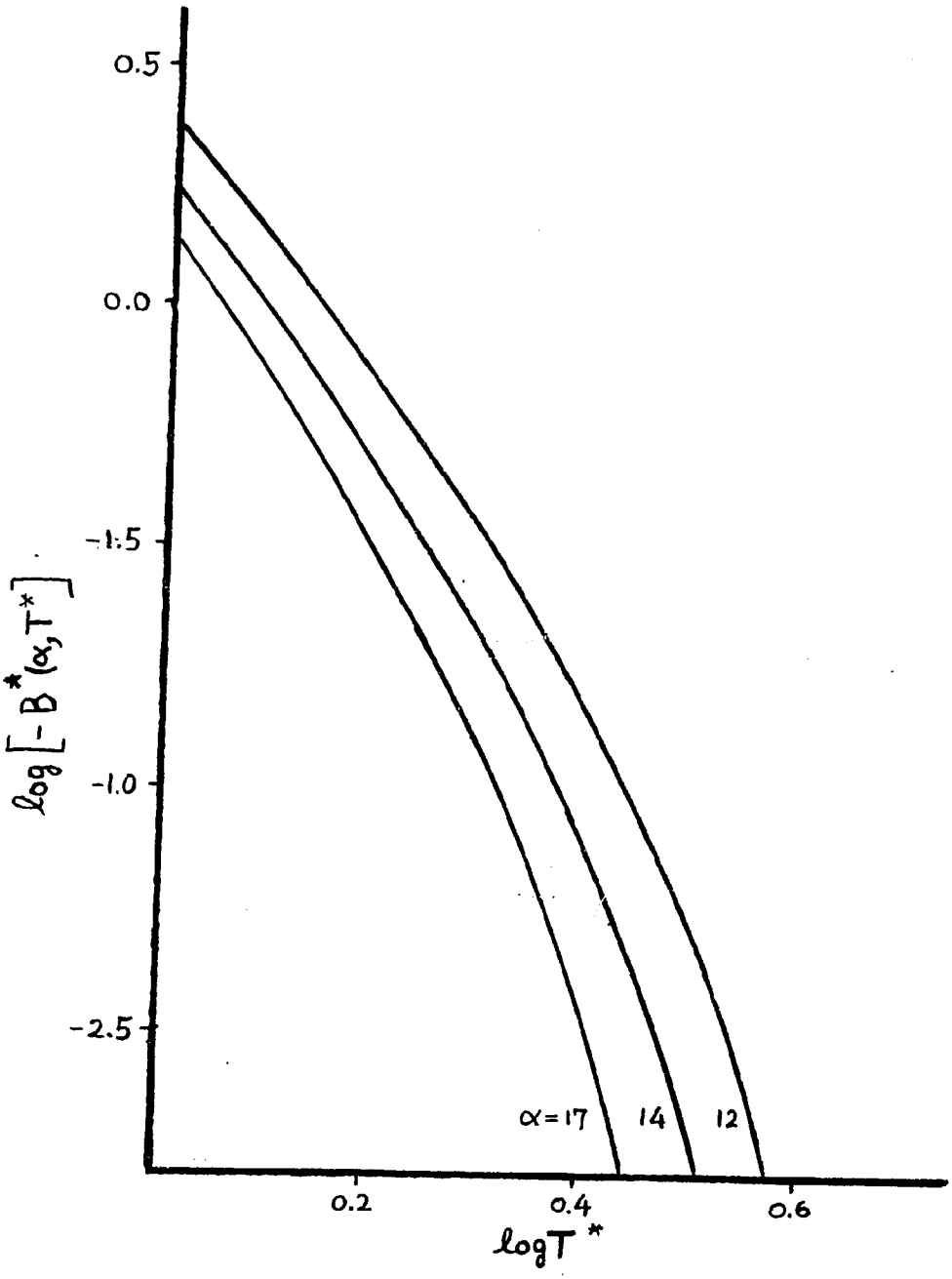

Fig. 2 A Plot of the Reduced Quantities for Virial Coefficients

that at most temperatures of interest the gases chosen had negative values of B(T).

An analogous procedure may be employed to obtain the potential parameters from viscosity data. Starting with the definition of T* and Eq. (8) to the third approximation, one obtains

$$\log \frac{10^7 \eta}{(MT)^{1/2}} = \log \frac{f_\eta^{(3)}}{\Omega^{(2,2)*}} + \log(266.93) - 2\log \eta_m$$

$$\log T = \log T^* + \log(\epsilon/k) \qquad (22)$$

As with the second virial coefficient, a plot of the theoretical quantities $\log \left[f_\eta^3 / \Omega^{(2,2)*} \right]$ vs $\log T^*$ yields a family of curves, over one of which the experimental quantities $\log \left[10^7 \eta / (MT)^{1/2} \right]$ vs $\log T$ may be superposed by parallel translation of axes. Translation along the η axis determines $\log \eta_m$, translation along the T axis determines $\log (\epsilon/k)$, and the particular theoretical curve over which the experimental data are superposed determines α explicitly. Figure 3 illustrates the nature of the graphs obtained when the theoretical quantities were plotted.

The procedures described above may be employed for any potential function, and during the early, exploratory stages of this research the available data were used to calculate the characteristic potential parameters of argon, methane and ethane for both the Exp-Six and Lennard-Jones potentials. The lack of data for ethane reduced the reliability of the results for that compound, but for argon and methane preliminary evaluations of the parameters were

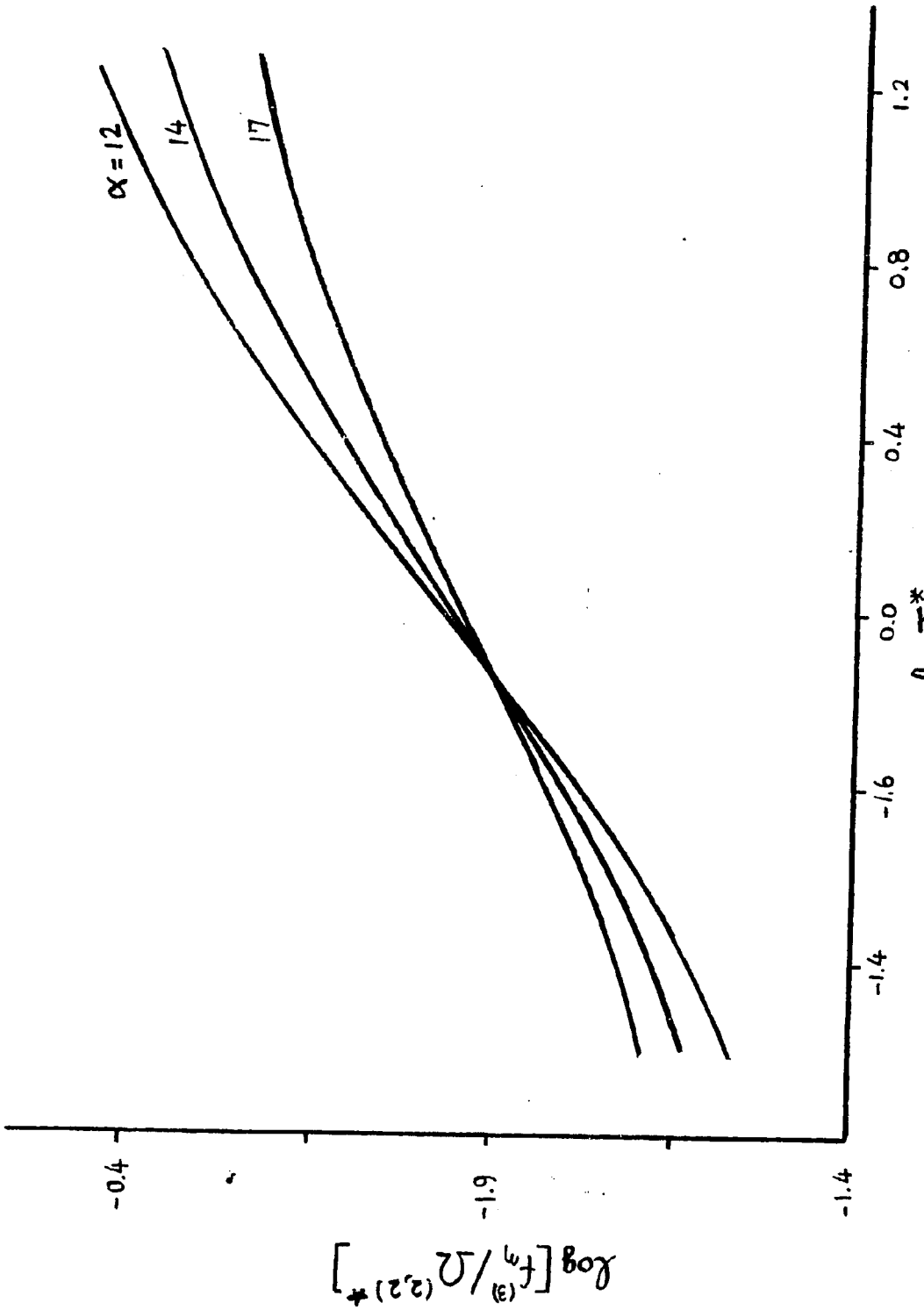

Fig. 3 A Plot of the Reduced Quantities for Viscosity

possible, and the calculated values agreed fairly well with the reported values. It was also observed that if the ratio of the characteristic distance parameters for the two different potentials was formed (σ/r_m), then the values obtained were very nearly equal. In view of this feature of the distance parameters, the corresponding ratio was calculated for most of the remaining inert gases (having spherically symmetric potentials), and it was found that for all of the gases examined, A, Ne, Kr, Xe, and CH_4, the ratio of the distance parameters was very nearly constant. Helium was not considered, since different values for the parameters were obtained depending on whether quantum or classical theory was used. For radon no reliable data were available.

Because the assumption that a formal relationship between the two parameters would serve as a method for estimating the first approximation to r_m when σ was known from the Lennard-Jones parameters, an equation was derived relating the ratio (σ/r_m) to α and the ratio of the depth of the minima observed for the (12-6) and Exp-Six potentials. In Appendix III it is shown that this equation has the form

$$(\sigma/r_m) = 2\beta^4 \left[\epsilon^*(26\beta^6-7)\frac{1}{\alpha}\frac{(\alpha-6)}{(\alpha-7)}\right]^{1/2} \qquad (23)$$

where β is a constant and $\epsilon^* = (\epsilon_L/\epsilon_E)$, the ratio of the depths of the two different potential wells. A fuller discussion of Eq. (23) can be found in Appendix III, along

with comparisons of "theoretical" values calculated from Eq. (23) and experimentally derived values of (σ/π_m). The agreement for spherically symmetric molecules is generally better than 1.0 percent, but for nitrogen, carbon monoxide and ethane the disagreement is as large as 2-3 percent, indicating that the assumption upon which Eq. (23) was based is probably wrong for molecules which do not have spherical symmetry.

PART THREE

EXPERIMENTAL DESIGN AND PROCEDURE

A. The Choice and Theory of the Method The experimental methods which have been employed for the determination of the viscosities of gases fall mainly into two groups. In the first method, the gas is forced through a capillary tube and the pressure difference between the ends of the tube, along with the volume transferred per unit time are measured. In the second method, a solid disc, cylinder or sphere is moved in the gas, in most cases very close to a fixed disc, cylinder, or concentric sphere, and the force exerted is measured in a suitable way. The two techniques are generally referred to as the "transpiration" and "viscous reaction" methods respectively. The transpiration method -- the method employed in this research -- was used as a comparitive method by Faraday[29], and later by Meyer[30]. More recent measurements by this technique have been made by Partington[31], and a large number of measurements have been reported by Trautz and collaborators[32].

The principle of the transpiration method depends on Poiseuille's law:

$$\frac{V}{t} = \frac{\pi}{8} \frac{P_1 - P_2}{L} \frac{r^4}{\eta} \qquad (24)$$

where V is the volume of the gas in cm^3, measured at a fixed temperature and under a mean pressure of $(P_1 + P_2)/2$, which flows in t secs. through a straight capillary of length L cm. and radius r cm. when the entrance and exit pressures are, respectively, P_1 and P_2 dynes-cm^{-2}. Poiseuille's equation

may be easily derived for an incompressible fluid[33], and Eq. (24) results. The application of Eq. (24) to a compressible fluid requires, however, some justification.

In the case of a gas, V varies with the pressure along the tube and also changes with temperature, being different for isothermal and adiabatic flow. For a very small pressure difference dP, Eq. (24) may be written as $dV = (\pi r^4/8\eta L)dP$, where dV represents the flow per second. Also $dV = dn\,(RT/P)$ for an ideal gas, and therefore

$$dn = \frac{\pi r^4}{8L\eta RT} P\,dP$$

or

$$n = \frac{\pi r^4}{8LR} \int \frac{P\,dP}{\eta T} \tag{25}$$

For isothermal flow (T constant) η is constant, hence:

$$m = \frac{\pi r^4}{8LRT\eta} \int_{P_2}^{P_1} P\,dP = \frac{\pi r^4}{8LRT\eta} \cdot \frac{P_1^2 - P_2^2}{2} = \frac{\pi r^4 (P_1 - P_2)}{8LRT\eta} \cdot \frac{P_1 + P_2}{2} \tag{26}$$

If the volume V is measured under an average pressure $(P_1 + P_2)/2 = \overline{P}$ then

$$\frac{mRT}{\overline{P}} = V = \frac{\pi}{8} \frac{P_1 - P_2}{L} \frac{r^4}{\eta} \tag{27}$$

showing that Eq. (24) or (27) is applicable to gases providing only that the gases be measured at the suitable pressure, $\overline{P}$. Several corrections have been suggested for the Poiseuille equation, some of which will now be discussed.

Firstly, Poiseuille's law holds only for stream-line flow through the capillary, a condition determined by the dimensions of the capillary, the pressure difference and the viscosity of the fluid gas, all of which regulate the linear velocity of fluid passing through the capillary. According to Reynolds, turbulent flow replaces laminar flow when the linear velocity V exceeds the value given by

$$\rho \frac{d V}{\eta} = 2000 \qquad (28)$$

where d is the diameter and ρ the density of the fluid and the quotient equal to 2000, is a dimensionless number called the Reynolds number. Eq. (28) applies also to gases, for which Dowling found a higher value of the Reynolds number[34]. The condition for laminar flow is that $v < V$, and it is easy to show that under the conditions of the experiments described herein, v was always appreciably less than V: e.g., oxygen at 27°C, with a viscosity of 2071×10^{-7} g-cm^{-1}-sec^{-1} in a capillary of 1.0 mm. diameter has a value of $V \doteqdot 2.9 \times 10^{4}$ cm-sec^{-1}, while v as calculated from the measured values of volume transfered per unit time at the same temperature has a value $v \doteqdot 2.9 \times 10^{2}$ cm-sec^{-1}, a coincidence of multipliers which results in the numerical ratio $v/V \doteqdot 0.01$.

Another amendment often suggested to the Poiseuille

equation is the so-called "Hagenbach correction"; an attempt to compensate for the kinetic energy of the moving fluid. This correction, however, becomes negligible for long and narrow capillaries (implying large t), and since the times measured in this research were of the order of hundreds of seconds at the lower temperatures to thousands of seconds at the higher temperatures, no attempts were made to apply the Hagenbach factor. Finally, at the ends of the capillaries, and particularly at the entry end, it is possible that the motion of the fluid is not laminar or parallel to the wall. The result is the same as if, on account of the greater resistance, the gas traverses a greater length of capillary than is actually the case. A method of obviating this difficulty is to add to the actual length of the capillary a fictitious length λ , which Couette found was approximately $\lambda \doteq 3d$, where d is the diameter of the capillary. However, since the viscosities were measured by a comparative technique, to be described in the following paragraph, such a correction was unnecessary and the Poiseuille law was used in the form of Eq. (24).

The method employed to determine the viscosity of a gas may be described as follows:

For a substantial flow Eq. (24) may be written as $\Delta V/\Delta t = (\pi r^4/8L)\frac{\Delta P}{\eta}$, and since for a fixed capillary r, L, are all constant, then $\Delta V/\Delta t = (K/\eta)\Delta P$. This implies that a plot of $\Delta \dot{V} = \Delta V/\Delta t$ versus ΔP should be a straight line whose slope is inversely proportional to the viscosity. If, therefore, some gas of known viscosity is

passed through the capillary at fixed temperature and the ratio (K/η) for this gas is compared with the corresponding quantity for some gas of unknown viscosity, then to the extent that the slopes are indeed constant (a question to be discussed in a later section) the ratio of the quantities (K/η) is inversely proportional to the ratio of the viscosities. Since the viscosity of the standard is assumed to be known, the unknown viscosity may be directly determined.

B. Apparatus Design The apparatus employed to measure the viscosities of argon, methane, and ethane may be briefly described as consisting of a pair of capillary tubes immersed in a constant temperature bath, with provision for measuring both the pressure difference developed across the capillaries and the volume of gas transported during a given time interval, i.e., the flow rate. Each of these components will now be discussed seperately.

a. The capillary system In order to avoid any problems arising from irregularly drawn capillaries, two capillary tubes of Trubore Pyrex were obtained from the Fish-Schurman Company, having internal diameters of 1.000 and 0.750 mm. with a tolerance of $\pm$0.001 mm.. The capillary system consisted of two capillary tubes of 10 and 15 cm. lengths (the longer being the capillary of bigger radius) joined to 7 mm. Pyrex tubing bent in the shape of a "U" of approximately 16 inches depth. The two U-shaped tubes were joined by means of two-way stopcocks to single inlet and outlet tubes which

extended beyond the stopcocks about 5 inches. Each of the extending tubes was provided with an outlet tube, containing a trap, which was joined to the two arms of an oil manometer by Tygon tubing. The total distance between the tips of the outlet and inlet tubes was 26 inches; between the stopcocks, 16 inches; and across the open end of the two U-shaped sections, 3 inches. In addition, a shunt tube containing a one-way stopcock led from one of the manometer outlets to the other. This shunt tube made it possible to flush the main sections of the capillary system with the experimental gas before the gas was allowed to pass through one of the capillaries, thereby producing a pressure difference across the manometer. In addition, the shunt could be used to divert experimental gas away from the capillaries, if the flow rate was so great as to produce unfavorably large pressure differences tending to cause overflow from one of the manometer arms. Figure 4 illustrates the capillary system.

b. The constant temperature bath The constant temperature bath consisted of a Pyrex cylinder-jar of 6 inch diameter and 14 inches high, embedded in a Styrofoam insulation jacket having a minimum thickness of 2 inches and resting on a platform securely attached to a metal lattice. Since the viscosities were measured at temperatures from ca. 200°K. to temperatures approaching 500°K., it became necessary to select as a fluid for the bath a substance suited to these conditions. For the region from 285°K. to 500°K. the bath was filled to a height of 12 inches with Dow Corning 550

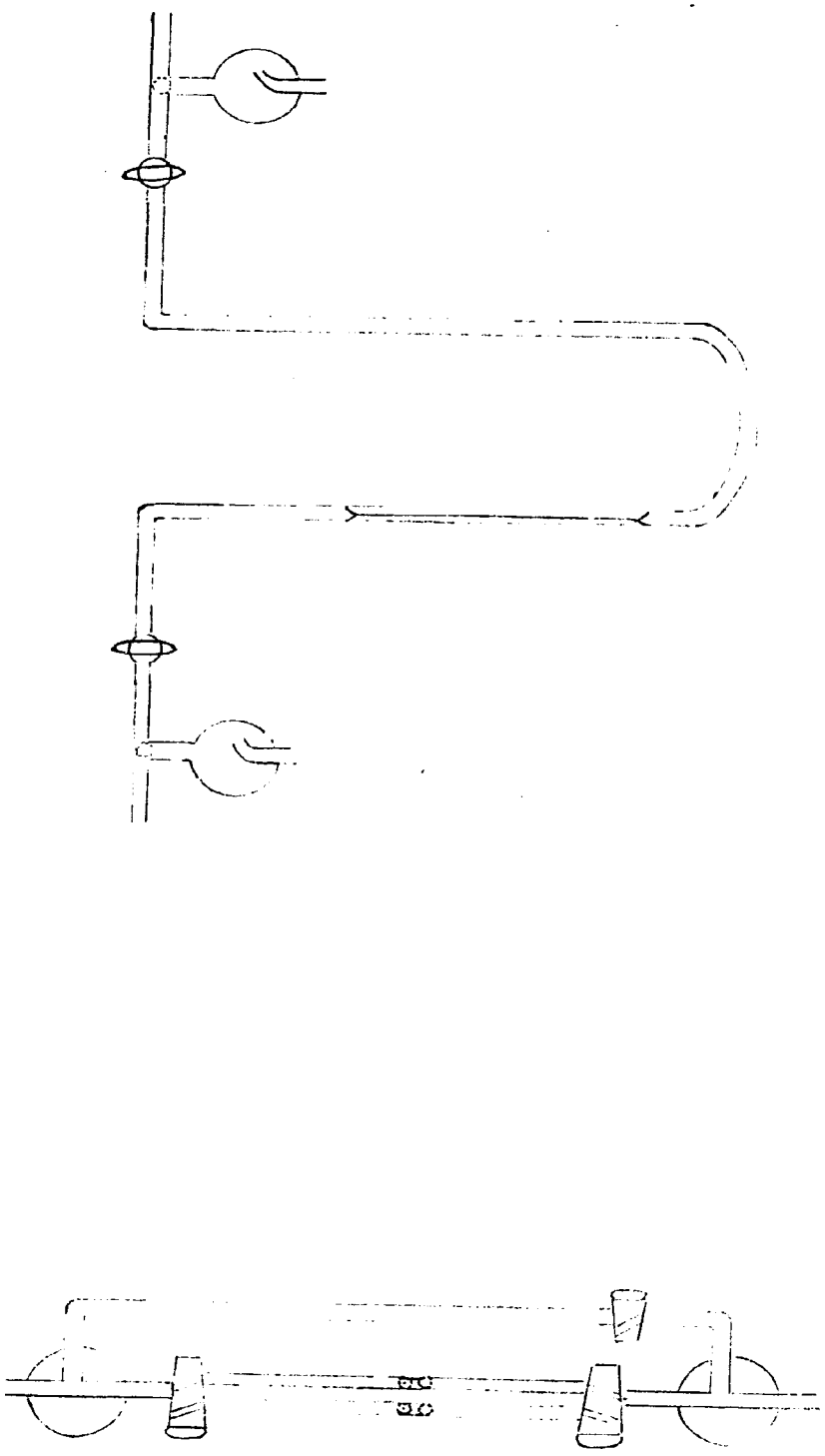

Fig. 4 The Capillary System

Fluid, a silicone oil of exceptional heat endurance, high resistivity to oxidation, low volatility, a high flash point, and a relatively flat viscosity-temperature slope even beyond 500 K.. For the measurements made at 0°C, -22.9°C and-63.5°C, the Pyrex jar and insulation were replaced by a large Dewar of four-liter capacity containing cracked ice and water at 0°C, and slush baths of carbon tetrachloride and chloroform at -22.9°C and -63.5°C respectively: the slush baths were prepared according to the instructions given by Sanderson[35].

From room temperature to 500°K., the bath temperature was regulated by a DeKhotinsky Thermoregulator, based on the expansion or contraction of a bimetallic strip with temperature changes. In order to prevent arcing across the Thermoregulator contacts, a 0.04 mfd. condensor, suitable for loads up to 150 watts, was connected across the contact leads. The heating element was a 125 watt, 115 volt Cenco Lagless Knife Type Blade Immersion Heater connected in series with the Thermoregulator. For convenience a General Electric AR 1 argon pilot lamp was joined in parallel across the heater to indicate when the regulator contacts were open or closed: this provided a qualitative estimate of the sensitivity of the Thermoregulator. The operation of the entire heating and regulating system was controlled by a switch in series with the pilot lamp. The bath was agitated by means of a 24 x ¼ inch stainless steel rod over which three 2 x 5/8 x 1/16 inch stainless steel blades were slipped through ¼ inch holes drilled in the center of the blades, and soldered into place at four inch intervals starting

3 inches from the bottom. The stirring mechanism was supported at the top by passing the upper end of the rod through a 4-inch metallic sleeve, made from a No. 3 cork borer, which was held in a 1-hole rubber stopper fitted into a 4-inch length of glass tubing of 2-inch O.D.. The glass sleeve was held in place by a 3-pronged clamp joined to a secure metal lattice, and passed through the upper level of Styrofoam insulation to a point just above the liquid level. At the bottom, the stirring-rod rode on a small screw set ¼ inch below the surface of a No. 12 solid rubber stopper with the bath fluid serving as an excellent lubricant. The stirring mechanism was driven by a Sargent Cone Drive Stirring Motor, and through removeable cylindrical sections cut from the sides of the insulating jacket, small shavings of rubber which had been added to the bath could be seen in agitated motion, even with the driving cone set at small diameters.

The cylindrical sections mentioned above served a second purpose, inasmuch as the bath temperature could be read through these openings from a National Bureau of Standards 3-inch immersion mercury thermometer, N.B.S. No. 26307, graduated in degrees from -15°C to 200°C. The temperatures could be read to a degree and estimated to ± 0.1 degree with a calibration error of not more than 0.1 degree over the whole temperature range and a quoted accuracy of 0.1 to 0.3 degree[36] (no measurable deviation could be observed at the ice point and boiling point of water).

In operation, no detectable changes could be observed

in the bath temperatures, even at temperatures approaching 200°C. Since the temperatures could be read to a spread of 0.2 degree, it may be claimed that the bath temperatures suffered no greater a variation than this; somewhat greater than the practical limit of the type of Thermoregulator employed. This limit on the possible variation of the temperature was entirely satisfactory for the purposes of this investigation, since it can be very easily shown that the changes produced in the viscosities of any of the gases employed and at all the temperatures considered (including the slush bath temperatures) were never more than ½ percent when the most unfavorable values for the Sutherland constant were selected. Figure 5 shows a cross-section of the temperature bath with the capillary system in place.

c. The oil manometer A very simple oil manometer was constructed by bending a piece of 7 mm. glass tubing in the form of a "U" to fit around a meter stick, to which the tubing was joined by fine copper wire passing around the tubing and through fine holes drilled in the meter stick. The manometer was supported by a simple wooden frame and attached by wood screws with cut-down rubber stoppers between the manometer and mounting acting as an insulation against sudden vibration or shock. The manometer was thoroughly cleaned with dichromate cleaning solution, rinsed, dried and half-filled with mineral oil. The open ends were joined by Tygon tubing to the leads provided by the capillary system.

d. The wet test meter The volumes transferred through

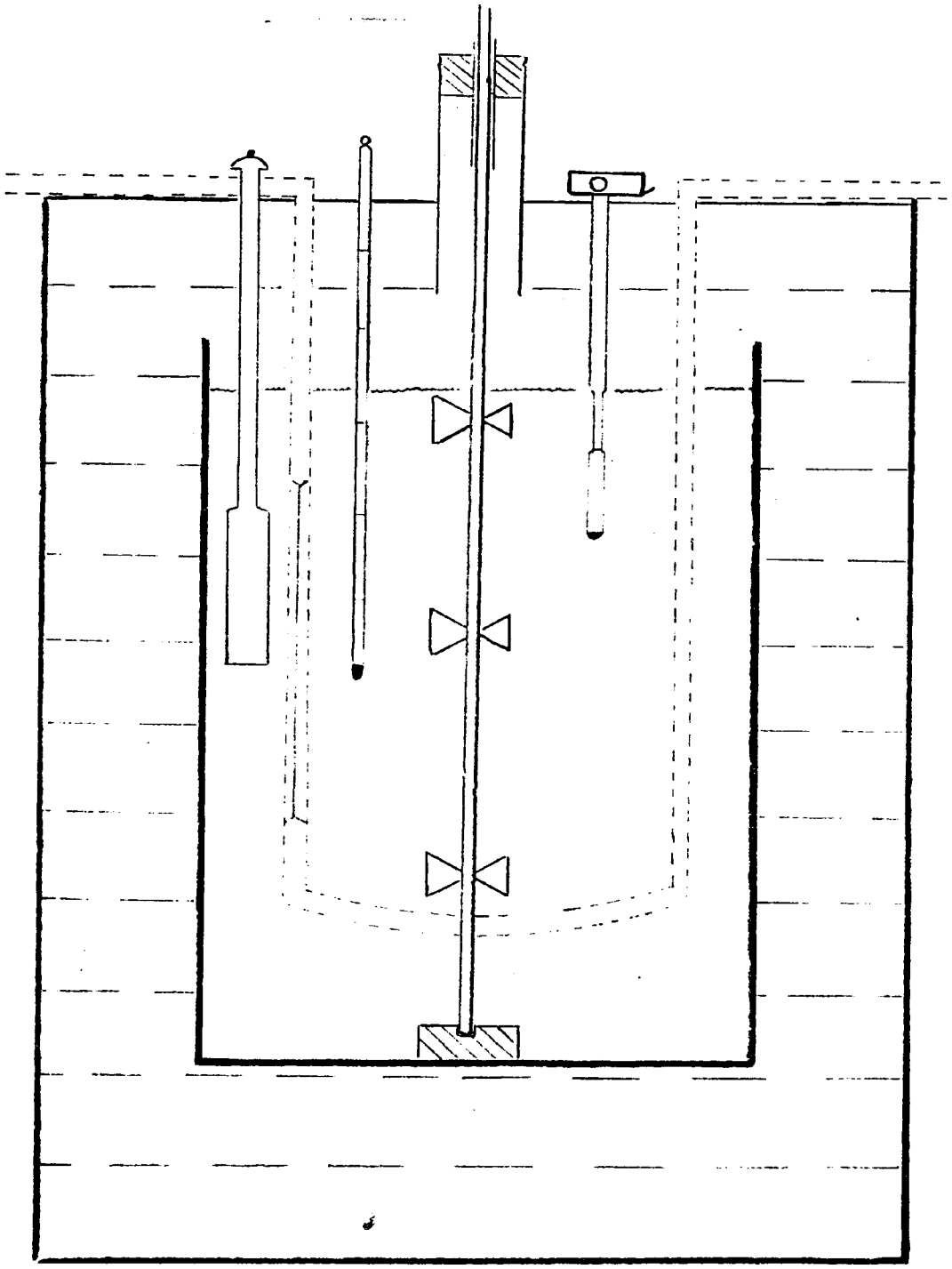

Fig. 5. The Constant Temperature Bath

the capillaries per second were measured by attaching a wet test meter, manufactured by the Precision Scientific Company, to the outlet tube of the capillary apparatus and timing a three liter flow by a Meylan Stop Watch, Type 200A. The measured flow rates were then corrected (following the procedure described by Burwell et al.[37]); first by reducing all the measured volumes to standard conditions, taking into account the vapor pressure of water at the temperature over which the gases were measured, and then by correcting to the average pressure along the capillary, taken as $P_2 + \Delta P/2$, where P_2 is the exit pressure and ΔP the pressure difference along the capillary. The flow rates may then be expressed either in liters per second or in moles per second, but for either case they should be linear with ΔP as long as ΔP is sufficiently small.

C. The Procedure and Standardization of the Method The primary standard upon which all of the measured viscosities were based was the known values of the viscosity of oxygen, chosen in the following manner: for all temperatures up to 300° K., the data of Johnston and McCloskey[38] were employed, which had been corrected to a uniform relative basis by selecting the viscosity of air at 23° C as 1833.0×10^{-7} g-cm^{-1}-sec^{-1}. Beyond 300° K. to the upper limit of the experimental measurements, the best smoothed data of Trautz and Melster[39], Trautz and Zink[40], States[41] and Wobser and Müller[42] were employed. As a check on suitability of the

standards, the viscosities of argon were measured and compared with those reported by several authors, notably Trautz[43] and co-workers, including measurements made by non-comparative techniques. The agreement was always better than ½ percent, and for the measurements made on methane and ethane the measured values of argon were employed as the standard since a large source of highly purified argon was available. As an auxiliary check on the suitability of the standardization, the viscosity of argon was determined at selected temperatures using helium as the reference gas: no significant changes were observed in the measured values of argon. The sources and purities of the gases studied are given in Appendix IV.

The best estimate of the accuracy of the method, based on the propagation of the intrinsic errors in the measurement of ΔV, ΔP, Δt, and T, is 0.5 percent. The agreement of our results with those previously reported for argon is very often better than 0.5 percent indicating, perhaps, that the estimated accuracy is too low. The major weakness of this technique rests in the necessity for having an "exact" standard, the reliability of the standard measuring directly the reliability of the results. It was for this reason that oxygen was chosen as the standard for this research, since a wealth of reliable data was available for oxygen.

The typical procedure followed in the measurement of a viscosity may be described as follows:

A cylinder of the gas to be measured was attached through a calcium chloride drying tube to the inlet of the

capillary system and with the shunt tube open, the system flushed with approximately a 3-liter flow. The bath had already been allowed to come to equilibrium at the desired temperature, and after the system was flushed, the gas diverted to one of the two capillaries by means of the two-way stopcocks, and by adjusting the needle valve on the tank, a pressure difference of approximately 10-15 cm. of oil was developed across the chosen capillary. In order to permit the pressure difference to equilibrate and the gas to equilibrate with the bath temperature, another 3-liter flow was allowed. No changes in the pressure difference were observed after 3-liters were permitted to pass through the system. The gas entered the system from the needle valve at a constant value of 36 p.s.i..

Another 3-liter transfer was then timed, and the ratio $\Delta \dot{V}/\Delta P$ computed in the following fashion. First the volume transferred was corrected to S.T.P. taking into consideration the vapor pressure of water at the temperature over which the gas transfer was measured. This value of ΔV was then cofrected to the average pressure along the capillary, taken as $P_2 + \Delta P/2$ and divided by the time interval and then by the pressure difference ΔP. The above procedure having been previously carried out for the reference gas, the ratio of the measured values of $\Delta \dot{V}/\Delta P$ and the chosen value for the reference viscosity were then compared to yield the unknown viscosity. It was found convenient first to measure $\Delta \dot{V}/\Delta P$ for argon at a fixed temperature and then to measure methane and ethane in succession at the same temperature. In this manner errors were presumably systematic for the

unknown gases.

Poiseuille's law predicts that a plot of $\Delta\dot{V}$ vs ΔP should be linear. Table 1 contains the experimental data obtained for argon and oxygen at 273.16°K; the last entry in each column corresponds to the value of ΔP below which no change in the ratio $\Delta\dot{V}/\Delta P$ was observed, i.e., the limiting slope. Figure 6 shows a plot of $\Delta\dot{V}$ vs ΔP for argon at 300.16°K.. In general, it was observed that as long as the values of $\Delta\dot{V}/\Delta P$ were computed for $\Delta P \leqslant$ 15 cm. of oil, the slopes were constant and the same as the value of the limiting slope determined graphically. In practice, therefore, the slope was determined only at a single point corresponding to $\Delta P \leqslant$ 15 cm., for each gas. This made the experimental procedure relatively rapid with no loss in accuracy.

TABLE 1

THE QUANTITY $\dot{\Delta V}/\Delta P$ FOR ARGON AND OXYGEN AT 273.16°K.

ΔV (liters)		Δt (sec.)		$\dot{\Delta V} \times 10^3$ (Lit-sec^{-1})		ΔP (cm.oil)		$(\dot{\Delta V}/\Delta P) \times 10^3$	
Argon	Oxygen	Argon	Oxygen	Argon	Oxygen	Argon	Oxygen	Argon	Oxygen
2.63	2.64	433.2	408.0	6.071	6.461	34.50	33.15	.17597	.19490
2.63	2.64	608.9	523.2	4.319	5.038	23.70	25.18	.18224	.20008
2.63	2.64	783.7	646.9	3.356	4.075	18.05	20.00	.18593	.20375
2.63	2.64	975.8	694.0	2.695	3.798	14.20	13.40	.18979	.20878

The viscosity of argon at 273.16° K.

$$\eta_{\text{argon}} = 1911 \times 10^{-7} \frac{.20878}{.18979} = 2102 \times 10^{-7} \text{ g-cm}^{-1}\text{-sec}^{-1}.$$

(cf. Table 2)

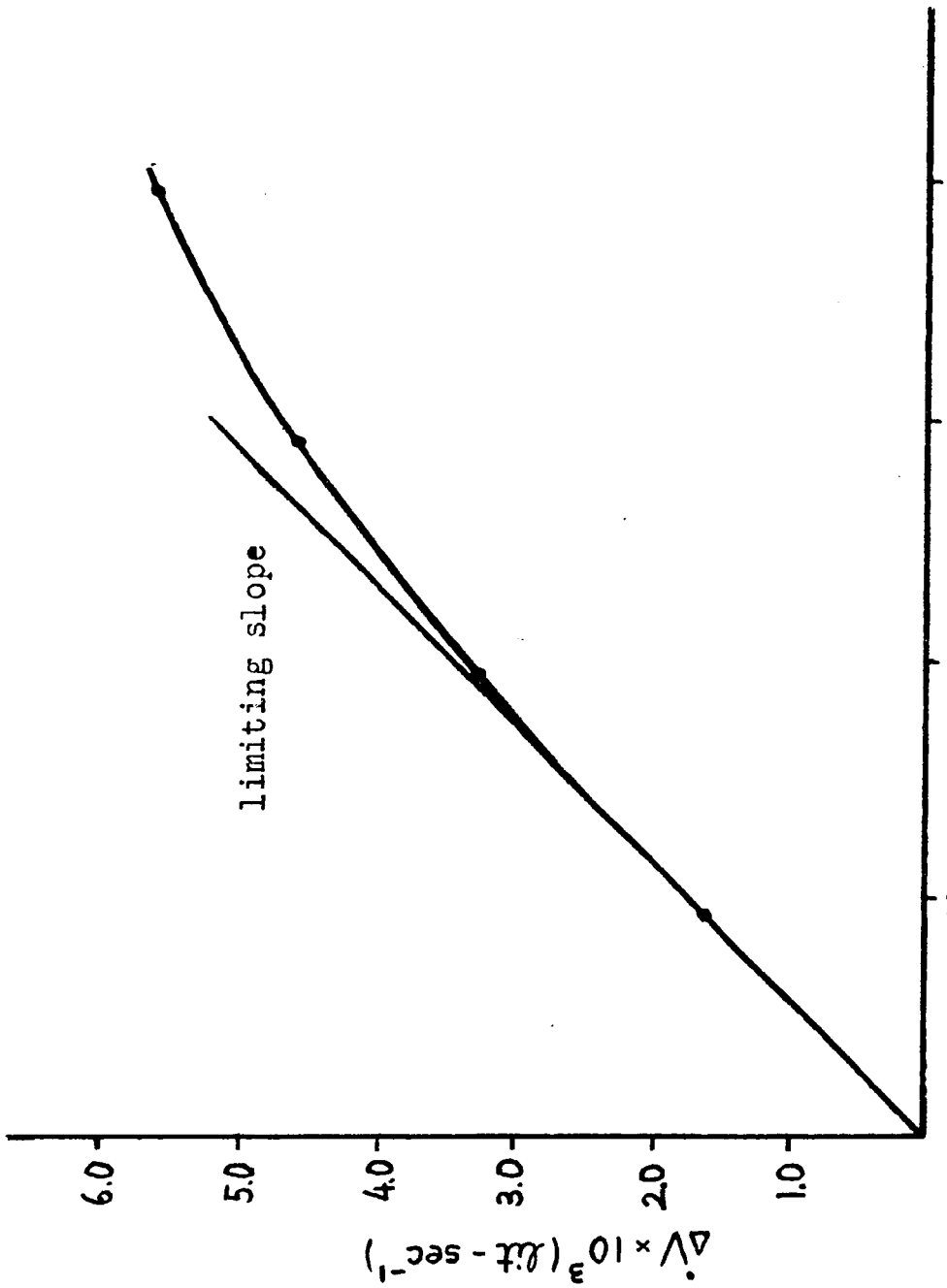

Fig. 6 A Plot of the Flow Rate of Argon vs ΔP

PART FOUR

RESULTS

A. Argon The values obtained for the viscosity of argon by the procedures previously described are collected in Table 2. From these values and the techniques described in Part II C, the following values were deduced for the potential parameters: $r_m = 3.867$ Å, $(\epsilon/k) = 123.0$, and $\alpha = 14$. Figure 7 shows a graph of the viscosity vs temperature computed from the parameters indicated above and Eq. (9). Included for comparison are the data of several other workers along with the present work.

The excellent agreement indicated by Fig. 7 cannot be taken alone as evidence for the suitability of the Exp-Six potential since the viscosity data were used to evaluate the parameters. More suitable evidence for the adequacy of the potential form may be found in a comparison of the calculated and measured values for the remaining transport coefficients, viz., thermal conductivity and self-diffusion coefficients, and for the virial coefficients. Tables 3 and 4 contain the transport coefficients while Figure 8 illustrates the second virial coefficient. The agreement in all cases is very good, giving strong evidence in support of the suitability of the Exp-Six potential form for representing the gaseous behavior of argon.

It was mentioned in the introduction that Mason and Rice[21] had been unable to fit the high temperature viscosity data for argon with an Exp-Six potential. Their suggestion was that the high temperature data for argon were low. Since the experimental data of this research, to the higher limit

TABLE 2

COMPARISON OF OBSERVED VISCOSITIES OF ARGON WITH THOSE CALCULATED FOR THE EXP-SIX POTENTIAL

	$10^7\eta$ g-cm-1-sec-1		
T,°K	Obs	Calc	Obs
210.7	1670	1675	
250.1	1952	1948	
273.16	2102	2095	2114[a*]
293.2	2220	2222	2212[a]
300.3	2267	2270	2273[b]
311.5	2340	2339	
320.3	2389	2392	
328.2	2446	2440	
337.7	2499	2495	
343.0	2523	2528	
353.4	2592	2588	
368.6	2674	2670	2660[a]
381.3	2735	2740	
396.4	2819	2822	
409.1	2896	2890	
423.7	2971	2967	
438.9	3050	3046	
448.2	3099	3094	
461.9	3170	3163	
471.4	3221	3216	3223[a]

a. M. Trautz and W. Ludewigs, Ann. Physik, 3, 409 (1929).
b. H. L. Johnston and E. R. Grilly, J. Phys. Chem., 46, 948 (1942).
* Extrapolated value.

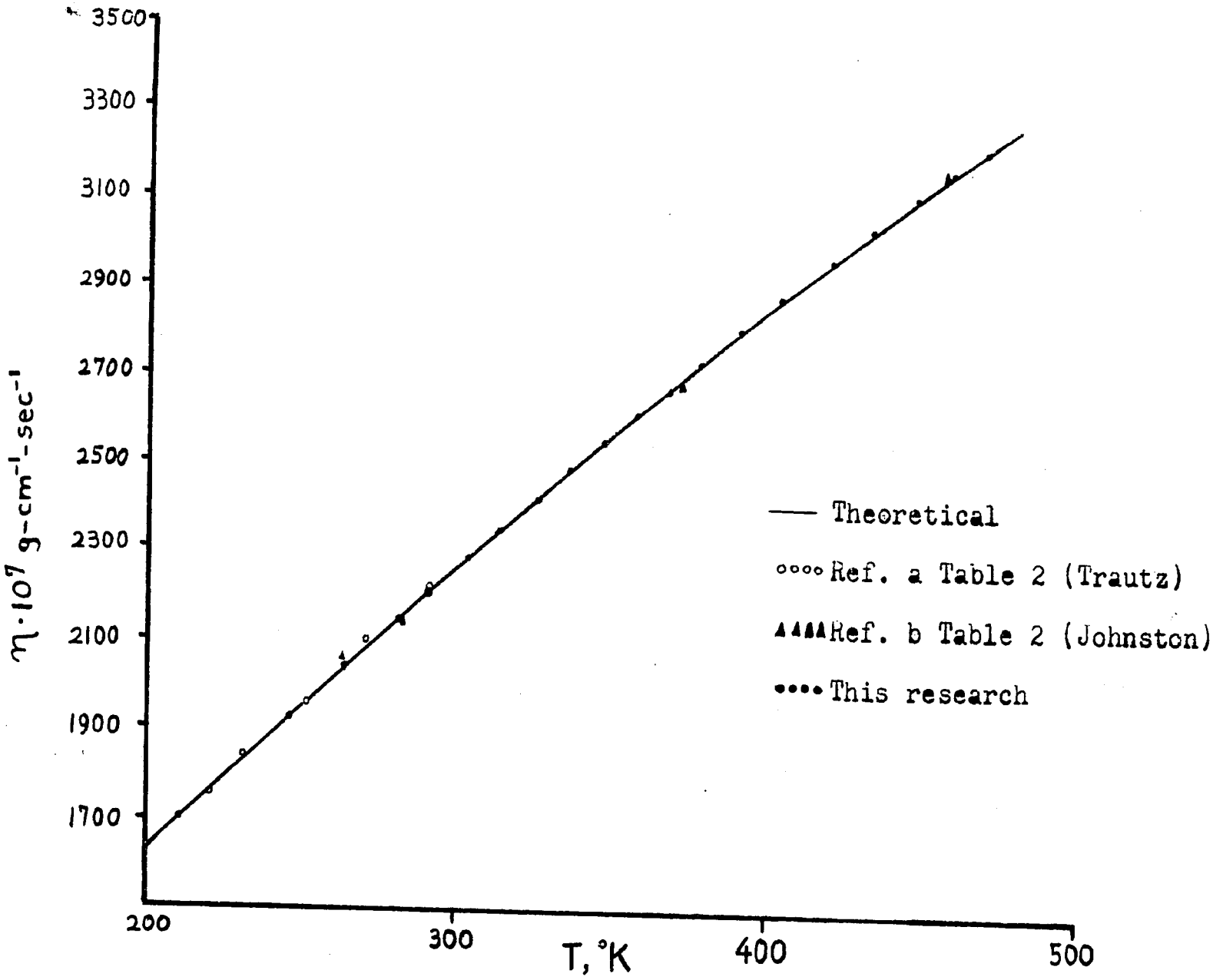

Fig. 7. The Viscosity of Argon vs Temperature

TABLE 3

THERMAL CONDUCTIVITY OF ARGON USING POTENTIAL PARAMETERS FROM VISCOSITY

$10^7\lambda$ cal-cm^{-1}-sec^{-1}-deg^{-1}		
T,°K.	Calc.	Exptl.
90.2	145	141[a]
194.7	293	293[a]
273.2	390	385[b] 390[c] 394[a]
373.2	505	506[a]
491.2	618	614[a]
579.1	690	685[a]

a. W. G. Kammuluik and E. H. Carman, Proc. Phys. Soc. (London), 65B, 70 (1952).
b. S. Weber, Ann. Physik, 54, 323 (1917).
c. T. L. Ibbs and A. A. Hirst, Proc. Roy. Soc. (London), A123, 134 (1929).

TABLE 4

COEFFICIENT OF SELF-DIFFUSION FOR ARGON USING POTENTIAL PARAMETERS FROM VISCOSITY

	D_{11} cm^2-sec^{-1}		
T,°K.	Exp-Six (present work)	Exptl.[a]	Exp-Six[b] (thermal diffusion)
77.7	.0134	.0134	.0134
90.2	.0181	.0180	.0181
194.7	.0825	.0830	.0824
273.2	.155	.156	.155
295.2	.178	.178	.178
353.2	.248	.249	.247

a. E. B. Winn, Phys. Rev., 80, 1024 (1950).
b. M. P. Madan, J. Chem. Phys., 23, 763 (1955).

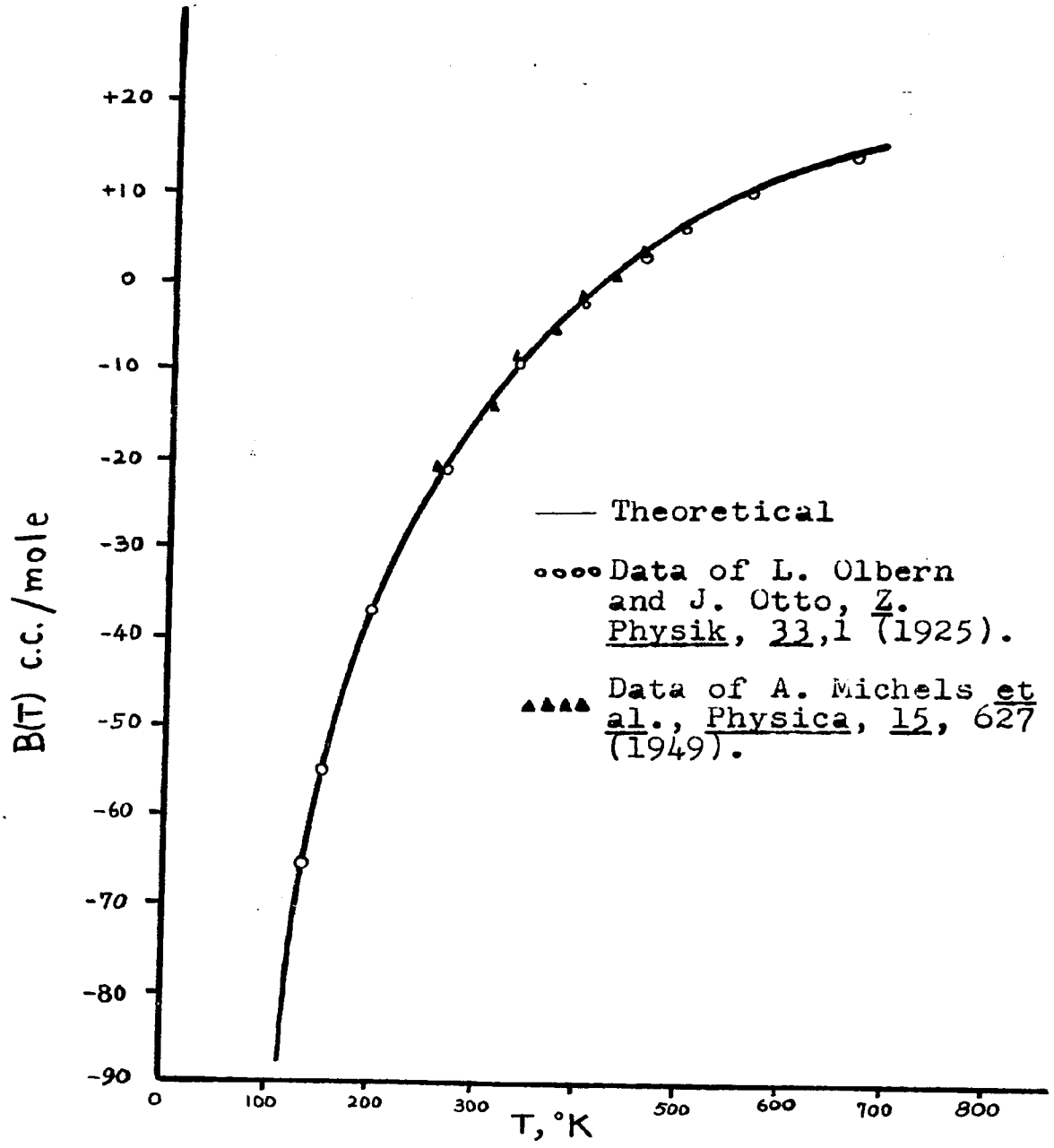

Fig. 8 The Second Virial Coefficient of Argon

of measurement, agree to within 1.0 percent with previously reported values, and furthermore, since the extrapolated values for the calculated curve based on the parameters reported herein always lie very near to the curve of Mason and Rice[21], then it is necessary to conclude in agreement with Mason and Rice that the high temperature viscosities reported for argon are very probably low. Experiments in this direction would be highly valuable.

B. Methane Table 5 contains the present results for the viscosity of methane along with calculated values based on the potential parameters $r_m = 4.209$ Å, $(\epsilon/k) = 152.4$ and $\alpha = 14$, deduced from viscosity. Figure 9 illustrates the temperature dependence of the viscosity and includes data of other workers. The data of this research are on the average about 2.0 percent higher than the previously reported values, and do not show the unusually strong dependence on temperature reported by Trautz for temperatures higher than 400° K.. The rather limited data of Lambert et al. are about 3.0 percent lower than our values but also do not indicate the strong dependence reported by Trautz.

The suitability of the potential function must be tested, however, by properties other than the one employed to deduce the parameters. Each property will now be discussed separately.

The theory of Enskog and Chapman provides no exact method for calculating the thermal conductivity of polyatomic

TABLE 5

COMPARISON OF OBSERVED VISCOSITIES OF METHANE WITH THOSE CALCULATED FOR THE EXP-SIX POTENTIAL

	$10^7\eta$ g-cm^{-1}-sec^{-1}		
T, °K.	Obs.	Calc.	Obs.
210.7	810	815	
250.1	967	960	
273.16	1031	1038	1022[a]
292.7	1103	1104	1087[a]
300.7	1125	1128	
308.2	1155	1152	1112[b]
320.7	1189	1193	1175[a] 1150[b]
328.7	1220	1218	1206[b]
337.3	1253	1248	1238[b]
351.1	1281	1285	
363.1	1322	1321	
373.2	1355	1353	1331[a]
387.9	1391	1395	
397.4	1419	1423	
407.2	1449	1452	
424.4	1506	1503	1474[a]
439.9	1541	1546	
451.6	1574	1578	
459.4	1594	1600	
473.16	1635	1638	1603[a]

a. M. Trautz and R. Zink, Ann. Physik, 7, 427 (1930).
b. J. D. Lambert et al., Proc. Roy. Soc. (London), A231, 280 (1955).

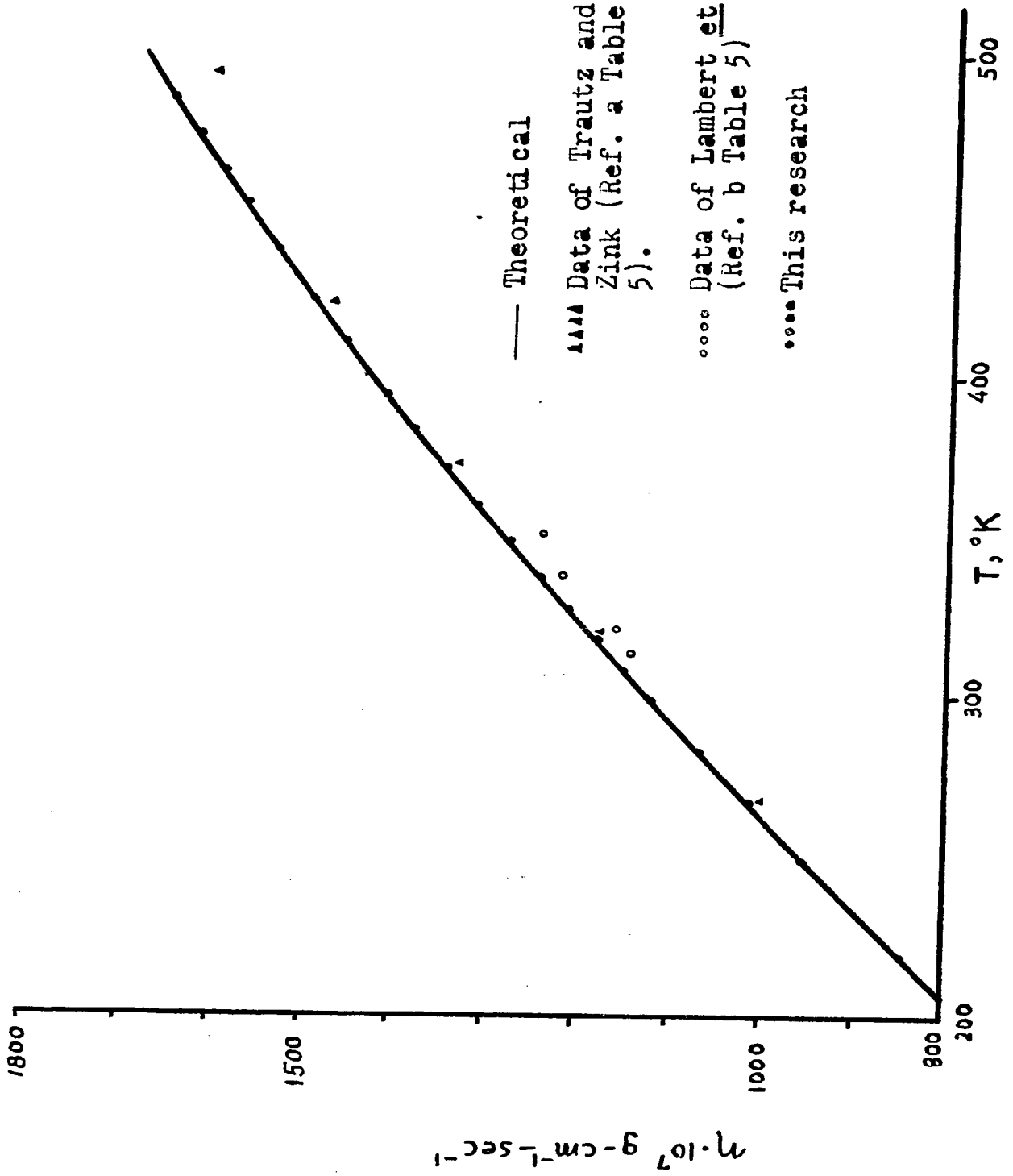

Fig. 9 The Viscosity of Methane vs Temperature

molecules. It was mentioned earlier (cf. Eq. (12)) that the simple correction suggested by Eucken was applicable only to the case where interchange and equilibrium between external and internal degrees of freedom was rapid. A previous attempt to calculate the thermal conductivity of methane was unsuccessful[44], and led to the suggestion that the Eucken correction was not applicable to methane[21]. Lambert and Rowlinson have studied ultrasonic dispersion in methane, and they have found that even up to temperatures as high as 600 °K the relaxation times are of the order of 10^{-7} sec., implying that thousands of collisions are required in order to establish equilibrium between external and internal degrees of freedom (vibrational relaxation times). It is not surprising, therefore, that the Eucken correction is unsuitable for methane, and for this reason no attempt has been made to calculate the thermal conductivity of methane.

The diffusion coefficient, on the other hand, is unaffected by the presence of internal degrees of freedom, and Table 6 contains a comparison of calculated values and experimental data. The agreement is fairly good, but by no means as satisfactory as the agreement previously indicated for argon.

In Figure 10 the virial coefficients of methane are plotted against temperature, and the agreement between the calculated curve and the experimental data is very good.

C. Ethane The viscosity data, summarized in Table 7,

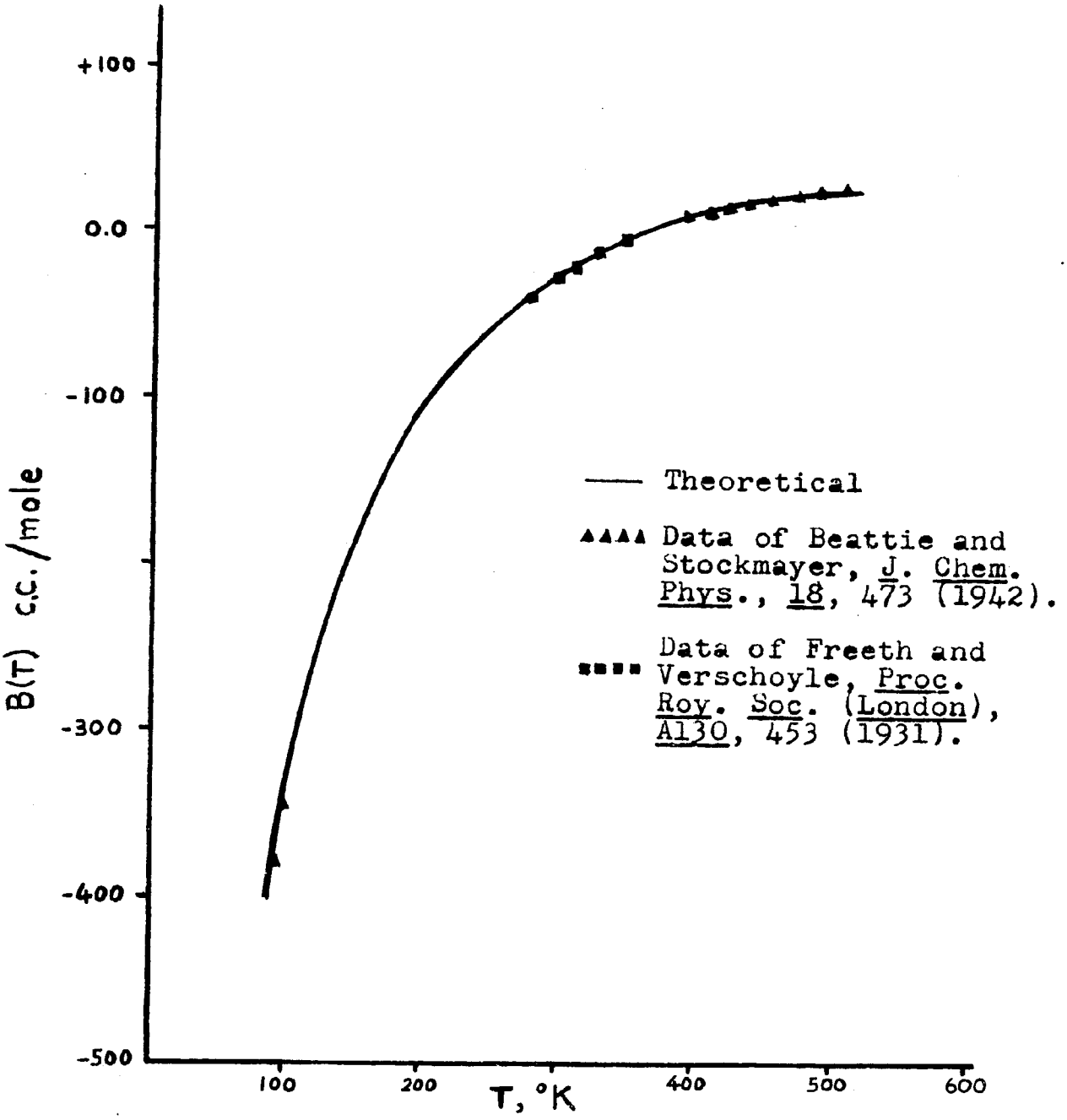

Fig. 10 The Second Virial Coefficient of Methane

TABLE 6
COEFFICIENT OF SELF-DIFFUSION FOR METHANE
USING POTENTIAL PARAMETERS FROM VISCOSITY

	D_{11} cm^2-sec^{-1}		
T, ° K.	Exp-Six (present work)	Exptl.[a]	Exp-Six[b] (thermal diffusion)
90.2	.0217	.0266	.0216
194.7	.100	.0992	.100
273.2	.193	.206	.192
298.2	.227	.240	.226
353.2	.310	.318	.308

a. E. B. Winn, Phys. Rev., 80, 1024 (1950).
b. M. P. Madan, J. Chem. Phys., 23, 763 (1955).

TABLE 7

COMPARISON OF OBSERVED VISCOSITIES OF ETHANE WITH THOSE CALCULATED FOR THE EXP-SIX POTENTIAL

	$10^7\eta$ g-cm^{-1}-sec^{-1}		
T, ° K	Obs.	Calc.	Obs.
250.1	795	801	
273.16	869	873	851[a]
292.7	930	930	909[a] 929[b]
300.7	950	954	
308.2	970	975	
320.7	1010	1013	990[a] 1000[c]
328.7	1035	1034	1034[b]
337.3	1064	1060	
351.1	1101	1098	1096[c]
363.1	1127	1132	
373.2	1155	1158	1142[a] 1167[b]
387.9	1204	1200	1245[b]
397.4	1230	1225	
407.2	1254	1251	
424.4	1289	1295	1278[a]
439.9	1341	1335	
451.6	1372	1367	
459.4	1390	1387	
473.16	1418	1422	1408[a]

a. M. Trautz and K. G. Sorg, Ann. Physik, 10, 81 (1931).
b. T. Titani, Bull. Chem. Soc. Japan, 5, 98 (1930).
c. J. D. Lambert et al., Proc. Roy. Soc. (London), 231A, 280 (1955).

permitted the following assignment for the potential parameters of ethane: $r_m = 4.905$ Å, $(\epsilon/k) = 229.1$, and $\alpha = 16$. A comparison of the calculated curve and the data may be found in Figure 11. Our data are 1.0 to 2.0 percent higher than those of Trautz and Sorg and of Lambert *et al.*, but are somewhat lower (*ca.* 2.0 percent) than those of Titani at temperatures greater than 350°K.. The slope of our curve is in good agreement with all previous investigations, although Titani's data appear to have a somewhat larger slope at higher temperatures.

Comparison of theory and experiment becomes difficult with ethane for several reasons; the lack of sufficient diffusion data and the same difficulties for λ as those encountered for methane leave only the virial coefficients as a check on the suitability of the potential function. The results are disappointing.

In a recent paper, Castle, Jansen and Dawson[46] have discussed a solution to the problem of calculating the second virial coefficients for nonspherical molecules. They concluded that for ethane the deviation from spherical symmetry, at least as far as long range forces were concerned, was small compared to such molecules as nitrogen, carbon monoxide, carbon dioxide and nitrous oxide. Independently, our results for the (σ/r_m) of ethane seemed to indicate essentially the same result. It was, therefore, surprising that the calculated curve for the second virial coefficient of ethane (computed from viscosity) should deviate so much

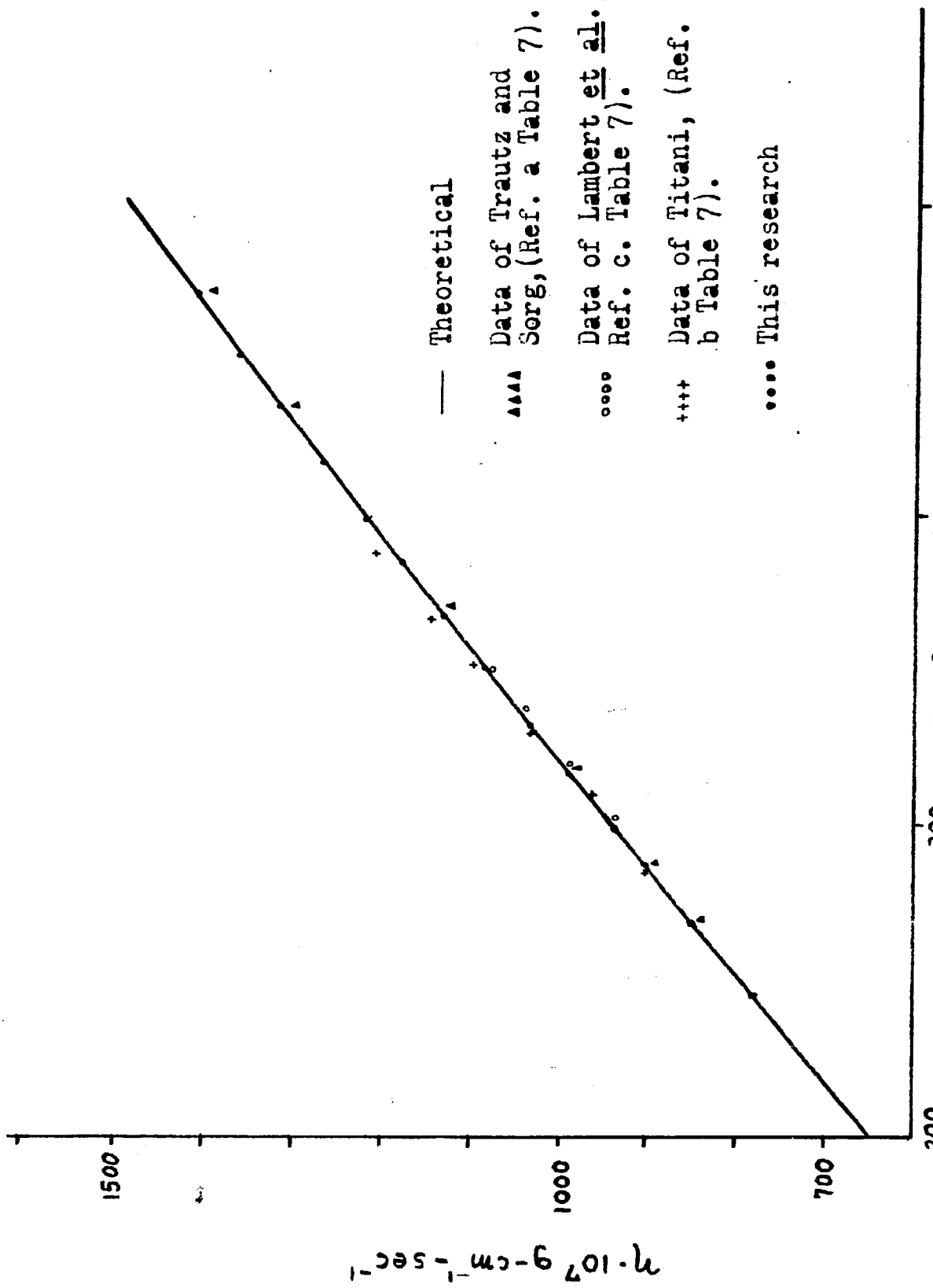

Fig. 11 The Viscosity of Ethane

from the experimental data. Figure 12 shows the second virial coefficient of ethane plotted against temperature, and the failure of a single set of Exp-Six parameters to reproduce the measured values is clear. A second set of parameters deduced from virial coefficient data $r_m = 5.226$ Å, $(\epsilon/k) = 249.5$, $\alpha = 16$ fit the data well, but this reduces the Exp-Six potential to the status of an unnecessarily complicated interpolation function. It is interesting to note, however, that the different values determined for r_m are in accord with the fact that the virial coefficients are more determined by the attractive forces than the repulsive forces, and vice versa for viscosity.

Table 8 contains a comparison of the potential parameters obtained from this research and those reported by other workers. The differences, although small in most cases, are significant enough to permit our parameters to fit better the existing data whenever comparison is possible. No previous results have been reported for ethane.

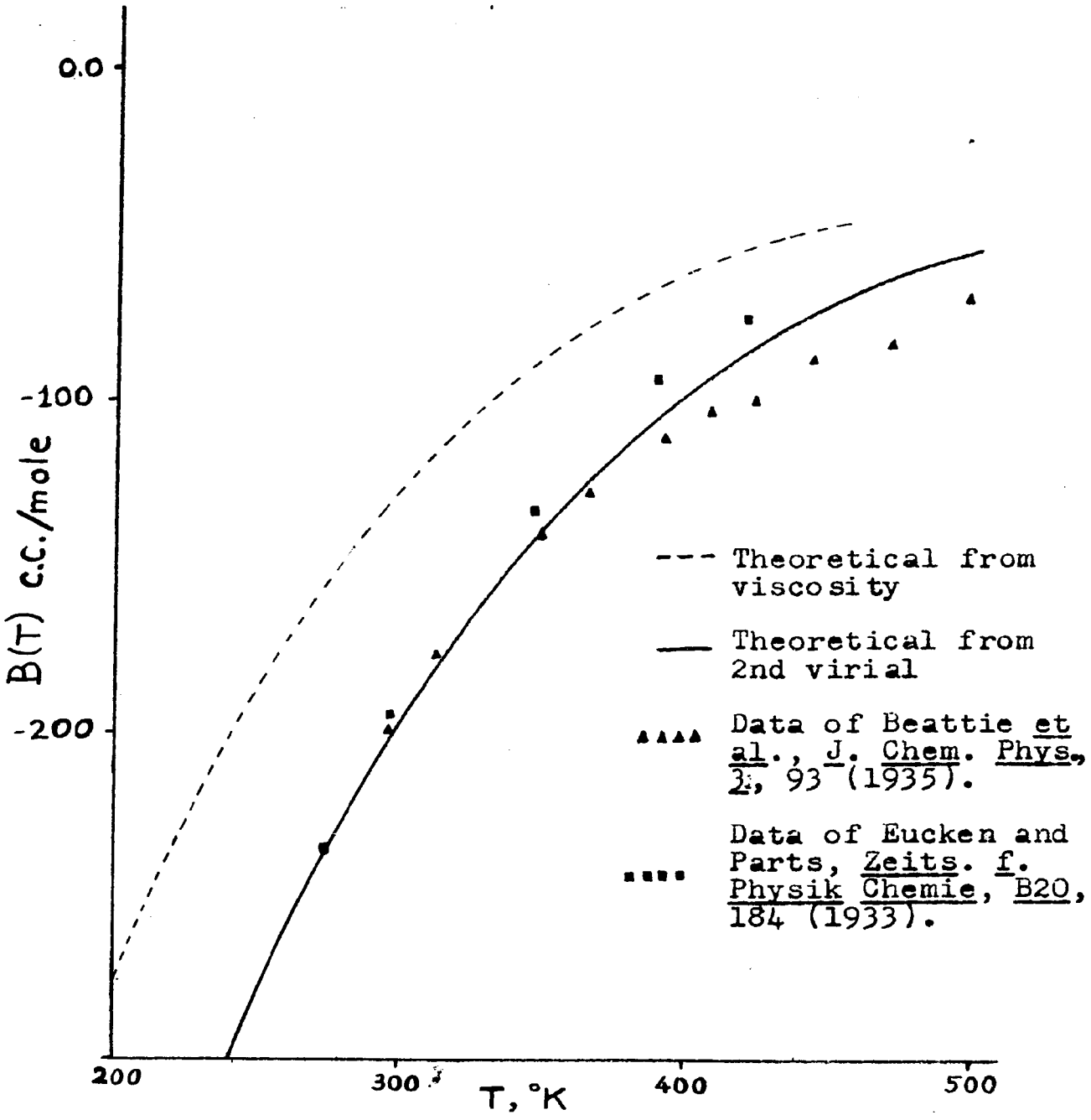

Fig. 12 The Second Virial Coefficient of Ethane

TABLE 8

COMPARISON OF VALUES OF THE POTENTIAL PARAMETERS BY DIFFERENT METHODS

	α	(ϵ/k)	r_m (Å)	Method	Reference
Argon	14	123.0	3.867	Visc.	a
	14	123.2	3.866	Visc.2nd Virial, Crystal	b
	14	122.46	3.868	Visc.	c
	14	122.9	3.868	Thermal Diffusion	c
Methane	14	152.4	4.209	Visc.	a
	14	152.8	4.206	Visc.2nd Virial, Crystal	b
	14	152.20	4.203	Visc.	c
	14	150.6	4.222	Thermal Diffusion	c
Ethane	16	229.1	4.905	Visc.	a
	16	249.5	5.226	2nd Virial	a
Lennard-Jones		230	4.418	Visc.	d
		243	3.954	2nd Virial	d

a. This research.
b. E. A. Mason and W. E. Rice, J. Chem. Phys., 22, 843 (1954).
c. M. P. Madan, J. Chem. Phys., 23, 763 (1955).
d. R. B. Bird, J. O. Hirschfelder and C. F. Curtiss, "Survey of the Equation of State and Transport Properties of Gases and Liquids", University of Wisconsin Publication, CM-758 (1952), generously supplied by Prof. J. O. Hirschfelder.

PART FIVE

CONCLUSIONS AND SUMMARY

It is apparent from the discussions of the preceding sections that the Exp-Six potential is entirely suitable for spherical molecules, and if thermal conductivity is omitted, even for spherical polyatomic molecules, while for nonspherical molecules, it appears to fail. The question arises whether the primary fault rests with the potential form or with the basic theory, which assumes spherically symmetric potentials and elastic intermolecular collisions. From the results of of this research and those of Mason and Rice[21], it appears fair to judge that the basic responsibility for the failure of the Exp-Six potential with nospherical molecules lies primarily with the theory. It will prove interesting to see whether the new theory of Curtiss[47] will be any more successful than the Enskog-Chapman theory, since the former explicitly includes the nonspherical case. It may then be possible to judge, under stronger circumstances, the relative merits of the Lennard-Jones and Exp-Six potential forms.

From the results of this research, certain problems immediately suggest themselves. Experimentally, the measurement of the viscosity of argon at high temperatures ($T > 600^{\circ}K$) would permit a more fitting comparison of theory and experiment in a region where the limited data available are considerably lower than the calculated results. In addition the careful measurement of the self-diffusion coefficients (or thermal diffusion ratios) for ethane would permit a check on the suitability of the potential form deduced from the viscosity data. It is possible that a

single set of parameters would be sufficient to describe all the transport properties of ethane, while failing for the equation of state. Theoretically, the gaps are enormous. It is to be expected that in the future machine methods of calculation will permit the solution to a rigorous, general kinetic theory, as yet undeveloped. Furthermore, the methods of quantum mechanics and the use of highly developed computational techniques may yet prove successful enough to permit a greater fundamental understanding of intermolecular forces.

The results of this research are summarized below:

1. A capillary viscometer was built and the viscosities of argon, methane and ethane measured from 210°K to 473°K. The results were in essential agreement with the previously reported data, although for methane and ethane they were a few percent higher than the previously reported values.

2. A set of potential parameters for the Exp-Six potential function were deduced from the viscosity data and the calculated properties of the gases compared with experimental data. For argon and methane agreement was in all cases good: but for ethane a single set of parameters was unable to reproduce both viscosity and virial coefficient data. It was concluded that the Enskog-Chapman theory failed for the nonspherical ethane molecule.

APPENDIX I

A REVIEW OF THE KINETIC THEORY OF DILUTE GASES

In this appendix an attempt is made to review the principal results of the kinetic theory of dilute gases. In the limited space available it has not been possible to proceed with complete rigor from step to step, but no essential detail has been sacrificed for brevity. The notation and format of the review essentially follow that presented in Hirschfelder[9] but numerous changes have been made where simplicity of presentation was to be gained.

A. Outline of the Problem and Method of Approach A rigorous development of the kinetic theory of gases is based upon a detailed knowledge of the distribution function $f_i(\vec{r}, \vec{v}_i, t)$, which represents the number of molecules of the i th species which at a time, t, lie in a unit volume element about the point $\vec{r}$ and which have velocities within a unit range about $\vec{v}_i$. When the system is not at equilibrium, the distribution function satisfies the Boltzmann integro-differential equation. If, however, equilibrium is assumed where no gradients exist in the composition, velocity and temperature of the gas, then $f_i(\vec{r}, \vec{v}_i, t)$ reduces to the Maxwellian distribution $f_i^{[0]} = n_i \left(\frac{m_i}{2\pi\theta}\right)^{3/2} \exp(-m_i v_i^2/2\theta)$, where $\theta = kT$.

Generally, one is interested only in those properties of gases which are slightly removed from equilibrium and for which the flux vectors are linear in the derivatives. In this limit the usual definitions of the transport coefficients apply and the Boltzmann equation can be solved by a

perturbation method developed by Chapman and Enskog. The final result is that all the transport coefficients can be expressed in terms of a set of integrals $\Omega^{(\ell,s)}$ which involve explicitly the dynamics of a molecular encounter and, hence, the intermolecular force law.

B. The Description of Non-Equilibrium Systems It is virtually impossible to give a complete dynamical description of the state of a complex macroscopic system. The problem of predicting the probable behavior of a system from incomplete information about the system at any given time is essentially a statistical one. It is convenient to represent the system by an ensemble consisting of a very large number of replicas of the single system. The ensemble is then described by a generalized distribution function $f^{(N)}(\vec{r}^N, \vec{p}^N, t)$ -- where $\vec{r}^N$ and $\vec{p}^N$ are vectors in a 3N-dimensional space representing the location and linear momentum of N particles-- so chosen that averages over the ensemble are in agreement with macroscopic measurements on the system at any given time. In other words, the probable behavior of the macroscopic system is taken to be the average behavior of the members of the representative ensemble.

The variation of the distribution function $f^{(N)}(\vec{r}^N, \vec{p}^N, t)$ with time is described by the Liouville equation,

$$\frac{\partial f^{(N)}}{\partial t} + \left[f^{(N)}, H\right] = 0 \qquad (I.1)$$

where $[f^{(N)}, H]$ is a well-known notation for the Poisson bracket. This equation involving 6N variables is difficult to solve, but, fortunately, a less complete description of the system than that afforded by $f^{(N)}$ is satisfactory. Generally, one of the lower-order distribution functions $f^{(h)}(\vec{r}^h, \vec{p}^h, t)$, obtained by integration of $f^{(N)}$ over the $N-h$ molecules not included in the group 1, 2, 3, ... h, is suitable and particular interest is focused on those distribution functions with h = 1 and h = 2. For a system of identical particles, $f^{(N)}$ is symmetric in the coordinates of all the molecules, since no physical experiment differentiates among them. The function $f^{(1)}$ is then suitable for those properties of gases which do not depend on the relative positions of two or more molecules and, therefore, contains the level of information needed to study the behavior of moderately dilute gases. For more dense gases, however, higher-order functions are needed. If, however, the potential energy may be written in the form $\Phi(\vec{r}^N) = \frac{1}{2}\sum_{i,j} \varphi_{ij}$, then $f^{(2)}$ is sufficient to describe all the macroscopic properties of the system: $f^{(2)}$ is then the distribution function in the phase space of pairs.

C. <u>The Boltzmann Equation</u> A rigorous derivation of the Boltzmann equation can be made from the Liouville equation, but a somewhat simpler physical approach often gives a clearer understanding of its significance.

Consider a monatomic gas mixture in a non-equilibrium

state, sufficiently dilute that all collisions higher than two-body are unimportant. For further generality let the molecules of the i th species be acted upon by an external force $\vec{X}_i(\vec{r},t)$, with the property that $\vec{X}_i(\vec{r},t) \ll \frac{\partial}{\partial \vec{r}_i} \cdot \Phi(\vec{r})$, i.e., the external force is always much smaller than the forces acting during a molecular encounter.

Each component of the mixture has a distribution function in the molecule phase space (μ) of the form $f_i^{(1)}(\vec{r},\vec{p}_i,t)$, where the function is written in terms of the linear momentum $\vec{p}_i$ rather than the velocity $\vec{v}_i$. The function is given meaning by the property that the number of molecules of the i th species which at a time t lie in a range $d\vec{r}$ about $\vec{r}$ and $d\vec{p}_i$ about $\vec{p}_i$ is $f_i^{(1)}(\vec{r},\vec{p}_i,t)d\vec{r}\,d\vec{p}_i$. The problem is to determine the flow of phase points through a six-dimensional phase space, in which each point represents a molecule which interacts with others. In the absence of interaction, the behavior of $f_i^{(1)}$ would be described by the Liouville equation and the likely situation, therefore, is for $f_i^{(1)}$ to be described by a Liouville equation modified by the addition of terms to account for molecular collisions.

Imagine a region of extension $d\vec{r}\,d\vec{p}_i$ located about the point $(\vec{r},\vec{p}_i)$ containing $f_i^{(1)}\,d\vec{r}\,d\vec{p}_i$ phase points. In the absence of collisions the molecules associated with these phase points move in such a way that at time $t + dt$ the independent variables assume the values $[\vec{r} + (\vec{p}_i/m_i)\,dt]$ and $(\vec{p}_i + \vec{X}_i\,dt)$. If no other points arrive at this latter position (in the absence of collisions), then,

$$f_i^{(1)}(\vec{r}, \vec{p}_i, t)\, d\vec{r}\, d\vec{p}_i$$

$$= f_i^{(1)}\left(\left[\vec{r} + \frac{\vec{p}_i}{m_i} dt\right], \left[\vec{p}_i + \vec{X}_i\, dt\right], \left[t + dt\right]\right) d\vec{r}\, d\vec{p}_i \qquad (I.2)$$

Collisions, however, are taking place and therefore some of the phase points at $(\vec{r}, \vec{p}_i)$ do not arrive at $\left(\left[\vec{r} + \frac{\vec{p}_i}{m_i} dt\right], \left[\vec{p}_i + \vec{X}_i dt\right]\right)$ after an interval dt. Furthermore, there are some phase points not associated with $(\vec{r}, \vec{p}_i)$ which after a time dt are associated with $\left(\left[\vec{r} + \frac{\vec{p}_i}{m_i} dt\right], \left[\vec{p}_i + \vec{X}_i dt\right]\right)$ as a result of collisions. Let $\Gamma_{ij}^{(-)} d\vec{r}\, d\vec{p}_i\, dt$ be the number of molecules of the i th species lost from the momentum range $\vec{p}_i$ to $\vec{p}_i + d\vec{p}_i$ in the position range $\vec{r}$ to $\vec{r} + d\vec{r}$ during an interval dt through collisions with the j-type molecules. Correspondingly, let $\Gamma_{ij}^{(+)} d\vec{r}\, d\vec{p}_i\, dt$ be those gained in the same fashion. Equation (I.2) now takes the form

$$f_i^{(1)}\left(\left[\vec{r} + \frac{\vec{p}_i}{m_i} dt\right], \left[\vec{p}_i + \vec{X}_i dt\right], \left[t + dt\right]\right) d\vec{r}\, d\vec{p}_i$$

$$= f_i^{(1)}(\vec{r}, \vec{p}_i, t)\, d\vec{r}\, d\vec{p}_i + \sum_j \left[\Gamma_{ij}^{(+)} - \Gamma_{ij}^{(-)}\right] d\vec{r}\, d\vec{p}_i\, dt \qquad (I.3)$$

The left-hand side of Eq. (I.3) may be expanded in a Taylor series about the point $(\vec{r}, \vec{p}_i, t)$, and if terms higher than the first order are dropped, the result may be combined with Eq. (I.3) to give a form the the Boltzmann Equation:

$$\frac{\partial f_i^{(1)}}{\partial t} + \frac{1}{m_i}\left(\vec{p}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{r}}\right) + \left(\vec{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{p}_i}\right) = \sum_j \left(\Gamma_{ij}^{(+)} - \Gamma_{ij}^{(-)}\right) \qquad (I.4)$$

This result agrees with the Liouville equation except for the addition of the collision terms on the right side.

The right-hand side of Eq. (I.4) is usually written in a somewhat different form, in terms of the "collision integrals". In order to deduce the proper form for the collision integrals, the following problem must be solved: the calculation of the probability that a molecule of the type i, located at the point $(\vec{r},\vec{p}_i)$ will experience a collision with a molecule of type j, in the time interval dt and characterized by a range db in the impact parameter b. The result has the following form,

$$\Gamma_{ij}^{(-)} = 2\pi \iint f_i^{(1)} f_j^{(1)} g_{ij}\, b\, db\, d\vec{p}_j \qquad (I.5)$$

where g_{ij} is the initial relative velocity of the molecules i and j, and is defined as $\vec{g}_{ji} = \frac{\vec{p}_j}{m_j} - \frac{\vec{p}_i}{m_i}$ with the obvious property that $|\vec{g}_{ji}| = g_{ji} = g_{ij}$. In Eq. (I.5) $\Gamma_{ij}^{(-)}$ represents the contribution to $\partial f_i^{(1)}/\partial t$ due to the removal from the group of molecules i by collisions with molecules of type j.

The result for $\Gamma_{ij}^{(+)}$ may be written as

$$\Gamma_{ij}^{(+)} = 2\pi \iint f_i^{(1)'} f_j^{(1)'} g_{ij}\, b\, db\, d\vec{p}_j \qquad (I.6)$$

where $f_i^{(1)'}$ and $f_j^{(1)'}$ are the distribution functions for i and j <u>after</u> collision. In the derivation of Eq. (I.6) use is made of the following properties of g_{ij}, b and $d\vec{p}_i d\vec{p}_j$: for potential functions which are spherically symmetric there

must be conservation of energy and angular momentum leading to the results that $g_{ij} = g'_{ij}$ and $b = b'$; furthermore, since the position vectors of the two molecules are not changed in the collision, the transformation $(\vec{p}_i, \vec{p}_j) \rightarrow (\vec{p}'_i, \vec{p}'_j)$ is a so-called "contact-transformation" and its Jacobian is unity leading to the result that $d\vec{p}_i d\vec{p}_j = d\vec{p}'_i d\vec{p}'_j$.

The final form of the Boltzmann equation may, therefore, be written by combination of Eq.'s (I.5), (I.6) and (I.4) as,

$$\frac{\partial f_i^{(1)}}{\partial t} + \frac{1}{m_i}\left(\vec{p}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{r}}\right) + \left(\vec{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{p}_i}\right) = 2\pi \sum_j \iint \left(f_i^{(1)'} f_j^{(1)'} - f_i^{(1)} f_j^{(1)}\right) g_{ij}\, b\, db\, d\vec{p}_j \qquad (I.7)$$

The law of force implicitly enters into the integrals on the right-hand side of Eq. (I.7), since $f_i^{(1)'}$, $f_j^{(1)'}$ are functions of $\vec{p}'_i$ and $\vec{p}'_j$ which can be calculated from dynamical principles when $\vec{p}_i$, $\vec{p}_j$ and b are given, along with the intermolecular potential energy.

In most problems of kinetic theory, it is more convenient to work in terms of a distribution function $f_i(\vec{r}, \vec{v}_i, t)$ rather than $f_i(\vec{r}, \vec{p}_i, t)$. In a fashion entirely analogous to the one described above, the Boltzmann equation may be shown in terms of $f_i(\vec{r}, \vec{v}_i, t)$ to have the form,

$$\frac{\partial f_i^{(1)}}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{r}}\right) + \frac{1}{m_i}\left(\vec{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{v}_i}\right) = 2\pi \sum_j \iint \left(f_i^{(1)'} f_j^{(1)'} - f_i^{(1)} f_j^{(1)}\right) g_{ij}\, b\, db\, d\vec{v}_j \qquad (I.8)$$

Eq. (I.8) serves as the basis for the discussion of the transport properties of moderately dilute non-polar gases.

D. The Flux Vectors and the Equations of Change The hydrodynamic equations of change for mass, momentum and energy may be derived from Eq. (I.8). In connection with this problem, and the associated problem of the flux vectors, certain definitions of various velocities are required and are presented below.

The linear velocity of a molecule of the j th type is denoted by $\vec{V}_j$ and has components v_{jx}, v_{jy}, v_{jz} the magnitude of $\vec{V}_j$, $|\vec{V}_j| = v_j$, is called the molecular speed. For the j th species at a number density n_j, the average velocity $\overline{\vec{V}_j}$, is defined by

$$\overline{\vec{V}_j}(\vec{r},t) = \frac{1}{n_j} \int \vec{V}_j f_j(\vec{r},\vec{V}_j,t)\, d\vec{V}_j \qquad (I.9)$$

From Eq.(I.9), in which $\overline{\vec{V}_j}$ represents the macroscopic rate of flow of the j th species, it is clear that if $\alpha(\vec{r},t)$ is any function of the velocity, then the average value of $\alpha(\vec{r},t)$ is given by

$$\overline{\alpha}(\vec{r},t) = \frac{1}{n_j} \int \alpha(\vec{V}_j) f_j(\vec{r},\vec{V}_j,t)\, d\vec{V}_j \qquad (I.10)$$

If one denotes the density of the gas at a particular point by $\rho(\vec{r},t) = \sum_j n_j m_j$, then the mass average velocity has the form

$$\vec{V}_o(\vec{r},t) = \frac{1}{\rho} \sum_j n_j m_j \overline{\vec{V}_j} \qquad (I.11)$$

The mass average velocity has the property of being a weighted mean, with each molecule weighted according to its mass. In addition, the momentum of the gas per unit volume

is the same as if all the molecules were moving at the mass average velocity $\vec{v}_o$; $\vec{v}_o$ is often called the <u>stream-</u> or <u>flow-velocity</u>.

The velocity of a molecule with respect to an axis moving with the velocity $\vec{v}_o$ is called the <u>peculiar velocity</u> and has the form $\vec{V}_j = \vec{v}_j - \vec{v}_o$. The <u>diffusion velocity</u>, $\overline{\vec{V}_j}$, may be regarded as the average of the peculiar velocity and written in the form

$$\overline{\vec{V}_j} = \frac{1}{n_j}\int(\vec{v}_j - \vec{v}_o)\, f_j(\vec{r},\vec{v}_j,t)\, d\vec{v}_j = \overline{\vec{v}_j} - \vec{v}_o \qquad (I.12)$$

The mechanism of the transport of mass, momentum and kinetic energy may be treated similarly and these properties may be given the collective symbol ψ_j . Consider now the macroscopic transport of these properties ψ . Imagine in the gas a small element of surface, dS, moving with the stream velocity $\vec{v}_o$. The orientation of this surface may be designated by a unit vector $\vec{n}$ normal to the surface dS. The molecules of the j th species have a velocity relative to dS of $\vec{V}_j$, and all such molecules contained in a cylinder of length $|\vec{V}_j|\,dt$ and cross-section dS will cross dS per unit time. The designated cylinder has a volume $(\vec{n}\cdot\vec{V}_j)\,dS\,dt$, and since there are $f_j\, d\vec{V}_j$ molecules per unit volume having a velocity $\vec{V}_j$, then the number of molecules crossing dS during the interval dt is $f_j(\vec{n}\cdot\vec{V}_j)\,d\vec{V}_j\,dS\,dt$. If the property ψ_j , whose magnitude depends on $\vec{V}_j$, is associated with each molecule,

then the flux of ψ (the ammount crossing unit area per unit time) may be written as $\psi_j f_j (\vec{n}\cdot\vec{V}_j)\, d\vec{V}_j$. The total flux is, therefore

$$\int \psi_j f_j (\vec{n}\cdot\vec{V}_j)\, d\vec{V}_j = (\vec{n}\cdot\int \psi_j f_j \vec{V}_j\, d\vec{V}_j) = (\vec{n}\cdot\vec{\Psi}) \qquad (I.13)$$

where the <u>flux vector</u> $\vec{\Psi}$ associated with the property is defined as

$$\vec{\Psi} = \int \psi_j f_j \vec{V}_j\, d\vec{V}_j \qquad (I.14)$$

Consider now Eq. (I.14) and the transport of mass, momentum and kinetic energy.

Case 1. Transport of Mass

if $\psi_j = m_j$, then

$$\vec{\Psi} = m_j \int f_j \vec{V}_j\, d\vec{V}_j = n_j m_j \vec{V}_j = \vec{j}_j \qquad (I.15)$$

where $\vec{j}_j$ is the mass flux vector.

Case 2. Transport of Momentum

if $\psi_j = m_j V_{jx}$, then

$$\vec{\Psi} = m_j \int V_{jx} \vec{V}_j f_j\, d\vec{V}_j = n_j m_j \overline{V_{jx}\vec{V}_j} \qquad (I.16)$$

represent the flux vector associated with the transport of the x-component of momentum relative to $\vec{V}_o$. This vector may be written, along with its y-and-z - components, as

$$\vec{\Psi}_{jx} = n_j m_j \left(\vec{\alpha}\,\overline{V_{jx}V_{jx}} + \vec{\beta}\,\overline{V_{jx}V_{jy}} + \vec{\gamma}\,\overline{V_{jx}V_{jz}}\right),$$

$$\vec{\Psi}_{jy} = n_j m_j \left(\vec{\alpha} \overline{V_{jy} V_{jx}} + \vec{\beta} \overline{V_{jy} V_{jy}} + \vec{\gamma} \overline{V_{jy} V_{jz}} \right)$$

$$\vec{\Psi}_{jz} = n_j m_j \left(\vec{\alpha} \overline{V_{jz} V_{jx}} + \vec{\beta} \overline{V_{jz} V_{jy}} + \vec{\gamma} \overline{V_{jz} V_{jz}} \right) \qquad \text{(I.17)}$$

The three flux vectors defined by Eqs. (I.17) form a symmetric second order tensor with components

$$(p_j)_{xx} = m_j \int f_j V_{jx} V_{jx} \, d\vec{V}_j = n_j m_j \overline{V_{jx} V_{jx}}$$

$$(p_j)_{xy} = (p_j)_{yx} = n_j m_j \overline{V_{jx} V_{jy}} \qquad \text{(I.18)}$$

. . . , or symbolically

$$\mathcal{P}_j = n_j m_j \overline{\vec{V}_j \vec{V}_j}$$

where $\mathcal{P}_j$ is the tensor associated with the parital pressure of the j th species in the gas. The <u>pressure tensor</u> for the mixture is defined as

$$\mathcal{P} = \sum_j \mathcal{P}_j = \sum_j n_j m_j \overline{\vec{V}_j \vec{V}_j} \qquad \text{(I.19)}$$

for which the diagonal elements p_{xx}, p_{yy}, p_{zz} are normal stresses and the non-diagonal elements represent the so-called shear stresses.

Case 3. Transport of Kinetic Energy

If $\psi_j = \frac{1}{2} m_j V_j^2$, then

$$\vec{\Psi}_j = \frac{1}{2} m_j \int V_j^2 \vec{V}_j f_j \, d\vec{V}_j = \frac{1}{2} n_j m_j \overline{V_j^2 \vec{V}_j} = \vec{q}_j \qquad \text{(I.20)}$$

where $\vec{q}_j$ is the flux vector associated with the transport of kinetic energy of the j th species. The heat flux vector, $\vec{q}$, is the sum of the $\vec{q}_j$'s, viz.,

$$\vec{q} = \sum_j \vec{q}_j = \sum_j \tfrac{1}{2} m_j n_j \overline{V_j^2 \vec{V}_j} \tag{I.21}$$

In terms of the flux vectors defined above, the usual definitions for the transport coefficients are

$$\Psi = \begin{cases} j_{iz} = -D \dfrac{dn_j}{dz} \\ P_{yz} = -\eta \dfrac{dv_x}{dz} \\ q_z = -\lambda \dfrac{dT}{dz} \end{cases} \tag{I.21a}$$

It is not necessary to specify the exact form of the distribution functions f_i in order to derive the fundamental hydrodynamic equations of continuity, motion and energy balance from the Boltzmann equation. If the Boltzmann equation for the i th species Eq. (I.8) is multiplied by the quantity, ψ_i , associated with the i th species and then integrated over $\vec{V}_i$, one obtains

$$\int \psi_i \left\{ \frac{\partial f_i^{(1)}}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{r}}\right) + \frac{1}{m_i}\left(\vec{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{v}_i}\right) \right\} d\vec{v}_i$$

$$= 2\pi \sum_j \iint \psi_i \left(f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)} \right) g_{ij}\, b\, db\, d\vec{v}_j\, d\vec{v}_i \tag{I.22}$$

The three terms on the left-hand side of Eq. (I.22) may be easily transformed as follows:

$$\int \psi_i \frac{\partial f_i^{(1)}}{\partial t} d\vec{v}_i = \frac{\partial}{\partial t} \int \psi_i f_i^{(1)} d\vec{v}_i - \int f_i^{(1)} \frac{\partial \psi_i}{\partial t} d\vec{v}_i$$

$$= \frac{\partial (n_i \overline{\psi_i})}{\partial t} - n_i \overline{\frac{\partial \psi_i}{\partial t}} \qquad \text{(I.23)}$$

, and

$$\int \psi_i v_{ix} \frac{\partial f_i^{(1)}}{\partial x} d\vec{v}_i = \frac{\partial}{\partial x} \int \psi_i v_{ix} f_i^{(1)} d\vec{v}_i - \int f_i^{(1)} v_{ix} \frac{\partial \psi_i}{\partial x} d\vec{v}_i$$

$$= \frac{\partial}{\partial x} (n_i \overline{\psi_i v_{ix}}) - n_i \left(\overline{v_{ix} \frac{\partial \psi_i}{\partial x}} \right) \qquad \text{(I.24)}$$

, and

$$\int \psi_i \frac{\partial f_i^{(1)}}{\partial v_{ix}} d\vec{v}_i = \iint \left[\psi_i f_i^{(1)} \right]_{v_{ix} = -\infty}^{v_{ix} = +\infty} dv_{iy}\, dv_{iz} - \int f_i^{(1)} \frac{\partial \psi_i}{\partial v_{ix}} d\vec{v}_i$$

$$= -n_i \overline{\frac{\partial \psi_i}{\partial v_{ix}}} \qquad \text{(I.25)}$$

where the last two equations have been written only for the x-components and in which the quantities $\vec{r}$, $\vec{v}_i$ and t are taken as the independent variables. Combination of Eqs. (I.23), (I.24) and (I.25) with Eq. (I.22) leads finally to Enskog's general equation of change for a physical quantity ψ_i, viz.,

$$\frac{\partial}{\partial t}(n_i \overline{\psi_i}) + \left(\frac{\partial}{\partial \vec{r}} \cdot n_i \overline{\psi_i \vec{v}_i} \right) - n_i \left\{ \frac{\partial \psi_i}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial \psi_i}{\partial \vec{r}} \right) + \left(\frac{\vec{X}_i}{m_i} \cdot \frac{\partial \vec{\psi}_i}{\partial \vec{v}_i} \right) \right.$$

$$= 2\pi \sum_j \iint \psi_i \left(f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)} \right) g_{ij}\, b\, db\, d\vec{v}_i\, d\vec{v}_j \,, \qquad \text{(I.26)}$$

summation of Eq. (I.26) over i gives the equation of change of ψ for the entire gas.

An important property of the collision integrals (the right hand side of Eq. (I.26)) is that when the quantities m_i , $m_i \vec{V}_i$, or $\frac{1}{2} m_i V_i^2$ are substituted for ψ_i , the integrals vanish. The validity of the property may be shown in the following manner. Certainly

$$\iiint \psi_i (f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)}) g_{ij} b \, db \, d\vec{v}_i \, d\vec{v}_j$$

$$= \iiint \psi_i' (f_i^{(1)} f_j^{(1)} - f_i^{(1)\prime} f_j^{(1)\prime}) g_{ij}' b' \, db' \, d\vec{v}_i' \, d\vec{v}_j' \,, \qquad \text{(I.27)}$$

where the second integral is written in terms of the inverse collisions; furthermore, $g_{ij} = g_{ij}'$, $b = b'$ and $d\vec{v}_i \, d\vec{v}_j = d\vec{v}_i' \, d\vec{v}_j'$ for the reasons cited in deriving Eq. (I.7). Therefore, the second integral of Eq. (I.27) may be written as

$$- \iiint \psi_i' (f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)}) g_{ij} b \, db \, d\vec{v}_i \, d\vec{v}_j \qquad \text{(I.28)}$$

Since both the integrals in Eq. (I.27) are equal then they each equal one-half the sum of both with the result that

$$\iiint \psi_i (f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)}) g_{ij} b \, db \, d\vec{v}_i \, d\vec{v}_j$$

$$= \frac{1}{2} \iiint (\psi_i - \psi_i') (f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)}) g_{ij} b \, db \, d\vec{v}_i \, d\vec{v}_j \,. \qquad \text{(I.29)}$$

If $\psi_i = m_i$, then certainly $(\psi_i - \psi_i') = (m_i - m_i') = 0$, since mass is conserved during a collision. Furthermore, Eq. (I.29)

may be summed over both i and j and the dummy indicies interchanged to give

$$\sum_{ij} \iiint \psi_i \left(f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)} \right) g_{ij}\, b\, db\, d\vec{v}_i\, d\vec{v}_j$$

$$= \frac{1}{4} \sum_{ij} \iiint \left(\psi_i + \psi_j - \psi_i' - \psi_j' \right) \left(f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)} \right) g_{ij}\, b\, db\, d\vec{v}_i\, d\vec{v}_j \qquad \text{(I.30)}$$

The quantity $(\psi_i + \psi_j - \psi_i' - \psi_j')$ must certainly vanish for the properties $m_i \vec{V}_i$ and $\frac{1}{2} m_i V_i^2$ since both are conserved separately during a collision. This analysis establishes that the collision integrals must vanish for the summational invariants.

It is now possible to derive explicit expressions for the equations of change by substituting $\psi_i = m_i$, $\psi_i = m_i \vec{V}_i$ and $\psi_i = \frac{1}{2} m_i V_i^2$ into Eq. (I.26). If the indicated substitutions are made and the necessary manipulations performed, it is possible to establish the validity of the following equations:

a. the equation of continuity

$$\frac{\partial \rho}{\partial t} + \left(\frac{\partial}{\partial \vec{r}} \cdot \rho \vec{V}_o \right) = 0$$

b. the equation of motion of the gas

$$\frac{\partial \vec{V}_o}{\partial t} + \left(\vec{V}_o \cdot \frac{\partial}{\partial \vec{r}} \vec{V}_o \right) = -\frac{1}{\rho} \left(\frac{\partial}{\partial \vec{r}} \cdot \mathcal{P} \right) + \frac{1}{\rho} \sum_i n_i \vec{X}_i$$

c. the equation of energy balance

$$\frac{\partial}{\partial t} \left(\rho \hat{U}^{(tr.)} \right) + \left(\frac{\partial}{\partial \vec{r}} \cdot \rho \hat{U}^{(tr.)} \right) + \left(\frac{\partial}{\partial \vec{r}} \cdot \vec{q} \right)$$

$$+ \left(\mathcal{P} : \frac{\partial \vec{V}_o}{\partial \vec{r}} \right) - \sum_i n_i \left(\vec{X}_i \cdot \overline{\vec{V}_i} \right) = 0 . \qquad \text{(I.31)}$$

In Eq. (b), $\mathcal{P}$ is the pressure tensor defined by Eq. (I.19): in Eq. (c) $\hat{U}^{(tr)}$ is the translational contribution to the internal energy per unit mass defined by $\hat{U}^{(tr)} = \rho^{-1} \sum_i \frac{1}{2} n_i m_i \overline{V_i^2}$ and the "double-dotted" notation for the tensor $\mathcal{P}$ is defined by the operation $(\mathcal{P} : \mathcal{P}') \equiv \sum_\alpha \sum_\beta \mathcal{P}_{\alpha\beta} \mathcal{P}'_{\beta\alpha} = (\mathcal{P}' : \mathcal{P})$. It is also to be noted that Eq. (I.31 c) does not apply to a gaseous molecule having internal degrees of freedom.

E. Enskog's Solution of the Boltzmann Equation For the case of equilibrium, the Boltzmann equation may be solved rather easily to yield the Maxwellian distribution. The solution makes use of the famous H-theorem which indicates in this connection that not only the term on the right side of Eq. (I.8) is zero, but also the integrand of each integral is identically zero, leading to a proof of the statistical principle of "detailed balance". It is now necessary to consider the non-equilibrium case.

The Boltzmann equation may be written in the form:

$$\frac{\partial f_i^{(1)}}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{r}}\right) + \frac{1}{m_i}\left(\vec{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{v}_i}\right) = \sum_j J(f_i^{(1)}, f_j^{(1)}) \qquad (I.32)$$

where $J(f_i^{(1)} f_j^{(1)})$ has the so-called bilinear form:

$$J(f_i^{(1)}, f_j^{(1)}) = 2\pi \iint (f_i^{(1)\prime} f_j^{(1)\prime} - f_i^{(1)} f_j^{(1)}) g_{ij} b \, db \, d\vec{v}_j \qquad (I.33)$$

Enskog's series solutions to the Boltzmann equation are obtained by defining a perturbation parameter ϵ in such a way that $\frac{1}{\epsilon}$ measures the frequency of the collisions.

In addition, the parameter ϵ is introduced into the Boltzmann equation in such a way that the frequency of the collisions can be varied arbitrarily without influencing the relative frequency of a particular kind of collision. Consider, then, a problem for which the Boltzmann equation has the form:

$$\frac{\partial f_i^{(1)}}{\partial t} + (\vec{v}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{r}}) + \frac{1}{m_i}(\vec{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \vec{v}_i}) = \frac{1}{\epsilon}\sum_j J(f_i^{(1)}, f_j^{(1)}) \qquad (I.34)$$

If ϵ were small, collisions would occur frequently and the gas would behave like a continuum maintaining everywhere local equilibrium. (NOTE: henceforth, only first order distribution functions are considered, and the notation $f_i^{(1)}$ is changed to f_i in order to avoid confusion with the symbolism to be employed relating to the degree of approximation to f_i .)

If the distribution function, f_i , is expanded as a power series in ϵ as follows,

$$f_i = \sum_{K=0}^{\infty} \epsilon^K f_i^{[K]} \qquad (I.35)$$

and the series (I.35) introduced into Eq. (I.34), then upon equating the coefficients of equal powers of ϵ , one obtains the following set of equations for the functions $f_i^{[0]}, f_i^{[1]}, f_i^{[2]}, \ldots$

$$0 = \sum_j J(f_i^{[0]}, f_j^{[0]})$$

$$\frac{\partial f_i^{[0]}}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial f_i^{[0]}}{\partial \vec{r}}\right) + \frac{1}{m_i}\left(\vec{X}_i \cdot \frac{\partial f_i^{[0]}}{\partial \vec{v}_i}\right) = \sum_j \left[J(f_i^{[0]}, f_j^{[1]}) + J(f_i^{[1]}, f_i^{[0]})\right]$$

$$\frac{\partial f_i^{[1]}}{\partial t} + \left(\vec{v}_i \cdot \frac{\partial f_i^{[1]}}{\partial \vec{r}}\right) + \frac{1}{m_i}\left(\vec{X}_i \cdot \frac{\partial f_i^{[1]}}{\partial \vec{v}_i}\right) = \sum_j \left[J(f_i^{[0]}, f_j^{[2]}) + J(f_i^{[1]}, f_j^{[1]}) + J(f_i^{[2]}, f_j^{[0]})\right] . \qquad \text{(I.36)}$$

The first of these coupled equations represents the equilibrium solution of the Boltzmann equation and this implies immediately that $f_i^{[0]}$ must be the Maxwellian function $f_i^{[0]} = n_i (m_i/2\pi\theta)^{3/2} \exp\left(-m_i(\vec{v}_i - \vec{v}_0)^2/2\theta\right)$. Chapman and Cowling[48] show that each of the remaining integral equations of Eqs. (I.36) along with the auxiliary conditions listed below specifies uniquely a set of functions $f_i^{[n]}$.

$$\text{a.} \quad \int f_i^{[n]} d\vec{v}_i = 0 \qquad n = 1, 2, 3, \ldots$$

$$\text{b.} \quad \sum_i m_i \int \vec{v}_i f_i^{[n]} d\vec{v}_i = 0 \qquad n = 1, 2, 3, \ldots \qquad \text{(I.37)}$$

$$\text{c.} \quad \frac{1}{2}\sum_i m_i \int (\vec{v}_i - \vec{v}_0)^2 f_i^{[n]} d\vec{v}_i = 0 \qquad n = 1, 2, 3, \ldots$$

The set of functions for $f_i^{[n]}$ so defined is used as a solution of the Boltzmann equation.

The equation for $f_i^{[1]}$ may be written in terms of a perturbation function φ_i defined by the equation,

$$f_i^{[1]}(\vec{r},\vec{V}_i,t) = f_i^{[0]}(\vec{r},\vec{V}_i,t)\,\varphi_i(\vec{r},\vec{V}_i,t) \qquad (I.38)$$

If Eq. (I.38) is substituted into the second of the Eqs. (I.36), the necessary differentiations performed, the time derivatives eliminated by means of the equations of change Eqs. (I.31) and account taken of Eqs. (I.37), then the resulting equation for the perturbation function φ_i may be written

$$f_i^{[0]}\left[\frac{n}{n_i}(\vec{V}_i\cdot\vec{d}_i) + (\mathbf{b}:\frac{\partial\vec{V}_0}{\partial\vec{r}}) - (\frac{5}{2}-\vec{W}_i^2)(\vec{V}_i\cdot\frac{\partial \ln T}{\partial\vec{r}})\right]$$

$$= 2\pi\sum_j\iint f_i^{[0]}f_j^{[0]}(\varphi_i'+\varphi_j'-\varphi_i-\varphi_j)\,g_{ij}\,b\,db\,d\vec{V}_j \,, \qquad (I.39)$$

where

$$\vec{d}_i = \frac{\partial}{\partial\vec{r}}\left(\frac{n_i}{n}\right) + \left(\frac{n_i}{n}-\frac{n_i m_i}{\rho}\right)\frac{\partial \ln p}{\partial\vec{r}} - \frac{n_i m_i}{p\rho}\left[\frac{\rho}{m_i}\vec{X}_i - \sum_j n_j\vec{X}_j\right]$$

and

$$\mathbf{b} = 2\left[\vec{W}_i\vec{W}_i - \tfrac{1}{3}W_i^2\,\mathbf{U}\right] \qquad (I.40)$$

In the second of Eqs. (I.40) $\mathbf{U}$ is the unit tensor and $\vec{W}_i$ is a dimensionless velocity defined by $\vec{W}_i = \sqrt{m_i/2\theta}\,\vec{V}_i$.

The perturbation function φ_i may be shown to have the form:

$$\varphi_i = -\left(\vec{A}_i \cdot \frac{\partial \ln T}{\partial \vec{r}}\right) - \left(\mathbb{B}_i : \frac{\partial \vec{v}_0}{\partial \vec{r}}\right) + n \sum_j \left(\vec{C}_i^{(j)} \cdot \vec{d}_j\right), \qquad \text{(I.41)}$$

where $\vec{A}_i$, $\mathbb{B}_i$, $\vec{C}_i^{(j)}$ are functions of $\vec{W}_i$, the local composition and temperature.

If Eq. (I.41) is substituted into Eq. (I.39) and the coefficients of similar gradients equated, then separate integral equations result for the functions $\vec{A}_i$, $\mathbb{B}$ and $\vec{C}_i^{(j)}$. It may be shown that any vector function of $\vec{W}_i$, the only vector variable, is the vector itself multiplied by some scalar function of the absolute value of the vector $\vec{W}_i$, and since $\vec{A}_i$, $\mathbb{B}_i$ and $\vec{C}_i^{(j)}$ are functions only of n_i , T and $\vec{W}_i$, then certainly $\vec{A}_i$ and $\vec{C}_i^{(j)}$ are of the form:

$$\vec{C}_i^{(j)} = \vec{W}_i \, C_i^{(j)}(W_i)$$
$$\vec{A}_i = \vec{W}_i \, A_i(W_i) \qquad \text{(I.42)}$$

while the tensor $\mathbb{B}_i$ must be of the form:

$$\mathbb{B}_i = \left\{\vec{W}_i\vec{W}_i - \tfrac{1}{3} W_i^2 \mathbb{U}\right\} B_i(W_i) \qquad \text{(I.43)}$$

Furthermore, the auxiliary relations have the form:

$$\sum_i \sqrt{m_i} \int \left(\left[\vec{C}_i^{(j)} - \vec{C}_i^{(k)}\right] \cdot \vec{W}_i\right) f_i^{[0]} \, d\vec{V}_i = 0$$
$$\qquad \text{(I.44)}$$
$$\sum_i \sqrt{m_i} \int \left(\vec{A}_i \cdot \vec{W}_i\right) f_i^{[0]} \, d\vec{V}_i = 0$$

Solutions to these integral equations have been obtained by two equivalent methods both of which expand the scalar function $C_i^{(j)}(W_i)$, $B_i(W_i)$ and $A_i(W_i)$ in a series of Sonine polynomials. The manipulations required to express the transport coefficients in terms of the Sonine polynomials are long, difficult and tedious. No attempt will be made to follow these derivations exactly and rigorously, but an outline of the method along with the significant result will be presented in the following section. The interested reader is referred to the works of Chapman and Cowling[48] and Hirschfelder, Curtiss and Bird[9].

F. The Sonine Polynomial Expansion The solution of the integral equations is made by means of a variational principle, in which a set of trial functions are so chosen that solution of the integral equations requires that the integral of the "double-dotted" product of the trial function and the appropriate quantity, $\vec{A}_i$, B_i or $\vec{C}_i^{(j)}$ be a maximum. In this connection it has been found convenient to make use of the Sonine polynomials, $S_n^{(m)}(x)$, defined by

$$S_n^{(m)}(x) = \sum_j \frac{(-1)^j (m+n)!}{(n+j)!\,(m-j)!\,j!}\, x^j , \qquad (I.45)$$

which satisfy the orthogonality condition,

$$\int_0^\infty x^n e^{-x} S_n^{(m)}(x)\, S_n^{(m')}(x)\, dx = \frac{(n+m)!}{m!}\, \delta_{mm'} \qquad (I.46)$$

It is interesting that these functions, except for the normalization, are the same as the associated Laguerre polynomials. The trial functions, $t_i^{(h,k)}$, are then chosen to be a finite linear combination of the Sonine polynomials as follows,

$$\vec{t}_i^{(h,k)}(\vec{W}_i) = \mathscr{W}_i \sum_{m=0}^{\xi-1} t_{im}^{(h,k)}(\xi)\, S_m^{(m)}(W_i^2) \qquad (I.47)$$

where the tensor, $\mathscr{W}_i$ and the index, n, have different values depending on which of the quantities $\vec{A}_i$, $\mathscr{B}_i$, or $\vec{C}_i^{(j)}$ is being considered. The solution of the varational problem results in an equation for the Sonine polynomial coefficients, $t_{im}^{(h,k)}(\xi)$, (where ξ indicates the order of approximation): this in turn permits evaluation of the functions $\vec{A}_i$, $\mathscr{B}_i$ and $\vec{C}_i^{(j)}$ which lead directly to the perturbation function φ_i. Finally, the perturbation function is employed to calculate $f_i^{[1]}$ from Eq. (I.38), and $f_i^{[1]}$ provides the information needed for the evaluation of the transport coefficients.

The final results for the transport coefficients in terms of the Sonine polynomial expansion are summarized below:

$$D_{ij}(\xi) = \left(\frac{\rho}{3n m_j}\right)\sqrt{\frac{m_i}{2kT}} \sum_{m=0}^{\xi-1} C_{im}^{(ji)}(\xi) \int V_i^2 S_{3/2}^{(m)}(W_i^2) f_i^{[0]} d\vec{V}_i$$

$$\eta(\xi) = \frac{1}{15}\sum_j \frac{m_j^2}{2kT} \sum_{m=0}^{\xi-1} b_{jm}(\xi) \int S_{5/2}^{(m)}(W_j^2) V_j^4 f_j^{[0]} d\vec{V}_j \qquad (I.48)$$

$$\lambda'(\xi) = -\frac{\sqrt{2}}{3} k\sqrt{kT} \sum_j \sum_{m=0}^{\xi-1} \frac{1}{\sqrt{m_j}} a_{jm}(\xi) \int S_{3/2}^{(m)}(W_j^2)\left(\frac{5}{2} - W_j^2\right) W_j^2 f_j^{[0]} d\vec{V}_j$$

where D_{ij} is the binary diffusion coefficient, η is the coefficient of viscosity, and λ' is the ordinary thermal conductivity excepting that it carries also a term related to thermal diffusion: the coefficients $c_{im}^{(j,i)}$, b_{jm} and a_{jm} are the Sonine expansion coefficients $t_{im}^{(h,k)}$, and ξ is related to the order of approximation, i.e., the number of terms used in the finite series trial function.

The coefficients $t_{im}^{(h,k)}$ may be written in terms of a set of integrals $\Omega_{ij}^{(\ell,s)}$ defined as

$$\Omega_{ij}^{(\ell,s)} = \sqrt{\frac{2\pi kT}{\mu_{ij}}} \int_0^\infty\int e^{-\gamma_{ij}^2} \gamma_{ij}^{2s+3} (1-\cos^\ell \chi) b\, db\, d\gamma_{ij} \quad \text{(I.49)}$$

where $\Omega_{ij}^{(\ell,s)}$ refer to collisions between molecules of types i and j, μ_{ij} is the reduced mass, γ_{ij} is the reduced relative initial speed of the colliding molecules defined as $\gamma_{ij} = \sqrt{\frac{\mu_{ij}}{2kT}}\, g_{ij}$ χ is the angle by which the molecules are deflected and b is the impact parameter. The dynamics of the collisions enters into the description of the transport coefficients through the "collision integrals" defined by Eq. (I.49) in the following manner: in order to evaluate $\Omega^{(\ell,s)}$, χ must be known as a function of g_{ij} and b, and from the dynamics of the collision process it can be shown that

$$\chi(b,g) = \pi - 2b \int_{r_m}^\infty \frac{dr/r^2}{\sqrt{1-[\varphi(r)/\frac{1}{2}\mu g^2] - b^2/r^2}} \quad \text{(I.50)}$$

where r_m is the distance of closest approach. Hence if $\varphi(r)$

is given, $\Omega^{(\ell,s)}$ may be computed. The usefulness of the integrals $\Omega^{(\ell,s)}$ can be easily appreciated if one considers that the transport coefficients may be written (after much manipulation) in practical units, to the first approximation as,

$$D_1 \times 10^7 = 26280 \frac{\sqrt{T^3/M}}{p \sigma_m^2 \Omega^{(1,1)}}$$

$$\eta_1 \times 10^7 = 266.93 \frac{\sqrt{MT}}{\sigma_m^2 \Omega^{(2,2)}} \qquad \text{(I.51)}$$

$$\lambda_1 \times 10^7 = 1989.1 \frac{\sqrt{T/M}}{\sigma_m^2 \Omega^{(2,2)}}$$

where

D = coefficient of self-diffusion in cm^2-sec^{-1}

η = coefficient of viscosity in g-$cm^{-1}$$sec^{-1}$

λ = thermal conductivity in cal-cm^{-1}-sec^{-1}-deg^{-1}

T = absolute temperature

M = molecular weight

p = pressure in atmospheres

r_m = the collision diameter given by $\varphi'(r_m) = 0$.

Higher approximations to the transport coefficients may all be written in the same form, viz.,

$$\Gamma_k = \Gamma_1 f_\Gamma^{(k)} \qquad \text{(I.52)}$$

where $f_\Gamma^{(k)}$ is a very slowly varying function of the integrals $\Omega^{(\ell,s)}$ (and hence T) and differs only slightly from unity, and Γ_k represents any of the transport coefficients.

Eqs. (I.48) and (I.51) represent respectively the

theoretical and practical solutions of the Boltzmann equation for the transport coefficients following the methods of Enskog and Chapman. More recently, Grad[49] had evolved a very powerful method (the 13-moment approximation) for solving the Boltzmann equation which justifies the first approximation of Enskog but which, in addition, permits many higher order levels of description. The formal theory of polyatomic molecules has been developed by Wang-Chang and Uhlenbeck[50], and very recently Curtiss[47] has published a theory for nonspherical molecules. The principal difference between the two approaches lies in the fact that Curtiss restricts the problem by considering only classical mechanics, while the former workers solve the quantum mechanical problem. The primary disadvantage of the quantum mechanical treatment is difficulty associated with the evaluation of the angular dependent inelastic cross-sections, which do not appear in the theory of Curtiss. No numerical computations have been performed for either theory, but Curtiss has promised them for his theory. It remains to be seen just how effective his theory will be in practice.

APPENDIX II

THE COLLISION INTEGRALS $\Omega^{(l,s)*}(\alpha, T^*)$ FOR CALCULATING THE TRANSPORT COEFFICIENTS FOR THE MODIFIED BUCKINGHAM POTENTIAL

T^* \ α	12	13	14	15	16	17
0.1	3.2524	3.1726	3.1205	3.0691	3.0160	2.9639
0.2	2.6064	2.5324	2.4920	2.4494	2.4080	2.3645
0.3	2.2709	2.2131	2.1805	2.1285	2.1089	2.0743
0.4	2.0176	1.9783	1.9545	1.9275	1.9017	1.8767
0.5	1.8130	1.7880	1.7723	1.7536	1.7300	1.7184
0.6	1.6474	1.6321	1.6235	1.6114	1.6003	1.5888
0.7	1.5136	1.5060	1.5015	1.4944	1.4885	1.4818
0.8	1.4082	1.4092	1.4084	1.4048	1.4028	1.4005
0.9	1.3159	1.3168	1.3189	1.3182	1.3180	1.3184
1.0	1.2422	1.2458	1.2500	1.2515	1.2538	1.2568
1.2	1.1287	1.1260	1.1431	1.1857	1.1533	1.1587
1.4	1.0463	1.0560	1.0651	1.0715	1.0789	1.0872
1.6	0.9843	0.9955	1.0060	1.0141	1.0229	1.0320
1.8	0.9362	0.9487	0.9600	0.9693	0.9797	0.9895
2.0	0.8978	0.9113	0.9232	0.9336	0.9440	0.9553
2.5	0.8289	0.8445	0.8572	0.8695	0.8815	0.8945
3.0	0.7830	0.7998	0.8131	0.8269	0.8400	0.8537
3.5	0.6496	0.7677	0.7815	0.7962	0.8104	0.8247
4.0	0.7240	0.7429	0.7573	0.7727	0.7876	0.8026
5.0	0.6862	0.7065	0.7221	0.7385	0.7544	0.7701
6.0	0.6589	0.6756	0.6970	0.7140	0.7305	0.7476
7.0	0.6376	0.6597	0.6777	0.6950	0.7123	0.7301

APPENDIX II (con't)

T* \ α	12	13	14	15	16	17
8.0	0.6202	0.6320	0.6619	0.6795	0.6976	0.7157
9.0	0.6054	0.6287	0.6486	0.6664	0.6854	0.7037
10	0.5926	0.6165	0.6370	0.6551	0.6742	0.6934
12	0.5713	0.5961	0.6177	0.6361	0.6559	0.6762
14	0.5540	0.5794	0.6019	0.6201	0.6410	0.6615
16	0.5305	0.5654	0.5885	0.6075	0.6285	0.6493
18	0.5268	0.5532	0.5768	0.5963	0.6176	0.6388
20	0.5158	0.5428	0.5666	0.5863	0.6080	0.6295
25	0.4933	0.5214	0.5454	0.5658	0.5880	0.6101
30	0.4756	0.5043	0.5285	0.5497	0.5721	0.5946
35	0.4613	0.4908	0.5145	0.5365	0.5592	0.5821
40	0.4492	0.4795	0.5028	0.5253	0.5482	0.5710
45	0.4390	0.4697	0.4929	0.5158	0.5389	0.5617
50	0.4299	0.4612	0.4840	0.5075	0.5305	0.5536
60	0.4152	0.4466	0.4692	0.4936	0.5168	0.5399
70	0.4032	0.4358	0.4573	0.4824	0.5057	0.5288
80	0.3933	0.4264	0.4473	0.4730	0.4962	0.5195
90	0.3849	0.4185	0.4388	0.4651	0.4883	0.5116
100	0.3777	0.4116	0.4314	0.4582	0.4813	0.5047
200	0.3361	0.3724	0.3887	0.4186	0.4413*	0.4609*

* Extrapolated values.

APPENDIX III

A RELATION BETWEEN THE CHARACTERISTIC DISTANCE PARAMETERS OF THE LENNARD-JONES AND EXPONENTIAL-SIX POTENTIAL FUNCTIONS

The Lennard-Jones (L.J.) function may be written as

$$\varphi_L(r) = 4\epsilon_L\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad \text{(III.1)}$$

and the Exp-Six function as

$$\varphi_E(r) = \frac{\epsilon_E}{1-6/\alpha}\left[\frac{6}{\alpha}\, e^{\alpha(1-r/r_m)} - \left(\frac{r_m}{r}\right)^{6}\right] \qquad \text{(III.2)}$$

Eq. (III.2) contains a spurious maximum at very small r and for convenience, $\varphi(r) = \infty$, if $r < r_{max}$ (<u>cf.</u> pg.3 of the text).

The basic assumption from which the ratio (σ/r_m) will be derived may be expressed as

$$\left[\lim_{r\to r_{min}} \frac{d^2\varphi_L}{dr^2} \Big/ \lim_{r\to r_{min}} \frac{d^2\varphi_E}{dr^2}\right] = 1 \qquad \text{(III.3)}$$

In Eq. (III.3) it must be understood that, in general, $\varphi_L(r) \neq \varphi_E(r)$ and, therefore, the value of r for which each function becomes a minimum, r_{min} is in general different for the two functions. The significance of Eq. (III.3) will be discussed later.

Straightforward differentiations of Eqs. (III.1) and (III.2) leads to

$$\varphi_L''(r) = \frac{24\epsilon_L}{\sigma^2}\left(\frac{\sigma}{r}\right)^{8}\left[26\left(\frac{\sigma}{r}\right)^{6} - 7\right] \qquad \text{(III.4)}$$

and

$$\varphi''_E(r) = \frac{6\epsilon_E}{(1-6/\alpha)r_m^2}\left[\alpha e^{\alpha(1-r/r_m)} - 7\left(\frac{r_m}{r}\right)^8\right] \qquad \text{(III.5)}$$

where ϵ_L and ϵ_E are the depths of the wells for the (L.J.) and Exp-Six functions respectively. As $r \to r_{min}$ the ratio (σ/r) for the (L.J.) function approaches a constant value of 0.8909 (β). hence

$$\lim_{r \to r_{min}} \varphi''_L(r) = \frac{24\epsilon_L}{\sigma^2}\beta^8\left[26\beta^6 - 7\right] \qquad \text{(III.6)}$$

For Eq. (III.5), as $r \to r_{min}$ the exponential term approaches α , and the term in r^{-8} approaches the number seven, therefore

$$\lim_{r \to r_{min}} \varphi''_E(r) = \frac{6\epsilon_E}{(1-6/\alpha)r_m^2}(\alpha - 7) \qquad \text{(III.7)}$$

Substitution of (III.6) and (III.7) into Eq. (III.3) and rearrangement leads, finally to the equation,

$$(\sigma/r_m) = 2\beta^4\left[\epsilon^*(26\beta^6 - 7)\frac{1}{\alpha}\frac{(\alpha-6)}{(\alpha-7)}\right] \qquad \text{(III.8)}$$

in which $\epsilon^* = (\epsilon_L/\epsilon_E)$.

Table IIIA shows values of (σ/r_m) as calculated from Eq. (III.8) for integral values of α from 12 to 17, and for selected values of ϵ^* from 0.90 to 1.20. The entries are

TABLE III A

(σ/Π_m) FOR SELECTED VALUES OF ϵ^* AND ALPHA

ϵ^* \ α	12	13	14	15	16	17
.90	.92491	.87621	.83564	.80099	.77074	.734996
.92	.93516	.88592	.84490	.80986	.77928	.75224
.94	.94521	.89544	.85399	.81857	.78766	.76033
.96	.95524	.90494	.86304	.82725	.79601	.76839
.98	.96510	.91429	.87196	.83579	.80424	.77633
.99	.97007	.91899	.87644	.84009	.80837	.78032
1.00	.97494	.92361	.88084	.84431	.81243	.78424
1.02	.98468	.93283	.88964	.85275	.82055	.79207
1.04	.99445	.94209	.89847	.86121	.82869	.79993
1.06	1.0042	.95132	.90727	.86964	.83681	.80777
1.08	1.0129	.95961	.91519	.87723	.84411	.81481
1.10	1.0227	.96887	.92401	.88569	.85225	.82267
1.15	1.0451	.99011	.94427	.90510	.87093	.84070
1.20	1.0676	1.0113	.96453	.92452	.88961	.85874

judged accurate to within two figures in the fifth decimal place.

The derivation of Eq. (III.8) was based on Eq. (III.3) and some discussion of this point is required. In Eq. (III.3) the limits were taken as the (L.J.) and Exp-Six functions approached their respective minima. It has been considered a fair assumption by most workers that in this region both functions may be represented as parabolas. Since the two functions are not coincident, then they may be represented by two parabolas having different origins and characterized by different values of the parameter p , the distance from the focus to the directrix. The parabolas may, therefore, be written as

$$\begin{aligned} (\pi - h_L)^2 &= 2 p_L (\varphi_L - k_L) \\ (\pi - h_E)^2 &= 2 p_E (\varphi_E - k_E) \end{aligned} \qquad \text{(III.9)}$$

where the pairs of coordinates (h_L, k_L), (h_E, k_E) locate the origins of the parabolas on a $\varphi(\pi)$ vs π plot. From Eq. (III.9) it follows directly that

$$\begin{aligned} \varphi_L''(\pi) &= (1/p_L) \\ \varphi_E''(\pi) &= (1/p_E) \end{aligned} \qquad \text{(III.10)}$$

and from Eqs. (III.10) that

$$\left[\varphi_L''(\pi)/\varphi_E''(\pi)\right] = p_E/p_L \qquad \text{(III.11)}$$

It is clear, therefore, that Eq. (III.3) is equivalent to assuming that $(\rho_E / \rho_L) = 1$, a condition that physically requires both functions, $\varphi_L(r)$ and $\varphi_E(r)$, to have exactly the same shape sufficiently close to their respective minima even though their origins may be different. The extent to which Eq. (III.3) agrees with experiment is probably a measure of the accuracy of this assumption. Table IIIB contains a comparison of calculated and experimental values of (σ / r_m) for several gases of presumed spherical symmetry. Included for comparison are three non-spherical cases. The (L.J.) parameters used for the calculation were all taken from Hirschfelder[9], as were the Exp-Six values for all the gases excepting argon, methane and ethane, which were taken from the results of this research.

It is clear from Table IIIB that as a molecule becomes less spherically symmetric (implying rather high values for α, i.e. $\alpha \geq 16$), the agreement between experimental and calculated values for (σ / r_m) is attenuated. This is in harmony with the observation that as α gets large a single set of potential parameters is incapable of reproducing both the transport and virial coefficients. In this connection, it is interesting to note that of the non-spherical gases, ethane seems to show the slightest deviation, a fact which finds substantiation elsewhere in the very recent literature[46].

In conclusion, the principal ultility of Eq. (III.8) lies in it ability to predict the location of r_m rather well

TABLE III B

A COMPARISON OF EXPERIMENTAL AND CALCULATED VAULES FOR (σ/r_m)

Gas	(σ/r_m) Expt'l.	(σ/r_m) Calc.	ϵ^*	α
Argon	0.884	0.884	1.01	14.0
Neon	0.886	0.883	1.04	14.5
Krypton	0.890	0.906	0.90	12.3
Xenon	0.911	0.909	0.97	13.0
Methane	0.923	0.920	1.09	14.0
Nitrogen	0.917	0.735	0.90	17.0
Carbon Monoxide	0.912	0.752	0.92	17.0
Ethane	0.892	0.812	1.00	16.0

once the parameters α and (ϵ/k) have been determined and a choice of σ and (ϵ/k) for the corresponding (L.J.) potential has been made. Conversely, if r_m and (ϵ/k) are known, then by application of an extended form of Table IIIA, a self-consistent value for α may be selected.

APPENDIX IV

SOURCE AND PURITY OF THE GASES

A purity of 99 percent in the gases employed was in all cases adequate, since even in the extreme case, a 1.0 percent impurity would not be expected to change the measured viscosity by more than 0.4 percent. For example, a 1.0 percent methane impurity in ethane at 100°C would produce, assuming linearity, a change in the measure value of ethane of 0.26 percent.

The following gases were employed:

1. Oxygen, 99.6%, The Matheson Company, Inc.
2. Argon, 99.9%, The Matheson Company, Inc.
3. Methane, 99.0%, The Matheson Company, Inc.
4. Ethane, 99.9 mol%, The Phillips Petroleum Company
5. Helium, 99.99%, Airco Company, Bureau of Mines, "XXX" grade.

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