ARRANGEMENT OF TABLES AND FIGURES

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'TRANSPORT COEFFICIENTS OF BINARY GAS MIXTURES'

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All the tables, except for tables numbered 3 and 4 placed in appendix A (commencing on p.185), follow serial order.

All the figures, except for figures numbered 46 to 48 (following p.162) and 49 to 51 (following p.164), are placed in serial order.

TRANSPORT COEFFICIENTS OF BINARY GAS MIXTURES

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PREFACE

This thesis describes original work carried out by the candidate at the Australian National University. Wherever it has been necessary to use others' work proper acknowledgement has been made in the form of references.

Suresh C. Gupta.

Suresh Chander Gupta

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SUMMARY

Expressions of the transport coefficients for a binary gas mixture have been developed in terms of irreducible tensors and matrices. They have been shown to be completely equivalent to those of Chapman and Cowling but are more suitable for writing a computor programme for a calculation to any given order. This programme has not to be changed from one order to the next and has been used to carry out a much more extensive and systematic study of the higher order contributions, for rigid sphere and Lennard-Jones potentials than the ones available in the literature.

For the rigid sphere potential, for a given set of parameters, the rate of decrement of the first four orders is more rapid for the coefficient of viscosity than any other coefficient for a simple gas and for a binary gas mixture. The approach to the following limits was also studied for the coefficients of thermal-conductivity, diffusion and thermal diffusion ratios. The limits are : (1) $M_1 \gg M_2$, $n_1 \gg n_2$ (2) $M_1 \gg M_2$, $\sigma_{11} \gg \sigma_{22}$ (3) $M_1 \gg M_2$, $n_2 \gg n_1$ (4) $M_1 \gg M_2$, (4) $M_1 \gg M_2$, $\sigma_{22} \gg \sigma_{11}$. It is found that the absolute values of these coefficients do not have a common limit for the (1) and (2) or for the limits (3) and (4). However :
except for thermal - conductivity, the relative

magnitudes of the higher orders to the first do have a common limit for the cases (1) and (2). For the Lennard-Jones potential, the rate of decrement of the first four orders with temperature and concentration is most rapid for the coefficient of viscosity and the least for thermal-diffusion ratio. The higher order contributions for the simple gas and for Ar-Ne mixture are important only at high temperature. The value of thermal-diffusion ratio for Ar-Ne is negative below 100° K for all orders.

Finally, a comparison of the higher orders of the theory with the experimental data for Ar-Ne, Kr-Ne, Kr-He and Xe-Kr mixtures shows that for the unlike molecules there is a need for better and more accurate sets of force constants than those given by the combination rules. A method of estimating these constants, using the experimental data of viscosity and thermal-conductivity in a more direct fashion has been outlined.

For more details about the contents of this work, refer to Table of Contents and Introduction. (p.11-14, Ch. I).

TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

A. The distribution function and the transport coefficients

Expressions for transport coefficients for a simple gas, or for a multi-component gas-mixture, have been obtained by solving a set of Boltzmann equations by the usual method of Chapman and Enskog. The details of the solution are discussed by Chapman and Cowling and Hirschfelder et al (Chs. 7 and 8, C.C-52; Chs. 7 and 8, H.C.B-64). Basically the procedure involves the solution of the Boltzmann equation (or equations) by a method of successive approximation. For the simple gas, the relevant Boltzmann equation may be written in the form

$$\mathfrak{D}\, f = - J(f\, f_1) \quad , \tag{1-1}$$

where

$$\mathfrak{D} = \frac{\partial}{\partial t} + \underline{c} \cdot \frac{\partial}{\partial \underline{r}} + \underline{X} \cdot \frac{\partial}{\partial \underline{c}} \quad , \tag{1-2}$$

and

$$J(f\, f_1) = \iint (f\, f_1 - f'\, f_1')\, \sigma(g,\chi)\, d\, \hat{g}'\, d\underline{c}_1 \quad . \tag{1-3}$$

The various symbols have their usual meaning (p. 108, C.C-52).

For ordering equations corresponding to different approximations, a parameter $1/\varepsilon$ is introduced on the r.h.s. of eqn. (1-1) and f is expanded in a power series in ε. Equating different powers of ε on both sides of eqn. (1-1) an infinite set of equations corresponding to different approximations is obtained. The first approximation ($f^{(0)}$) gives the Maxwellian distribution function. For a non-equilibrium situation, this choice of $f^{(0)}$ gives rise to a set of subsidiary conditions which must be satisfied by higher approximations to f. (For details, see ch. 7, C.C-52)

With this $f^{(0)}$ and the associated set of subsidiary conditions, the second and higher approximations are completely determined (for second and third approximations, Chs. 7 and 15, C.C-52). In practice it is even difficult to work with the second approximation (i.e. $f^{(1)}$) not to speak of higher approximations. It is the second approximation to the distribution function (i.e. ($f^{(0)} + f^{(1)}$)) which is of interest to us in this work and is adequate for systems near equilibrium. It depends linearly on gradients of temperature and velocity.

On using the expression for the second approximation to determine heat and momentum flow, coefficients of thermal conductivity (λ) and viscosity (η), of a simple gas, are automatically defined. In particular λ (eqn. 7.4-1, C.C-52) is

$$\lambda = \frac{2\,k^2\,T}{3\,m}\,[\underline{A},\underline{A}] \quad , \qquad (1\text{-}4)$$

where $\underline{A}$ is an infinite sum of Sonine polynomials (eqns. 7.51-1, -2, C.C-52). $[\underline{A},\underline{A}]$ is an integral function, related to the integral part of the Boltzmann equation, and commonly called 'square bracket' (for definition, refer to eqn. (4.4-8, C.C-52)). The square bracket in the expression for λ is formally shown to be equivalent to an infinite order determinant, each element of which is essentially a square bracket for certain Sonine polynomials (see sec. 7.51, C.C-52). Furthermore each of these individual square brackets may be expressed in terms of so-called collision integrals ($\Omega^{(\ell,s)}$). These integrals depend on the intermolecular forces and the temperature of the gas (Ch. 9, C.C-52). The coefficient of viscosity (η) is determined in a similar manner (Chs. 7 and 9, C.C-52). Therefore, at least in principle, once the collision integrals are known, the corresponding coefficients can be evaluated.

In practice, the associated infinite order determinants must, of course, be truncated to a finite size for these calculations to be done. Therefore one speaks of an n th order approximation to a particular coefficient when the relevant determinant is truncated to an $(n \times n)$ size.

In the case of a binary gas-mixture, the same procedure is adopted for solving the two relevant Boltzmann equations (for details, see Ch. 8, C.C-52). However, there are minor points of difference. The first is being that four transport coefficients (coefficients of viscosity, thermal-conductivity, diffusion and thermal-diffusion) are considered instead of two as in the case of the simple gas. The second is that, for a binary mixture, the general expressions of the coefficients are expressed in terms of more complex integral functions known as "curly brackets". These brackets are made up of several square brackets (for definition of curly brackets, refer to eqn. 4.4-12, C.C-52). Again the evaluation of the curly brackets follows the same pattern as the square brackets in the simple gas case (Chs. 8 and 9, C.C-52). Again, of course, the associated infinite order determinants must be truncated to a finite size.

Thus the formal structure for the calculations of the transport coefficients for a simple gas or a binary gas-mixture, upto an order 'n' , is complete (For details see Chs. 7,8,9, C.C-52). As is known and is further discussed here, explicit numerical calculations for a given order 'n' are not simple. The difficulties involved for such calculations are of the following types.

1. Explicit expressions for the square brackets corresponding to the given order 'n' must be developed. As is apparent from the procedure of Chapman and Cowling (Ch. 9, C.C-52), there are no simple set rules indicating firstly which of the collision integrals are needed for a particular square bracket and secondly how the corresponding coefficients for a given collision integral are to be evaluated. In fact, the latter step is very complex. This complexity is apparent from the works of Chapman and Cowling, Joshi, Saxena, Mason and Hirschfelder et al (C.C-52, Jo-65, S.J-63, Ma-57, H.BS-48) who have developed the expression for the first, second and third orders for various coefficients for a binary-mixture.

2. For a particular order, the calculations are further complicated by the number of parameters involved. These

parameters for a simple gas are temperature, mass and force constants (for a given intermolecular potential). For a gas-mixture, they are temperature, mass and relative concentrations of the individual components of the mixture and force constants for interactions between like and between unlike molecules for a particular potential. This is why there are only a few computed results available for specific values of the parameters.

In view of the complexity of the Chapman-Cowling procedure, as outlined above, for doing higher-order calculations and computations, there is a need to simplify the whole structure for a simple gas or a gas-mixture, for various coefficients.

B Convergence Studies

Having outlined the complexity of C.C[1] procedure for higher order calculations, we wish to emphasise that these calculations are really essential in order to provide more stringent tests of the theory. To date the experimental data has been compared to the first order theory alone while the higher order contributions have always been assumed to be very small. As is

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[1] C.C. = Chapman-Cowling.

discussed below there is only partial evidence to support this assumption.

In practice it is obviously simpler to calculate second and third order contributions for a simple gas than for a gas-mixture because of the less number of parameters involved. Again, the structure of the brackets is simpler in the former case. The rapid rate of decrement for the first three orders for the simple gas for different intermolecular potentials is well established (C.C-52, Ma-55, H.C.B-64). Due to obvious difficulties in the calculations for a binary mixture, as outlined above, enough computed values to establish the general rapid rate of decrement for the first three orders[1], are not available. The available computed values are :

1. Lorentzian Gas. (L.G.M.)

   In this case, the mass and concentration of the heavier component is much greater than that of the lighter. Convergence for the infinite orders is established for this case for different types of potentials (Ma-57a, De-66, C.C-52).

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[1] Limitations to the computor programmes based on C.C. procedures e.g. those mentioned by Devoto (De-66) are discussed later (p.9).

2. Quasi-Lorentzian Gas (Quasi L.G.M.)

In this case, the concentration of the heavier component is much less than that of the lighter. Convergence is implied by the decreasing contributions for the first three orders for the coefficients of thermal diffusion and diffusion for the inverse power and Lennard-Jones potentials. (Ma-57a, De-66).

3. Isotopic Mixtures.

In this case also, convergence is implied by the decreasing contributions for the first three orders for the coefficients of thermal-diffusion and diffusion. (Ma-57a).

4. Joshi and Saxena have done calculations, using second and third order expressions of viscosity for a binary gas-mixture, for rigid sphere molecules (Jo-65, J.S-65). They computed only for two specific sets of parameters which are given below :

(i) $M_1 = 10\ M_2$, $\sigma_{11} = \sigma_{22}$, $x_1 = x_2 = 0.5$. ~~$X_1 = X_2 = 0.5$~~ .

(ii) $M_1 = 10\ M_2$, $\sigma_{11} >> \sigma_{22}$, $x_1 = x_2 = 0.5$. ~~$X_1 = X_2 = 0.5$~~ .

All the symbols have their usual meanings.

Also they have done calculations for an Ar-He system using the second order expression for viscosity for the exp-6 potential (S.J.-63).

In the general case, the above set of calculations is not enough to establish a definite pattern for the rapid rate of decrement for the first three orders for various coefficients. This is because the extreme cases, such as L.G.M. or Quasi L.G.M., are not good enough for generalisation to the types of mixtures ordinarily encountered. Recently Devoto (De-66) computerised the second and third order expressions for a binary gas-mixture and showed that the L.G.M. and Quasi-L.G.M. limits are reached when the mass and concentration ratios are of the order of 10^{-6} or 10^{-7}. Since these limits are well-beyond the limits encountered in practice (e.g. see Th. 60), there is a need to study more general mixtures to establish the definite pattern.

Devoto's approach was, clearly, a step forward to know more about the computed values for orders higher than the first for different sets of parameters. Apparently, he was forced to write separate computer programmes for each of the orders he considered. Although the explicit expressions of the square brackets for these orders were already available, still it

involved a lot of work. For computation of higher orders, one would have to develop the expressions for the brackets involved in them before writing a computer programme.

Thus we conclude that the present procedure, of studying higher order contributions for various transport coefficients, due to Chapman and Cowling (Ch. 9, C.C-52) is somewhat cumbersome. This is particularly so in the case of gas-mixtures.

C. Aims of Present Study.

In subsequent work, our aim is to simplify the whole structure of calculations for a binary gas-mixture. This has become feasible because of an alternative formulation of the Chapman-Enskog method by Kumar (Ku-67). On the basis of this reformulation, the various difficulties associated with the Chapman-Enskog method, as mentioned earlier, are overcome in the following way.

Firstly, final expressions for the transport coefficients are derived as an inverse of a certain matrix (equivalent to $[\underline{A},\underline{A}]$ (eqn. (1.4) for the simple gas case, see Ku-67). The matrices are again truncated for a finite order calculation but they are more suitable for writing a computer programme than

the truncated determinants of Chapman and Cowling. The elements of these matrices can be expressed as finite sums of the product of two Talmi coefficients and the interaction integrals ($V^{\ell}_{nn'}$) (For Talmi coefficients, see Ku-66a, for other information, see Ku-67). Explicit general expressions are now available in these terms. Their advantage is that they provide an easy set of rules for finding the number of interaction integrals needed in calculation of a particular order and for evaluating the numerical coefficients for these interaction integrals.

Secondly, since the expressions for the coefficients based on the reformulation are more suitable for computational work, the study for the different sets of parameters, for a given order 'n' calculation, now becomes possible with the use of a computer. Moreover this computer programme has not to be modified from one order to the next.

In the present work, firstly we develop expressions for the transport coefficients for a binary-mixture using Kumar's reformulation. As stated above, these expressions are particularly convenient for computational purposes. Secondly, using these expressions, we study the rate of decrement for

first four orders for Lennard-Jones and rigid sphere potentials for various sets of parameters. Thirdly, from the above study, we conclude that the rate of decrement is more rapid for viscosity and thermal-conductivity than for diffusion and thermal-diffusion. Therefore the first order expressions for viscosity and thermal-conductivity are more useful to study force constants for interactions between unlike molecules than the corresponding expressions for diffusion and thermal-diffusion as presently done in literature (S.M.-53).

Finally, a brief summary of the contents of various Chapters is given below.

In Chapter II and III, two Boltzmann equations for a binary gas-mixture are essentially solved by the Chapman-Enskog method. The solution is developed in terms of spherical irreducible tensors and matrices. Expressions for transport coefficients are derived. These expressions may be used to build up an automatic computer programme for a given order 'n' and this has not to be modified while going from one order to the next. Also these expressions are shown to be equivalent to the general expressions of Chapman and Cowling (Ch. 8, C.C-52) which, as already discussed, are not very

convenient for computation. As a preliminary to this derivation, various properties of the differential and integral parts of the Boltzmann equation are discussed.

In Chapter IV, steps needed to write the computer programme from the general expressions of Chapter III have been outlined. Explicit expressions, of the coefficients for various orders, in terms of mass ratios, concentration ratios and interaction integrals are given in appendix C. These expressions may be subjected to the same types of studies as the corresponding expressions in Chapman-Cowling work (Br-59,-65, S.J.-65, H.C.B.-64, Ma-57, S.J.-64a). A possibility of the Kihara type approximation for the expressions of thermal-conductivity, diffusion and thermal-diffusion have been pointed out. The relation between the interaction and collision integrals have been put in a form more suited to out work. Some specific cases are given in appendix B. In appendix A, the interaction integrals for rigid sphere and Lennard-Jones potentials are tabulated.

In Chapter V the computer programme, developed in Chapter IV, is used to carry out a systematic study of

the rate of decrement. This has been done for various sets of parameters, for various orders, for rigid sphere and Lennard-Jones potentials and for different coefficients. Further, the effects of the diffusive term on the thermal-conductivity of a gas-mixture are considered for both the potentials. Also in the literature the same limits (C.C-52, Ma-57a, De-66) have been considered of interest. The limits are (1) $M_1 \gg M_2$; $x_1 \gg x_2$; (2) $M_1 \gg M_2$, $\sigma_{11} \gg \sigma_{22}$; (3) $M_2 \gg M_1$, $x_2 \gg x_1$; (4) $M_2 \gg M_1$, $\sigma_{22} \gg \sigma_{11}$. We study the full range of variation of the parameters involved and approach to the limiting values, for the rigid sphere potential.

In Chapter VI, a comparison of the higher orders of the theory and the experimental data is made for Ar-Ne, Kr-Ne, Kr-He and Xe-Kr mixtures for different coefficients for the Lennard-Jones potential. Also an accurate and efficient way of handling the experimental data of viscosity and thermal-conductivity of a binary gas-mixture for determining the force constants of unlike molecules is discussed. This is shown to be better than another method occurring in the literature which involves calculation of the diffusion coefficients from the data of these coefficients as an intermediate step.

CHAPTER II

IRREDUCIBLE TENSORS, MATRICES AND THE EXPANSION OF THE DISTRIBUTION FUNCTION

Introduction

In this chapter, the velocity distribution function is expanded in terms of the polynomials of the velocity vector using the notation of Fano and Racah (F.R.-59). This expansion is useful because we can exploit the concept of irreducibility using spherical polar coordinates. Thus it is necessary to rewrite various gas properties such as number density, temperature, mass average velocity, pressure tensor, rate-of-shear tensor, thermal-flux vector and the average velocity (C.C.-52) in terms of the coefficients of the expansion of the distribution function used here. (Section A).

The integral part of the Boltzmann equation, in the usual standard work of Chapman and Cowling (C.C-52) is related to the bracket expressions. Here it is expressed using the above expansion and the Talmi coefficients (Ku-66) for transforming the polynomials of the velocity vector or the product of these polynomials to the center of mass and the relative velocity coordinates. It is related to the collision matrix which is defined later in this chapter. The advantage of dealing with the integral part of the Boltzmann equation in this way is it finally involves integration over the relative velocity

coordinate g only while the integration over the other variables is performed easily using the orthogonality of the spherical harmonics and the velocity vector polynomials.

The diagonal character and symmetry properties of the matrices for like and unlike molecules have been discussed. Also, the matrices are shown to be equivalent to the bracket expressions. (Section B).

Finally, in the second approximation of the Chapman-Enskog method, the differential part of the Boltzmann equation (C.C.-52) has been analysed into its scalar, vector and tensor parts using the above form of the distribution function. (Section C).

The results of sections A and C are needed only for chapter III, while those of section B are needed for chapters III, IV and appendices A and C.

A Notation and Definitions

(a) IRREDUCIBLE TENSORS

The notation for standard and contrastandard tensors, in the present work, is the same as discussed by Fano and Racah (F.R.-59). Thus a standard tensor of rank ℓ will be denoted by $\Phi_m^{(\ell)}$, while a contrastandard

tensor will be written $\phi_m^{[\ell]}$, where m can have $(2\ell+1)$ values. Tensors of particular rank ℓ and standardisation, are distinguished by including another superscript viz. $\phi_m^{(\nu\ell)}$ and $\phi_m^{[\nu\ell]}$, where ν can have values $0,1,2,\ldots$.

The spherical harmonic is represented by a contrastandard tensor of rank ℓ and the relation between this representation and the usual representation is

$$Y_m^{[\ell]} = i^{\ell} \; Y_{\ell m} \quad . \tag{2.1}$$

The relation between two types of tensors is

$$Y_m^{[\ell]} = Y_m^{(\ell)*} = (-)^{\ell-m} \; Y_{-m}^{\ell} \quad . \tag{2.2}$$

A velocity vector $\underline{C}(=C_1,C_2,C_3)$ is related to its spherical components by the following set of equations :

$$C_{\pm 1}^{(1)*} = C_{\pm 1}^{[1]} = \frac{(\mp iC_1 + C_2)}{\sqrt{2}} = \mp \frac{i}{\sqrt{2}} C \sin\theta \, e^{\pm i\varphi} \tag{2.3}$$

$$C_0^{(1)*} = C_0^{[1]} = i\, C_3 = i\, C \cos\theta \tag{2.4}$$

where C is the magnitude of $\underline{C}$.

(b) POLYNOMIALS

The irreducible tensor polynomials of the velocity vector $\underline{C}$, to be used in expanding the velocity distribution function, are the same as those used by several other workers (Bu-35, C.C.-52, Wa-60).

$$\phi_m^{(\nu\ell)}(\underline{C}) = N_{\nu\ell}\left(\frac{C}{\sqrt{2}}\right)^{\ell} S^{(\nu)}_{\ell+1/2}\left(\frac{1}{2}C^2\right) Y_m^{(\ell)}(\theta,\phi)$$

$$= R_{\nu\ell}(C)\, Y_m^{(\ell)}(\hat{\underline{C}})$$

$$= \phi^{(\underline{\nu})}(C) \tag{2.5}$$

where

$$N^2_{\nu\ell} = 2\pi^{3/2}\,\Gamma(\nu+1)/\Gamma(\nu+\ell+{}^3/_2) \tag{2.6}$$

$$R_{\nu\ell} = N_{\nu\ell}\left(\frac{C}{\sqrt{2}}\right)^{\ell} S^{(\nu)}_{\ell+1/2}\left(\frac{1}{2}C^2\right) \tag{2.7}$$

and $S^{(\nu)}_{\ell+1/2}\left(\frac{1}{2}C^2\right)$ is the Sonine or generalised Laugerre polynomial.

The orthogonality relation for the polynomials is

$$\int \bar{w}(\alpha,C)\,\phi_m^{(\nu\ell)}(\alpha\underline{C})\,\phi_{m'}^{[\nu'\ell']}(\alpha\underline{C})\;d\,\underline{C}$$

$$= \delta_{\nu\nu'}\;\delta_{\ell\ell'}\;\delta_{mm'} \tag{2.8}$$

where the weight function $\bar{w}(\alpha,C)$ is given by

$$\bar{w}(\alpha,C) = \left(\frac{\alpha^2}{2\pi}\right)^{3/2} e^{-\frac{1}{2}\alpha^2 C^2} \tag{2.9}$$

and

$$\int \bar{w}(\alpha,C)\, d\underline{C} = 1 .$$

These polynomials depend upon five parameters. Four of these $(\alpha(\underline{r},t)$, $\underline{c}_0(r,t))$ come through the weight function. $\underline{c}_0$ is hidden in the choice of the coordinate system for c . $n(\underline{r},t)$, the fifth parameter is related to the normalisation. As will be seen later α is related to temperature.

(c) DISTRIBUTION FUNCTION.

The velocity distribution function $f_i(r,\underline{c},t)$ can be written in two parts; the first depending upon the velocity vector and the second depending upon the space. We take $\underline{C}_0$ as the origin of the velocity coordinate system. Then the peculiar velocity $\underline{C} = c - c_0$, or $\underline{c} = \underline{C} + \underline{c}_0$. Hence the distribution function $f_i(\underline{r},\underline{c},t)$ becomes $f_i(\underline{r},\underline{C}+\underline{c}_0,t)$, which will later be written $f_i(\underline{r},\underline{C},t)$.

$$f_i(\underline{r},\underline{C}_i,t) = n_i\bar{w}(\alpha_i C_i) \sum_{\nu\ell m} \mathcal{F}_m^{(\nu\ell)}(\alpha_i,\underline{r},t)\, \phi_m^{(\nu\ell)}(\alpha_i\underline{C}_i) \tag{2.10}$$

where

$$\mathcal{F}_m^{(\nu\ell)}(\alpha_i,\underline{r},t) = \frac{1}{n}\int \phi_m^{(\nu\ell)}(\alpha_i,\underline{C})\, f_i(\underline{r},\underline{C},t)\, d\underline{C} \qquad (2.11)$$

and

$$n_i(r,t) = \int f_i(\underline{r},\underline{C},t)\, d\,\underline{C} \quad . \qquad (2.11a)$$

So that $\mathcal{F}_m^{(\nu\ell)}(\alpha_i,\underline{r},t)$ becomes the average value of the polynomials, i.e.

$$\mathcal{F}_m^{(\nu\ell)}(\alpha_i,\underline{r},t) \equiv \mathcal{F}_{i\,m}^{(\nu\ell)} = \left\langle \phi_m^{(\nu\ell)}(\alpha_i\,\underline{C}_i)\right\rangle \qquad (2.12)$$

where

$$\alpha_i = \sqrt{\frac{m_i}{kT}}$$

where m_i is the mass of the particle, k is the Boltzmann constant and T is the temperature.

(d) NUMBER DENSITY, TEMPERATURE AND MASS AVERAGE VELOCITY.

The expansion of the distribution function $f_i\,(r,\underline{C}_i,t)$ for a particular species i of a gas mixture requires five parameters. These are temperature, number density and mass average velocity.

If n_i in eqn. (2.11a) is taken as the number density, then

$$\mathcal{F}_{i\ 0}^{(00)} = 1 \quad . \tag{2.13}$$

The total number density n , is

$$n = \sum_i n_i \quad . \tag{2.14}$$

The temperature is defined by mean kinetic energy.

$$\text{Mean kinetic energy} = \frac{1}{n} \sum_i \left\langle \tfrac{1}{2} n_i m_i (C^2) \right\rangle$$

$$= \frac{3}{2} k T , \tag{2.15}$$

where the $(\langle \quad \rangle)$ denotes the average value. From eqns. (2.5) and (2.11), we have

$$\mathcal{F}_{i\ 0}^{(10)} = \sqrt{\frac{1}{6}} \left(3 - \langle \alpha_i^2 \cdot C_i^2 \rangle \right). \tag{2.16}$$

Substituting for α_i, we get from the above eqns

$$\sum_i n_i \mathcal{F}_{i\ 0}^{(10)} = 0 \quad . \tag{2.17}$$

The average velocity $\underline{C}_i$ is defined as

$$\left\langle (C_i)_m^{(1)} \right\rangle = \frac{1}{\alpha_i} \mathcal{F}_{i\ m}^{(01)} . \tag{2.18}$$

The above relation follows from eqns. (2.5) and (2.11). Now $\underline{C}_i = \underline{c}_i - \underline{c}_0$ where $\underline{c}_0$ is the mass average velocity defined by

$$\rho \underline{c}_0 = \sum_i \rho_i \langle \underline{c}_i \rangle \tag{2.19}$$

where is the total mass density and ρ_i is the mass density of species i,

$$\rho_i = m_i n_i \; ; \qquad \rho = \sum_i \rho_i \tag{2.20}$$

so that,

$$\sum_i n_i \alpha_i^2 \, . \, (\langle \underline{c}_1 \rangle - \underline{c}_0) = 0 \tag{2.21}$$

From eqn. (2.18) we have

$$\sum_i n_i \alpha_i \mathcal{F}_{i\,m}^{(01)} = 0 \, . \tag{2.22}$$

(e) PRESSURE TENSOR

The pressure $\underline{\underline{P}}$, of a gas mixture is the sum of the partial pressure tensors of individual components, and is given by

$$\underline{\underline{P}} = \sum_s \underline{\underline{P}}(s) \tag{2.23}$$

where s is the number of components of the mixture. The

scalar hydrostatic pressure, p , is the sum of the partial pressures, i.e.

$$p = \sum_s p_s \quad = n\,k\,T \tag{2.24}$$

The pressure tensor $\underline{\underline{P}}_s$ of any component of a mixture is a symmetric tensor whose components $\underline{\underline{P}}_{ij}$ are

$$\underline{\underline{P}}_{ij} \quad (s) = \left\langle \rho_s \; C_{is} \; C_{js} \right\rangle \tag{2.25}$$

The above equation can be put in irreducible notation using eqns. (2.3), (2.4), (2.5), (2.6), (2.7) and (2.12)

$$\frac{P_{ij}^{\;(s)}}{P_s} = \delta_{ij} + \sqrt{\frac{4}{3}} \sum_{m=-2}^{2} (ij\,|2m)^* \; \mathcal{F}_m^{[02]}(s) \tag{2.26}$$

where the matrices $(ij\,|2m)$ are (Ku-66)

$$(ij\,|2,0) = \frac{1}{2} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{vmatrix}, \qquad (ij\,|2,\pm 1) = \frac{3}{8} \begin{vmatrix} 0 & 0 & \pm 1 \\ 0 & 0 & 1 \\ \pm 1 & 1 & 0 \end{vmatrix}$$

$$(ij|2, \pm 2) = \sqrt{\frac{3}{8}} \begin{vmatrix} -1 & \pm 1 & 0 \\ \pm 1 & 1 & 0 \\ 0 & 0 & 0 \end{vmatrix} \tag{2.27}$$

Using eqn. (2.24) and (2.26), the expression for $\underline{\underline{P}}_{ij}$ is

$$\underline{\underline{P}}_{ij} = p\,\delta_{ij} + \sqrt{\frac{4}{3}} \sum_{m=-2}^{2} (ij|2m)^{*} \mathcal{H}_m^{[\bar{0}2]} \tag{2.28}$$

where

$$\mathcal{H}_m^{[\bar{0}2]} = \sum_s \mathcal{H}_m^{[\bar{0}2]}(s) \quad .$$

(f) THE RATE-OF-SHEAR TENSOR AND VISCOSITY

The rate-of-shear tensor is a traceless symmetric tensor, and, in cartesian components, is given by

$$S_{ij} = \frac{1}{2} \frac{\partial \underline{c}_{0i}}{\partial x_j} + \frac{\partial \underline{c}_{0j}}{\partial x_i} - \frac{1}{3} \left(\sum_{k=1}^{3} \frac{\partial \underline{c}_{0k}}{\partial x_k} \right) \delta_{ij} \tag{2.29}$$

where i, j = 1, 2, 3.

The corresponding quantity in the present notation is $\mathcal{S}_m^{[2]}$ where

$$\mathcal{S}_m^{[2]} = \sum_{\mu} (1\,\mu\;1m\,-\mu|2m)\; \partial^{[1]}(c_0)^{[1]}{}_{m-\mu} \tag{2.30}$$

$\partial^{[1]}$ is the gradient operator and $(1\,\mu\;1m\,-\mu|2m)$ or

$(\ell m\ \ell' m'\ LM)$ are the Clebsch-Gordon coefficients. This notation for the Clebsch-Gordon coefficient is equivalent to $C(\ell\ \ell'\ L;\ m,m')$ used by Rose (Ro-57).

The relation between $\underline{\underline{S}}_{ij}$ and $\mathcal{S}_m^{[2]}$ is (Ku-67)

$$\underline{\underline{S}}_{ij} = \sqrt{\frac{2}{3}} \sum_{m=-2}^{2} (ij|2m)^* \ \mathcal{S}_m^{[2]} \tag{2.31}$$

where $(ij|2m)$ is given by eqn. (2.27).

The viscosity of a mixture of s-components, η_{mix}, is related to $\underline{\underline{P}}_{ij}$ and $\underline{\underline{S}}_{ij}$ by

$$\underline{\underline{P}}_{ij} = p\delta_{ij} - 2\,\eta_{mix}\ \underline{\underline{S}}_{ij} \tag{2.32}$$

Comparing eqns. (2.28), (2.31) and the above equation, we obtain the basic equation which determines the coefficient of viscosity:

$$\mathcal{F}_m^{(02)} = -\sqrt{2}\ \eta_{mix}\ \mathcal{S}_m^{(2)} \tag{2.33}$$

(g) THERMAL FLUX VECTOR AND THERMAL-CONDUCTIVITY

The thermal flux vector of any component of a mixture is

$$q_s = \frac{1}{2}\rho_s \left\langle C^2\ \underline{C}_s \right\rangle \tag{2.34}$$

In the present notation, using eqns. (2.4), (2.5), (2.6), (2.7)

and (2.12), the above equation becomes

$$q_m^{(1)}(s) = \sqrt{\frac{5}{2}}\frac{p_s}{\alpha_s}\left(\sqrt{\frac{5}{2}}\,\mathcal{J}_m^{(01)}(s) - \mathcal{J}_m^{(11)}(s)\right) . \quad (2.35)$$

Like the pressure, the thermal flux vector of a mixture is the sum of the partial thermal flux vectors of each component

$$q_m^{(1)} = \sum_s q_m^{(1)}(s) \quad . \quad (2.36)$$

The thermal-conductivity of a mixture, λ_{mix}, is the coefficient of $(-\partial_m^{(1)} T)$ in the above equation.

(h) AVERAGE VELOCITY AND DIFFUSION COEFFICIENTS

The average velocity $\langle \underline{C} \rangle$, in our notation, is written as $\frac{1}{\alpha}\mathcal{J}_m^{(01)}(\alpha\underline{C})$.

When the average velocities of molecules of two types of gas are not the same, the gases are said to diffuse into each other. The difference between the average velocities is related to the diffusion coefficients (D_{12}) and the thermal diffusion coefficient (D_T) by the following eqn. (eqn. (8.41-7) C.C.-52)

$$\frac{1}{\alpha_1}\mathcal{J}_m^{(01)}(\alpha_1\underline{c}_1) - \frac{1}{\alpha_2}\mathcal{J}_m^{(01)}(\alpha_2\underline{c}_2)$$

$$= -\frac{n^2}{n_1 n_2}\left[D_{12}\,(d_{12})_m^{(1)} + D_T\,\partial_m^{(1)}\log T\right] \quad (2.37)$$

where $(d_{12})_m^{(1)}$ is given by eqn. (3.49) in the next chapter

B. Talmi coefficients, the Integral part of the Boltzmann equations and the Bracket expressions

(a) TALMI COEFFICIENTS

The evaluation of the integral part of the Boltzmann equation, to be discussed in section (II B-b), needs the distribution function f or the polynomials ϕ's to be transformed to polynomials in the center of mass and relative velocities coordinate systems. This transformation is done by the use of Talmi coefficients. They are written as

$$T\left(\begin{matrix}(\Gamma)\ NLM \\ (\gamma)\ n\ell m\end{matrix}\ \middle|\ \begin{matrix}(\alpha_1)\ \nu_1\ell_1 m_1 \\ (\alpha_2)\ \nu_2\ell_2 m_2\end{matrix}\right) = T(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\nu_1,\alpha_2\nu_2) \qquad (2.38)$$

with

$$\Gamma^2 = \alpha_1^2 + \alpha_2^2 \quad ; \quad \gamma^2 = \left(\frac{\alpha_1^2\ \alpha_2^2}{\alpha_1^2+\alpha_2^2}\right); \quad \alpha_i = \sqrt{\frac{m_i}{kT}}$$

and $N = (NLM)$; $\underline{n} = (n\ell m)$; $\nu_1 = (\nu_1\ell_1 m_1)$; $\nu_2 = (\nu_2\ell_2 m_2)$.

Only two properties of these coefficients (ku-66a, ku-67) are needed for our work :

(1) $$T(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu},\alpha_2\underline{0}) = (-)^{\ell}\left(\frac{\alpha_1}{\alpha_2}\right)^{P-p} T(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{0},\alpha_2\underline{\nu})$$

with (2.39)

$P = 2N+L$; $p = 2n+\ell$.

(2) $$\sum_{M,m} T(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu}_1,\alpha_2\underline{0})T(\Gamma\underline{N},\gamma\underline{n}'|\alpha_1\nu_3,\alpha_2\underline{0})$$

$$= \delta_{\ell_3\ell_1}\,\delta_{m_3m_1}\,(-)^{n+n'+\nu_1+\nu_3}\,\frac{\bar{N}^2_{NL}\,\bar{N}_{n\ell}\,\bar{N}_{n'\ell}}{\bar{N}_{\nu_1\ell_1}\,\bar{N}_{\nu_3\ell_1}}$$

$$\left(\frac{\alpha_1}{\Gamma}\right)^{2P+p+p'}\left(\frac{\alpha_2}{\alpha_1}\right)^{p+p'}\sigma^2(\ell\ L\ \ell_1). \qquad (2.40)$$

where

$$\bar{N}^2_{\nu\ell} = \frac{2\,\pi^{3/2}}{\nu!\,(\nu+\ell+1/2)!}\ ,\quad p' = 2\,n' + \ell\ ,$$

$$\underline{\nu}_3 = (\nu_3,\ \ell_3,\ m_3)\ .$$

$$\sigma(\ell_1\ell_2\ell_3) = (i)^{\ell_1+\ell_2-\ell_3}\sqrt{\frac{(2\ell_1+1)(2\ell_2+1)}{4\,\pi\,(2\ell_3+1)}}\,(\ell_1 0\ell_2 0|\ell_3 0) \qquad (2.40a)$$

$(\ell_1 0\ \ell_2 0|\ell_3 0)$ is again a Clebsch-Gordon coefficient.

The above set of properties simplify further for a pure gas case when $\alpha_1 = \alpha_2 = \alpha$.

(b) INTEGRAL PART OF THE BOLTZMANN EQUATION

The evaluation of the integral part, discussed by Chapman and Cowling (C.C.-52) , is related to the bracket expressions, square or curly, which in turn are written in terms

of the collision integrals $\Omega^{(\ell,s)}$. The corresponding quantities in the present work are collision matrices and inter-action integrals $V^{\ell}_{n\,n'}$. Though a general evaluation of the integral part has been done elsewhere (Ku-66), we will outline a few steps because, firstly, we wish to derive some of the properties of the collision matrices which are needed for chapters III and IV and secondly the explicit form of the interaction integrals is required for chapter IV and appendix A.

The usual form of the integral part $J_{12}(f_1 f_2)$ is

$$J_{12}(f_1 f_2) = \iint (f_1 f_2 - f_1' f_2') g\, \sigma\, (g,\chi) d\hat{\underline{g}}'\, d\underline{C}_2 \qquad (2.41)$$

$$= J\,(\underline{C}_1) \quad .$$

where the various symbols are

$f_i' \equiv f_i'\,(\,\underline{C}_i'\,,\,\underline{r}\,,\,t\,)$

$f_i \equiv f_i\,(\,\underline{C}_i\,,\,\underline{r}\,,\,t\,)$ distribution functions

$\underline{C}_i$ - velocities of particles before collision.

$\underline{C}_i'$ - velocities of particles after collision.

$g = |C_1 - C_2|$ magnitude of the relative

$g' = |C_1' - C_2'|$ velocity vectors before and after the collision.

$\hat{g}'$ - angular part of the relative velocity vector after collision

$\sigma(g,\chi)$ - scattering cross-section

χ - angle of deflection i.e. angle between $\hat{g}$ and $\hat{g}'$.

Expanding $J(C_1)$ in a form similar to eqn. (2.10), we obtain

$$J(\underline{C}_1) = \bar{w}\,(\alpha_1 C_1) \sum_{\underline{\nu}_3} J^{(\underline{\nu}_3)}(\alpha_1)\, \phi^{[\underline{\nu}_3]}(\alpha_1 \underline{C}_1) \quad ,$$

So that $$J^{(\underline{\nu}_3)}(\alpha_1) = \int J(\underline{C}_1)\, \phi^{(\underline{\nu}_3)}(\alpha_1 \underline{C}_1)\, d\underline{C}_1 \quad . \qquad (2.42)$$

To obtain the expansion of $J^{(\underline{\nu}_3)}(\alpha_1)$ in terms of $\mathcal{F}$'s we substitute eqn. (2.31) in the above eqn. and expand f_1, f_2, f_1' and f_2' in the form of eqn. (2.10) ,

$$J^{\underline{\nu}_3}(\alpha_1) = \sum_{\underline{\nu}_1, \underline{\nu}_2} (\alpha_1 \underline{\nu}_3 | J | \alpha_1 \underline{\nu}_1, \alpha_2 \underline{\nu}_2)\, \mathcal{F}^{(\underline{\nu}_1)}(\alpha_1)\, \mathcal{F}^{(\underline{\nu}_2)}(\alpha_2)$$

where

$$(\alpha_1 \underline{\nu}_3 | J | \alpha_1 \underline{\nu}_1, \alpha_2 \underline{\nu}_2)$$

$$= \int \bar{w}\,(\alpha_1 C_1) \bar{w}(\alpha_2 C_2) \phi^{(\underline{\nu}_3)}(\alpha_1 \underline{C}_1)$$

$$[\phi^{[\underline{\nu}_2]}(\alpha_2 \underline{C}_2)\ \phi^{[\underline{\nu}_1]}(\alpha_1 \underline{C}_1) -$$

$$- \phi^{[\underline{\nu}_2]}(\alpha_2 \underline{C}_2')\ \phi^{[\underline{\nu}_1]}(\alpha_1 \underline{C}_1')]\ d\ \underline{V} \qquad (2.43)$$

with

$$d\ \underline{V} = \sigma\ (g, \chi)\ g\ d\ \underline{C}_1\ d\ \underline{C}_2\ d\ \hat{g}'\ .$$

The above eqn. (2.43) represents the basic J-matrix which is of particular interest to us, and will be discussed in subsequent work. Special forms of this matrix are related to the collision matrix and the bracket expressions of Chapman and Cowling.

For changing the variables of integration in the basic J-matrix integral, the following relations between the velocity vectors are relevant.

$$\underline{C}_1 - \underline{C}_2 = \underline{g}\ , \quad \Gamma^2\ \underline{G} = \alpha_1^2\ \underline{C}_1 + \alpha_2^2\ \underline{C}_2\ , \qquad (2.44)$$

$$\underline{C}_1' = \underline{C}_2' = \underline{g}'\ , \quad \Gamma^2\ \underline{G}' = \alpha_1^2\ \underline{C}_1' + \alpha_2^2\ \underline{C}_2'\ . \qquad (2.45)$$

$\underline{G}$ and $\underline{G}'$ are the center of mass velocity vectors before and after the collision respectively and therefore $\underline{G} = \underline{G}'$ always, also $g^2 = g'^2$.

The required relations between the volume elements are

$$d\,\underline{\hat{g}}'\;d\,\underline{g}\;d\,\underline{G} = d\,\underline{\hat{g}}\;d\,\underline{g}'\;d\,\underline{G} \tag{2.46}$$

and

$$d\,\underline{C}_1\;d\,\underline{C}_2\;d\,\underline{\hat{g}}' = d\,\underline{C}_1'\;d\,\underline{C}_2'\;d\,\hat{g} \tag{2.46a}$$

From eqns. (2.34) and (2.9)

$$\bar{w}\,(\alpha_1,C_1)\;\;\bar{w}\,(\alpha_2,C_2) = \bar{w}\,(\Gamma,G)\;\;\bar{w}\,(\alpha,g) \tag{2.47}$$

To evaluate the J-matrix (eqn. 2.43) we transform seperately the polynomial in $(\underline{\nu}_3)$ and the product of polynomials in ($[\underline{\nu}_2]$ and $[\underline{\nu}_1]$) to the product of the polynomials in the center of mass and the relative velocity coordinate system by means of Talmi coefficients. We change the variables of integration by means of eqn. (2.46) and (2.46a), substituting eqn. (2.47) and integrate the transformed integrand over variable $\underline{G}$. The result is

$$(\alpha_1\underline{\nu}_3|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{\nu}_2) =$$

$$= \sum_{\underline{N},\underline{n},\underline{n}'} T\,(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu}_1,\alpha_2\underline{\nu}_2)\; T'\,(\Gamma\underline{N},\gamma\underline{n}',|\alpha_1\underline{\nu}_3,\alpha_2\underline{0})$$

$$\int w(\gamma,g)\,[\phi^{[\underline{n}]}(\gamma\underline{g}) - \phi^{[\underline{n}]}(\gamma\underline{g}')]\;\phi^{[\underline{n}_1']}(\gamma\underline{g})g\;\sigma\,(g,\chi)\;d\hat{g}'\;d\underline{g} \tag{2.48}$$

where

$$\underline{n}' = (n',\ell',m') \quad , \quad \underline{n} = (n\ell m) \quad , \quad \underline{N} = (NLM) \quad .$$

Integration over the angular part is simplified by expanding the differential scattering cross-section $\sigma(g,\chi)$ as

$$\sigma(g,\chi) = \sum_{\lambda=0}^{\infty} \sum_{\mu=-\lambda}^{\lambda} \sigma_\lambda(g)\;\; Y_\mu^{[\lambda]}\,(\hat{\underline{g}})\; Y_\mu^{(\lambda)}\,(\hat{\underline{g}}') \tag{2.49}$$

and

$$\sigma_\lambda(g) \;=\; 2\,\pi \int \sigma\,(g,\chi)\;\; P_\lambda(\cos\,\chi)\;d(\cos\,\chi) \tag{2.50}$$

Substituting $\sigma(g,\chi)$ and using the orthogonality relations of the spherical harmonics, eqn. (2.48) becomes

$$(\alpha_1\underline{\nu}_3|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{\nu}_2)$$

$$= \sum_{\underline{N},\underline{n},\underline{n}'} T\,(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu}_1,\alpha_2\underline{\nu}_2)\; T'\,(\Gamma\underline{N},\gamma\underline{n}'|\;\alpha_1\underline{\nu}_3,\alpha_2\underline{0})$$

$$V^{\ell}_{nn'}\,(12) \tag{2.51}$$

and from now on $\underline{n}' = (n'\ell m)$

$$V^{\ell}_{nn'}(12) = \int_0^{\infty} \bar{w}(\gamma,g)\, R_{n\ell}(\gamma g)\, R_{n'\ell}(\gamma g)$$

$$(\sigma_0 - \sigma_\ell(g))\, g^3\, dg \qquad (2.52)$$

where $\bar{w}(\gamma,g)$, $R_{n\ell}(\gamma g)$ and $\sigma_\ell(g)$, $\sigma_0(g)$ are defined by eqns. (2.9), (2.6) and (2.50) respectively.

In the present work, due to linearisation of the Chapman-Enskog method, one set of indices is always zero, i.e. $\underline{\nu}_2 = (0,0,0)$. Since $\phi^{[0]} = 1$, the eqns. (2.43) and (2.51) become

$$(\alpha_1\underline{\nu}_3|\underline{J}|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) = \int \bar{w}(\alpha_1,\underline{C}_1)\bar{w}(\alpha_2,C_2)$$

$$\phi^{[\underline{\nu}_3]}(\alpha_1\underline{C}_1)\,[\phi^{[\underline{\nu}_1]}(\alpha_1\underline{C}_1) - \phi^{[\underline{\nu}_1]}(\alpha_1\underline{C}_1')]\, d\,\underline{V}$$

$$= \sum_{\underline{N},\underline{n},n'} T(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu}_3,\alpha_2\underline{0})\; T(\Gamma\underline{N},\gamma\underline{n}'|\alpha_1\underline{\nu}_1,\alpha_2\underline{0})\; V^{\ell}_{nn'}(12)$$

(2.53)

The expression on the l.h.s. of the above equation will be known as the collision matrix in further work.

(c) CHAPMAN-COWLING SQUARE BRACKETS AND COLLISION MATRICES FOR UNLIKE MOLECULES.

The square bracket may be written as (eqn. (4.4-10), C.C-52)

$$[F_1, G_1]_{12} = \int \bar{w}\,(\alpha_1, C_1)\,\bar{w}\,(\alpha_2, C_2)\,G_1\,(F_1 - F_1')\,d\,\underline{V}\,. \qquad (2.54)$$

Using eqn. (2.43), we get the square bracket of the polynomials ϕ's as

$$[\phi^{[\underline{\nu}_3]}(\alpha_1\underline{C}_1), \phi^{[\nu_1]}(\alpha_1\underline{C}_1)]_{12} = (\alpha_1\underline{\nu}_3|J|\alpha_1\underline{\nu}_1, \alpha_2\underline{0})\,. \qquad (2.55)$$

Three other arrangements of $\alpha_1\,\underline{C}_1$ and $\alpha_2\,\underline{C}_2$ are possible in two positions within this bracket giving rise to different matrices, In terms of the Talmi-coefficients these are :

$$(\alpha_1\underline{\nu}_3|J|\alpha_1\underline{0}, \alpha_2\underline{\nu}_1) = [\phi^{(\underline{\nu}_3)}(\alpha_1\underline{C}_1)\,,\ \phi^{[\underline{\nu}_1]}(\alpha_2\underline{C}_2)]_{12}$$

$$= \sum_{\underline{N},\underline{n},n'} T\,(\Gamma\underline{N}, \gamma\underline{n}|\alpha_1\underline{\nu}_3, \alpha_2\underline{0})\,T'\,(\Gamma\underline{N}, \gamma\underline{n}'|\alpha_1\underline{0}, \alpha_2\underline{\nu}_1)\,V^{\ell}_{nn'}\,(12) \qquad (2.56)$$

$$(\alpha_2\underline{\nu}_3|J|\alpha_1\underline{\nu}_1, \alpha_2\underline{0}) = [\phi^{(\underline{\nu}_3)}(\alpha_2\underline{C}_2),\ \phi^{[\underline{\nu}_1]}(\alpha_1\underline{C}_1)]_{12}$$

$$= \sum_{\underline{N},\underline{n},n'} T\,(\Gamma\underline{N}, \gamma\underline{n}|\alpha_1\underline{0}, \alpha_2\underline{\nu}_3)\,T'\,(\Gamma\underline{N}, \gamma\underline{n}'|\alpha_1\underline{\nu}_1, \alpha_2\underline{0})\,V^{\ell}_{nn'}\,(12) \qquad (2.57)$$

$$(\alpha_2\underline{\nu}_3|J|\alpha_1\underline{0},\alpha_2\underline{\nu}_1) = [\phi^{(\underline{\nu}_3)}(\alpha_2\underline{C}_2),\ \phi^{[\underline{\nu}_1]}(\alpha_2\underline{C}_2)]_{12}$$

$$= \sum_{\underline{N},\underline{n},n'} T\,(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{0},\alpha_2\underline{\nu}_3)\ T\,(\Gamma\underline{N},\gamma\underline{n}'|\alpha_1\underline{0},\alpha_2\underline{\nu}_1)\ V^{\ell}_{nn'}(12) \tag{2.58}$$

Each of the eqns. (2.53, 2.56 - 2.58) has a different set of Talmi coefficients. In order to establish relations between the transposes of the matrices, we need the same set of Talmi coefficients in each of these eqns. This is achieved by using the transformation property (2.39) of the Talmi coefficients. The resulting eqns. are

$$(\alpha_1\underline{\nu}_3|J|\alpha_1\underline{0}\ ,\alpha_2\underline{\nu}_1) =$$

$$= \sum_{\underline{N},\underline{n},n'} (-)^{\ell} \left(\frac{\alpha_2}{\alpha_1}\right)^{P-p'} T\,(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu}_3,\alpha_2\underline{0})\ ,$$

$$T\,(\Gamma\underline{N},\gamma\underline{n}'|\alpha_1\underline{\nu}_1,\alpha_2\underline{0})\ V^{\ell}_{nn'}(12)\ , \tag{2.59}$$

$$(\alpha_2\underline{\nu}_3|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) =$$

$$= \sum_{\underline{N},\underline{n},n'} (-)^{\ell} \left(\frac{\alpha_2}{\alpha_1}\right)^{P-p} T\,(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\underline{\nu}_3,\alpha_2\underline{0}\ )$$

$$T\,(\Gamma\underline{N},\gamma\underline{n}'|\alpha_1\underline{\nu}_1,\alpha_2\underline{0})\ V^{\ell}_{nn'}(12)\ , \tag{2.60}$$

$$(\alpha_2\nu_3|J|\alpha_1\underline{0},\alpha_2\nu_1) =$$

$$= \sum_{\underline{N},\underline{n},n'} \left(\frac{\alpha_2}{\alpha_1}\right)^{2P-p-p'} T\,(\Gamma\underline{N},\gamma\underline{n}|\alpha_1\nu_3,\alpha_2\underline{0})$$

$$T\,(\Gamma\underline{N},\gamma\underline{n}'|\alpha_1\nu_1,\alpha_2\underline{0})\; V^{\ell}_{nn'}\;(12) \quad . \tag{2.61}$$

(d) PROPERTIES OF COLLISION MATRICES OF UNLIKE MOLECULES

(i) Diagonal character

The collision matrix becomes diagonal in ℓ and m because of the orthogonality (2.40) of the Talmi coefficients.

$$(\alpha_1\nu_3|J|\alpha_1\nu_1,\alpha_2\underline{0}) = (\alpha_1\nu_3\ell_1m_1|J^{\ell_1}|\alpha_1\nu_1\ell_1m_1,\alpha_2\underline{0})\delta_{\ell_1\ell_3}\,\delta_{m_3m_1} \tag{2.62}$$

This diagonal character is independent of the α's and ν's. Hence all the other three matrices (2.59 - 2.61) are diagonal.

(ii) Transposes of the matrices

We define the ν-transpose of the collision matrices of section (II B-C) for ν indices alone, leaving all the other indices in their original position. Denoting this ν-transpose by a tilda, we have

$$(\alpha_1\nu_3|\tilde{J}|\alpha_1\nu_1,\alpha_2\underline{0}) = (\alpha_1\nu_1|J|\alpha_1\nu_3,\alpha_2\underline{0}) \tag{2.63}$$

$$(\alpha_1\underline{\nu}_3|\tilde{J}|\alpha_1\underline{0},\alpha_2\underline{\nu}_1) = (\alpha_1\underline{\nu}_1|J|\alpha_1\underline{0},\alpha_2\underline{\nu}_3) \tag{2.64}$$

$$(\alpha_2\underline{\nu}_3|\tilde{J}|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) = (\alpha_2\underline{\nu}_1|J|\alpha_1\underline{\nu}_3,\alpha_2\underline{0}) \tag{2.65}$$

$$(\alpha_2\underline{\nu}_3|\tilde{J}|\alpha_1\underline{0},\alpha_2\underline{\nu}_1) = (\alpha_2\underline{\nu}_1|J|\alpha_1\underline{0},\alpha_2\underline{\nu}_3) \tag{2.66}$$

Using the defining eqns. (2.53), (2.46 - 2.48) and expressing the r.h.s. of the above set of eqns in the corresponding Talmi coefficients, it can be shown that

$$(\alpha_1\underline{\nu}_3|\tilde{J}|\alpha_1\underline{\nu}_1;\alpha_2\underline{0}) = (\alpha_1\underline{\nu}_3|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) \tag{2.67}$$

$$(\alpha_1\underline{\nu}_3|\tilde{J}|\alpha_1\underline{0},\alpha_2\underline{\nu}_1) = (\alpha_2\underline{\nu}_3|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) \tag{2.68}$$

$$(\alpha_2\underline{\nu}_3|\tilde{J}|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) = (\alpha_1\underline{\nu}_3|J|\alpha_1\underline{0},\alpha_2\underline{\nu}_1) \tag{2.69}$$

$$(\alpha_2\underline{\nu}_3|\tilde{J}|\alpha_1\underline{0},\alpha_2\nu_1) = (\alpha_2\underline{\nu}_3|J|\alpha_1\underline{0},\alpha_2\underline{\nu}_1) \tag{2.70}$$

(e) COLLISION MATRICES FOR LIKE MOLECULES AND THEIR PROPERTIES

For like molecules $\alpha_1 = \alpha_2 = \alpha$ and velocity variables become $\underline{C}$ and $\underline{C}_1$ instead of $\underline{C}_1$ and $\underline{C}_2$. The square bracket, in C.C. notation (eqn. (4.4-7), C.C.-52) is

$$[F,G]_1 = \int \bar{w}\,(\alpha,C)\;\bar{w}\,(\alpha,C_1)\;G\,(F-F')\;d\,\underline{V} \tag{2.71}$$

From (eqn. (3.54-3), C.C.-52)

$$[F,G]_1 = \frac{1}{2} \int \bar{w}\,(\alpha,C)\;\bar{w}\,(\alpha,C_1)(G-G')(F-F')\;d\,\underline{V} \quad . \tag{2.72}$$

For the polynomials ϕ's , the above equation is

$$[\phi^{[\underline{\nu}_3]}(\alpha\underline{C}_1),\ \phi^{(\underline{\nu}_1)}(\alpha\underline{C}_1)]\ ,$$

$$= \frac{1}{2} \int \bar{w}\,(\alpha,C)\;\bar{w}\,(\alpha,C_1)(\phi^{[\underline{\nu}_3]}(\alpha\underline{C}_1)-\phi^{[\underline{\nu}_3]}(\alpha\underline{C}_1')$$

$$(\phi^{(\underline{\nu}_1)}(\alpha\underline{C}_1) - \phi^{(\underline{\nu}_1)}(\alpha\underline{C}_1'))\;d\,\underline{V} \quad . \tag{2.73}$$

Simplifying the r.h.s. of the above equation in the same way as was done eqn. (2.43) and using the transformation property of Talmi coefficients (eqn. (2.39)) for $\alpha_1 = \alpha_2 = \alpha$, we get

$$[\phi^{[\underline{\nu}_3]}(\alpha\underline{C}_1),\ \phi^{(\underline{\nu}_1)}(\alpha\underline{C}_1)] = (\alpha\underline{\nu}_3|J|\alpha\underline{\nu}_1,\alpha\underline{0}) \quad . \tag{2.74}$$

The r.h.s. of this equation is also diagonal in ℓ and m . Defining the transpose of the matrices for like molecules, as before, it can be shown that

$$(\alpha\ \underline{\nu}_3|\tilde{J}|\alpha\ \underline{\nu}_1,\alpha\ \underline{0}) = (\alpha\ \underline{\nu}_3|J|\alpha\ \underline{\nu}_1,\alpha\ \underline{0}) \tag{2.75}$$

This result is independent of α .

Eqn. (2.64) is not identical to eqns. (2.53, 2.56 - 2.68), in definition. The definition of square brackets for like molecules (eqn. (2.73)) is different from that of unlike molecules (eqn. (2.54)).

(f) CHAPMAN-COWLING CURLY BRACKETS

The C.C. curly bracket is (eqn. (4.4-12), C.C.-52) :

$$n_1 n_2 \{F,G\} = n_1^2 [F,G]_1 + n_1 n_2 ([F_1,G_1]_{12} + [F_1,G_2]_{12}$$

$$+ [F_2,G_1]_{12} + [F_2,G_2]_{12}) + n_2^2 [F,G]_2 \quad . \qquad (2.76)$$

In terms of the polynomials ϕ's and the collision matrices, from eqns. (2.43, 2.46 - 2.48, 2.64), we have

$$n_1 n_2 \{\phi^{[\underline{\nu}_3]}(\alpha\underline{C}), \phi^{(\underline{\nu}_1)}(\alpha\underline{C}_1)\}$$

$$= n_1^2 (\alpha_{1\underline{-3}}\nu_{\underline{-3}}|J|\alpha_{1\underline{-1}}\nu_{\underline{-1}},\alpha_{1\underline{-}}0) + n_1 n_2 [(\alpha_{1\underline{-3}}\nu_{\underline{-3}}|J|\alpha_{1\underline{-1}}\nu_{\underline{-1}},\alpha_{2\underline{-}}0)$$

$$+ (\alpha_{1\underline{-3}}\nu_{\underline{-3}}|J|\alpha_{1\underline{-}}0,\alpha_{2\underline{-1}}\nu_{\underline{-1}}) + (\alpha_{2\underline{-3}}\nu_{\underline{-3}}|J|\alpha_{1\underline{-1}}\nu_{\underline{-1}},\alpha_{2\underline{-}}0)$$

$$+ (\alpha_{2\underline{-3}}\nu_{\underline{-3}}|J|\alpha_{1\underline{-}}0,\alpha_{2\underline{-1}}\nu_{\underline{-1}})] + n_2^2 (\alpha_{2\underline{-3}}\nu_{\underline{-3}}|J|\alpha_{2\underline{-1}}\nu_{\underline{-1}},\alpha_{2\underline{-}}0) \quad . \qquad (2.77)$$

As shown earlier, all the collision matrices in this equation are diagonal in ℓ and m. Hence the curly bracket itself is proportional to $\delta_{\ell_1 \ell_3} \; \delta_{m_1 m_3}$.

B. Differential Operator of the Boltzmann Equation.

The usual differential operator for the i th component of a gas-mixture (C.C.-52) is

$$\mathcal{D}_i \, f_i = \left(\frac{\partial}{\partial t}\right) + \underline{C} \cdot \frac{\partial}{\partial \underline{r}} + \underline{X}_i \cdot \frac{\partial}{\partial \underline{C}} \Big) \, f_i \tag{2.78}$$

where $\underline{X}_i$ is the external force acting on the i th component.

Expanding f_i (eqn. (2.10)), multiplying the above equation by $\phi^{[\underline{\nu}]}(\alpha_i \, \underline{C}_i)$ and integrating w.r.t. $\underline{C}_i$, we obtain

$$\int \phi^{[\underline{\nu}]}(\alpha_i \underline{C}_i) \, \underline{\mathcal{D}}_i \, f_i \; d\,\underline{C}_i = \sum_{\underline{\nu}_1} (\nu | \, \underline{\mathcal{D}}_i | \underline{\nu}_1) \; \mathcal{F}^{(\underline{\nu}_1)}(\alpha_i, \underline{r}, t) \tag{2.79}$$

Using the summation convention for $\underline{\nu}_1$, we have

$$(\underline{\nu} | \, \underline{\mathcal{D}}_i | \underline{\nu}_1) \; \mathcal{F}^{(\underline{\nu}_1)}(\alpha_i, \underline{r}, t) =$$

$$= \int \phi^{[\underline{\nu}]}(\alpha_i \, \underline{C}_i) \, \underline{\mathcal{D}}_i \, n \, \bar{w}(\alpha_i, C_i) \; \phi^{(\underline{\nu}_1)}(\alpha_i \underline{C}_i) \; \mathcal{F}^{(\underline{\nu}_1)}(\alpha_i, \underline{r}, t) d\underline{C}_i \tag{2.80}$$

Since we propose to work only up to the second approximation of the Chapman-Enskog method we can set $\underline{\nu}_1 = (0,0,0)$. It can be shown (Ku-67) that $(\underline{\nu}|\ \mathcal{D}_i|\underline{0})$ breaks up into the scalar $(\delta_{\ell 0})$, vector $(\delta_{\ell 1})$ and tensor $(\delta_{\ell 2})$ parts.

$$(\underline{\nu}|\ \underline{\mathcal{D}}_i|\underline{0}) = U\ \delta_{\nu 1}\delta_{\ell 0}\ \delta_{m0}$$

$$+ (U^{(1)}_{i\ m}\ \delta_{\nu 0} - \sqrt{\tfrac{5}{2}}\ \frac{1}{\alpha_i}\ \partial^{(1)}_m \log T\ \delta_{\nu 1})\ \delta_{\ell 1}$$

$$+ \sqrt{2}\ \mathcal{D}^{(2)}_m\ \delta_{\nu 0}\ \delta_{\ell 2} \quad . \tag{2.81}$$

where

$$U = -\frac{1}{2}\partial_1 \log T - \frac{1}{2}\underline{c}_0 \cdot \partial \log T - \frac{1}{3}\underline{\nabla} \cdot \underline{c}_0 \tag{2.82}$$

and

$$U^{(1)}_{i\ m} = \frac{1}{\alpha_i}\left(\frac{1}{n_i}\partial^{(1)}_m n_i + \partial^{(1)}_m \log T + \alpha_i^2\left(\partial_t\ c^{(1)}_{0\ m}\right)\right.$$

$$\left. + \alpha_i^2\left(\underline{c}_0 \cdot \partial^{(1)}_m\right)\underline{c}_0\right) \quad . \tag{2.83}$$

∂_t denotes the time derivative.

For the calculation of the transport coefficients in the next chapter, two values of i (=1,2) are needed. The structure of $(\underline{\nu}|\underline{\mathcal{D}}_1|\underline{0})$ and $(\underline{\nu}|\underline{\mathcal{D}}_2|\underline{0})$ can be rewritten by replacing subscript i by 1 and 2 respectively in eqns. (2.81-2.83).

CHAPTER III

EXPRESSIONS FOR THE TRANSPORT COEFFICIENTS

therefore of the $\underline{\underline{\mathcal{K}}}$ -matrix, and the breakup of the differential part of the Boltzmann equation into scalar, vector and tensor components, the equations of different tensorial characters may be separated. (Section B).

(3) Using the Euler's equations of motion, the scalar component vanishes.

The subsidiary conditions (see Introduction) are identically satisfied by the tensor component as they do not involve the tensor component. On the other hand, we have to modify the structure of the $\underline{\underline{\mathcal{K}}}$ -matrix (to be denoted $\underline{\underline{\mathcal{K}}}^1$-matrix in subsequent work) for the vector component so that it satisfies the subsidiary conditions.

Incorporating the subsidiary conditions, the set of equations corresponding to the vector and tensor components is solved in terms of the inverse of the appropriate $\underline{\underline{\mathcal{K}}}$ -matrix which is denoted by $\underline{\underline{\mathcal{L}}}$ for convenience. (Section C).

(4) The solution of the tensor part is related to the coefficient of viscosity and that of the vector part to the other coefficients, in particular, coefficients of Diffusion, Thermal diffusion and Thermal-conductivity. The expressions for these coefficients are written in forms which may directly be used for computation. These forms of the expressions are shown to be equivalent to the

general expressions of Chapman and Cowling (C.C.-52) which are not very suitable for computation. (Sections D and E).

A The Set of two Boltzmann Equations and $\mathcal{K}$ -matrix

(a) BOLTZMANN EQUATIONS FOR A BINARY GAS-MIXTURE

The usual set of two Boltzmann equations for a binary gas-mixture is

$$\mathcal{D}_1 f_1 = - J_{11}(ff_1) - J_{12}(f_1 f_2) \tag{3.1}$$

$$\mathcal{D}_2 f_2 = - J_{22}(ff_2) - J_{21}(f_2 f_1) \tag{3.2}$$

where $\mathcal{D}$ and J have defined by eqns. (2.78) and (2.41) respectively. Now in the above set of equations, substitute the expansion of the distribution function f_i , (2.10), for f_1 and f_2 . Multiply the resulting equations by $\phi^{(\underline{\nu})}(\alpha_1 \underline{C}_1)$ and $\phi^{(\underline{\nu})}(\alpha_2 \underline{C}_2)$ and integrate with respect to $\underline{C}_1$ and $\underline{C}_2$ respectively. The resulting equations are

$$(\underline{\nu}|\underline{D}_1|\underline{\nu}')\mathcal{F}_1^{(\underline{\nu}')} =$$

$$= - n_1 (\alpha_1 \underline{\nu}|J|\alpha_1\underline{\nu}_1,\alpha_1\underline{\nu}_2)\mathcal{F}_1^{(\underline{\nu}_2)} \mathcal{F}_1^{(\underline{\nu}_1)}$$

$$- n_2 (\alpha_1\underline{\nu}|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{\nu}_2) \mathcal{F}_2^{(\underline{\nu}_2)} \mathcal{F}_1^{(\underline{\nu}_1)} . \tag{3.3}$$

$$(\underline{\nu}|\underline{D}_2|\underline{\nu}')\,\mathcal{F}_2^{(\underline{\nu}')} =$$

$$= -\,n_1\,(\alpha_2\underline{\nu}|J|\alpha_2\underline{\nu}_2,\alpha_1\underline{\nu}_1)\,\mathcal{F}_1^{(\underline{\nu}_1)}\,\mathcal{F}_2^{(\underline{\nu}_2)}$$

$$-\,n_2\,(\alpha_2\underline{\nu}|J|\alpha_2\underline{\nu}_2,\alpha_2\underline{\nu}_2)\,\mathcal{F}_2^{(\underline{\nu}_2)}\,\mathcal{F}_2^{(\underline{\nu}_1)} \qquad (3.4)$$

where we have used summation convention for $\underline{\nu}'$ on the l.h.s. of these equations and for $\underline{\nu}_1$ and $\underline{\nu}_2$ on the r.h.s. of these equations.

(i) <u>First Approximation</u> : To solve the above equation for $\mathcal{F}_1^{(\underline{\nu}')}$ and $\mathcal{F}_2^{(\underline{\nu}')}$ up to the second approximation, as was done for a pure gas (ku -67) , multiply the r.h.s. of these equations by $(1/\varepsilon)$ and expand $\mathcal{F}$'s in powers of . Comparing the powers of ϵ on both sides of the resulting equation, we get a set of equations for different orders of approximations. The solution of the first approximation, as for pure gas, is

$$^0\mathcal{F}_1^{(\underline{\nu}')} = \delta_{\underline{\nu}'\underline{0}} \qquad (3.5)$$

$$^0\mathcal{F}_2^{(\underline{\nu}')} = \delta_{\underline{\nu}'\underline{0}} \qquad (3.6)$$

Now, as for the pure gas,tthe normalised distribution

function is

$$f_1^{(0)} = n_1 \bar{w}(\alpha_1, \underline{C}_1)$$

$$= n_1 \left(\frac{m_1}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_1 C_1^2}{2kT}\right) \tag{3.7}$$

and

$$f_2^{(0)} = n_2 \bar{w}(\alpha_2, \underline{C}_2)$$

$$= n_2 \left(\frac{m_2}{2\pi kT}\right)^{3/2} \exp\left(-\frac{m_2 C_2^2}{2kT}\right). \tag{3.8}$$

where $\underline{C}_1 = {}_1 - \underline{c}_0$ and $\underline{C}_2 = \underline{c}_2 - \underline{c}_0$. In the above equations n_1, n_2, T and $\underline{c}_0$ are arbitrary parameters at this stage. Now if we want to refer $f_1^{(0)}$ and $f_2^{(0)}$ as Maxwell-Boltzmann distribution functions for the two species of gases, n_1 and n_2 should correspond to number density, T to the temperature and $\underline{c}_0$ to the mass average velocity. In consequence of our choice, from eqns. (2.13), (2.17) and (2.22) we have identically

$$n_i = n_i \mathcal{F}_i^{(00)}{}_0 \equiv n_i \; {}^0\mathcal{F}_i^{(00)}{}_0 \tag{3.9}$$

$$n_1 \alpha_1 \mathcal{F}_1^{(01)} + n_2 \alpha_2 \mathcal{F}_2^{(01)} m =$$

$$= n_1 \alpha_1 \; {}^0\mathcal{F}_1^{(01)} + n_2 \alpha_2 \; {}^0\mathcal{F}_2^{(01)} m \equiv 0 \tag{3.10}$$

$$n_1 \mathcal{F}_1^{(1\ )}{}_0 + n_2 \mathcal{F}_2^{(\ 0)} = n_1\ {}^0\mathcal{F}_1^{(10)}{}_0 + n_2\ {}^0\mathcal{F}_2^{(10)}{}_0 \equiv 0 \tag{3.11}$$

Then, further approximations to $\mathcal{F}$ must satisfy the relations

$$\sum_{r=1}^{\infty} {}^r\mathcal{F}_i^{(00)} = 0 \tag{3.12}$$

$$\sum_{r=1}^{\infty} (n_1\alpha_1\ {}^r\mathcal{F}_1^{(10)}{}_m + n_2\alpha_2\ {}^r\mathcal{F}_2^{(01)}{}_m) = 0 \tag{3.13}$$

$$\sum_{r=1}^{\infty} (n_1\ {}^r\mathcal{F}_1^{(10)}{}_0 + n_2\ {}^r\mathcal{F}_2^{(10)}{}_0) = 0 \tag{3.14}$$

Only this choice of the parameters leads to properly order forms for the whole solutions $f_1\ (\mathcal{F}_1)$ and $f_2\ (\mathcal{F}_2)$ and is a part of Chapman-Enskog method (C.C.-52). The equations (3.12 - 3.14) are called subsidiary conditions. They should be satisfied by any solution .

(ii) <u>Second Approximation</u>

Substituting the first approximation and introducing k-matrix, we get, from eqns. (3.3) and (3.4) for the second approximation of the C-E method

$$(\underline{\nu}|\underline{D}_1|\underline{0}) = - n_1 \, [k_{11}]_{\underline{\nu},\underline{\nu}'} \, {}^1\mathcal{F}_1(\underline{\nu}') - n_2 \, [k_{12}]_{\underline{\nu},\underline{\nu}'} \, {}^1\mathcal{F}_2(\underline{\nu}') \tag{3.15}$$

$$(\underline{\nu}|\underline{D}_2|\underline{0}) = - n_1 \, [k_{21}]_{\underline{\nu},\underline{\nu}'} \, {}^1\mathcal{F}_1(\underline{\nu}') - n_2 \, [k_{22}]_{\underline{\nu},\underline{\nu}'} \, {}^1\mathcal{F}_2(\underline{\nu}') \tag{3.16}$$

where

$$[\underline{\underline{k}}_{11}]_{\underline{\nu},\underline{\nu}'} = [\, (\alpha_1\underline{\nu}|J|\alpha_1\underline{\nu}',\alpha_1\underline{0}) + (\alpha_1\underline{\nu}|J|\alpha_1\underline{0},\alpha_1\underline{\nu}') + (n_2/n_1)\,(\alpha_1\underline{\nu}|J|\alpha_1\underline{\nu}',\alpha_2\underline{0})\,] \tag{3.17}$$

$$[\underline{\underline{k}}_{12}]_{\underline{\nu},\underline{\nu}'} = (\alpha_1\underline{\nu}|J|\alpha_1\underline{0},\ \alpha_2\underline{\nu}') \tag{3.18}$$

$$[\underline{\underline{k}}_{21}]_{\underline{\nu},\underline{\nu}'} = (\alpha_2\underline{\nu}|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}) \tag{3.19}$$

$$[\underline{\underline{k}}_{22}]_{\underline{\nu},\underline{\nu}'} = [\, (\alpha_2\underline{\nu}|J|\alpha_2\underline{\nu}',\alpha_2\underline{0}) + (\alpha_2\underline{\nu}|J|\alpha_2\underline{0},\alpha_2\underline{\nu}') + (n_1/n_2)\,(\alpha_2\underline{\nu}|J|\alpha_1\underline{0},\alpha_2\underline{\nu}')\,] \tag{3.20}$$

Each of the matrices is an infinite square matrix in $\underline{\nu}$ and $\underline{\nu}'$. The explicit form will be given later.

Introducing a (2×2) $\underline{\underline{\mathcal{K}}}$ -matrix each element of which is

an infinite square matrix, we can write eqns. (3.7) and (3.8) for ${}^1\mathcal{F}$ as

$$\underline{\Psi} = \underline{\underline{\mathcal{K}}}\ {}^1\underline{\mathcal{F}} \tag{3.21}$$

where we have suppressed the actual indices and

$$\underline{\underline{\mathcal{K}}} = \begin{pmatrix} (\underline{\underline{k}}_{11})_{\underline{\nu},\underline{\nu}'} & (\underline{\underline{k}}_{12})_{\underline{\nu},\underline{\nu}'} \\ (\underline{\underline{k}}_{21})_{\underline{\nu},\underline{\nu}'} & (\underline{\underline{k}}_{22})_{\underline{\nu},\underline{\nu}'} \end{pmatrix} \tag{3.22}$$

$${}^1\mathcal{F} = \begin{pmatrix} -n_1 & {}^1\mathcal{F}_1(\underline{\nu}') \\ -n_2 & {}^1\mathcal{F}_2(\underline{\nu}') \end{pmatrix} \tag{3.23}$$

$$\underline{\Psi} = \begin{pmatrix} (\underline{\nu}|D_1|\underline{0}) \\ (\underline{\nu}|D_2|\underline{0}) \end{pmatrix} \tag{3.24}$$

Or in terms of the components introduced in eqn. (2.81)

$$\Psi = u\ \underline{\xi}_1\ \delta_{\ell 0}\ \delta_{m0} + \sqrt{2}\ \underline{\xi}_0\ \delta_{\ell 2}\mathcal{S}^{(2)}_m$$

$$+ (\underline{\underline{\mathcal{U}}}^{(1)}_m\ \underline{\underline{\mathcal{B}}}\ \underline{\xi}_0 - \sqrt{\tfrac{5}{2}}\ (\partial^{(1)}_m \log T)\ \underline{\underline{\mathcal{B}}}\ \underline{\xi}_1)\ \delta_{\ell 1} \tag{3.25}$$

where

$$\underline{\xi}_1 = \begin{pmatrix} \delta_{\nu 1} \\ \delta_{\nu 1} \end{pmatrix}, \qquad \underline{\xi}_0 = \begin{pmatrix} \delta_{\nu 0} \\ \delta_{\nu 0} \end{pmatrix} \tag{3.26}$$

$$\underline{\zeta}_0 = \begin{pmatrix} \delta_{\nu 0} \\ 0 \end{pmatrix}, \qquad \underline{\zeta}_1 = \begin{pmatrix} 0 \\ \delta_{\nu 1} \end{pmatrix} \tag{3.27}$$

$$\underline{\underline{\mathcal{B}}} = \begin{pmatrix} -\dfrac{1}{n_1\alpha_1} & \dfrac{1}{\alpha_1} \\ -\dfrac{1}{n_2\alpha_2} & \dfrac{1}{\alpha_2} \end{pmatrix} \delta_{\nu\nu'} \tag{3.28}$$

$$\underline{\underline{\mathcal{U}}}_m^{(1)} = \begin{pmatrix} n_1\alpha_1(U_1)^{(1)}{}_m & 0 \\ 0 & -n_2\alpha_2(U_2)^{(1)}{}_m \end{pmatrix} \delta_{\nu\nu'} \tag{3.29}$$

U , $(U_1)^{(1)}{}_m$, $(U_2)^{(1)}{}_m$ and $\mathcal{S}^{(2)}{}_m$ have been defined by eqns. (2.82), (2.83) and (2.30) respectively.

Eqn. (3.25) gives $\underline{\Psi}$ as the sum of a scalar, vector and tensor parts.

(b) PROPERTIES OF $\underline{\underline{k}}$- and $\underline{\underline{\mathcal{K}}}$ -matrices

(i) Diagonal Character

All the k-matrices are made up of the collision matrices. The collision matrices given in eqn. (2.52) are shown to be diagonal in ℓ and m. Therefore all the $\underline{\underline{k}}$- and $\underline{\underline{\mathcal{K}}}$ -matrices will be diagonal in ℓ and m, i.e.,

$$[\underline{\underline{k}}_{ij}]_{\underline{\nu},\underline{\nu}'} = [\underline{\underline{k}}^{\ell}_{ij}]_{\nu,\nu'} \; \delta_{\ell\ell'} \; \delta_{mm'} \tag{3.30}$$

$$[\underline{\underline{\mathcal{K}}}]_{\underline{\nu},\underline{\nu}'} = [\underline{\underline{\mathcal{K}}}^{\ell}]_{\nu,\nu'} \; \delta_{\ell\ell'} \; \delta_{mm'} \quad . \tag{3.31}$$

(ii) Transpose of the matrices

We will differentiate between two types of transposes. One is for the (2×2) $\underline{\underline{\mathcal{K}}}$ -matrix and the other is for the $\underline{\underline{k}}$-matrices.

The total transpose for the $\underline{\underline{\mathcal{K}}}$ -matrix consists of the transpose of the (2×2) matrix and the transpose of the ν-indices for the individual elements of the matrix; while the transpose for the $\underline{\underline{k}}$-matrices is only for the ν-indices.

We have already discussed the ν-transpose of the collision matrices eqns. (2.63 - 2.66, 2.75) . Since the $\underline{\underline{k}}$-matrices are

made up of the collision matrices (eqns. (3.17 - 3.20)) and denoting the ν-transpose of the $\underline{\underline{k}}$-matrices by tilda again, we have

$$[\tilde{\underline{\underline{k}}}_{ij}]_{\underline{\nu},\underline{\nu}'} = [\underline{\underline{k}}_{ij}]_{\underline{\nu}',\underline{\nu}} \tag{3.31}$$

where $i, j = 1,2$.

As shown earlier all the collision matrices are symmetric (2.67 - 2.70), it follows that the $\underline{\underline{k}}$-matrices are also symmetric i.e.

$$[\underline{\underline{k}}_{ij}]_{\underline{\nu}',\underline{\nu}} = [\underline{\underline{k}}_{ji}]_{\underline{\nu},\underline{\nu}'} \quad . \tag{3.32}$$

Denoting the total transpose of the $\underline{\underline{\mathcal{K}}}$-matrix by the superscript T , we have

$$[\underline{\underline{\mathcal{K}}}^{T}] = \begin{pmatrix} (\tilde{\underline{\underline{k}}}_{11})_{\underline{\nu},\underline{\nu}'} & (\tilde{\underline{\underline{k}}}_{21})_{\underline{\nu},\underline{\nu}'} \\ (\tilde{\underline{\underline{k}}}_{12})_{\underline{\nu},\underline{\nu}'} & (\underline{\underline{k}}_{22})_{\underline{\nu},\underline{\nu}'} \end{pmatrix} . \tag{3.33}$$

Using eqn. (3.32), we have

$$[\underline{\underline{\mathcal{K}}}^{T}] = [\underline{\underline{\mathcal{K}}}] \quad . \tag{3.34}$$

As will be seen later, this $\underline{\underline{\mathcal{K}}}$-matrix is the cause of simplification of the mathematical structure and, thus,

provides the justification for introducing this quantity.

(c) STRUCTURE OF THE $\underline{k}$-MATRICES AND THE $'\underline{\mathcal{F}}$-COLUMNS

Each of the k-matrices, diagonal in ℓ and m is an infinite square matrix in ν and ν'. A typical structure is

$$[\underline{\underline{k}}^{\ell}_{ij}] = \begin{pmatrix} (\underline{\underline{k}}^{\ell}_{ij})_{00} & (\underline{\underline{k}}^{\ell}_{ij})_{01} & (\underline{\underline{k}}^{\ell}_{ij})_{02} & -- & (\underline{\underline{k}}^{\ell}_{ij})_{0n} & --- \\ (\underline{\underline{k}}^{\ell}_{ij})_{10} & (\underline{\underline{k}}^{\ell}_{ij})_{11} & (\underline{\underline{k}}^{\ell}_{ij})_{12} & -- & (\underline{\underline{k}}^{\ell}_{ij})_{1n} & --- \\ - & - & - & - & - & - & - & - & - \\ - & - & - & - & - & - & - & - & - \\ (\underline{\underline{k}}^{\ell}_{ij})_{n0} & (\underline{\underline{k}}^{\ell}_{ij})_{n1} & (\underline{\underline{k}}^{\ell}_{ij})_{n2} & -- & (\underline{\underline{k}}^{\ell}_{ij})_{nn} & --- \\ - & - & - & - & - & - & - & - & - \\ - & - & - & - & - & - & - & - & - \end{pmatrix} \tag{3.35}$$

Also each of the $'\underline{\mathcal{F}}$'s is an infinte column matrix in ν i.e.

$$
{}^{1}\mathcal{F}_{1} = \begin{pmatrix} {}^{1}\mathcal{F}_{1}{}^{(0\ell)}{}_{m} \\ {}^{1}\mathcal{F}_{1}{}^{(1\ell)}{}_{m} \\ {}^{1}\mathcal{F}_{1}{}^{(2\ell)}{}_{m} \\ \vdots \\ {}^{1}\mathcal{F}_{1}{}^{(n\ell)}{}_{m} \\ \vdots \end{pmatrix} \tag{3.36}
$$

In both cases $n \to \infty$.

B. <u>Separation for different tensorial components</u>

Eqn. (3.20) is

$$
\underline{\Psi} = \underline{\underline{\mathcal{K}}} \; \underline{{}^{1}\mathcal{F}} \; . \tag{3.20a}
$$

Since the $\underline{\underline{\mathcal{K}}}$ -matrix is diagonal in ℓ and m and $\underline{\Psi}$ (eqn. 3.25)) consists of a scalar, vector and tensor part, there is no coupling among various terms of different tensor character. Because of this the above equation separates into

the following set of equations i.e.

$$\underline{\Psi}^{(\nu 0)}{}_{0} = [\underline{\underline{\mathcal{K}}}^{0}]_{\nu,\nu'} \; {}^{1}\underline{\mathcal{F}}^{(\nu' 0)}{}_{0} \tag{3.37}$$

$$\underline{\Psi}^{(\nu 1)}{}_{m} = [\underline{\underline{\mathcal{K}}}^{1}]_{\nu,\nu'} \; {}^{1}\underline{\mathcal{F}}^{(\nu' 1)}{}_{m} \tag{3.38}$$

$$\underline{\Psi}^{(\nu 2)}{}_{m} = [\underline{\underline{\mathcal{K}}}^{2}]_{\nu,\nu'} \; {}^{1}\underline{\mathcal{F}}^{(\nu' 2)}{}_{m} \tag{3.39}$$

$$\underline{\Psi}^{(\nu \ell)}{}_{m} \quad 0 = [\underline{\underline{\mathcal{K}}}^{\ell}]_{\nu,\nu'} \; {}^{1}\underline{\mathcal{F}}^{(\nu' \ell)}{}_{m}\} \quad \text{for} \quad \ell \geq 3 \; . \tag{3.40}$$

i.e. $$ {}^{1}\underline{\mathcal{F}}^{(\nu' \ell)}{}_{m} = 0$$

where from (3.26) to (3.29)

$$\underline{\Psi}^{(\nu 0)}{}_{0} = U \, \underline{\xi}_{1} \, \delta_{\ell_0} \, \delta_{m_0} \; , \tag{3.41}$$

$$\underline{\Psi}^{(\nu 1)}{}_{m} = (\underline{\underline{\mathcal{U}}}^{(1)}{}_{m} \, \underline{\underline{\mathcal{B}}} \, \underline{\xi}_{0} - \sqrt{\tfrac{5}{2}} \, \partial^{(1)}{}_{m} \log T \, \underline{\underline{\mathcal{B}}} \, \underline{\xi}_{1}) \delta_{\ell_1} \; , \tag{3.42}$$

$$\underline{\Psi}^{(\nu 2)}{}_{m} = \sqrt{2} \; \mathcal{S}^{(2)}{}_{m} \; \underline{\xi}_{0} \; \delta_{\ell_2} \tag{3.43}$$

The various ${}^{1}\underline{\mathcal{F}}$'s are given by eqn. (3.23).

C. Euler's Equations of Motion

Eqns. (3.41) and (3.21) involve the rate of change of the

temperature T and the mass average velocity $\underline{c}_0$ with time through U (eqn. (2.72)) and $(U_1)^{(1)}_m$ and $(U_2)^{(1)}_m$ (eqn. (2.73)) respectively. Following the C-E method, in the second approximation for $\mathcal{F}_1$ and $\mathcal{F}_2$, these time derivatives are to be eliminated using Euler's equations of motion.

The form of the Euler's equations for a binary gas mixture is

$$(\underline{\nu}^*|\underline{\mathcal{D}}_1|\underline{0}) + (\underline{\nu}^*|\underline{\mathcal{D}}_2|\underline{0}) = 0 \tag{3.44}$$

where

$$\underline{\nu}^* = (0,0,0) \text{ ; or } (0,1,m) \text{ ; or } (0,2,m) \text{ .}$$

The equation corresponding to $\underline{\nu}^* = (0,0,0)$ is not needed For $\underline{\nu}^* = (0,1,m)$, we have

$$\rho\{(\underline{c}_0 \cdot \partial^{(1)}_m)\, \underline{c}_0 - \partial_t\, (c_0)^{(1)}_m\}$$

$$= \rho_1\, X_1{}^{(1)}_m + \rho_2\, X_2{}^{(1)}_m - \partial^{(1)}_m\, p \tag{3.45}$$

where X_1 and X_2 are the external forces acting on the two components of the gas-mixture.

For $\underline{\nu}^* = (1,0,0)$, the two terms in the Euler's equation are identical viz.

$$- \frac{1}{2} \partial_t \log T - \frac{1}{2} \underline{c}_0 \cdot \underline{\partial} \log T - \frac{1}{3} \underline{\nabla} \cdot \underline{c}_0 = 0 \qquad (3.46)$$

Eliminating the time derivative of T in the scalar part in eqn. (3.41), using eqn. (3.46), it follows that

$$U = 0 \quad . \qquad (3.47)$$

Hence, in the second approximation of the Chapman-Enskog method of solution, the scalar part is always zero.

Eliminating the time-derivative of $\underline{c}_0$ by using eqn. (3.38) and rearranging the terms we get expressions for $(U_1)^{(1)}_m$ and $(U_2)^{(1)}_m$ (defined by eqn. (2.82)) in terms of ρ_1 , ρ_2 , ρ and p ;)

$$(U_1)^{(1)}_m = \frac{n}{n_1 \alpha_1} (d_{12})^{(1)}_m \quad , \qquad (3.48)$$

with

$$(d_{12})^{(1)}_m = \partial^{(1)}_m \left(\frac{n_1}{n}\right) - \frac{\rho_1 \rho_2}{p\ \rho} (\chi_1{}^{(1)}_m - \chi_2{}^{(1)}_m)$$

$$+ \frac{n_1 n_2}{n\ \rho} \quad (m_2 - m_1)\ \partial^{(1)}_m p \quad , \qquad (3.49)$$

and

$$(U_2)^{(1)}_m = \left(\frac{n}{n_2 \alpha_2} \right) (d_{21})^{(1)}_m \quad , \qquad (3.50)$$

with

$$(d_{21})^{(1)}_{m} = -(d_{12})^{(1)}_{m} \quad . \tag{3.51}$$

Using these relations in eqn. (3.29), $\mathcal{U}^{(1)}_{m}$ becomes

$$\mathcal{U}^{(1)}_{m} = n\,(d_{12})^{(1)}_{m} \cdot \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad . \tag{3.52}$$

Substituting this in eqn. (3.42), it follows that

$$\underline{\Psi}^{(\nu 1)}_{m} = \left(\underline{\zeta}_0\, n\,(d_{12})^{(1)}_{m} - \underline{\zeta}_1 \sqrt{\tfrac{5}{2}}\, \partial^{(1)}_{m} \log T\right) \quad . \tag{3.53}$$

(a) SUBSIDIARY CONDITIONS AND REDUNDANT EQUATIONS

Within the second approximation of the C-E method, the subsidiary conditions, from eqns. (3.12 - 3.14), are

$$n_i\, {}^{1}\mathcal{F}_{i}{}^{(00)}_{0} = 0 \quad , \tag{3.54}$$

$$n_1\, {}^{1}\mathcal{F}_{1}{}^{(10)}_{0} + n_2\, {}^{1}\mathcal{F}^{(10)}_{0} = 0 \tag{3.55}$$

$$n_1\alpha_1\, {}^{1}\mathcal{F}_{1}{}^{(01)}_{m} + n_2\alpha_2\, {}^{1}\mathcal{F}_{2}{}^{(01)}_{m} = 0 \quad . \tag{3.56}$$

Now, from eqns (3.37 - 3.40), ${}^{1}\mathcal{F}$ has scalar, vector and tensor components only while for all the higher-rank tensors

$^{1}\underline{\mathcal{F}}$ is zero. We have shown earlier that the scalar part is also zero, so $^{1}\underline{\mathcal{F}}$ involves only vector and tensor components. Now these components of $^{1}\underline{\mathcal{F}}$ must satisfy these conditions. Since the tensor component is not involved in these conditions, so, they are identically satisfied by the tensor component of $^{1}\underline{\mathcal{F}}$. For the vector part of $^{1}\underline{\mathcal{F}}$, first two conditions are again identically satisfied. Here we will discuss how the last condition (3.56) is taken into account for the vector part.

Dropping inessential indices e.g. setting $\Psi_{1\ m}^{(\nu 1)} = \Psi_1^{\nu}$, we have from eqns. (3.15), (3.16) and (3.38)

$$\Psi_1^{\nu} = (k'_{11})_{\nu\nu'}\, n_1\, \mathcal{F}_1^{\nu'} + (k'_{12})_{\nu\nu'}\, \mathcal{F}_2^{\nu'} \tag{3.57}$$

$$\Psi_2^{\nu} = (k'_{21})_{\nu\nu'}\, n_1\, \mathcal{F}_1^{\nu'} + (k'_{22})_{\nu\nu'}\, n_2\, \mathcal{F}_2^{\nu'} \quad . \tag{3.58}$$

Each of these eqns. represents an infinite set of equations corresponding to the values of ν and ν' from zero to infinity. For a finite order calculation we will truncate this infinite set of equations with the same justification as Chapman and Cowling (C.C-52) truncate their infinite-order determinants. For a calculation upto (N+1) order, ν and ν' will have values from zero to N . Using the expansion of Ψ_i^{ν} (3.42), the explicit forms for a set (2 N+2) of equations is

$$\frac{1}{n_1\alpha_1}(d_{12})^{(1)}_m = (k'_{11})_{00}\, n_1\, \mathcal{F}_1^0 + (k'_{11})_{01}\, n_1\, \mathcal{F}_1^1 + \cdots + (k'_{11})_{0N}\, n_1\, \mathcal{F}_1^N$$

$$+ (k'_{12})_{00}\, n_2\, \mathcal{F}_2^0 + (k'_{12})_{01}\, n_2\, \mathcal{F}_2^1 + \cdots + (k'_{12})_{0N}\, n_2\, \mathcal{F}_2^N \qquad (3.57a)$$

$$-\frac{1}{\alpha_1}\sqrt{\frac{5}{2}}\,\partial^{(1)}_m \log T = (k'_{11})_{10}\, n_1\, \mathcal{F}_1^0 + (k'_{11})_{11}\, n_1\, \mathcal{F}_1^1 + \cdots + (k'_{11})_{1N}\, n_1\, \mathcal{F}_1^N$$

$$+ (k'_{12})_{10}\, n_2\, \mathcal{F}_2^0 + (k'_{12})_{11}\, n_2\, \mathcal{F}_2^1 + \cdots + (k'_{12})_{1N}\, n_2\, \mathcal{F}_2^N \qquad (3.57b)$$

$$0 = (k'_{11})_{N0}\, n_1\, \mathcal{F}_1^0 + (k'_{11})_{N1}\, n_1\, \mathcal{F}_1^1 + \cdots + (k'_{11})_{NN}\, n_1\, \mathcal{F}_1^N$$

$$+ (k'_{12})_{N0}\, n_2\, \mathcal{F}_2^0 + (k'_{12})_{N1}\, n_2\, \mathcal{F}_2^1 + \cdots + (k'_{12})_{NN}\, n_2\, \mathcal{F}_2^N \qquad (3.57n)$$

$$-\frac{1}{n_2\alpha_2}\,(d_{12})^{(1)}_m = (k'_{21})_{00}\,n_1\,\mathcal{F}_1^0 + (k'_{21})_{01}\,n_1\,\mathcal{F}_1^1 + \text{---} + (k'_{21})_{0N}\,n_1\,\mathcal{F}_1^N$$

$$+ (k'_{22})_{00}\,n_2\,\mathcal{F}_2^0 + (k'_{22})_{01}\,n_2\,\mathcal{F}_2^1 + \text{---} + (k'_{22})_{0N}\,n_2\,\mathcal{F}_2^N \qquad (3.58a)$$

$$-\frac{1}{\alpha_2}\sqrt{\frac{5}{2}}\,\partial^{(1)}_m \log T = (k'_{21})_{10}\,n_1\,\mathcal{F}_1^0 + (k'_{21})\,n_1\,\mathcal{F}_1^1 + \text{---} + (k'_{21})_{1N}\,n_1\,\mathcal{F}_1^N$$

$$+ (k'_{22})_{10}\,n_2\,\mathcal{F}_2^0 + (k'_{22})_{11}\,n_2\,\mathcal{F}_2^1 + \text{---} + (k'_{22})_{1N}\,n_2\,\mathcal{F}_2^N \qquad (3.58b)$$

$$0 = (k'_{21})_{N0}\,n_1\,\mathcal{F}_1^0 + (k'_{21})_{N1}\,n_1\,\mathcal{F}_1^1 + \text{---} + (k'_{21})_{NN}\,n_1\,\mathcal{F}_1^N$$

$$+ (k'_{22})_{N0}\,n_2\,\mathcal{F}_2^0 + (k'_{22})_{N1}\,n_2\,\mathcal{F}_2^1 + \text{---} + (k'_{22})_{NN}\,n_2\,\mathcal{F}_2^N \qquad (3.58n)$$

Combining this set of $(2\ N + 2)$ equations with the subsidiary condition (3.56), we have $(2\ N + 3)$ equations while the number of unknowns in these equations is $(2\ N + 2)$. Obviously the problem is overdetermined. However, as will be shown later, there is one redundant equation in $(2\ N + 3)$ equations and a unique solution may be obtained.

Multiplying eqn. (3.57a) by $n_1\ \alpha_1$ and (3.58a) by $n_2\ \alpha_2$ and adding, we see that the l.h.s. is zero while each term of the r.h.s. is identically zero because the coefficients of ${}^0\mathcal{H}$'s satisfy the following identities.

$$n_1\ \alpha_1\ (k^1_{11})_{0N} + n_2\ \alpha_2\ (k^1_{21})_{0N} \equiv 0 \tag{3.59}$$

$$n_1\ \alpha_1\ (k_{12})_{0N} + n_2\ \alpha_2\ (k_{22})_{0N} \equiv 0 \tag{3.60}$$

These identities follow from eqns. (3.17 - 3.20, 2.39 and 2.74).

This vanishing of each term on the r.h.s. shows that eqns. (3.57a and 3.58a) are linearly dependent. However the eqn. (3.56) giving the subsidiary condition is linearly independent of the rest of $(2\ N + 2)$ eqns. So by neglecting one of the linearly dependent equations of the whole set of $(2\ N + 3)$

eqns., we are left with $(2\,N + 2)$ equations. Hence a unique solution may be obtained.

Incorporating the subsidiary conditions (3.56) for the vector part, the modified form of eqn. (3.38) is

$$\underline{\Psi}'^{(\nu 1)}_{m} = [\,\underline{\underline{\mathcal{K}}}'\,]_{\nu\nu'}\;\underline{\mathcal{F}}'^{(\nu' 1)}_{m} \tag{3.61}$$

where

$$\underline{\underline{\Psi}}'^{(\nu 1)}_{m} = \underline{\underline{\mathcal{B}}}\,(\underline{\zeta}_0\, n\,(d_{12})^{(1)}_{m} - \underline{\zeta_1}\,\sqrt{\tfrac{5}{2}}\,\partial^{(1)}_{m}\,\log T) \tag{3.62}$$

with

$$\underline{\underline{\mathcal{B}}}' = \begin{pmatrix} 0 & \dfrac{1}{\alpha_1} \\ \dfrac{1}{n_2\alpha_2} & \dfrac{1}{\alpha_2} \end{pmatrix} \delta_{\nu\nu'} \quad . \tag{3.63}$$

$$[\,\underline{\underline{\mathcal{K}}}'\,]_{\nu\nu'} = \begin{pmatrix} (\underline{\underline{k}}'_{11})_{\nu\nu'} & (\underline{\underline{k}}'_{12})_{\nu\nu'} \\ (\underline{\underline{k}}'_{21})_{\nu\nu'} & (\underline{\underline{k}}'_{22})_{\nu\nu'} \end{pmatrix} \tag{3.64}$$

with

$$(\underline{\underline{k}}'_{11})' = \begin{bmatrix} \alpha_1 & 0 & 0 & 0 & -- & 0 \\ (\underline{\underline{k}}'_{11})_{10} & (\underline{\underline{k}}'_{11})_{11} & (\underline{\underline{k}}'_{11})_{12} & (\underline{\underline{k}}'_{11})_{13} & -- & (\underline{\underline{k}}'_{11})_{1N} \\ - & - & - & - & - & - \\ - & - & - & - & - & - \\ - & - & - & - & - & - \\ (\underline{\underline{k}}'_{11})_{N0} & (\underline{\underline{k}}'_{11})_{N1} & (\underline{\underline{k}}'_{11})_{N2} & (\underline{\underline{k}}'_{11})_{N3} & -- & (\underline{\underline{k}}'_{11})_{NN} \end{bmatrix} \tag{3.65}$$

$$(\underline{\underline{k}}^1_{12})' = \begin{bmatrix} \alpha_2 & 0 & 0 & 0 & -- & 0 \\ (\underline{\underline{k}}'_{12})_{10} & (\underline{\underline{k}}'_{12})_{11} & (\underline{\underline{k}}'_{12})_{12} & - & - & (\underline{\underline{k}}'_{12})_{1N} \\ - & - & - & - & - & - \\ - & - & - & - & - & - \\ - & - & - & - & - & - \\ (\underline{\underline{k}}'_{12})_{N0} & (\underline{\underline{k}}'_{12})_{N1} & - & - & - & (\underline{\underline{k}}'_{12})_{NN} \end{bmatrix} \tag{3.66}$$

while $(\underline{\underline{k}}'_{21})$ and $(\underline{\underline{k}}'_{22})$ remains unchanged. The choice of modifying $\underline{\underline{k}}'_{11}$ and $\underline{\underline{k}}'_{12}$ or $\underline{\underline{k}}'_{21}$ and $\underline{\underline{k}}'_{22}$ is entirely ours. However, only care should be taken, when we modify $\underline{\underline{k}}'_{21}$ and $\underline{\underline{k}}'_{22}$ we should incorporate corresponding modification in $\underline{\underline{\mathcal{B}}}'$.

From now onwards, we will use the modified form of $\underline{\underline{\mathcal{K}}}'$-matrix i.e. $(\underline{\underline{\mathcal{K}}}')'$-matrix. This matrix is no longer symmetric.

Chapman and Cowling use $(2N + 1)$ eqns. instead of the $(2N + 2)$ eqns. derived here. They achieve this by dropping one of the linearly dependent equations and using the subsidiary condition (3.56) to eliminate either ${}'\mathcal{F}_1{}^{(01)}{}_m$ or ${}'\mathcal{F}_2{}^{(01)}{}_m$. Thus they are able to eliminate, one row, one column and one unknown from the Eq (3.57) and (3.58) to get a $((2N + 1) \times (2N + 1))$ matrix equation for $(2N + 1)$ unknowns.

(b) THE SOLUTION FOR ${}'\mathcal{F}$.

The general equation (3.20)

$$\underline{\Psi} = \underline{\underline{\mathcal{K}}}\ {}'\underline{\mathcal{F}} \tag{3.20b}$$

may still be retained formally by making appropriate modifications

to the vector part i.e. $\underline{\Psi}_m^{(\nu 1)}$ of this equation as given by eqn. (3.61) and $(\underline{\underline{\mathcal{K}}}^{1})$ of the eqn. known as $(\underline{\underline{\mathcal{K}}}^{1})'$ is given by eqns. (3.64 - 3.66). $(\underline{\underline{\mathcal{K}}}^{1})'$ is no more symmetric but is still diagonal in ℓ and m.

The equations may be solved formally for ${}^{1}\underline{\mathcal{F}}$, in particular

$$ {}^{1}\underline{\mathcal{F}} = \underline{\underline{\mathcal{L}}}\ \underline{\Psi}\ , \tag{3.67} $$

$(\underline{\underline{\mathcal{L}}})$ is the left inverse of $(\underline{\underline{\mathcal{K}}})$. The various components of $(\underline{\underline{\mathcal{L}}}^{\ell})$ are infinite matrices and like all other matrices are diagonal in the indices ℓ and m; that is

$$ [\underline{\underline{\mathcal{L}}}]_{\underline{\nu}',\underline{\nu}} = [\underline{\underline{\mathcal{L}}}^{\ell}]_{\nu',\nu}\ \delta_{\ell\ell'}\ \delta_{mm'} \tag{3.68} $$

The components of $\underline{\underline{\mathcal{L}}}$ or of $\underline{\underline{\mathcal{L}}}^{\ell}$ can be written with the help of eqns. (3.7) and (3.8). They are

$$ (\underline{\underline{\mathcal{L}}}^{\ell}{}_{11})_{\nu',\nu} = + \{[\underline{\underline{k}}_{12}^{\ell^{-1}}\ \underline{\underline{k}}_{11}^{\ell} - \underline{\underline{k}}_{22}^{\ell^{-1}}\ \underline{\underline{k}}_{21}^{\ell}]^{-1}\ [\underline{\underline{k}}_{12}^{\ell^{-1}}]\}_{\nu',\nu}, \tag{3.69} $$

$$ (\underline{\underline{\mathcal{L}}}^{\ell}{}_{12})_{\nu',\nu} = - \{[\underline{\underline{k}}_{12}^{\ell^{-1}}\ \underline{\underline{k}}_{11}^{\ell} - \underline{\underline{k}}_{22}^{\ell^{-1}}\ \underline{\underline{k}}_{21}^{\ell}]^{-1}\ [\underline{\underline{k}}_{22}^{\ell^{-1}}]\}_{\nu',\nu}, \tag{3.70} $$

$$ (\underline{\underline{\mathcal{L}}}^{\ell}{}_{21})_{\nu',\nu} = + \{[\underline{\underline{k}}_{11}^{\ell^{-1}}\ \underline{\underline{k}}_{12}^{\ell} - \underline{\underline{k}}_{21}^{\ell^{-1}}\ \underline{\underline{k}}_{22}^{\ell}]^{-1}\ [\underline{\underline{k}}_{11}^{\ell^{-1}}]\}_{\nu',\nu}, \tag{3.71} $$

$$(\mathcal{L}^{\ell}_{22})_{\nu',\nu} = -\{[k^{\ell^{-1}}_{11}\, k^{\ell}_{12} - k^{\ell^{-1}}_{21}\, k^{\ell}_{22}]^{-1}\, [k^{\ell^{-1}}_{21}]\}_{\nu',\nu} \quad (3.72)$$

with the replacements $K^{1}_{11} \to K^{1'}_{11}$ and $K^{1}_{12} \to K^{1'}_{12}$ where needed.

Introducing indices, eqn. (3.67) may be written as

$$^{1}\mathcal{F}^{(\nu'\ell')}_{m'} = [\mathcal{L}^{\ell}]_{\nu',\nu}\, \underline{\Psi}^{(\nu\ell)}_{m}\, \delta_{\ell\ell'}\, \delta_{mm'} \quad . \quad (3.73)$$

From eqns. (3.39) and (3.73), the tensor part is

$$^{1}\mathcal{F}^{(\nu'2)}_{m} = \sqrt{2}\, \mathcal{S}^{(2)}_{m}\, (\mathcal{L}^{2})_{\nu'\nu}\, \underline{\xi}_0\, \delta_{\nu_0} \quad , \quad (3.74)$$

From eqns. (3.61), (3.62) and (3.73), the vector part is

$$^{1}\mathcal{F}^{(\nu'1)}_{m} = (\mathcal{L}^{1})\, \mathcal{B}'\, (\underline{\zeta}_0\, n\, (d_{12})^{(1)}_{m} - \underline{\zeta}_1 \sqrt{\tfrac{5}{2}}\, \partial^{(1)}_{m} \log T) \quad . \quad (3.75)$$

Having obtained the values of $^{1}\mathcal{F}^{(\nu 2)}_{m}$ and $^{1}\mathcal{F}^{(\nu 1)}_{m}$ in terms of inverted $\mathcal{L}^{2}$ and $\mathcal{L}^{1}$-matrices respectively, we are in a position to derive the general expressions of various transport coefficients in terms of $\underline{k}$-matrices. These expressions may be handled directly for doing any computational work for an order 'n'.

D. Viscosity

The coefficient of viscosity (η_{mix}) is related to the tensor part of ${}^1\mathcal{F}$. The computational form for η_{mix} in terms of k-matrices is derived. Also an equivalence of this form with that of Chapman and Cowling is shown.

(a) COMPUTATIONAL FORM

We try the form for

$$\underline{{}^1\mathcal{F}}_m^{(\nu'2)} = \sqrt{2}\ \mathcal{S}_m^{(2)}\ \underline{Z} \tag{3.76}$$

where indices on $\underline{Z}$ have been suppressed. Obviously the quantity Z like ${}^1\mathcal{F}$ (eqn. (3.23)) is a two row column with components Z_1 and Z_2. Each of the Z_1 and Z_2 is an infinite column vector. From eqns. (3.74) and (3.76), the structure of Z is

$$\underline{Z} = \mathcal{L}^2\ \underline{\xi}_0 \tag{3.77}$$

where $\underline{\xi}_0$ is given by eqn. (3.26).

From eqn. (3.23)

$${}^1\mathcal{F}_m^{(\nu'2)} = \begin{pmatrix} -n_1 & {}^1\mathcal{F}_{1\,m}^{(\nu'2)} \\ -n_2 & {}^1\mathcal{F}_{2\,m}^{(\nu'2)} \end{pmatrix} \tag{3.78}$$

Combining eqns. (3.78), (3.77) and (3.76), the values of $\mathcal{F}_{1\,m}^{(\nu'2)}$ and $\mathcal{F}_{2\,m}^{(\nu'2)}$ for the second approximation are known. Now we will use these values to write the expressions for η_{mix}.

From the basic pressure tensor-viscosity relationship (eqn. (2.33)), the expression for the coefficient of viscosity, in the second approximation of the C-E method, is

$$k\,T\,(n_1\,{}^1\mathcal{F}_{1\,m}^{(02)} + n_2\,{}^1\mathcal{F}_{2\,m}^{(02)}) = -\sqrt{2}\,\eta_{mix}\,\mathcal{S}_m^{(2)}. \tag{3.79}$$

Rewriting this equation in the present notation, we have

$$k\,T\,(n_1\,{}^1\mathcal{F}_{1m}^{(02)} + n_2\,{}^1\mathcal{F}_{2\,m}^{(02)}) = -\,k\,T(\underline{\xi}_0^T\,{}^1\mathcal{F}_m^{(\nu 2)})$$

$$= -\sqrt{2}\,\eta_{mix}\,\mathcal{S}_m^{(2)}, \tag{3.80}$$

where $\underline{\xi}_0^T$ is the row matrix corresponding to the column $\underline{\xi}_0$ (eqn. (3.26)).

Substituting the value of ${}^1\mathcal{F}_m^{(\nu'2)}$ from eqn. (3.66) and $\underline{Z}$ from (3.77), we get the value of η_{mix} from the above equation as

$$\frac{\eta_{mix}}{k\ T} = (\underline{\xi}_0^T \quad \mathcal{L}^2 \quad \underline{\xi}_0) \qquad . \tag{3.81}$$

Since the r.h.s. of this equation is the product of a row, (2 × 2)-matrix and a column, the result is a function of various parameters of the gas mixture and the computed result for a particular set of parameters is a number.

Writing the form of $\mathcal{L}^2$ explicitly from eqns. (3.69 - 3.72) and carrying out the multiplication, we obtain the zero-zero element of a certain matrix as the coefficient of viscosity. The explicit expression is

$$\frac{\eta_{mix}}{k\ T} = [((k^2_{12})^{-1}\ k^2_{11} - (k^2_{22})^{-1}\ k^2_{21})^{-1}\ ((k^2_{22})^{-1} - (k^2_{12})^{-1})$$

$$+ ((k^2_{11})^{-1}\ k^2_{12} - (k^2_{21})^{-1}\ k^2_{22})^{-1}\ ((k^2_{22})^{-1} - (k^2_{11})^{-1})]_{00}$$

(3.82)

The computation of η_{mix} consists in the setting up of k-matrices for a particular potential and order and carrying out the various matrix manipulations. Details of computation will be given in Chapter IV.

(b) EQUIVALENCE WITH CHAPMAN-COWLING EXPRESSIONS

From eqns. (3.21), (3.43) and (3.76), we have

$$\underline{\xi}_0 = (\underline{\underline{\mathcal{K}}}^2 \underline{Z}) \quad . \tag{3.83}$$

Taking the transpose and multiplying both sides by $\underline{Z}$, we have

$$(\underline{\xi}_0^T \underline{Z}) = (\underline{Z}^T \underline{\underline{\mathcal{K}}}^2 \underline{Z}) \quad , \tag{3.84}$$

where we have used

$$\underline{\underline{\mathcal{K}}}^{2^T} = \underline{\underline{\mathcal{K}}}^2 \quad ; \tag{3.85}$$

which follows from diagonal nature of $\underline{\underline{\mathcal{K}}}$.

From eqns. (3.76) and (3.80), an alternative expression for viscosity may be obtained. This is

$$\frac{\eta_{mix}}{k\ T} = (\underline{\xi}_0^T \underline{Z}) \quad . \tag{3.86}$$

On using (3.84), it therefore follows that

$$\frac{\eta_{mix}}{k\ T} = (\underline{Z}^T \underline{\underline{\mathcal{K}}}^2 \underline{Z}) \quad . \tag{3.87}$$

On comparing the tensor part in the expansion of the distribution function (eqns. (8.31-1,-2), CC.-52) with eqn. (3.39), the value of the second-rank tensor $\underline{\underline{B}}_{1\ m}^{(2)}$ and $\underline{\underline{B}}_2^{(2)}$ of Chapman and Cowling in the present notation are

$$\underline{\underline{B}}_{1\,m}^{(2)} = -\sqrt{2}\sum_{\nu_1} Z_1^{\nu_1}\ \phi_m^{(\nu_1 2)}\ (\alpha_1 \underline{C}_1) \quad , \tag{3.88}$$

$$\underline{\underline{B}}_{2\,m}^{(2)} = -\sqrt{2}\sum_{\nu_1} Z_2^{\nu_1}\ \phi_m^{(\nu_1 2)}\ (\alpha_2 \underline{C}_2) \quad , \tag{3.89}$$

where Z_1 and Z_2 are the components of Z . These are obtained by comparing the corresponding components of the two column vectors of eqns. (3.77).

The Chapman-Cowling curly bracket (eqn. (2.77)) for $\underline{\underline{B}}$'s is

$$n_1 n_2\ \{\underline{\underline{B}},\underline{\underline{B}}\} = \sum_m n_1 n_2 \{\underline{\underline{B}}_{1\,m}^{(2)} + \underline{\underline{B}}_{2\,m}^{(2)}\ ,\ \underline{\underline{B}}_{1\,m}^{[2]} + \underline{\underline{B}}_{2\,m}^{[2]}\} \tag{3.90}$$

As shown in chapter II, the curly bracket consists of several collision matrices. Since all the collision matrices are independent of ℓ and m , and the coefficients of $\delta_{mm'}$ are independent of m , when the summation over m is carried out we get a factor $(2\ \ell + 1)$ corresponding to $(2\ \ell + 1)$, m-values. Using eqns. (2.77), (3.17-3.20), we get

$$\begin{aligned} n_1 n_2 \{\underline{\underline{B}},\underline{\underline{B}}\} &= -10[Z_1^T\, k^2_{11}\, Z_1 + Z^T_1\, k^2_{12}\, Z_2 + Z^T_2\, k^2_{21}\, Z_1 \\ &\qquad + Z^T_2\, k^2_{22}\, Z_2] \\ &= -10(\underline{Z}^T\ \underline{\underline{\mathcal{K}}}^2\ \underline{Z}) \quad . \end{aligned} \tag{3.91}$$

The expression of viscosity in Chapman and Cowling work ((8.52-7), C.C-52) is

$$n_1 n_2 \{\underline{B}, \underline{B}\} = - \frac{10}{kT} \quad \eta_{mix} \quad . \tag{3.92}$$

Comparing eqns. (3.87), (3.91) and (3.92), the equivalence is established.

E. Vector Part.

The vector part, eqn. (3.75) is

$$^{1}\mathcal{J}_{m}^{(\nu'1)} = (\mathcal{L}^{1})\mathcal{D}_{..} \; (\underline{\zeta}_0 \; n \; (d_{12})_{m}^{(1)} - \underline{\zeta}_1 \sqrt{\tfrac{5}{2}} \; \partial_{m}^{(1)} \log T). \tag{3.93}$$

Using this expression the coefficients of diffusion, thermal-diffusion and thermal-conductivity may be defined. (The first two coefficients are discussed in the following subsection (a) and the last coefficient in the next subsection (b)). Finally, as with viscosity, for each coefficient, we will write the computational form and show that it is equivalent to the corresponding expressions of Chapman and Cowling (C.C.-52).

(a) DIFFUSION AND THERMAL DIFFUSION

The gases are said to diffuse when the average velocities of the molecules are not the same. In the present notation, the difference between $\langle \underline{C}_1 \rangle - \langle \underline{C}_2 \rangle$ is (eqn. (2.37))

$$\frac{1}{\alpha_1} \mathcal{F}_{1\,m}^{(01)} - \frac{1}{\alpha_2} \mathcal{F}_{2\,m}^{(01)} = - \frac{n^2}{n_1 n_2} [D_{12} (d_{12})_m^{(1)} +$$

$$+ D_T \, \partial_m^{(1)} \log T] \quad . \tag{3.94}$$

where $(d_{12})_m^{(1)}$ is given by eqn. (3.49).

As in the previous sections, on suppressing certain indices, we try the form

$$^1 \underline{\mathcal{F}}_m^{(\nu 1)} = \underline{X} \, n \, (d_{12})_m^{(1)} + \underline{Y} \sqrt{\frac{5}{2}} \, \partial_m^{(1)} \log T \quad , \tag{3.95}$$

where $\underline{X}$ and $\underline{Y}$ are

$$\underline{X} = (\underline{\underline{\mathcal{L}}}^{1} \, \underline{\underline{\mathcal{B}}}' \, \underline{\zeta}_0) \quad , \tag{3.96}$$

$$\underline{Y} = (- \underline{\underline{\mathcal{L}}}^{1} \, \underline{\underline{\mathcal{B}}}' \, \underline{\zeta}_1) \quad . \tag{3.97}$$

These are obtained by comparing eqns. (3.93) and (3.95). Like Z , these are column vectors with the components are

X_1 , X_2 and Y_1 , Y_2 respectively.

Now, in the second approximation ot the C-E method, the expression on the l.h.s. of eqn. (3.94) is given by

$$\frac{1}{\alpha_1} \; {}^1\mathcal{J}_1{}^{(01)}_{m} - \frac{1}{\alpha_2} \; {}^1\mathcal{J}_2{}^{(01)}_{m} \equiv - ({}^1\underline{\mathcal{J}}^T \; \underline{\underline{\mathcal{B}}} \; \underline{\xi}_0) \; . \quad (3.98)$$

Substituting the value of ${}^1\mathcal{J}_r{}^{(\nu 1)}_{m}$ from eqn. (3.95) in the above eqn. and comparing coefficients of $(d_{12})^{(1)}_{m}$ and $(\partial^{(1)}_{m} \log T)$ from eqn. (3.94), we may obtain expressions for diffusion (D_{12}) and thermal-diffusion (D_T) . In particular, they are

$$D_{12} = \frac{n_1 n_2}{n} \; (\underline{X}^T \; \underline{\underline{\mathcal{B}}} \; \underline{\xi}_0) \quad , \quad (3.99)$$

$$D_T = \sqrt{\frac{5}{2}} \; \frac{n_1 n_2}{n^2} \; (\underline{Y}^T \; \underline{\underline{\mathcal{B}}} \; \underline{\xi}_0) \quad . \quad (3.100)$$

i) Computational form

On substituting in eqns. (3.99) and (3.100), the values of $\underline{X}$ and $\underline{Y}$ from eqns. (3.96) and (3.97) and the value of $\underline{\underline{\mathcal{L}}}^{1}$ from eqns. (3.69 - 3.72) , D_{12} is obtained as the zero-zero element and D_T as the zero-one element of certain matrices. The explicit expressions are

$$D_{12} = -\frac{n_1 n_2}{n}\Big[\frac{1}{n_1\alpha_1}\Big\{(k^1_{12})'^{-1}(k^1_{11})' - (k^1_{22})^{-1}(k^1_{21})\Big\}^{-1}\Big\{\frac{1}{n_2\alpha_2}(k^1_{22})^{-1}\Big\}$$

$$-\frac{1}{n_2\alpha_2}\Big\{(k^1_{11})'^{-1}(k^1_{12}) - (k^1_{21})^{-1}(k^1_{22})\Big\}^{-1}\Big\{\frac{1}{n_2\alpha_2}(k^1_{21})^{-1}\Big\}\Big]_{00} \qquad (3.101)$$

$$D_T = \sqrt{\frac{\xi}{2}}\,\frac{n_1 n_2}{n^2}\Big[\frac{1}{n_2\alpha_2}\Big\{(k^1_{11})'^{-1}(k^1_{12})' - (k'_{21})^{-1}(k^1_{22})\Big\}^{-1}\Big\{\frac{1}{\alpha_1}(k^1_{11})'^{-1} - \frac{1}{\alpha_2}(k^1_{21})^{-1}\Big\}$$

$$-\frac{1}{n_1\alpha_1}\Big\{(k^1_{12})'^{-1}(k^1_{11})' - (k^1_{22})^{-1}(k^1_{21})\Big\}^{-1}\Big\{\frac{1}{\alpha_1}(k^1_{12})'^{-1} - \frac{1}{2}(k^1_{22})^{-1}\Big\}\Big]_{01}$$

(3.102)

Thermal-diffusion ratio k_T is defined by

$$k_T = D_T/D_{12} \qquad (3.103)$$

The computation of D_T, D_{12} and k_T is similar to that for η_{mix}, The matrices in all cases are constructed from the same formulae (3.17 - 3.20), by using appropriate values of ℓ. It should be remembered, however, that for $\ell = 1$, the matrices are modified by putting $(k^1_{11})_{00} = \alpha_1$, $(k^1_{12})_{00} = \alpha_2$ and all other elements of the first row zero. After this the inversion is similar again.

(ii) <u>Equivalence with Chapman-Cowling expressions</u>

By comparing the vector parts in the expansion of th distribution functions of eqns. (8.31-1,-2,C.C-52) with eqns. (3.38) and (3.95) we get the values of the vector quantities $(D_1)^{(1)}_m$, $(D_2)^{(1)}_m$, $(A_1)^{(1)}_m$, $(A_2)^{(1)}_m$ used in Chapman and Cowling in the present notation as

$$(D_1)^{(1)}_m = - \sum_\nu X^\nu_1 \, \phi^{(\nu 1)}_m \, (\alpha_1 \underline{C}_1) \tag{3.10.4}$$

$$(D_2)^{(1)}_m = - \sum_\nu X^\nu_2 \, \phi^{(\nu 1)}_m \, (\alpha_2 \underline{C}_2) \tag{3.10.5}$$

$$(A_1)^{(1)}_m = \sqrt{\frac{5}{2}} \sum_\nu Y^\nu_1 \, \phi^{(\nu 1)}_m \, (\alpha_1 \underline{C}_1) \tag{3.10.6}$$

$$(A_2)^{(1)}_m = \sqrt{\frac{5}{2}} \sum_\nu Y^\nu_2 \, \phi^{(\nu 1)}_m \, (\alpha_2 \underline{C}_2) \tag{3.10.7}$$

The values of X_1, X_2, Y_1 and Y_2 are obtained by comparing the corresponding elements of the two columns in eqns. (3.96) and (3.97) respectively.

Again, the Chapman-Cowling curly bracket is

$$n_1 n_2 \quad \{\underline{D},\underline{D}\} = n_1 n_2 \sum_m \{(D_1)^{(1)}_m + (D_2)^{(1)}_m , (D_1)^{[1]}_m + (D_2)^{[1]}_m\} \tag{3.108}$$

As in case of viscosity, the factor due to summation over m will be 3 in the present case since $\ell = 1$. Now substituting from eqns. (3.104) and (3.105) and using eqn. (2.77), we have

$$n_1 n_2 \quad \{\underline{D},\underline{D}\} = 3\,(\underline{X}^T \underline{\underline{\mathcal{K}}}^1 \underline{X}) \quad . \tag{3.109}$$

By substituting eqn. (3.95) and using eqn. (3.53) for the l.h.s., we obtain by comparing the two sides of eqn. (3.38)

$$\underline{\underline{\mathcal{K}}}' \underline{X} = \underline{\underline{\mathcal{B}}} \underline{\zeta}_0 \tag{3.110}$$

$$\underline{\underline{\mathcal{K}}}' \underline{Y} = \underline{\underline{\mathcal{B}}} \underline{\zeta}_1 \tag{3.111}$$

Thus from eqns. (3.109)and (3.110), we have

$$n_1 n_2 \quad D,D \quad = 3 \; (\underline{X}^T \; \underline{\underline{\mathcal{B}}} \; \underline{\zeta}_0) \tag{3.112}$$

The expression for D_{12} in Chapman and Cowling work eqn. (8.4-4, CC.-52) is

$$n_1 n_2 \; \{D,D\} = - \frac{3n}{n_1 n_2} \; D_{12} \quad . \tag{3.113}$$

Comparing eqns. (3.99) and (3.112), (3.113), we establish the equivalence.

Similarly from eqns. (3.104 - 3.108), we have

$$n_1 n_2 \; \{\underline{D},\underline{A}\} = 3 \sqrt{\frac{5}{2}} \; (Y^T \; \underline{\underline{\mathcal{B}}} \; \underline{\zeta}_0) \quad . \tag{3.114}$$

Eqn. (3.100) is then seen to be equivalent to eqn. (8.4-5, C.C.52) which is

$$n_1 n_2 \; \{D,A\} = - \frac{3 \; n^2}{n_1 n_2} \; D_T \quad . \tag{3.115}$$

The only remaining step here is to show that X and Y are obtained by solving (2 N + 1) eqns. as is done in Chapman-Cowling work (C.C.-52). How this is to be done has already been indicated at the end of section (III - C.b).

(b) THERMAL-CONDUCTIVITY

The expression of the thermal-flux vector for a binary gas-mixture obtained by combining eqns. (2.35) and (2.36) is

$$q^{(1)}_{m} = \frac{5}{2} kT \left\{\frac{n_1}{\alpha_1} \mathcal{F}_1^{(01)}{}_m + \frac{n_2}{\alpha_2} \mathcal{F}_2{}^{(01)}_m\right\}$$

$$- \sqrt{\frac{5}{2}}\, kT \left\{\frac{n_1}{\alpha_1} \mathcal{F}_1{}^{(11)}_m + \frac{n_2}{\alpha_2} \mathcal{F}_2{}^{(11)}_m\right\} \qquad (3.116)$$

By definition, the thermal-conductivity is the coefficient of $(- \partial^{(1)}_m T)$ in the above expression of $q^{(1)}_m$. The first term in the expression is equal to $\frac{5}{2} kT\, (n_1\langle \underline{C}_1\rangle + n_2\langle \bar{\underline{C}}_2\rangle)$ Chapman and Cowling and will not contribute to the gradients of temperature in the system as it represents the heat flow resulting from the flux of molecules $(n_1\langle \underline{C}_1\rangle + n_2\langle \underline{C}_2\rangle)$ per unit time relative to mass velocity vector $\underline{c}_0$. (This contribution can also be shown to be independent of terms containing $(- \partial^{(1)}_m T)$ by using eqns. (3.94) and (3.95).) The second term in the second approximation is

$$\left(\frac{n_1}{\alpha_1}\ {}^1\mathcal{F}_1{}^{(1)}_m + \frac{n_2}{\alpha_2}\ {}^1\mathcal{F}_2{}^{(1)}_m\right) \equiv - \left(\underline{\zeta}_1^T\ \underline{\underline{\Phi}}^T\ {}^1\underline{\mathcal{F}}^{(\nu 1)}_m\right)$$

(3.117)

Now ${}^{1}\mathcal{F}^{(\nu 1)}_{m}$ from eqn. (3.95) has a term depending on $(d_{12})^{(1)}_{m}$ and another depending on $(\partial^{(1)}_{m} \log T)$. But from eqn. (3.88), $(d_{12})^{(1)}_{m}$, can be expressed in terms of $(\frac{1}{\alpha_1} \; {}_1{}^{(01)}_{m} - \frac{1}{\alpha_2} \; {}_2{}^{(01)}_{m})$ and $\partial^{(1)}_{m} \log T$. Since thermal conductivity is the coefficient of $(-\partial^{(1)}_{m} T)$ in the expression on the r.h.s. of the above equation, we will have to eliminate $(d_{12})^{(1)}_{m}$ in the equation (3.94) of ${}^{1}\mathcal{J}^{(\nu 1)}_{m}$. Carrying out this elimination in eqn. (3.94), the expression for ${}^{1}\mathcal{F}^{(\nu 1)}_{m}$ is

$$
{}^{1}\mathcal{F}^{(\nu 1)}_{m} = - [\underline{X} \left(\frac{n_1 n_2}{n} \left(\frac{1}{\alpha_1} \mathcal{F}_1{}^{(01)}_{m} - \frac{1}{\alpha_2} \mathcal{F}_2{}^{(01)}_{m}\right) + \right.
$$

$$
+ n \, D_T \, \partial^{(1)}_{m} \log T] \, / \, D_{12} + \sqrt{\tfrac{5}{2}} \, \underline{Y} \, \partial^{(1)}_{m} \log T. \quad (3.118)
$$

Hence

$$
(\underline{\zeta}_1^T \; \underline{\underline{\mathcal{B}}}^T \; {}^{1}\mathcal{J}^{(\nu 1)}_{m}) = \sqrt{\frac{2}{5}} \frac{n \, D_T}{D_{12}} \left(\frac{1}{\alpha_1} \mathcal{J}_1{}^{(01)}_{m} - \frac{1}{\alpha_2} \mathcal{J}_2{}^{(01)}_{m}\right)
$$

$$
+ \sqrt{\frac{2}{5}} \frac{n^3}{n_1 n_2} \frac{D_T^2}{D_{12}} \partial^{(1)}_{m} \log T
$$

$$
- \sqrt{\frac{5}{2}} \; \underline{\zeta}_1^T \; \underline{\underline{\mathcal{B}}}^T \; \underline{Y} \; \partial^{(1)}_{m} \log T \qquad (3.119)
$$

where in the first and second terms, we have used the identity

$$\underline{\zeta}_1^T \; \underline{\underline{\mathcal{B}}}^T \; \underline{X} \equiv + (\underline{Y}^T \; \underline{\underline{\mathcal{B}}} \; \underline{\zeta}_0)$$

$$= \sqrt{\frac{2}{5}} \; \frac{n^2}{n_1 n_2} \; D_T \quad . \tag{3.120}$$

The second equality follows from eqns. 3.114 and 3.115.

Finally, from eqns. (3.119) and (3.117), the expression for $q^{(1)}_m$ (eqn. (3.118)) becomes

$$q^{(1)}_m = \frac{5}{2} kT \left(\frac{n_1}{\alpha_1} \mathcal{J}_1{}^{(01)}_m + \frac{n_2}{\alpha_2} \mathcal{J}_1{}^{(01)}_m\right)$$

$$+ n \, kT \, k_T \left(\frac{1}{\alpha_1} \mathcal{F}_1{}^{(01)}_m - \frac{1}{\alpha_2} \mathcal{F}_2{}^{(01)}_m\right)$$

$$- kT \left(- \frac{n^2}{T n_1 n_2} \frac{D_T}{D_{12}} - \frac{5}{2T} (\underline{\zeta}_1^T \; \underline{\underline{\mathcal{B}}}^T \; \underline{Y})\right) \partial^{(1)}_m T \; , \tag{3.121}$$

This expression for $q^{(1)}_m$ is identical to eqn. (8.41-3 C.C-52) of Chapman and Cowling and, therefore, the explanation for each of the terms contributing to $q^{(1)}_m$ is the same as given by Chapman and Cowling. The first term has already been explained. The second term is due to thermal diffusion. The third term is proportional to the gradients of temperature $(- \partial^{(1)}_m T)$ in the system. The coefficient of $(- \partial^{(1)}_m T)$ in the third

term, by definition, is equal to the thermal conductivity, λ_{mix}, of a binary gas-mixture. Therefore

$$\lambda_{mix} = \lambda'_{mix} - \frac{n^3 k}{n_1 n_2} \frac{D_T^2}{D_{12}} \tag{3.122}$$

where

$$\lambda_{mix} = - \frac{5}{2} k (\underline{\zeta}_1^T \underline{\underline{\mathcal{B}}}^T \underline{Y})_1 \tag{3.123}$$

the second term in this expression for λ_{mix} being much smaller than the first.

(i) Computational form

An explicit expression for λ'_{mix} is obtained from eqns. (3.123) by substituting the value of $\underline{Y}$ from eqn. (3.97) and the value of $\underline{\underline{\mathcal{B}}}$ and $\underline{\zeta}_1$ from eqns. (3.28) and (3.27) respectively.

The resulting expression is

$$\lambda'_{mix} = \frac{5}{2} k \Big[\frac{1}{\alpha_1} \{(k^1_{22})^{-1} k^1_{(1} - (k^1_{12})' (k^1_{11})'\}\{\frac{1}{\alpha_1} (k^1_{12})' - \frac{1}{\alpha_2} (k^1_{22})^{-1}\} + \frac{1}{\alpha_2} \{(k^1_{21})^{-1} k^1_{22} - (k^1_{11})' (k^1_{12})'\} \{\frac{1}{\alpha_1} (k^1_{11})'^{-1} - \frac{1}{\alpha_2} (k^1_{21})^{-1}\}\Big]_{11} \tag{3.124}$$

The computation is done in a way similar to that for D_T, D_{12} and k_T.

(ii) Equivalence with Chapman-Cowling expressions

Using the forms given by eqns (3.104 - 3.107) for $(D_1)^{(1)}_m$, $(D_2)^{(1)}_m$, $(A_1)^{(1)}_m$, $(A_2)^{(1)}_m$, and defining the bracket expressions in the same way as before for diffusion and thermal-diffusion, the following relations follow :

$$n_1 n_2 \{\underline{A},\underline{D}\} = - \frac{3\, n^2}{n_1 n_2} D_T \tag{3.125}$$

and

$$n_1 n_2 \{\underline{A},\underline{A}\} = \frac{15}{2} (\underline{Y}^T \underline{\underline{\mathcal{K}}}^1 \underline{Y}) \quad . \tag{3.126}$$

From eqn. (3.111), the above eqn. becomes

$$n_1 n_2 \{\underline{A},\underline{A}\} = - \frac{15}{2} \underline{\zeta}_1^T \underline{\underline{\mathcal{B}}}^T \underline{Y} \tag{3.127}$$

The expression for thermal-conductivity in Chapman-Cowling notation is (eqn. (8.41-4), C.C.-52)

$$\lambda_{mix} = \frac{1}{3} k\, n_1 n_2 \, [\{\underline{A},\underline{A}\} - \{\underline{A},\underline{D}\}^2/\{\underline{D},\underline{D}\}] \, . \tag{3.128}$$

Substituting the values of $\{\underline{A},\underline{A}\}$, $\{\underline{A},\underline{D}\}$ and $\{\underline{D},\underline{D}\}$ from eqns. (3.127), (3.125) and (3.112), the above equation takes the form of eqn. (3.122).

CHAPTER IV

CALCULATION OF THE COLLISION MATRICES AND THE TRANSPORT COEFFICIENTS

Introduction

The expressions for the transport coefficients (eqns. 3.82, 3.101-.103, 3.124) derived in the last chapter, may be written in terms of collision matrices (using eqns. (3.9 to 3.12)). In this chapter we discuss the method of calculating the coefficients numerically for a general order 'n' and give algebraic expressions for the collision matrices in terms of interaction integrals and masses of the individual components of the mixture. The results of these numerical calculations for a rigid sphere and a Lennard-Jones potential are given in the next two chapters.

We have already discussed the advantages of doing numerical calculations using the general expressions derived in Chapter III over the Chapman-Cowling procedure (See Introduction). Here we have summed up the argument for sake of completion and emphasis.

The usual procedure of Chapman-and Cowling consists in expressing the coefficients in terms of infinite order determinants where each element is a finite sum of the square brackets (Chs. VIII and IX, C.C-52). Each of the square brackets is expressed as a finite sum of the collision integrals ($\Omega^{(\ell,s)}$) . This step is the most tedious part of the

calculations. The amount of difficulty experienced in writing these expressions for orders higher than the first is apparent from the works of Joshi, Saxena, Mason and Devoto (De-66, Jo-65, Ma-57, S.J.-63).

On calculating the expressions for the first few orders using the C.C. procedure, one can see a definite pattern of terms depending upon different $\Omega^{(\ell,s)}$. Unfortunately there is no simple set of conditions which will indicate which of these integrals are to be included for a given order 'n'. Moreover it is desirable to have a simple computer programme for calculating the coefficients of the $\Omega^{(\ell,s)}$ for the given order 'n'. It is not very convenient to build up such a programme in the C.C. formulation (C.C.-52).

In the present formulation, these disadvantages are removed. The improvement is particularly noticeable for the higher order calculations. This is the main reason for dealing with the collision matrices.

Before we indicate the steps to write a computer programme, it may be worthwhile to point out that the algebraic expressions of the collision matrices in terms of interaction integrals and

mass-ratios, for a fourth order calculation for viscosity and diffusion and for a third order calculation for thermal-conductivity and thermal-diffusion, are given in appendix C. These expressions may be used to compare the corresponding algebraic expressions for the corresponding coefficients obtained by using Chapman-Cowling procedure (C.C-52, De-66, Ma-57, Jo-65, S.J-63). Also these expressions of appendix C can be subjected to the type of studies to which the algebraic expressions of the Chapman-Cowling procedure have been subjected. In particular these studies are

(1) Approximation studies

Kihara, Brokaw, Mason, Saxena and others (Br-59, Br-65, S.J-65, H.C.B-54, Ma-57, S.J-64) have approximated the exact expressions by neglecting a number of terms depending upon different collision integrals in such a way that the accuracy of the approximate expressions for all practical purposes is as good as that of the original expressions and they are much easier to handle for computation.

(2) Consistency of different experimental data

First and higher-order expressions (W.M-62, W-65, S.A-61, S.M-66, S.M-65) have been used to establish certain approximate relations among various transport coefficients. These relations

help us to check the consistency of different experimental data. Also, from the measured values of a particular coefficient, we can predict approximate experimental values for other coefficients for which no measurements are available.

(3) Computation of the transport coefficients

By using the tabulated values of the collision integrals for various potentials, we can compute the theoretical values (Th.-61, S.G-66) of the coefficients for various orders on a desk calculator.

The only difference in working with the present expressions will be that the approximations will be made for the interaction integrals $V^{\ell}_{nn'}$ or the matrices instead of the collision integrals $\Omega^{(\ell,s)}$. However during the course of calculations for a rigid sphere potential, only a brief study of these Kihara-type approximations is made in section H).

Having discussed above the advantages of dealing with the collision matrices and, thereby, of the present form of the general expressions of the transport coefficients (Ch. III), the method of calculation of the coefficients consists of the following steps

(1) The collision matrices for unlike molecules are expressed in terms of the $V^{\ell}_{nn'}$ and a function $X\,(NL,\, n\ell,\, n' | \ell_1\, \nu_1 \nu_2)$ (to be introduced in section A).

(2) The sets of indices N,L,n,ℓ,n' , consistent with the conditions on Talmi coefficients for which the function $X(\quad)$ is non vanishing, are calculated (Section B).

(3) The function $X(\quad)$ is calculated in terms of mass-ratios for specific values of $N,L,n,\ell,$ and n' (Section C).

(4) The interaction integrals $V^{\ell}_{nn'}$ are calculated for specific values of ℓ , n and n' obtained in step (2). These integrals can be computed in one of two ways (Section D).

a) They may be computed directly from the definition of $V^{\ell}_{nn'}$ for a particular potential. These calculations for a rigid sphere and a Lennard-Jones potential are discussed in Appendix A.

b) In order to save labor in direct computation of the $V^{\ell}_{nn'}$ they can be computed from the available tabulations of the $\Omega^{(\ell,s)}$. A general relationship between $V^{\ell}_{nn'}$ and $\Omega^{(\ell,s)}$ is given. A few specific examples are considered in

appendix B. Also for a ready reference to the tabulated collision integrals available, a table is given indicating the type of potential, temperature range and the values of ℓ and s for which they are available.

(5) The collision matrices for unlike molecules for a given order 'n' are calculated in section E. Also algebraic expressions for these matrices for the order 'n' may be written in terms of masses and the $V^{\ell}_{nn'}$. As an example the explicit expressions for (4 × 4) size of the collision matrices are given in appendix C.

(6) In the sixth step the collision matrices for like molecules are calculated (Section F).

(7) In section G, we combine all the information to compute the transport coefficients using the general expression developed in Chapter III.

A The Function X( )

The collision matrices for unlike molecules are discussed in chapter II. It was shown that these matrices are diagonal in ℓ and m. Using an alternative notation,

these may be written as

$$(\alpha_1\underline{\nu}_1|J|\alpha_1\underline{\nu}_2,\alpha_2\underline{0}) \equiv J^{\ell_1}_{\nu_1\nu_2}(12)\,\delta_{\ell_1\ell_2}\,\delta_{m_1m_2} \quad . \tag{4-1}$$

$$(\alpha_1\underline{\nu}_1|J|\alpha_1\underline{0}\ ,\ \alpha_2\underline{\nu}_2) \equiv \underline{J}^{\ell_1}_{\nu_1\nu_2}(12)\,\delta_{\ell_1\ell_2}\,\delta_{m_1m_2} \quad . \tag{4-2}$$

$$(\alpha_2\underline{\nu}_1|J|\alpha_1\underline{\nu}_1,\alpha_2\underline{0}\ ) \equiv J^{\ell_1}_{\nu_1\nu_2}(21)\,\delta_{\ell_1\ell_2}\,\delta_{m_1m_2} \quad . \tag{4-3}$$

$$(\alpha_2\underline{\nu}_1|J|\alpha_1\underline{0}\ ,\ \alpha_2\underline{\nu}_1) \equiv \underline{J}^{\ell_1}_{\nu_1\nu_2}(21)\,\delta_{\ell_1\ell_2}\,\delta_{m_1m_2} \quad . \tag{4-4}$$

In this notation, the symmetry properties proved in chapter II, yield

$$\tilde{J}^{\ell_1}_{\nu_1\nu_2}(12) = J^{\ell_1}_{\nu_1\nu_2}(12) \quad . \tag{4-5}$$

$$\tilde{\underline{J}}^{\ell_1}_{\nu_1\nu_2}(12) = J^{\ell_1}_{\nu_1\nu_2}(21) \quad . \tag{4-6}$$

$$\tilde{J}^{\ell_1}_{\nu_1\nu_2}(21) = \underline{J}^{\ell_1}_{\nu_1\nu_2}(12) \quad . \tag{4-7}$$

$$\tilde{\underline{J}}^{\ell_1}_{\nu_1\nu_2}(21) = \underline{J}^{\ell_1}_{\nu_1\nu_2}(21) \quad . \tag{4-8}$$

Each of the above matrices is related to the product of

two Talmi coefficients. For example from eqn. (2.53)

$$(\alpha_1 \underline{\nu}_1 | J | \alpha_1 \underline{\nu}_2 \ , \ \alpha_2 \underline{0}) = \sum_{\underline{N},\underline{n},n'} T(\Gamma \underline{N}, \gamma \underline{n} | \alpha_1 \underline{\nu}_1, \alpha_2 \underline{0})$$

$$T(\Gamma \underline{N}, \gamma \underline{n}' | \alpha_1 \underline{\nu}_2, {}_2\underline{0}) \ V^{\ell}_{nn'} \quad (12).(4\text{-}9)$$

with $\underline{\nu}_1 = (\nu_1 \ \ell_1 \ m_1)$; $\underline{\nu}_2 = (\nu_2 \ \ell_2 \ m_2)$; $\underline{N} = (NLM)$;

$\underline{n} = (n \ell m)$; $\underline{n}' = (n' \ \ell \ m)$.

The Talmi coefficient $T(\Gamma \underline{N}, \gamma \underline{n} | \alpha_1 \underline{\nu}_1, \alpha_2 \underline{0})$ vanishes unless

$$2 \ N + L + 2n + \ell = 2 \ \nu_1 + \ell_1 \qquad (4\text{-}10)$$

$$L + \ell \geq \ell_1 \geq \left(|L - \ell| \right) \quad . \qquad (4\text{-}11)$$

The parity condition

$$(-)^{L+\ell} = (-)^{\ell_1} \qquad (4\text{-}12)$$

is absorbed in eqn. (4.10).

Using the orthogonality of the Talmi coefficients (eqn. 2.39)

$$(\alpha_1 \underline{\nu}_1 | J | \alpha_1 \underline{\nu}_2, \alpha_2 \underline{0}) \equiv J^{\ell_1}_{\nu_1 \nu_2} (12)\ \delta_{\ell_1 \ell_2}\ \delta_{m_1 m_2}$$

$$= \delta_{\ell_1 \ell_2}\ \delta_{m_1 m_2} \sum_{NLn\ell n'}$$

$$X\,(NL, n\ell, n' | \ell_1 \nu_1 \nu_2)\ V^{\ell}_{nn'}\,(12) \qquad (4\text{-}13)$$

where

$$J^{\ell_1}_{\nu_1 \nu_2} (12) = \sum_{NLn\ell n'} X\,(NL, n\ell, n' | \ell_1 \nu_1 \nu_2)\ V^{\ell}_{nn'}\,(12), \quad (4\text{-}14)$$

and

$$X(NL, n\ell, n' | \ell_1 \nu_1 \nu_2)$$

$$= (-)^{\nu_1 + \nu_2 + n + n'}\ \frac{N^2_{N_L}\ N_{n\ell}\ N_{n'\ell}}{N_{\nu_1 \ell_1}\ N_{\nu_2 \ell_1}}\ \left(\frac{\alpha_1}{\Gamma}\right)^{2P+p+p'}\ \left(\frac{\alpha_2}{\alpha_1}\right)^{p+p'}\ \sigma^2\,(\ell L \ell_1)$$

$$(4\text{-}15)$$

All symbols in X are defined by eqn. (2.40a) and the interaction integral $V^{\ell}_{nn'}\,(12)$ is given by eqn. (2.52).

Similarly the other collision matrices, eqns. (4.2 to 4.4), may be written in terms of this same function $X(\quad)$ being

$$J^{\ell_1}_{\nu_1\nu_2}(12) = \sum_{NLn\ell n'} (-)^{\ell} \left(\frac{\alpha_2}{\alpha_1}\right)^{P-p} X(NL,n\ell,n'|\ell_1\nu_1\nu_2)\, V^{\ell}_{nn'}(12) \,. \tag{4-16}$$

$$J^{\ell_1}_{\nu_1\nu_2}(21) = \sum_{NLn\ell n'} (-)^{\ell} \left(\frac{\alpha_2}{\alpha_1}\right)^{P-p'} X(NL,n\ell,n'|\ell_1\nu_1\nu_2)\, V^{\ell}_{nn'}(12) \,. \tag{4-17}$$

$$J^{\ell_1}_{\nu_1\nu_2}(21) = \sum_{NLn\ell n'} \left(\frac{\alpha_2}{\alpha_1}\right)^{2P-p-p'} X(NL,n\ell,n'|\ell_1\nu_1\nu_2)\, V^{\ell}_{nn'}(12) \,. \tag{4-18}$$

In these eqns. $X(NL,n\ell,n'|\ell_1\nu_1\nu_2)$ vanishes unless

$$2N + L + 2n + \ell = 2\,\nu_1 + \ell_1 \tag{4-19}$$

$$L + \ell \geq \ell_1 \geq \left(|L - \ell|\right) \tag{4-20}$$

$$n' = (\nu_1 - \nu_2) + n \tag{4-21}$$

The above set of conditions follow from those for the Talmi coefficients (4.10 and 4.11).

B Calculation of the significant sets of indices N, L, n, ℓ, n'

In writing any computer programme for the calculation of the J's, one of the intermediate steps is to find the set of indices N, L, n, ℓ, n' for which X is non-zero. To obtain this, we first calculate the upper and lower limits for N, L, n and ℓ, and then show the steps needed in calculating the set of indices consistent with the above set of equations.

(a) LIMITS FOR N, L, n AND ℓ.

The indices N, L, n and ℓ are all positive integers, the lower limits being obviously zero. We establish the upper limits as follows.

From eqn. (4.20)

$$\min.\ (L+\ell) = \ell_1 \quad . \tag{4-22}$$

Using this eqn., eqn. (4-19) becomes

$$\max.\ (N+n) = \nu_1 \quad , \tag{4-23}$$

i.e.

$$\left.\begin{aligned} \max.\ N &= \nu_1 \\ \max.\ n &= \nu_1 \end{aligned}\right\} \tag{4-24}$$

Thus the range of variation for N and n are

$$\left.\begin{array}{l} 0 \leq N \leq \nu_1 \\ 0 \leq n \leq \nu_1 \end{array}\right\} \quad . \tag{4-25}$$

From eqn. (4-19)

$$L + \ell = \ell_1 + 2\,(\nu_1 - N - n) \quad . \tag{4-26}$$

Because the minimum value of ℓ is zero, the maximum value of L is $(2\,\nu_1 + \ell_1)$. Thus the range of variation of L is

$$0 \leq L \leq (2\,\nu_1 + \ell_1) \quad . \tag{4-27}$$

Similarly the range of variation for ℓ is

$$0 \leq \ell \leq (2\,\nu_1 + \ell_1) \quad . \tag{4-28}$$

(b) SETS OF N, L, n, ℓ AND n' CONSISTENT WITH EQNS. (4.19-4.21).

The summation over these indices in eqns. (4.13, 4.16-4.18) can be performed in any order. We adopt the following procedure.

(1) Fix N, L and n. Vary ℓ between 0 to $(2\nu_1 + \ell_1)$. Find the set of values of ℓ consistent with eqns. (4.19 and 4.20). The sets of consistent values of N, L, n and ℓ are to be noted.

(2) Fix N and n. Vary L between 0 to $(2\nu_1 + \ell_1)$. For each L repeat step (1).

(3) Fix N. Vary n between 0 to ν_1. For each n go through step (2).

(4) Vary N between 0 to ν_1. For each N repaat step (3).

(5) Having obtained all the possible sets of indices N, L, n and ℓ for a given ℓ_1 and ν_1 in steps (1) to (4), we can find the values of n' for a given $\nu_1 + \nu_2$ from (4.21).

Thus we have obtained all the possible sets of indices N, L, n, ℓ and n'. As an example we give the values of N, L, n, ℓ and n' for $\ell_1 = 2$, $\nu_1 = \nu_2 = 2$ in Table 1, for which $X(\ )$ is not zero. $\ell = 0$ is not given as (from eqn. (2.52)) $V^0_{nn'}$ is zero.

TABLE 1.

Sets of indices N, L, n, ℓ and n' for given ℓ_1, ν_1 and ν_2 for which X is not zero. $\ell = 0$ case is not included.

ℓ_1	ν_1	ν_2	N	n	L	ℓ	n'
2	2	2	0	0	2	4	0
			0	0	3	3	0
			0	0	4	2	0
			0	1	1	3	1
			0	1	2	2	1
			0	1	3	1	1
			0	2	0	2	2
			0	2	1	1	2
			1	0	1	3	0
			1	0	2	2	0
			1	0	3	1	0
			1	1	0	2	1
			1	1	1	1	1
			2	0	0	2	0
			2	0	1	1	0

C. Calculation of $X(NL,n\ell,n')$

Having obtained the sets of indices N,L,n,ℓ and n' for which X is not zero, we are in a position to calculate $X(\quad)$ in order to determine the J's . All the factors in X have been defined by eqn. (2.40a) except for the Clebsch-Gordon coefficient $(L0\ \ell 0\ \ell_1 0)$ which is given by the following expression (Racah). (Ro-57).

$$(\ell_1 0\ \ell_2 0|\ell_3 0) = \Delta(\ell_1\ell_2\ell_3) \times$$

$$[(2\ell_3+1)\frac{(\ell_1+\ell_2-\ell_3)!\ (\ell_3+\ell_2-\ell_1)!\ (\ell_3+\ell_1-\ell_2)!}{(\ell_3+\ell_2+\ell_1+1)!}$$

$$\times\ (\ell_1!\ \ell_2!\ \ell_3!)$$

$$\times \sum_{\nu} \frac{(-)^{\nu}}{\nu!}\ [(\ell_1+\ell_2-\ell_3-\nu)!\ (\ell_1-\nu)!\ (\ell_2-\nu)!$$

$$(\ell_3-\ell_2+\nu)!\ (\ell_3-\ell_1+\nu)!\ ] \qquad (4\text{-}29)$$

where the integral index, ν , assumes only those values for which the factorial arguments are not negative, and $\Delta(\ell_1\ \ell_2\ \ell_3)$ means $\overline{\ell}_1 + \overline{\ell}_2 = \overline{\ell}_3$.

Now for specific values of indices N, N, n, ℓ and n' we may write the expressions for the different X's in terms of α_1 and α_2, where these parameters are defined by equation (2.16a).

D. Calculation of the interaction integrals

For computing the collision matrices, the values of the interaction integrals are necessary. They may be computed either directly or from the existing tabulation of the $\Omega^{(\ell,s)}$ for various potentials and different values of ℓ and s.

(a) DIRECT COMPUTATION

The values of the integrals for a rigid sphere and a Lennard-Jones potential are derived in appendix A. The advantage of the direct computation is that we can use it as a subroutine for the main programme for computing collision matrices by providing the proper force constants, temperature and the values of ℓ, n, n'.

(b) (i) RELATION BETWEEN INTERACTION INTEGRAL $V^{\ell}_{nn'}$ AND THE COLLISION INTEGRAL $\Omega^{(\ell,s)*}$

In kinetic theory work, it is usual to express all the relations in terms of the ratios $\Omega^{(\ell,s)*}$ instead of the integrals $\Omega^{(\ell,s)}$, $\Omega^{(\ell,s)*}$ being the ratio of the $\Omega^{(\ell,s)}$

for the given potential to the same $\Omega^{(\ell,s)}$ for the rigid sphere potential. Here we will give a relation between $V^{\ell}_{nn'}$ and $\Omega^{(\ell,s)*}$.

A relation between $V^{\ell}_{nn'}$ and $\Omega^{(\ell,s)}$ has been given elsewhere (Ku-67). Certain notational changes are required for our purposes. Accordingly, a modified derivation is given below.

From eqn. (2.50)

$$\sigma_{\lambda}(g) = 2\pi \int \sigma(g,\chi)\, P_{\lambda}\,(\cos\chi)\, d\,(\cos\chi) \tag{4-30}$$

where

$$\sigma(g,\chi) = \frac{1}{\sin\chi} \left| b\,\frac{db}{d\chi} \right| \tag{4-31}$$

$$\therefore\ \sigma_{\lambda}(g) = 2\pi \int P_{\lambda}\,(\cos\chi)\, d\,(\cos\chi) \tag{4-32}$$

and

$$P_{\lambda}\,(\cos\chi) = \sum_{r=0}^{N} a^{\lambda}_{r}\ \cos^{\lambda-2r}\chi \tag{4-33}$$

with $N = \lambda/_2$ for λ even and $N = \frac{(\lambda-1)}{2}$ for λ odd, and

$$a^{\lambda}_{r} = (-)^{r}\,\frac{(2\lambda-2r)!}{2^{\lambda}\, r!\,(\lambda-r)!\,(\lambda-2r)!} \quad . \tag{4-34}$$

Also, since

$$P_{\lambda}(1) = 1 \quad ,$$

$$\sum_{r=0}^{N} a_r^{\gamma} = 1 \quad . \tag{4-35}$$

$$\therefore \sigma_0(g) - \sigma_\lambda(g) = \sum_{r=0}^{N} a_r \; Q^{(\lambda-2r)}(g) \tag{4-36}$$

where $Q^{\ell}(g)$ eqn. (8.2-2) of H.C.B. (H.C.B.-54), is

$$Q^{\ell}(g) = 2\pi \int (1 - \cos^{\ell} \chi)\, b \, d\, b \; .$$

In terms of $x = (\gamma g/\sqrt{2})$, the expression for $V^{\lambda}_{nn'}$ (12) (eqn. (2.52) is

$$V^{\lambda}_{nn'}(12) = \frac{\sqrt{2}}{\gamma} \int w(x)\, R_{n_\lambda}(\sqrt{2}\, x)\, R_{n'_\lambda}(\sqrt{2}\, x)$$

$$\left(\sigma_0\left(\frac{\sqrt{2}\, x}{\gamma}\right) - \sigma_\lambda\left(\frac{\sqrt{2}\, x}{\gamma}\right)\right) x^3 \, dx \quad . \tag{4-37}$$

Now $[\{w(x)\}^{1/2} R_{n_\lambda}(\sqrt{2}\, x)]$ is the radial part of the simple harmonic oscillator wave function, hence it may be written in the following form using Moshinsky brackets (B.M.-60)

$$V^{\lambda}_{nn'} = \frac{\sqrt{2}}{\gamma} \sum_{p} B\,(n\lambda,\, n'\lambda,\, p)\, I_p \tag{4-38}$$

where

$$I_p = \frac{2}{\Gamma(p+3/2)} \int_0^\infty e^{-x^2} x^{2p+3} (\sigma_0-\sigma_\lambda)\, dX \,, \qquad (4\text{-}39)$$

and $B(n\lambda,n'\lambda,p)$ is the Moshinsky bracket.

In terms of x, $\Omega^{(\ell,s)}$ is

$$\Omega_{12}^{(\ell,s)} = \frac{1}{\sqrt{2}\pi\,\gamma} \int e^{-x^2} x^{2s+3}\, Q^\ell \left(\frac{\sqrt{2}\,x}{\gamma}\right) dx \quad . \qquad (4\text{-}40)$$

Substituting the value of $(\sigma_0-\sigma_\lambda)$ from eqn. (4-36); I_p in terms of $\Omega^{(\ell,s)}$ is

$$I_p = \frac{2\sqrt{2\pi}\,\gamma}{\Gamma(p+3/2)} \sum_{\gamma=0}^{N} a_r^\lambda\, \Omega_{12}^{(\lambda-2r,p)} \qquad (4\text{-}41)$$

Also the range of variation of p in eqn. (4-38) is

$$\lambda \leq p \leq (\lambda + n + n') \quad . \qquad (4\text{-}42)$$

As already mentioned, in kinetic theory work, it is customary to express all the relations in terms of $\Omega^{(\ell,s)*}$ instead of $\Omega^{(\ell,s)}$, $\Omega^{(\ell,s)*}$ as defined earlier is

$$\Omega_{12}^{(\ell,s)*} = \frac{\Omega_{12}^{(\ell,s)}}{[\,\Omega_{12}^{(\ell,s)}]\text{ rigid sphere}} \quad . \qquad (4\text{-}43)$$

Substituting the value of $[\Omega_{12}^{(\ell,s)}]$ rigid sphere , from Hirschfelder et al (eqn. (8.2-8), H.C.B., 54), we have

$$\Omega_{12}^{(\ell,s)} = \frac{1}{\gamma\sqrt{2\pi}} \frac{(s+1)!\,[(2+1) - (-)^{\ell}]}{4(\ell+1)} \pi\,\sigma_{12}^{2}\,\Omega_{12}^{(\ell,s)*} . \tag{4-44}$$

Finally the relation between $\Omega^{(\ell,s)*}$ and $V_{nn'}^{\lambda}(12)$ is

$$V_{nn'}^{\lambda}(12) = \sum_{p,r} \frac{\pi\sigma_{12}^{2}}{\gamma\sqrt{2}} \frac{(p+1)!}{\Gamma(p+3/2)} \frac{[(2\lambda-4r+1) - (-)^{\lambda-2r}]}{(\lambda-2r+1)}$$

$$a_r^{\lambda}\, B(n\lambda, n'\lambda, p)\, \Omega^{(\lambda-2r,p)*} \tag{4-45}$$

For numerical work, it is convenient to re-write this result in the following form

$$V_{nn'}^{\lambda}(12) = \sqrt{2\pi}\,\frac{\sigma_{12}^{2}}{\gamma} \sum_{p,r} A(\lambda,r,p)\, B(n\lambda, n'\lambda; p)\, \Omega^{(\lambda-2r,p)*} \tag{4-46}$$

where

$$A(\lambda,r,p) = \frac{\sqrt{\pi}}{2} \frac{(p+1)!}{\Gamma(p+3/2)} \frac{[2\lambda-4r+1) -- (-)^{\lambda-2r}]}{(\lambda-2r+1)}\, a_r^{\lambda} \tag{4-47}$$

Thus the value of the $V^{\lambda}_{nn'}$ (12) from the given tabulations of $\Omega^{(\ell,s)*}$ can be computed only if we know A( ) while the values of B( ) are tabulated by Brody and Moshinsky (B.M.60). A few specific cases of the relationship between the V^{λ} and the $\Omega^{(\ell,s)*}$ are given in appendix B.

(ii) POTENTIAL AND THE COMPUTED COLLISION INTEGRALS

The advantage of the above relation between $V^{\ell}_{nn'}$ and $\Omega^{(\ell,s)*}$ is that we can compute $V^{\ell}_{nn'}$ using the existing values of the collision integrals. We have collected the relevant information on $\Omega^{(\ell,s)*}$ for different potentials in Table 2 .

Table 2

(The values of temperature and ℓ and s for which the collision integrals are available are given below)

Potential	Temp.range($T^* = \frac{kT}{\epsilon}$)	Values of ℓ and s	References[+]
Exponential attractive	α(related to T^*) varies from 18 to 56	ℓ=1, s=1 ; ℓ=2, s=2	1
Exponential-repulsive	α varies from 3.50 to 28.50	ℓ=1, s=1 to 5 ; ℓ=2, s=2,3,4 ; ℓ=3, s=3	2
Inverse power		ℓ=1 to 3	3
Kihara	0.60 to 21.50	γ varies from 0.0 to 1.0 ℓ=1, s=1,2; ℓ=2,s=2,3	4
12-6 Lennard-Jones	0.05 to 400	ℓ=1, s=1 to 7; ℓ=2,s=2 to 6; ℓ=3, s=3,4,5; ℓ=4, s=4	4-12
9-6 Lennard-Jones	0.010 to 100.00	ℓ=1, s=1; ℓ=2, s=2	13
28-7 Lennard-Jones	0.010 to 100.00	ℓ=1, s=1; ℓ=2, s=2	13
Modified expo-6	0.10 to 20.0	α varies from 12 to 15 ℓ=1, s=1 to 7; ℓ=2, s=2 to 6; ℓ=3, s=3,4,5; ℓ=4, s=4	8, 14
Morse Potential	0.1 to 200	c varies from 1 to 10 ℓ=1, s=1; ℓ=2, s=2	6,15,16
Repulsive Screened Coulomb	0.010 to 100.00 .	ℓ=1, s=1; ℓ=2, s=2	17

Square-well	Q(related to T^*) varies from 0.1 to 4.0	d varies from 0.0 to 0.6 ℓ=1, s=1.2.3.5.7.9 ℓ=2, s=2,7	6,18,19,20
Stockmayer (12-6-3)	0.10 to 100.00	δ varies from (-2.5 to +2.5) ℓ=1, s=1; ℓ=2, s=2	10
Stockmayer (12-6-5)	0.10 to 100.00	q varies from 0.0 to 2.0 ℓ=1, s=1; ℓ=2, s=2	11
Sutherland	.250 to 50.0	ℓ=1, s=1,2,3 ℓ=2, s=2,3 ℓ=4, s=4	6,21

+ References for this table are given on p.218

E. Algebraic expressions and computation of the collision matrices.

Now we discuss the method of calculating the collision matrices upto a given order 'n' . By "calculation upto the order 'n'" we mean that the matrices $J^{\ell_1}_{\nu_1\nu_2}$ which are in fact infinite dimensional are truncated to $(n \times n)$ size with ν_1 and ν_2 ranging from zero to $(n - 1)$ for viscosity and diffusion and to $(n + 1) \times (n + 1)$ size with ν_1 and ν_2 ranging from zero to (n) for thermal-conductivity and thermal-diffusion ratio.

The method of writing X( ) in terms of α_1 and α_2 has been discussed in section C of this chapter. Now the algebraic expressions of different J-matrices may be written as a power series in α_1 , α_2 and $V^{\ell}_{nn'}$ (12) upto the order 'n' by using eqns. (4.14, 4.16 - 4.18). The advantages of writing these expressions in this form have already been discussed at the beginning of this chapter.

In order to minimise labour of writing the matrix elements of the matrices, we make use of the symmetry properties given by eqns. (4.5 to 4.8) and the following symmetry property.

From the definition of the collision matrix (eqn. (2.43)) and the transformation property of the Talmi coefficients (eqn. (2.29) and eqn. (4.21)), it follows that

$$J^{\ell_1}_{\nu_2\nu_1}(21) = \left(\frac{M_1}{M_2}\right)^{\nu_1-\nu_2} J^{\ell_1}_{\nu_1\nu_2}(21) \quad , \qquad (4\text{-}48)$$

where

$$M_1 = \frac{\alpha_1^2}{\alpha_1^2 + \alpha_2^2} = \frac{m_1}{m_1 + m_2} \quad , \qquad (4\text{-}49)$$

and

$$M_2 = \frac{\alpha_2^2}{\alpha_1^2 + \alpha_2^2} = \frac{m_2}{m_1 + m_2} \quad , \qquad (4\text{-}50)$$

As an example of the use of these symmetry properties, expressions for ν_1 and ν_2, ranging from zero to three for different collision matrices, for both the vector and tensor parts, are given in appendix C. As stated before, these expressions may be compared with those obtained by using Chapman-Cowling procedure (C.C-52). (To date only the third order expressions for the coefficients of viscosity, thermal conductivity and thermal diffusion and the fourth order

expressions for diffusion are known using this approach (C.C.-52, Jo-65, De-66, Ma-57, J.S-63).)

However for doing numerical work on the computer, we do not need these algebraic expressions. Having obtained the function X( ) for a particular gas-mixture in one subroutine and the $V^{\ell}_{nn'}$ for a particular potential, temperature and gas-mixture in another, we can compute the elements of the different J-matrices using eqns. (4.14, 4.16 - 4.18) upto the given order 'n' , inside the machine itself. This is to be contrasted with work of Devoto (De-66) who used the corresponding algebraic expressions of the various elements of the determinants for building the computer programme for each order following the Chapman-Cowling approach (CC-52).

F. Collision matrices for like molecules

Having discussed the method of calculation of the collision matrices for unlike molecules, for a given order 'n' , the method of calculation of the collision matrices for like molecules is relatively simple.

For like molecules, there are two matrices depending upon the two components of the mixture denoted by indices (1) and (2).

They are (eqn. (2.64))

$$(\alpha_{1-1}\nu_1|J|\alpha_{1-2}\nu_2,\alpha_{1-}0) = J^{\ell_1}_{\nu_1\nu_2}(11)\,\delta_{\ell_1\ell_2}\,\delta_{m_1m_2} \quad , \qquad (4\text{-}51)$$

$$(\alpha_{2-1}\nu_1|J|\alpha_{2-2}\nu_2,\alpha_{2-}0) = J^{\ell_1}_{\nu_1\nu_2}(22)\,\delta_{\ell_1\ell_2}\,\delta_{m_1m_2} \quad . \qquad (4\text{-}52)$$

Both these matrices were shown to be symmetrical in the ν-indices in Chapter II (eqn. (2.65)) i.e.

$$\tilde{J}^{\ell_1}_{\nu_1\nu_2}(ii) = J^{\ell_1}_{\nu_1\nu_2}(ii) \quad . \qquad (4\text{-}53)$$

These matrices may be expressed in terms of X( ) and $V^{\ell}_{nn'}$ with the only point of difference being that $\alpha_1 = \alpha_2 = \alpha$ in the definition of X( ) (eqn. (4.15)); as shown in Chapter II the odd-ℓ terms do not contribute to the sum of X and $V^{\ell}_{nn'}$ (12) is replaced by $V^{\ell}_{nn'}$ (11) or $V^{\ell}_{nn'}$ (22) . As an example the algebraic expressions for the vector and tensor parts can be obtained from eqns. (C.1 to C.10) and (C.31 to C.40) respectively by putting $M_1 = 0.5$, $M_2 = 0.5$ and noting that the odd-ℓ terms do not contribute to the sum.

Again for numerical computation we do not need the algebraic expressions. All that we need are two subroutines for X( ) and $V^{\ell}_{nn'}$ (ii) for a particular temperature, potential and gas.

G. Computation of the transport coefficients

Now that we have ~~Having~~ discussed the method of computations of the collision matrices for unlike and like molecules for a given set of parameters, (temperature, force constants and the gas mixture) we can compute all the six J-matrices ($J^{\ell_1}_{\nu_1\nu_2}$ (12) , $\underline{J}^{\ell_1}_{\nu_1\nu_2}$ (12) , $J^{\ell_1}_{\nu_1\nu_2}$ (21) , $\underline{J}^{\ell_1}_{\nu_1\nu_2}$ (21) , $J^{\ell_1}_{\nu_1\nu_2}$ (ii)) for a given ℓ_1 , ν_1 and ν_2 . Using this information, the coefficients are computed in the following way.

(1) Different k^{ℓ_1} -matrices are calculated using the set of eqns. (3.9 - 3.12) and (4.1 to 4.4, 4.51-52) for a given concentration ratio.

(2) Different coefficients are calculated from these matrices by the usual methods of matrix manipulations. Different coefficients correspond to different ℓ_1 - values.

(i) Coefficient of viscosity ($\ell_1 = 2$, tensor part) is calculated from the $\underline{k}^2$ -matrices using eqn (3.82).

(ii) Coefficients of thermal-conductivity, diffusion and thermal-diffusion ratio ($\ell_1 = 1$, vector part) are calculated by first forming the $(k^1_{11})'$, $(k^1_{12})'$, (k^1_{21}) and (k^1_{22}) matrices and, then, using eqns. (3.101), (3.103) and (3.124) respectively.

We have emphasised earlier that in the present method of computation, the programme has not to be changed from one order to the next. This is feasible in the following way :

Suppose we are interested in calculating all the values of a particular coefficient for a particular set of parameters from the first order to the n th order. All that is necessary is that we have to dimension each of the k-matrices to $(n \times n)$ size and initialise each element of these matrices to zero. Then start with the first order and calculate the coefficient with (1,1) element of k-matrices having the given value while all the other elements are zero. All the matrix manipulations are done in such a way that effectively we are dealing with $(|x|)$ matrix only for the second-order, (2×2) k-matrices are set up and the particular coefficient is calculated as if we are effectively dealing with various (2×2) k-matrices. A similar procedure is adopted for each higher-order till we

reach the highest order 'n' .

H. Kihara Type Approximation

In the present work, an approximation occurred which is in some ways similar to the kihara approximation (Ma-57). It is limited to the case in which the coefficients are dependent upon the vector part of the distribution for one. We deal with the elements of $(k^{1'}_{11})$ - and $(k^{1'}_{12})$ - matrices and put all the elements of the first column except the first one of these matrices equal to zero i.e.

$$(k^{1'}_{11})_{\nu_0} \text{ and } (k^{1'}_{12})_{\nu_0} = 0 \text{ for } \nu \neq 0 \quad . \quad (4\text{-}54)$$

It was found that the error introduced for the first four-orders in the calculation of λ'_{mix} for a rigid sphere potential for various types of mixture is 1 in 10^4 and for other coefficients, it is 1 in 10^6 . This is due to the fact that the dominant terms in the first columns of these two matrices are α_1 and α_2 .

This approximation makes $(k^{1'}_{11})$ - and $(k^{1'}_{12})$ - matrices symmetric and simplifies the exact algebraic expressions for all

orders without introducing any error. This is the type of work which has been attempted very often in literature (Br-58, Br-65, S.J.-63a) i.e. to simplify the exact first - and second - order expressions without introducing much error so as to ease computation.

There is some similarity between this and the Kihara approximation. We know that for Maxwellian molecules $V^{\ell}_{nn'}$ is $V^{\ell}_{nn}\,\delta_{nn'}$. Also we know that from eqns. (3.17, 3.18, 2.53, 2.56)

$$(k^{1'}_{11})_{\nu_0} \quad \text{and} \quad (k^{1'}_{12})_{\nu_0} \;\; \alpha \; V^{1}_{\nu_0} \qquad . \qquad (4\text{-}55)$$

So that when we neglect these columns for $\nu \neq 0$, we are neglecting off-diagonal V^1's . This is equivalent to neglecting off-diagonal collision integrals $\Omega^{(\ell,s)}$ (i.e. $s \neq 1$). However this analogy is not complete in as much as we do not neglect the contribution of $V^1_{\nu_0}$ $(\nu \neq 0)$ from other matrix elements, whereas in kihara approximation the corresponding Ω's are completely neglected (Ma-57).

This is an interesting study to make but has not been pursued further in this work.

CHAPTER V

CONVERGENCE AND TRANSPORT COEFFICIENTS

A Introduction

In the last chapter, we discussed the method of computing the transport coefficients for a given potential, gas-mixture and temperature. In this Chapter, using this facility, the rate of decrement of the first few orders, for all the four coefficients, is studied for a rigid sphere and a Lennard-Jones potential for different sets of parameters. A more extensive study of the rates of decrement for various gas-mixtures for a Lennard-Jones potential is done in the next chapter.

Before discussing the main problem, we would explain certain terms such as "approximations", "errors" and "convergence". These terms are not always used in the same way by different workers.

(a) APPROXIMATIONS

In the evaluation of the transport coefficients for dilute gases, three different types of approximations are involved. In order to avoid possible confusion we describe below what they are :

(i) Approximations in the Chapman-Enskog method

These approximations arise when we compare different

powers of ε on the two sides of the Boltzmann equations (p. Chapter III). Throughout our work we are dealing with the second approximation of this method. Although the third approximation in the sequence is sometimes discussed (C.C-52), it is usually neglected in the calculation of the transport coefficients for dilute gases.

(ii) Calculation of different Approximations of the Coefficients-Truncation of the Determinants

Within the above second approximation, Chapman and Cowling (C.C-52) express the transport coefficients of a pure gas and of a binary gas-mixture in terms of infinite dimensional determinants. For a practical calculation, they truncate these determinants to various sizes depending upon the particular order of approximation. The truncation of the determinants to $(n \times n)$ size for viscosity and diffusion and to $((n + 1) \times (n + 1))$ size for thermal-conductivity and thermal diffusion ratio has been termed an n th (order) approximation of these coefficients (the first (order) approximation for thermal-conductivity and thermal-diffusion ratio arises from (2×2) size determinants and is finite). This nomenclature of n th approximation has also been used by other workers also (Jo-65, S.J-63, S.M-66, Ma-57).

The above nomenclature is different from the one used by Hirschfelder et al and others (H.C.B-64, De-66, M.M-58) where for the nth aprroximation, the determinants are truncated to $(n \times n)$ size for all coefficients without exception. In this nomenclature the contribution of the first approximation to thermal-conductivity and thermal-diffusion ratio of a binary gas mixture is zero.

(iii) Approximations within the above approximation (ii)

These approximations are intended to simplify the expressions obtained by truncating the determinants in the above approximation (e.g. Ch. IV).

In order to distinguish more clearly the various levels of approximations, we shall refer to the n th approximation of type (ii) simply as n th order, where the particular order denotes the size of the determinant needed. Thus, from now onwards, we will deal with calculations upto the n th order. Also we will have various approximations (iii) within an order instead of within an approximation.

In our calculation, the truncation of determinants is equivalent to the truncation of matrices. Of the two nomenclatures described above, we adopt the one used by Chapman and Cowling.

(b) ERRORS

The theoretical errors can be grouped into four categories.

(i) Truncation errors

As discussed above, for an n th order calculation, we truncate the matrices to $(n \times n)$ size. In order to get the contribution for the n th order alone, we subtract the contribution of $((n-1) \times (n-1))$ matrix from this. Thus we can find out the corresponding contributions for all values of 'n'. Adding all these contributions, an infinite series is obtained. For the L.G.M. case $(m_1 >> m_2 , n_1 >> n_2)$, Chapman and Cowling (C.C-52) have shown that the series sum converges to a finite value. In practice the series is truncated after a certain number of terms 'n'. The difference between the truncated value and the finite value corresponding to the series sum may be called truncation error. These errors can be minimised by taking more and more terms into account. Due to the complexity of work involved, such errors have not been considered for any other gas-system, so far.

(ii) Approximation Errors

These errors arise in the study of approximations of type (iii). The difference between the values of the exact and

approximated expressions is known as the approximation error.

Errors belonging to this group have been discussed by different workers (Br-57, Br-63, J.S-64, Ma-57a, H.C.B-64). For purposes of comparing with experiments, these errors are over and above the truncation errors (if any known) for that order of calculation.

Errors associated with the Kihara type approximation (Section 4- H) belong to this group.

(iii) Computational Errors

Since the expressions of different orders for different transport coefficients (De-66, Jo-65, J.S-63, Ma-57, H.C.B-64) are written in terms of exact fractions and the collision integrals, the errors in computing the transport coefficients arises mainly from those in the computation of the collision integrals. This is so because the exact fractional part of the expressions can be computed to an accuracy of 1 in 10^7 and thus contributes negligible errors.

In the present work, we are dealing with the interaction integrals instead of the collision integrals. The interaction integrals for a rigid sphere can be evaluated exactly. The computational errors introduced for these integrals are 1 in 10^7 . For the Lennard-Jones potential, we have followed the

method of Smith and Munn (S.M-64) for evaluating the interaction integrals. The errors in the values of these integrals are 1 to 2 in 10^3. Previous calculations of the collision integrals, as summarised in table 2 have similar sort of accuracy.

These errors are in addition to the other errors discussed before. They can be improved upon by employing more accurate methods of numerical analysis.

(iv) Consistency errors

It is fairly common to check the consistency of different experimental data for different coefficients (We-64, M.W-62, S.G-65, S.A-62, We-63). Approximate relations between first order expressions of two different coefficients are established. Using these relations, we estimate the value of one of the coefficients from the measured value of the other coefficient. The difference between the estimated values and the actual measured values for the same coefficient may be called consistency errors.

By using the approximate relation between the two coefficients, measured value of one of the coefficients and the consistency error associated with that relation, the value of the other coefficient for different gas systems, for which no direct measurements are available, can be estimated. Such estimations

have been done fairly extensively for diffusion coefficients from the measured data of viscosity and thermal-conductivity of binary gas-mixtures (We-64, We-63, M.W-62, S.G-65, S.A-62). Recently, Kestin et al (K.N-66) have measured the diffusion coefficient for Ne-Co_2 mixture. This value agrees very well with the predicted value of Mason and Weissmann (M.W-62).

It may be remarked that these errors are not errors in the same sense as the first three ones are. It may be better to call them as numerical discrepencies for the estimated values.

(c) CONVERGENCE

The general expressions of the transport coefficients, obtained by Chapman and Cowling (C.C-52) are always assumed to be rapidly convergent because it is assumed that the major contribution to the coefficients is from the first order while the contributions from the higher-orders are small and rapidly decreasing.

For a simple gas, with rigid sphere molecules Chapman and Cowling (C.C-52) have shown that the magnitude of the second order is smaller than the first and that of the third order is smaller than the second. By comparing the contributions of the first

and third orders for a Lennard-Jones and expo-6 potentials, it has been reported (Ma-57) that the convergence of the series is rapid. In order to have an idea of the relative magnitudes of the first three orders for a Lennard-Jones potential, we have computed these using the collision integrals tabulated by Hirschfelder et al (H.C.B-64). Our results show that the convergence for the first three terms is faster for the Lennard-Jones potential than for the rigid sphere potential.

For a binary gas-mixture, algebraic expressions for the second and third orders (De-66, Jo-65, Ma-57, S.J-63, H.C.B-64) have been written but they are very complex to work with. Generally they are approximated to get some information for the rate of decrement in some extreme cases. It is convenient to separate these approximations for the coefficients of the vector part (diffusion, thermal diffusion ratio and thermal-conductivity) and the tensor part (viscosity). This separation is discussed below.

(i) <u>Vector part</u>

The special cases studied are

1) L.G.M. ($m_1 \gg m_2$, $n_1 \gg n_2$)

2) Quasi L.G.M. ($m_1 \gg m_2$, $n_1 \ll n_2$).

A complete series sum has been obtained for the L.G.M. (C.C-52), while the expressions are enormously simplified for the Quasi-L.G.M. case (Ma-57a). The rate of decrement of various order terms is not as rapid as the simple gas case for the corresponding potentials.

(ii) Tensor part

The special cases studied are

1) $M_1 = 10 \cdot i\, M_2$, $x_1 = x_2$; ~~$M_1 = 1000\, M_2$, $X_1 = X_2$~~, $\sigma_{11} = \sigma_{22}$ and $\sigma_{11} >> \sigma_{22}$ for a rigid sphere potential (Jo-65, S.J-64).

2) Ar-He case for second-order for expo-6 potentials. (S.J-63, S.J-63a).

3) Recently Storvick and Mason (S.M-66) have considered several extreme cases of concentration ratios for various gas mixtures for the second order calculation.

Regarding convergence, the conclusions of Mason and others (Ma-57, S.M-66) for binary gas-mixtures are based upon the above extreme cases only. Recently, Devoto (De-66) has shown that these limits (L.G.M. and Quasi-L.G.M.) are not reached until the mass and concentration ratios are of the order of 10^{-6} to 10^{-7}. These ratios are clearly far from any realised in nature and therefore the conclusions may not necessarily be appropriate.

Though we agree with the general physical nature of the conclusions for a simple gas and a binary gas-mixture that the series of the different coefficients is convergent but as discussed above, this conclusion does not have enough theoretical basis. In order to provide a more reasonable theoretical basis, we should study orders higher than the ones for which the calculations are available both for a simple gas and a binary gas mixture. Moreover, there is a need for studying more mass and concentration ratios which occur in practice for binary gas-mixtures.

With the general formulae developed in Chapter III and the method of computation discussed in Chapter IV, it is possible to automatically compute the transport coefficients for any order and potential.

We shall use this facility to study the convergence of the first five orders for a simple gas and of the first four orders for a binary gas-mixture for a rigid-sphere and Lennard-Jones potentials. Previous results are limited to third order only (Jo-65, C.C-52, H.C.B-64, Ma-57).

This will demonstrate the power of the present procedure and will provide a better picture of the relative magnitudes

of the first few orders and thereby of the convergence problem.

In this chapter, $T^{(n)}$ denotes the contribution of the first n orders to a particular transport coefficient e.g. $\eta^{(n)}$ denotes the contribution for first n orders to the coefficient of viscosity of the simple gas, while $\eta^{(n)}_{mix}$ denotes the contribution for the viscosity for a binary mixture and so on.

B. Rigid Sphere Potential

(a) SIMPLE GAS

As a preliminary check of the computer programme, we computed the first three orders for viscosity (η) and thermal-conductivity (λ). The ratios of the second and third orders to the first agreed completely with those calculated by Chapman and Cowling (C.C-52).

In table 5, we give the values of $(\eta^{(n)}/\eta^{(1)})$ and $(\lambda^{(n)}/\lambda^{(1)})$ for $n = 2,3,4,5$. It is clear that the difference between consecutive ratios becomes smaller. For example the difference between the ratios of the fourth and fifth orders to the first order, both for η and λ, is in the fifth and sixth decimal places. This shows a rapid convergence for the first five orders for a simple gas both for η and λ. Note that

Table 5.

Ratios of the first five orders to the first order for viscosity (η) and thermal-conductivity (λ) for a rigid sphere potential for a simple gas.

$\eta^{(2)}/\eta^{(1)}$	1·014852	$\lambda^{(2)}/\lambda^{(1)}$	1·022727
$\eta^{(3)}/\eta^{(1)}$	1·015879	$\lambda^{(3)}/\lambda^{(1)}$	1·024818
$\eta^{(4)}/\eta^{(1)}$	1·016006	$\lambda^{(4)}/\lambda^{(1)}$	1·025134
$\eta^{(5)}/\eta^{(1)}$	1·016028	$\lambda^{(5)}/\lambda^{(1)}$	1.025197

the convergence is independent of the nature of the gas and temperature. This independence holds for a ratio of any order 'n' to the first order and can be obtained from the general formulae of the simple gas in the following way.

The viscosity of a pure gas is given by

$$\eta = kT\,[J^2_{(11)}]^{-1}_{00} \quad : \tag{5-1}$$

This expression is obtained from eqn. (3.91) by putting $n_2 = 0$, $n_1 = 1$, $M_2 = M_1$ and $\sigma_{22} = \sigma_{11}$. From eqn. (4.14), we have

$$J^2_{\nu_1\nu_2}(11) = \sum_{NLn\ell n'} X(NLn\ell n'|2\ \nu_1\ \nu_2)V^{\ell}_{nn'}(11) \quad , \tag{5-2}$$

where X from eqn. (4.15) is a pure number independent of the mass of gas for $M_2 = M_1$. Now $V^{\ell}_{nn'}(11)$ from eqn. (4.46) is

$$V^{\ell}_{nn'}(11) = \sqrt{2\pi}\ \frac{\sigma^2_{11}}{\frac{2kT}{M_1}} \sum_{p,r} A(\ell,r,p)\ B(n\ell,n'\ell;p)$$

$$\Omega^{(\ell-2r,p)^*}_{11} \quad . \tag{5-3}$$

In the above equation, $V^{\ell}_{nn'}(11)$ is dependent only upon σ_{11},

T and M_1 while the other quantities are either constants or pure numbers. Combining this equation with eqn. (5.2), we get the expression of $J^2_{\nu_1\nu_2}(11)$ as

$$J^2_{\nu_1\nu_2}(11) = \sigma^2_{11} \sqrt{\frac{M_1}{T}}\; X'_{\nu_1\nu_2} , \qquad (5\text{-}4)$$

where $X'_{\nu_1\nu_2}$ contains all constants and other numerical factors dependent only upon the super- and sub-scripts of J .

Since the truncation and inversion of J^2-matrix affects only $X'_{\nu_1\nu_2}$, it is clear that $(\eta^{(n)}/\eta^{(1)})$ will be independent of σ_{11} , T and M_1 . The same argument applies to the J^1-matrix and therefore to the ratios of $(\lambda^{(n)}/\lambda^{(1)})$.

The above argument also leads to the well-known Eucken's expression that for the hard-sphere potential, the ratio of (η/λ) is independent of σ_{11} and T and is proportional to M or c_v , the specific heat at constant volume.

We find that the rate of decrement is faster for η than for λ .

(b) BINARY GAS-MIXTURES

The transport coefficients for a binary gas mixture depend

upon :

(1) masses and relative concentrations of the individual components of the mixture (M_1, M_2, n_1, n_2) ,

(2) force constants of interaction between like and unlike molecules $(\sigma_{11}, \sigma_{22}, \sigma_{12})$ and

(3) temperature (T).

In the literature (Jo-65, Ma-57, Ma-54, S.J-63, De-66), the algebraic expressions for orders upto the third have been written for all the coefficients but no systematic study for the convergence of all the three orders with different parameters is done. The main reason is that either till 1966, the higher-order expressions were not available, as in the case of thermal-conductivity, or the expressions were too complex to do any detailed study.

In this section, we have attempted a systematic study so as to exhaust most of the likely combinations and ranges of variation of these parameters $(T , M_1 , M_2 , \sigma_{11} , \sigma_{22} , n_1 , n_2)$. The various combinations are grouped as under.

In this section, subscript 1 refers to the heavier component and 2 to the lighter.

(1) Temperature dependence

Temperature dependence can be extracted from the general expressions of the coefficients given in Chapter III (eqns. 3.82, 3-101 to -103, 3.124). In particular, for viscosity, from eqns. (3.82, 3.17 - 3.20, 4.14, 4.46), it can be shown that for all orders

$$\eta_{mix} \propto \sqrt{T} \quad . \tag{5-5}$$

By taking the corresponding expressions for other coefficients a similar dependence on temperature is obtained.

(2) Convergence of first-four orders

With M_1 , M_2 , σ_{11} and σ_{22} fixed (σ_{11} , σ_{22} are the collision diameters of the two colliding molecules) on varying x_2 ($= \frac{n_2}{n_1+n_2}$, where n_1 and n_2 are the relative concentrations of the two components of the mixture) all the four coefficients for the first four orders are computed. In the case of diffusion, it is necessary to compute the first five orders in order to get the first

four orders of k_T . This computation has been done for Ar-Ne mixture for which the data is given below. This data has been taken from Hirschfelder et al (H.C.B.-64, Table 8.3-1).

M_1 (Molecular weight of Ar^{40}) = 39.44 gms.

M_2 (" " " " " Ne^{20}) = 20.18 gms.

$$\sigma_{11} = 3.64 \times 10^{-8} \text{ cms.}$$

$$\sigma_{22} = 2.58 \times 10^{-8} \text{ cms.}$$

$$\sigma_{12} = (\sigma_{11} + \sigma_{22})/2.$$

For viscosity (η_{mix}) and thermal-conductivity (λ'_{mix}) , we have placed the absolute values in tables 6 and 9 and the ratios (i.e. ($\eta^{(n)}_{mix}/\eta^{(1)}_{mix}$) and $\lambda'^{(n)}_{mix}/\lambda'^{(1)}_{mix}$) in tables 7 and 10. Figs (1) and (5) depict the variation of these ratios with x_2 . These ratios approach the pure gas limit for $x_2 = 0$ or 1 . This limit, as shown earlier (table 5) is independent of the nature of the gas.

For the diffusion (D_{12}) and the thermal-diffusion ratio (k_T) the absolute values and the ratios (i.e. ($D^{(n)}_{12}/D^{(1)}_{12}$) and ($k^{(n)}_T/k^{(1)}_T$)) are given in tables 17, 18, 24 and 12, 25. Also the absolute values and the ratios for these coefficients are plotted in figs. 15, 21 and 22.

(3) Variation with $(\sigma_{11}/\sigma_{22})$ ratios.

With M_1, M_2, x_1 and x_2 fixed, the first four orders of the coefficients for different $(\sigma_{11}/\sigma_{22})$ ratios (σ_{22} fixed) are calculated. The ratios of the second, third and fourth orders to the first for different $(\sigma_{11}/\sigma_{22})$ ratios are given in tables 8, 11, 19 and 26 and in figs. 2, 6, 16 and 22.

(4) Variation with mass ratios (M_1/M_2).

With σ_{11}, σ_{22} and M_2 fixed, the coefficients for the first three orders for different M_1 and x_2 $(0.1 \leq x_2 \leq 0.9)$ are calculated. The ratios of the second and third orders to the first order vs. x_2 for various M_1 are plotted in figs. 3, 7, 17 and 23.

(5) Approach to the L.G.M. and Quasi-L.G.M. Limits.

With σ_{11}, σ_{22} and M_2, the coefficients for the first three orders for different M, and (x_1/x_2) values are calculated. The ratios of the second order to the first order, are plotted in figs. 3, 10 + 11 for η_{mix} and λ'_{mix}. These ratios show an approach to the simple gas limit for (x_1/x_2) tending to zero and for (x_1/x_2) tending to infinity. For D_{12}

and k_T , ~~and η_{mix}~~ , these ratios approach limits different from the simple gas limit. The values of these ratios are given in tables ~~13, 15,~~ 20 + 28 and in figs. 18 + 24 . These limits have been termed as the L.G.M. and the Quasi-L.G.M. limits (C.C-52, Ma-57a).

(6) <u>Approach to the $(M_1 \gg M_2 , \sigma_{11} \gg \sigma_{22})$ and $(M_1 \gg M_2 , \sigma_{22} \gg \sigma_{11})$ limits.</u>

With x_1 , x_2 , M_2 and σ_{22} fixed, when $((\sigma_{11}/\sigma_{22}) \gg 1)$, the values of λ'_{mix} , η_{mix} , D_{12} and k_T are calculated for the first three orders for different M_1 and σ_{11} - values. The absolute values for the first two orders for these coefficients are given in tables 14, 23, 30 . The ratios of the second order to the first order are plotted in figs. 13, 19 + 25 for different mass ratios. For $((\sigma_{22}/\sigma_{11}) \gg 1)$, we perform the same calculation keeping σ_{11} fixed. The results of this calculation are given in tables 16, and in figs. 14 and 25.

The results of the above steps have been grouped together for each coefficient, unless otherwise specified, it was convenient to consider the ratio of the second order to the first order only.

The behaviour of the higher-order ratios is similar. Finally a comparison of the results for different coefficients is given in sec. (V-A.b- vi).

i) Viscosity (Tables 6-8, figs. 1-4)

An algebraic expression for the first order is given by Chapman and Cowling (C.C-52). Algebraic expressions for the second and third orders are given by Joshi and Saxena (Jo-65, S.J-63). Only numerical calculations available, done for the rigid sphere potential using the second and third order expressions are for the following specific cases (Jo-65, J.S-65).

1) $M_1 = 10\ M_2 = 10.0$ gms, $\sigma_{11} = \sigma_{22}$, $x_1 = x_2 = 0.5$.

2) $M_1 = 10\ M_2 = 10.0$ gms, $\sigma_{11} >> {}_{22}$, $x_1 = x_2 = 0.5$.

We also use this set of values to calculate the first four orders for different σ_{11} values (σ_{22} fixed).

Our results are placed in tables 6 to 8 and in figs. (1) to (4).

<u>Convergence of the first four orders.</u>

In table 6, the absolute values for η_{mix} for the first four orders for the Ar-Ne mixture are given for different values

Table 6.

Values of the first four order of viscosity (η_{mix}) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64 Å, σ_{11}=2.58 Å)

x_2	$\eta^{(1)}_{mix} \times 10^{-4}$	$\eta^{(2)}_{mix} \times 10^{-4}$	$\eta^{(3)}_{mix} \times 10^{-4}$	$\eta^{(4)}_{mix} \times 10^{-4}$
0.9	2.8348	2.8778	2.8810	2.8814
0.8	2.7107	2.7524	2.7556	2.7561
0.7	2.6011	2.6415	2.6446	2.6451
0.6	2.5038	2.5427	2.5457	2.5462
0.5	2.4166	2.4541	2.4570	2.4574
0.4	2.3382	2.3743	2.3771	2.3775
0.3	2.2674	2.3020	2.3047	2.3050
0.2	2.2030	2.2364	2.2389	2.2392
0.1	2.1442	2.1764	2.1787	2.1790

of x_2. It is clear that the viscosity of this mixture increases with decreasing values of x_2 for all the orders.

In table 7, the ratios of the second, third and fourth orders to the first order for η_{mix} are given for the Ar-Ne system and for different values of x_2. In fig. (1), these ratios for different x_2 are plotted to show the rate of decrement. Also we notice that the maximum contribution to a particular ratio or to an order is when $x_2 \simeq 0.5$.

In table 8, the values of $(\eta^{(n)}_{mix} / \eta^{(1)}_{mix})$ for $n = 2,3,4$ are given for different $(\sigma_{11}/\sigma_{22})$ ratios (σ_{22} fixed), for $x_1 = x_2 = 0.5$ and for $M_1 = 10\ M_2 = 10.0$ gms. We note that the limiting value for the ratios is reached when $(\sigma_{11}/\sigma_{22}) \simeq 10^3$. The difference of the values of $(\eta^{(2)}_{mix} / \eta^{(1)}_{mix})$ at $(\sigma_{11}/\sigma_{22}) = 10^2$ and at $(\sigma_{11}/\sigma_{22}) = 10^3$ is only in the fourth decimal place. The graph of $(\eta^{(n)}_{mix} / \eta^{(1)}_{mix})$ vs. $(\sigma_{11}/\sigma_{22})$ ratios in fig. (4) shows that, for all practical purposes, the limit for $(\eta^{(n)}_{mix} / \eta^{(1)}_{mix})$ is reached when $(\sigma_{11}/\sigma_{22}) \simeq 10$ to 10^2.

The values of the ratios of the second and third orders to the first order for $(\sigma_{11} = \sigma_{22})$ and for $(\sigma_{11} \gg \sigma_{22})$ are slightly different from the one given by Joshi and Saxena

Table 7.

Ratios of the first four orders to the first order for viscosity (η_{mix}) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, $\sigma_{11}=3.64\cdot A$, $\sigma_{22}=2.58\cdot A$)

x_2	$\eta^{(2)}_{mix}/\eta^{(1)}_{mix}$	$\eta^{(3)}_{mix}/\eta^{(1)}_{mix}$	$\eta^{(4)}_{mix}/\eta^{(1)}_{mix}$
0.1	1.01501	1.01609	1.01623
0.2	1.01516	1.01629	1.01645
0.3	1.01530	1.01647	1.01664
0.4	1.01541	1.01662	1.01679
0.5	1.01550	1.01672	1.01690
0.6	1.01554	1.01676	1.01694
0.7	1.01552	1.01673	1.01690
0.8	1.01542	1.01659	1.01675
0.9	1.01520	1.01632	1.01646

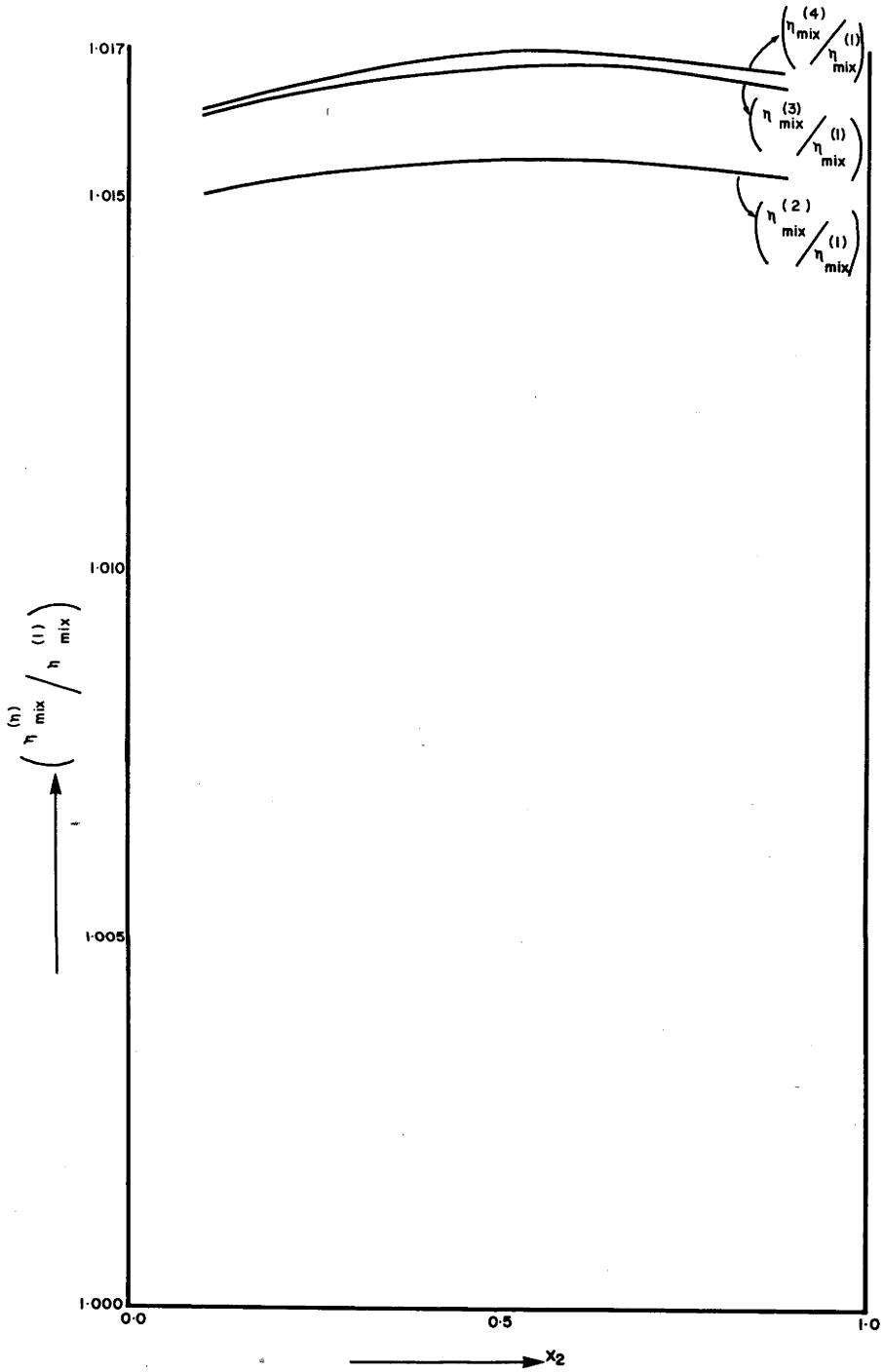

Fig. 1 .. For Ar-Ne , the ratios of the second, third and fourth order to the first order of viscosity have been compared for various concentrations of the lighter component. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A , σ_{22}=2.58·A).

Table 8.

Ratios of the first four orders to the first order for viscosity (η_{mix}) for a binary mixture for different (σ_{11}/σ_{22}) ratios. (Rigid sphere; M_1=10 M_2=10.0 gms, σ_{22}=1·A, ~~$x_1=x_2=0.5$~~ $x_1=x_2=0.5$).

σ_{11}/σ_{22}	$\eta_{mix}^{(2)}/\eta_{mix}^{(1)}$	$\eta_{mix}^{(3)}/\eta_{mix}^{(1)}$	$\eta_{mix}^{(4)}/\eta_{mix}^{(1)}$
1.0	1.0088	1.0094	1.0095
2.0	1.0155	1.0172	1.0176
10.0	1.0277	1.0323	1.0336
60.0	1.0305	1.0357	1.0373
1.0×10^2	1.0307	1.0359	1.0376
5.0×10^2	1.0309	1.0362	1.0378
1.0×10^4	1.0309	1.0362	1.0378
1.0×10^5	1.0309	1.0362	1.0378

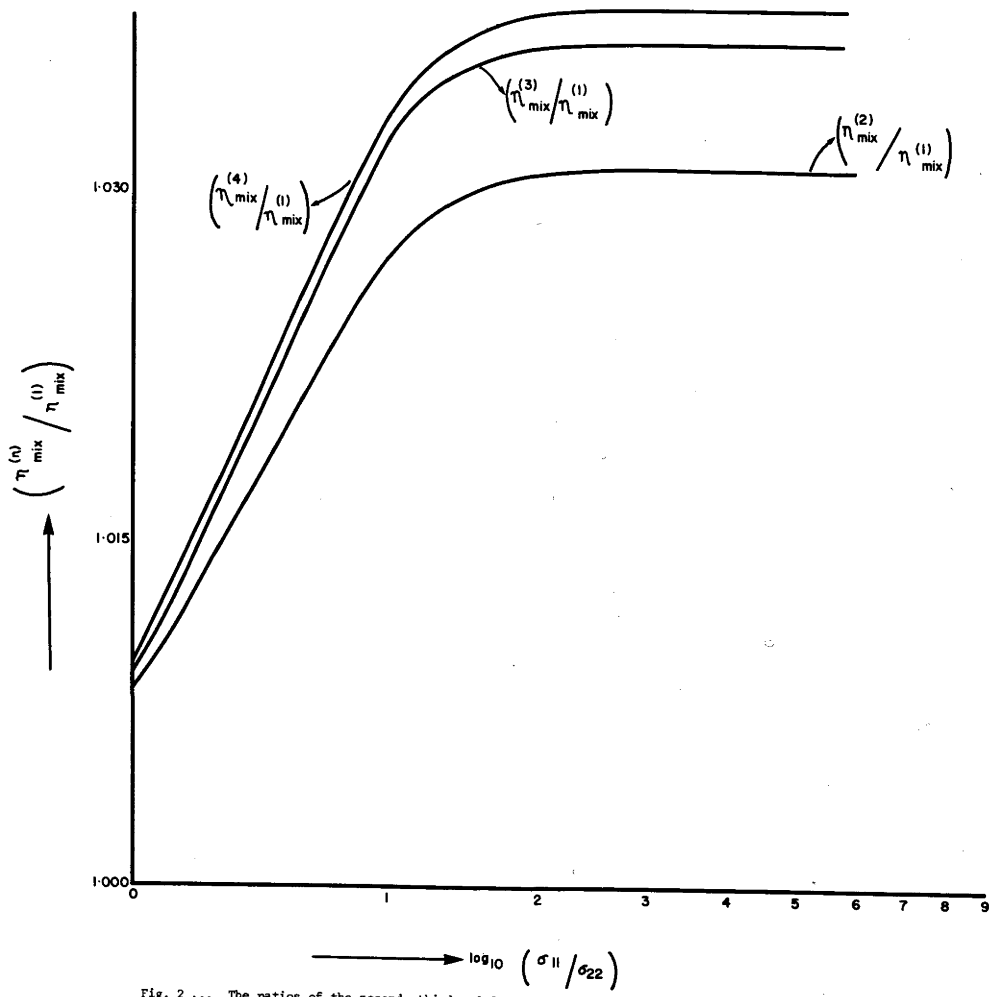

Fig. 2 ... The ratios of the second, third and fourth orders to the first order of viscosity have been compared for various $(\sigma_{11}/\sigma_{22})$ ratios. (Rigid sphere; $M_1=10$ $M_2=10$ gms, $\sigma_{22}=1\cdot A$, $X_1=X_2=0.5$).

(Jo-65, J.S-65).

Variation with mass-ratios.

In fig. (3), the values of ($\eta^{(2)}_{mix} / \eta^{(1)}_{mix}$) are plotted for various mass-ratios and for different values of x_2 . Some interesting features can be noted from this graph.

(1) The approach to the simple gas limit is steeper near $x_2 \simeq 1$ than near $x_2 \simeq 0$. This steepness increases with increasing mass-ratios.

(2) The curve corresponding to $M_1 = 39.44$ gms, $M_2 = 20.18$ gms, $\sigma_{11} = 3.64\text{Å}$, $\sigma_{22} = 2.58\text{Å}$ is the highest. The other curves corresponding to mass-ratios different from this lie in a descending order. After the mass-ratio $\frac{M_1}{M_2} \simeq 20$, there occurs an ascending sequence for higher M_2 mass-ratios in the region of small values of x_2 while for large values of x_2 the usual descending sequence continues. This shift from a descending to an ascending sequence shows that there is an increase in the second order contributions after a certain mass-ratio.

(3) There is a certain curvature in the curve for $M_1 = M_2$ which comes from the fact that $\sigma_{11} \neq \sigma_{22}$ One would expect a straight line in the case of a simple gas.

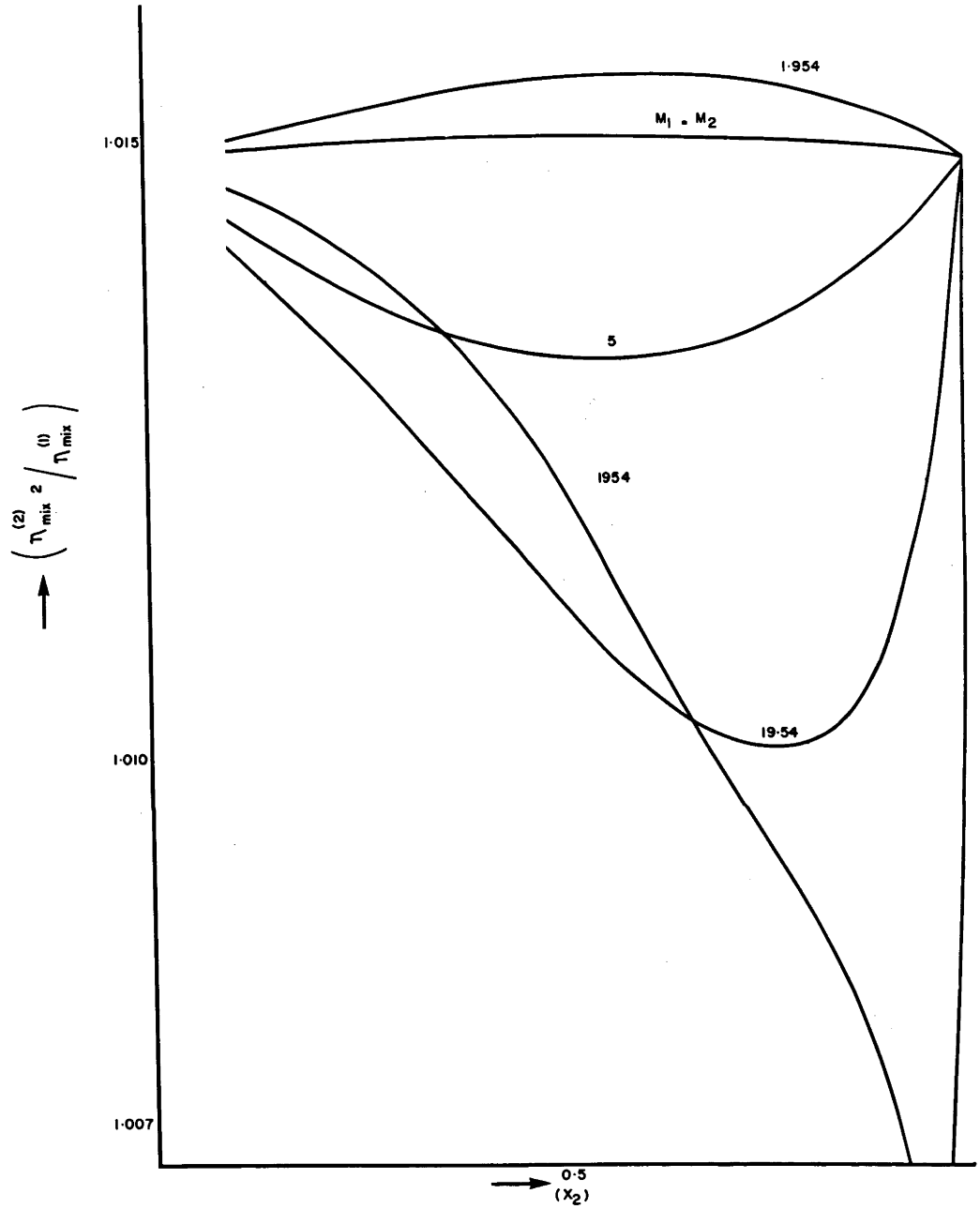

Fig. 3 .. The ratio of the second order to the first order of viscosity has been plotted versus various concentration of the lighter component for different mass-ratios. Number on each curve denotes M_1/M_2 ratio involved. (Rigid sphere; M_2=20.18 gms; σ_{11}=3.64'A , σ_{22}=2.58'A).

(4) From gas theory, it is well-known that, for viscosity, the heavier molecules are dominant momentum carriers. In order to study the effect of these carriers when they are in minority to the second order contribution for η_{mix}, ($\eta^{(2)}_{mix}$ / $\eta^{(1)}_{mix}$) vs. (M_1/M_2) is plotted for various values of x_2 in fig. 4. We observe that for $M_1/M_2 < 31.2$, the contribution of the heavier molecules to the ($\eta^{(2)}_{mix}$ / $\eta^{(1)}_{mix}$) is never dominant for every small values of x_1. But for mass-ratios greater than 31.2, the contribution of the heavier molecules is dominant when $x_1 \geqslant x_2/200$ For very high mass-ratios (i.e. $M_1/M_2 \gg 200$), the heavier molecules are dominant for values of x_1/x_2 less than $1/200$. This behaviour is not obvious in figs. (1) and (3). The statement of Storvick and Mason (S.M-66) that for viscosity, the dominant momentum carriers are heavy molecules and should contribute a maximum to the second order when they are in a minority, may be true only if qualified by restrictions on mass and concentration ratios.

(ii) <u>Thermal-Conductivity (Tables 9-16, Figs. 5-14).</u>

An algebraic expression for the first order for λ_{mix} is given by Chapman and Cowling (C.C-52) but no higher order expressions were written till as late as 1966 (De-66). The only

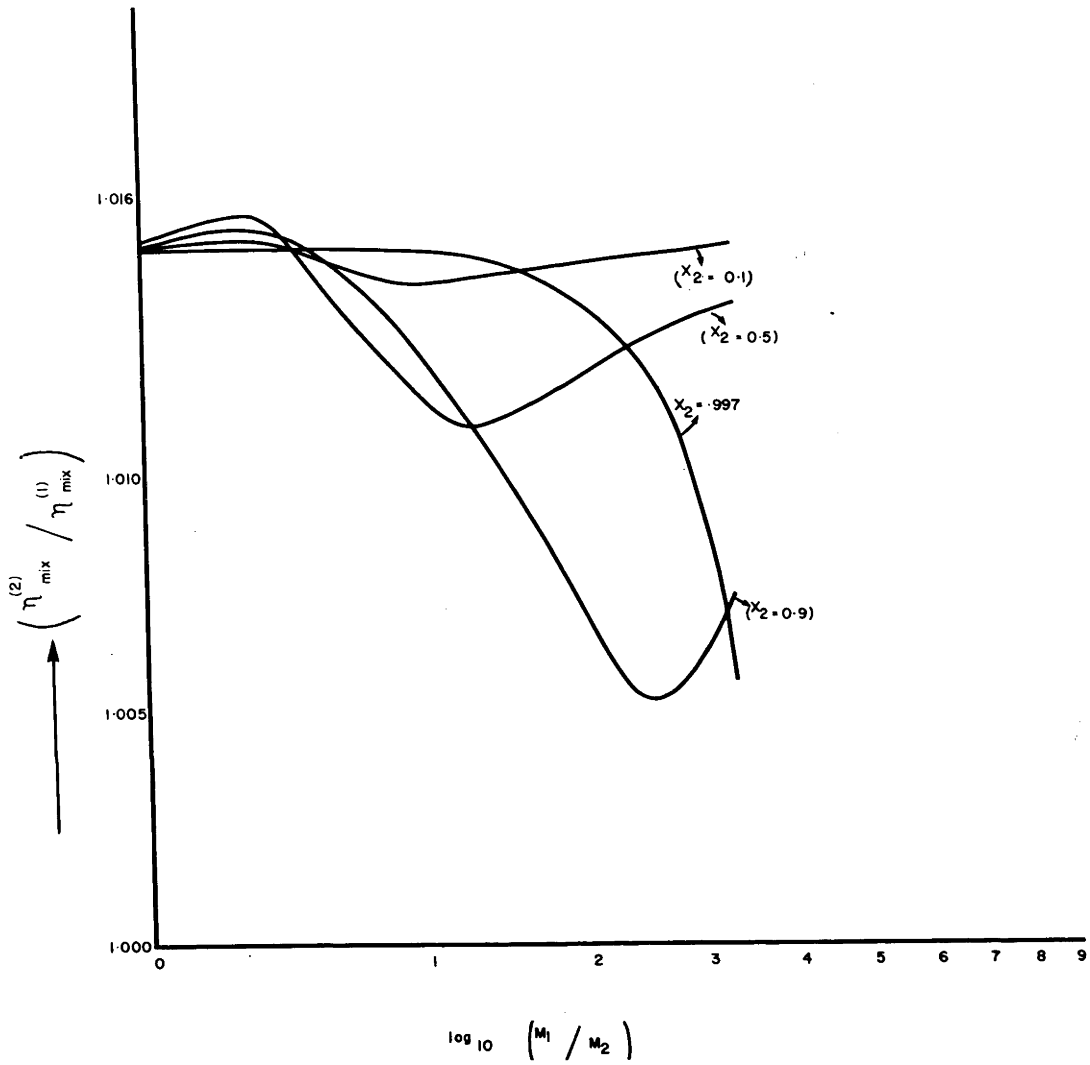

Fig. 4 .. The ratio of the second order to the first order of viscosity has been plotted versus mass ratios for different concentrations of the lighter component. (Rigid sphere; M_2=20.18 gms, σ_{11}=3.64.A, σ_{22}=2.58·A).

numerical calculation for orders higher than the first, for the rigid sphere molecules is for the L.G.M. case (C.C-52).

In this subsection only the λ'_{mix} part of the general expression of thermal-conductivity (eqn. (3.123)) is considered. The diffusive part of λ_{mix}, which is generally assumed to be small, is considered in the next sub-section. The results of the calculation for λ'_{mix} are given in tables 9 to 11 and in figs. 5 to 14.

Convergence of the first four Orders of λ'_{mix}.

The absolute values of λ'_{mix} for the first four orders are given in table 9 for different values of x_2. We note that the values continuously increase for decreasing values of x_2 for all orders.

In table 10, the ratios of the second, third and fourth orders to the first order for λ'_{mix} are given. It is clear from the table that for fixed values of x_2, the consecutive ratios decrease. Also these ratios are plotted in fig. (5). Again, as in viscosity there is a maximum in the contribution of λ'_{mix} for higher orders at $x_2 \simeq 0.5$.

Table 9.

Values of the first four orders of thermal conductivity (λ'_{mix}) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A, σ_{22}=2.58·A)

x_2	$\lambda'^{(1)}_{mix}$ X 10^3	$\lambda'^{(2)}_{mix}$ X 10^3	$\lambda'^{(3)}_{mix}$ X 10^3	$\lambda'^{(4)}_{mix}$ X 10^3
0.9	4.0751	4.1756	4.1856	4.1873
0.8	3.6335	3.7284	3.7885	3.7402
0.7	3.2565	3.3448	3.3546	3.3563
0.6	2.9313	3.0124	3.0215	3.0232
0.5	2.6481	2.7217	2.7301	2.7317
0.4	2.4000	2.4656	2.4731	2.4746
0.3	2.1798	2.2384	2.2450	2.2462
0.2	1.9844	2.0357	2.0413	2.0423
0.1	1.8096	1.8540	1.8585	1.8593

Table 10.

Ratios of the first four orders to the first order for thermal-conductivity (λ'_{mix}) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A , σ_{22}=2.58·A)

(x_2)	$\lambda'^{(2)}_{mix}/\lambda'^{(1)}_{mix}$	$\lambda'^{(3)}_{mix}/\lambda'^{(1)}_{mix}$	$\lambda'^{(4)}_{mix}/\lambda'^{(1)}_{mix}$
.9	1.02468	1.02714	1.02754
.8	1.02614	1.02889	1.02937
.7	1.02712	1.03010	1.03063
.6	1.02766	1.03078	1.03136
.5	1.02780	1.03097	1.03157
.4	1.02753	1.03067	1.03127
.3	1.02688	1.02991	1.03048
.2	1.02587	1.02867	1.02919
.1	1.02448	1.02698	1.02741

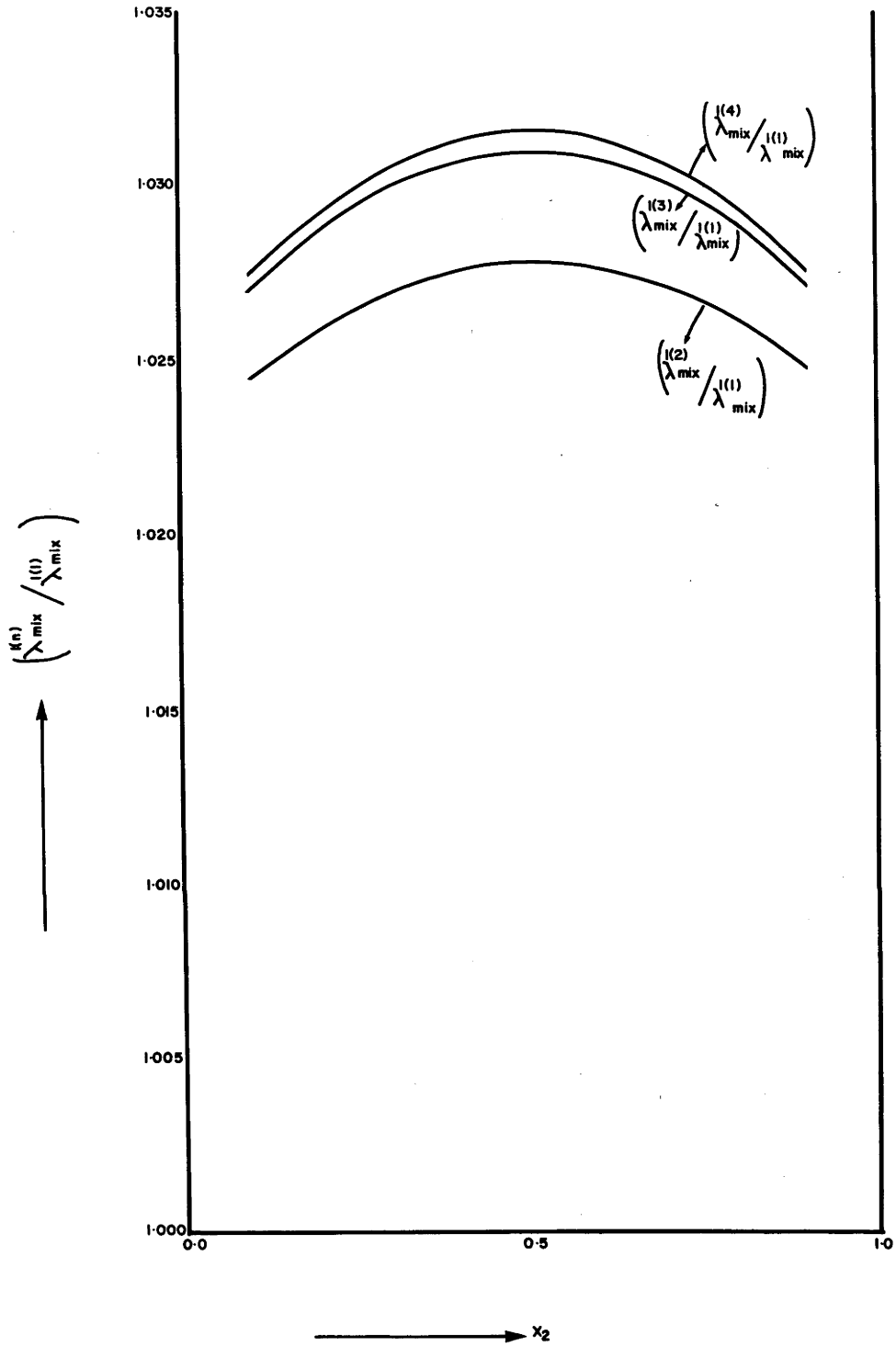

Fig. 5 .. For Ar-Ne , the ratio of the second, third and fourth orders to the first order of thermal-conductivity ($'_{mix}$) have been compared for various concentrations of the lighter component. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A , σ_{22}=2.58·A).

In table 11 and in fig. (6), the results of the variation of ($\lambda'^{(n)}_{mix} / \lambda'^{(1)}_{mix}$) for (n = 2,3,4) and for different (σ_{11}/σ_{22}) ratios are given. For this variation, the data used is M_1 = 10.0 gms, M_2 = 1.0 gms, $X_1 = X_2 = 0.5$ and σ_{22} = 1°A . It may be noted from the table that the limit is reached at $\sigma_{11}/\sigma_{22} \simeq 10^4$ for all orders but for all practical purposes, the limiting value is reached between $\sigma_{11}/\sigma_{22} \simeq 10$ to 100 (see fig. 6).

<u>Variation with mass-ratios.</u>

In fig. 7, a graph of the ($\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix}$) and ($\lambda'^{(3)}_{mix} / \lambda'^{(1)}_{mix}$) ratios for different values of x_2 and for different mass-ratios is given. Here M_2 = 20.18 gms, σ_{11} = 3.64°A, σ_{22} = 2.58°A are kept fixed. It is seen that the higher mass-ratios lie in an ascending order. Moreover, the spacing between the curves for the second and third orders goes on increasing for increasing mass-ratios.

Now, as in the case of viscosity, there is a definite value of the mass-ratio after which the contribution to the ($\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix}$) ratio approaches a maximum value. But, unlike viscosity, it happens when the lighter component is in a

Table 11.

Ratios of the first four orders to the first order for thermal conductivity (λ'_{mix}) for a binary mixture for different (σ_{11}/σ_{22}) ratios. (Rigid sphere; M_1=10 M_2=10.0 gms, σ_{22}=1·A, ~~$X_1=X_2=0.5$~~).
$x_1=x_2=0.5$).

σ_{11}/σ_{22}	$\lambda'^{(2)}_{mix}/\lambda'^{(1)}_{mix}$	$\lambda'^{(3)}_{mix}/\lambda'^{(1)}_{mix}$	$\lambda'^{(4)}_{mix}/\lambda'^{(1)}_{mix}$
1	1.04432	1.05255	1.05488
10	1.08917	1.11390	1.12351
10^2	1.09314	1.11956	1.13002
10^3	1.09335	1.11985	1.13033
10^4	1.09337	1.11987	1.13035
10^5	1.09337	1.11987	1.13035
10^6	1.09337	1.11987	1.13035

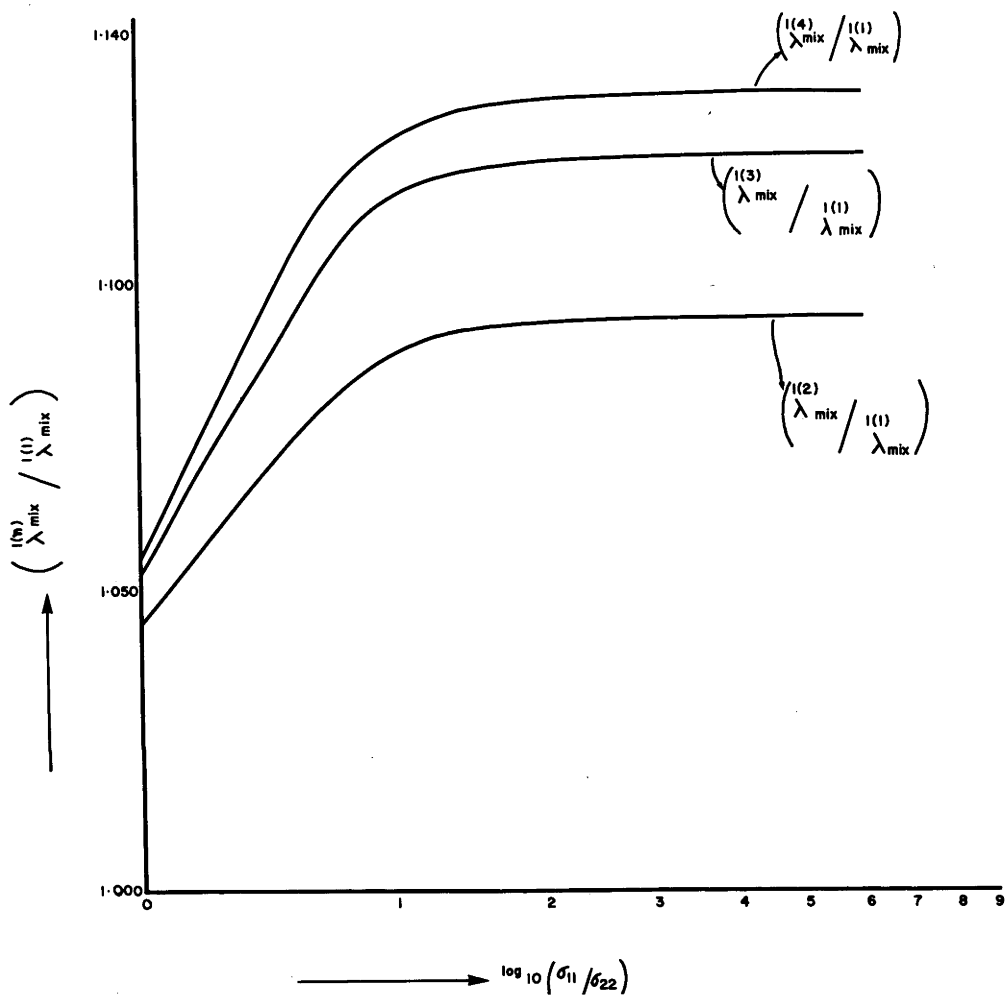

Fig. 6 .. The ratios of the second, third and fourth orders to the first order of thermal-conductivity (λ'_{mix}) have been compared for various (σ_{11}/σ_{22}) ratios. (Rigid sphere; M_1=10 M_2=10.0 gms, σ_{22}=1.0·A , X_1=X_2=0.5).

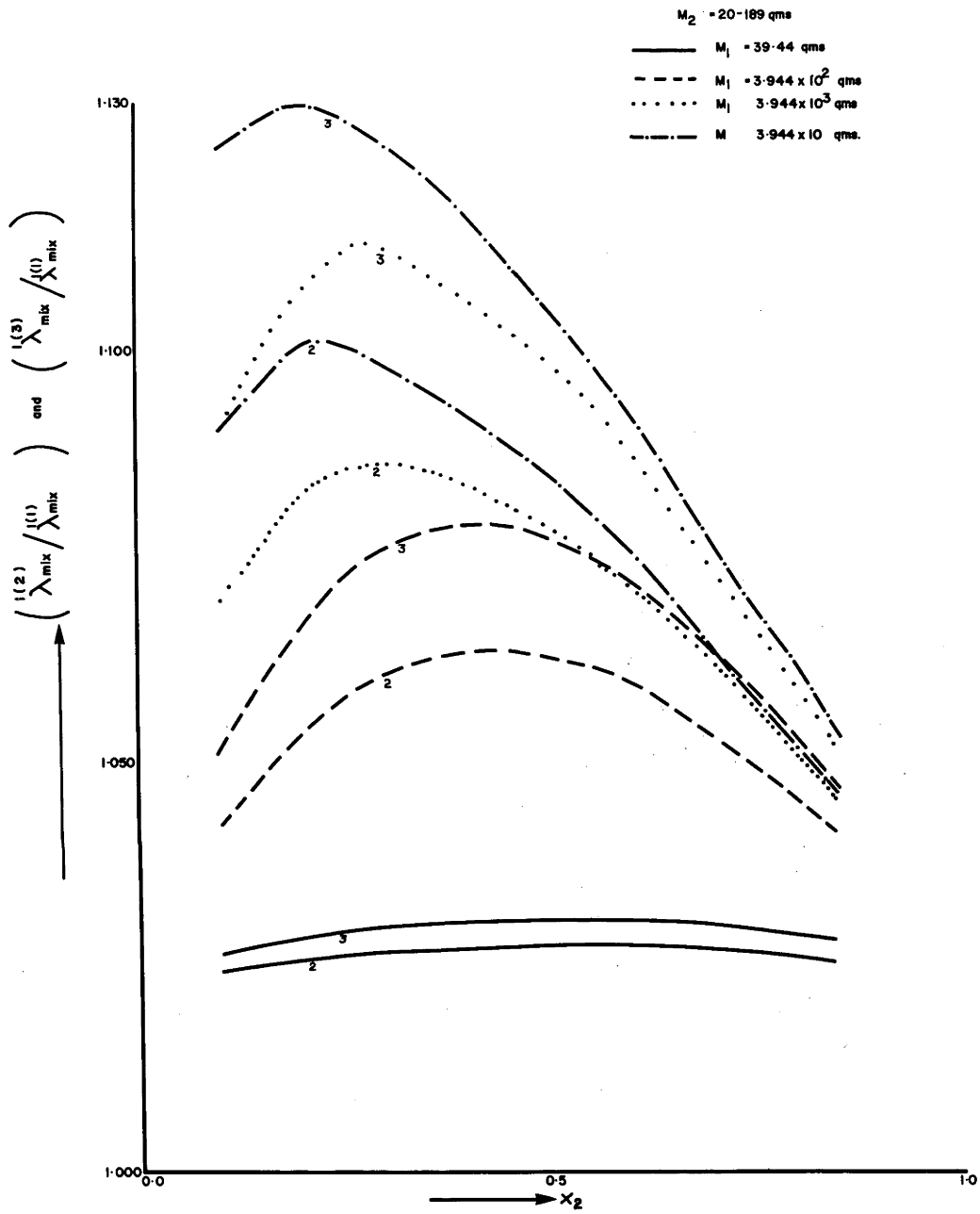

Fig. 7 .. The ratios of the second and third orders to the first order of thermal-conductivity (λ'_{mix}) have been plotted versus concentration of the lighter component for different mass ratios. Numbers (2) and (3) on different curves show the corresponding orders involved. (Rigid sphere; M_2=20.18 gms, σ_{11}=3.64·A, σ_{22}=2.58·A).

minority. These values of the $\left(\frac{(x_1/x_2)}{\sigma_{11}/\sigma_{22}}\right)$ and (M_1/M_2) ratios, for approaching this maximum, are interconnected. In fig. 8, we have drawn various curves for the different (n_1/n_2) and (M_1/M_2) ratios. It is clear that this contribution is dominant only when the $M_1/M_2 \geqslant 10^3$ and the $n_1/n_2 \simeq 10$, but when $n_1/n_2 \not\geqslant 10^5$, the contribution of the second order again, drops down the maximum level for all possible values of mass-ratios. This, just, shows that we need a certain minimum number of minority carriers for an effective second order contribution. This brings us to a point where we have shown the validity of Storvick and Mason (S.M-66) statement that for thermal-conductivity, the dominant energy carriers are light molecules and should contribute a maximum to the $(\lambda^{(2)}_{mix}/\lambda^{(1)}_{mix})$ ratio when they are in a minority provided it is qualified by restriction on the mass and concentration ratios.

It may be interesting to see the difference in behaviour of the $(\lambda'^{(2)}_{mix}/\lambda'^{(1)}_{mix})$ ratio and the absolute values of the second and third orders. In fig. 9, the absolute values of $\lambda'^{(2)}_{mix}$ and $\lambda'^{(3)}_{mix}$ are plotted for various mass ratios for $M_2 = 1.0$ gms, $\sigma_{11} = \sigma_{22} = 1$ A. Comparing figs. 8 and 9, we observe that the absolute values behave in an entirely different way because in fig. 9, the contribution to $\lambda'^{(2)}_{mix}$ increases when n_2 goes on

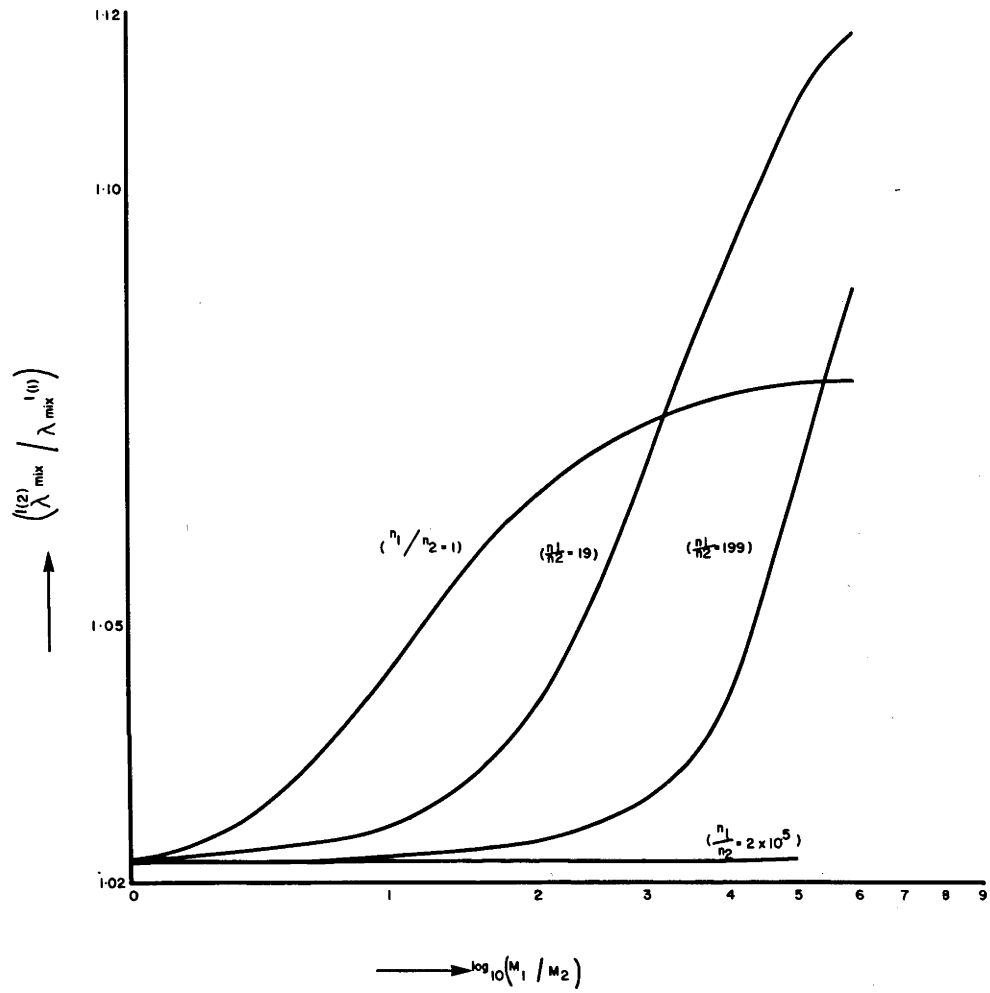

Fig. 8 .. The ratio of the second order to the first order of thermal-conductivity (λ'_{mix}) has been plotted versus mass ratios for different concentration ratios. (Rigid sphere; M_2=1.0 gm, $\sigma_{11}=\sigma_{22}$=1.0 Å).

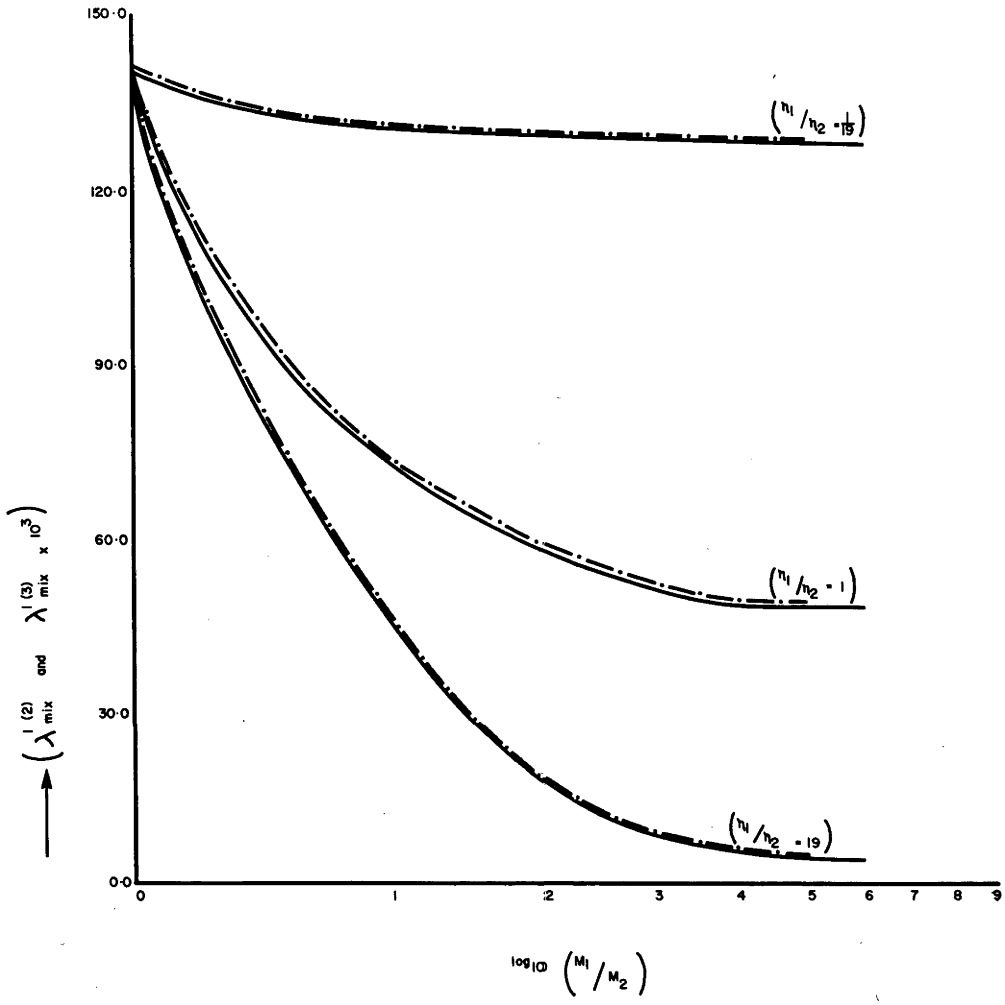

Fig. 9 .. The second- and third-order contributions to the thermal-conductivity (λ'_{mix}) have been plotted versus mass-ratios for different concentration ratios. (Rigid sphere; M_2=1.0 gm, $\sigma_{11}=\sigma_{22}$=1.0·A).

becoming greater than n_1, and vice-versa. The reason for this behaviour is not hard to see. In the former case, we are mainly concerned with the lighter component while in the latter (absolute values) case, the values are governed by heavy molecules and is roughly proportional to $1/_M$.

<u>The approach to the $(M_1 \gg M_2 , n_1 \gg n_2)$ and $(M_1 \gg M_2 , n_2 \gg n_1)$ limits.</u>

Now we shall study how the ratio $(\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix})$ for a simple mixture for which $n_1 \simeq n_2$ and $M_1 = M_2$, behaves when we approach the $(M_1 \gg M_2 , n_1 \gg n_2)$ L.G.M. limit and the $(M_1 \gg M_2 , n_1 \ll n_2)$ Quasi-L.G.M. limit. For this, in figs. 10 and 11, we plot the ratios for different mass and concentration ratios for $\sigma_{11} = \sigma_{22} = 1 \cdot A$ and for $M_2 = 1.0$ gm. It may be noted from these figures that for each mass ratio, the simple gas limit is attained though the approach differs with the mass-ratio. This conclusion also follows from the general formulae of chapter III.

<u>The approach to the $(M_1 \gg M_2 , \sigma_{11} \gg \sigma_{22})$ and $(M_1 \gg M_2 , \sigma_{22} \gg \sigma_{11})$ limits.</u>

Another interesting limit for the $(\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix})$ ratio

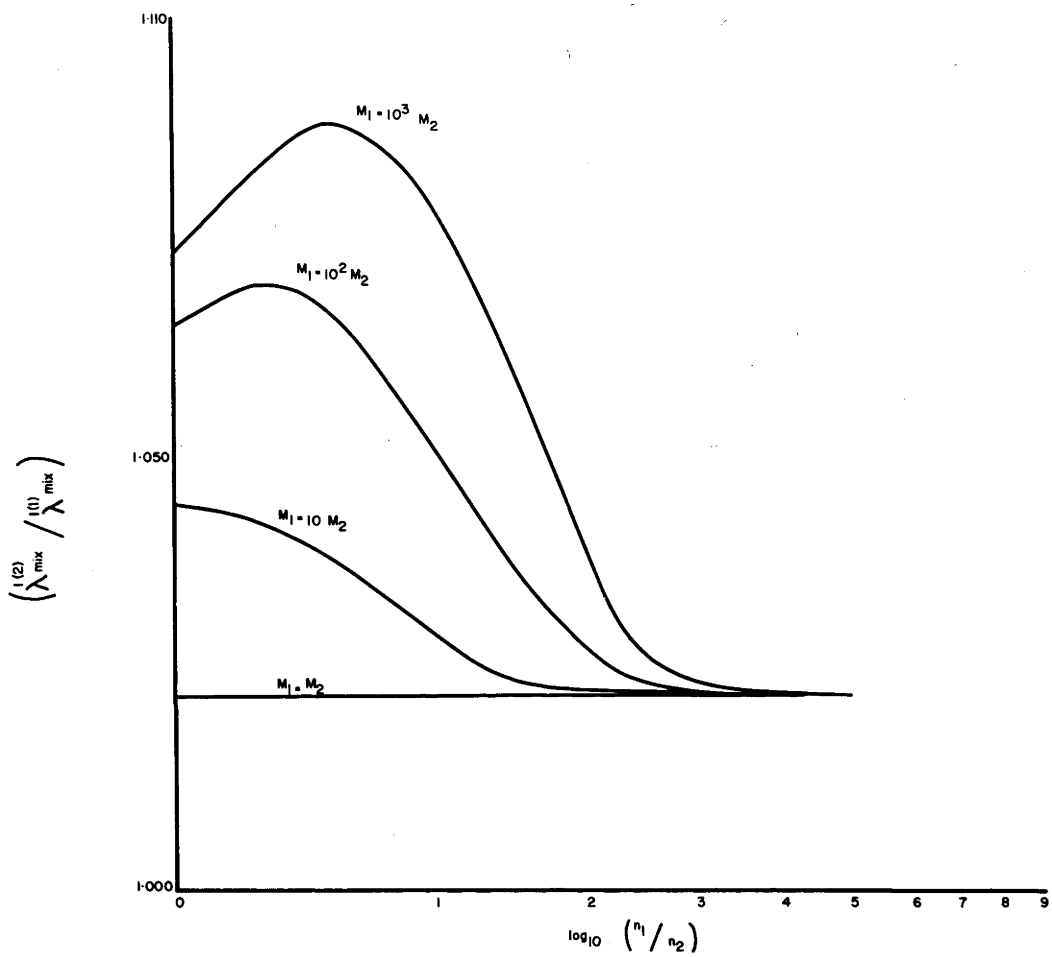

Fig. 10 .. The ratio of the second order to the first order of thermal-conductivity (λ'_{mix}) has been plotted versus concentration ratios for different mass ratios. (Rigid sphere; M_2=1.0 gm, $\sigma_{11}=\sigma_{22}$=1.0°A).

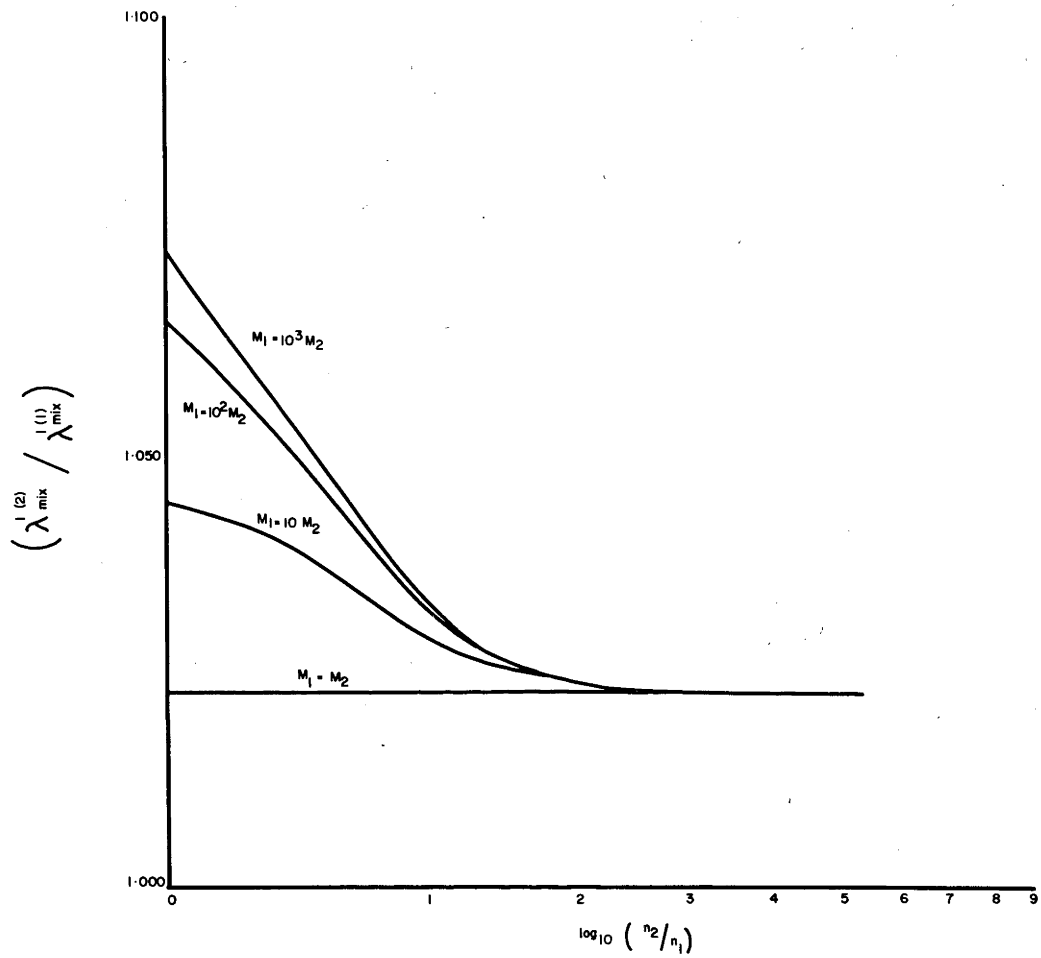

Fig. 11 .. The ratio of the second order to the first order of thermal-conductivity (λ'_{mix}) has been plotted versus concentration ratios for different mass ratios. (Rigid sphere; M_2=1.0 gm, $\sigma_{11}=\sigma_{22}$=1.0·A).

is when $(M_1 \gg M_2 , \sigma_{11} \gg \sigma_{22})$ or $(M_1 \gg M_2 , \sigma_{11} \ll \sigma_{22})$. For studying the former limit in figs. 12 and 13, this ratio is plotted for various mass and σ -ratios (σ_{22}-fixed) for $M_2 = 1.0$ gm, $x_1 = x_2 = 0.5$. In both the figures the limiting value of the ratio is reached when $(\sigma_{11}/\sigma_{22}) = 10$ to 100 and $M_1/M_2 \simeq 10^3$. The limiting values in these figures are different from the simple gas limit of fig. 10.

By comparing figs. 10 and 12, we observe that the behaviour of the $(\lambda^{(2)}_{mix} / \lambda^{(1)}_{mix})$ ratio for the limits $(M_1 \gg M_2 , n_1 \gg n_2)$ and $(M_1 \gg M_2 , \sigma_{11} \gg \sigma_{22})$ is not the same. Thus we conclude that this ratio does not observe the L.G.M. condition because according to the L.G.M. condition, the value of the ratio for the two limits should be the same.

For the $(M_1 \gg M_2 , \sigma_{11} \ll \sigma_{22})$ limit the λ'_{mix} -ratio is plotted in fig. 14 for different mass and σ -ratios (σ_{11} fixed) for $M_2 = 1.0$ gms and for $x_1 = x_2 = 0.5$. In this case, a limit lower than the simple gas limit is reached. Also this limit (Fig. 14) is lower than the limits of fig. 12. Thus the limit $(M_1 \gg M_2 , x_2 \gg x_1)$ in fig. 11 is not identical with the $(M_1 \gg M_2 , \sigma_{22} \gg \sigma_{11})$ limit for the λ'_{mix} - ratio.

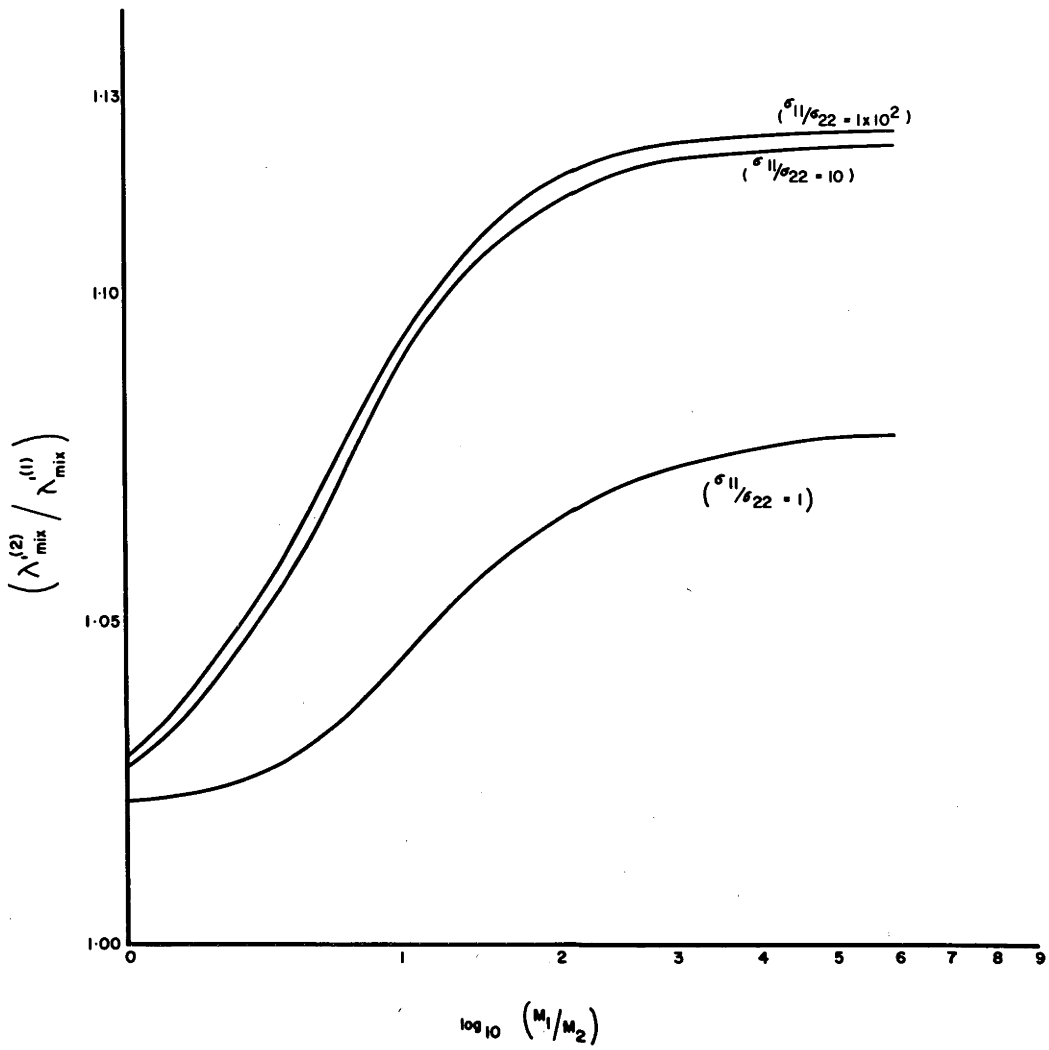

Fig. 12 .. The ratio of the second order to the first order of thermal-conductivity (λ'_{mix}) has been plotted versus mass-ratios for various (σ_{11}/σ_{22}) ratios. (Rigid sphere; M_2=1.0 gm, σ_{22}=1.0 Å, X_1=X_2=0.5).

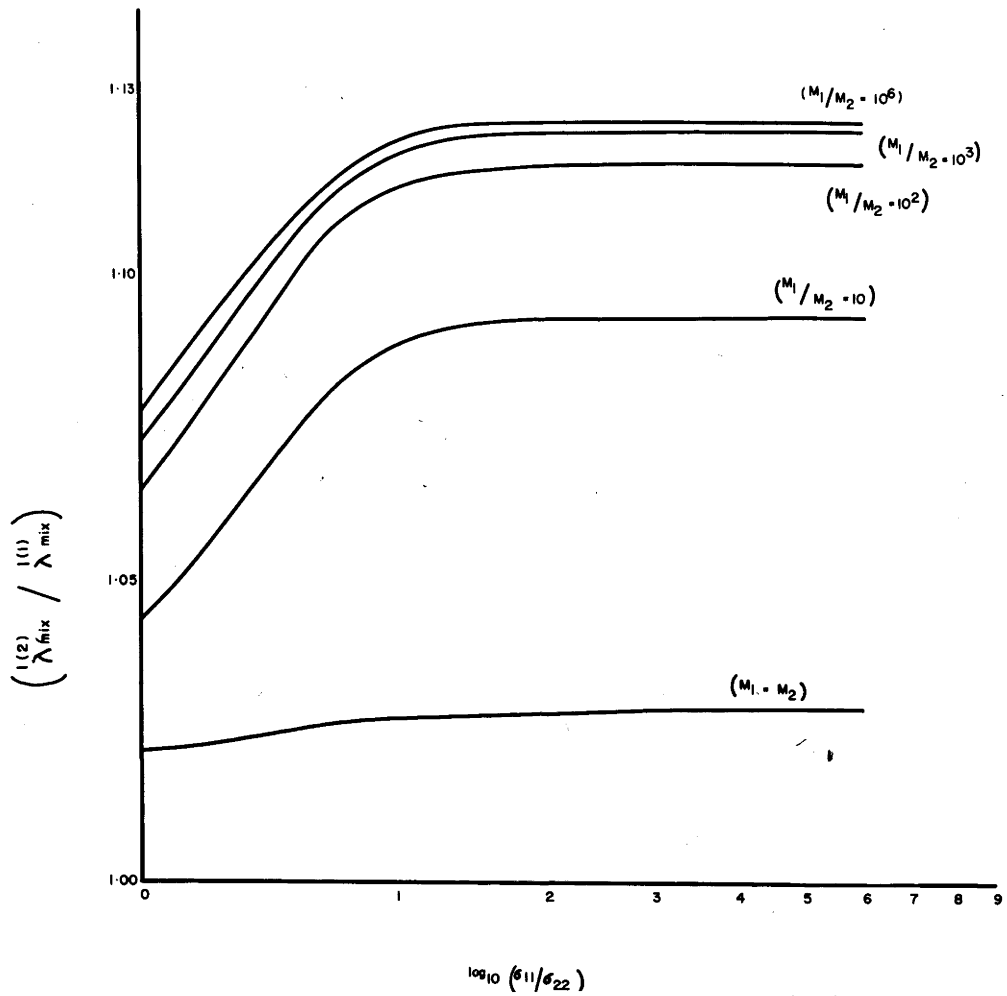

Fig. 13 .. The ratio of the second-order to the first order of thermal-conductivity (λ'_{mix}) has been plotted versus $(\sigma_{11}/\sigma_{22})$ ratios for various mass-ratios. (Rigid sphere; M_2=1.0 gm, σ_{22}=1.0·A , X_1=X_2=0.5).

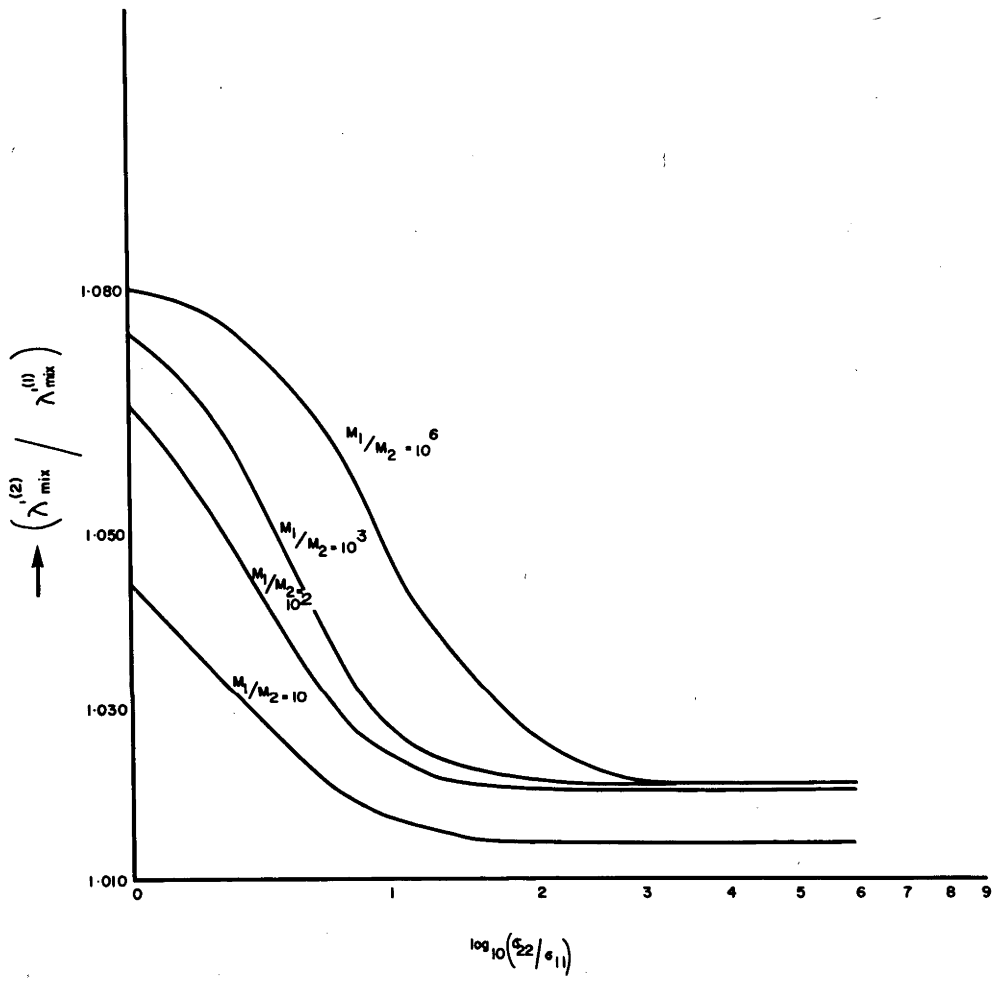

Fig. 14 .. The ratio of the second-order to the first order of thermal conductivity (λ'_{mix}) has been plotted versus (σ_{22}/σ_{11}) ratios for various mass ratios. (Rigid sphere; M_2=1.0 gm, σ_{11}=1.0°A, X_1=X_2=0.5).

iii) <u>Contribution of Diffusion Process to Thermal Conductivity</u> (Tables 12 - 16).

So far we have discussed the variation of λ'_{mix} with different sets of parameters as Mackenfuss and Curtiss (M.C-58) have argued that the diffusion term in λ_{mix} expression (3.122) does not contribute more than 2% to λ_{mix}. Here the contribution of this term is calculated for the following tye types of mixtures.

(1) For the Ar-Ne mixture, $0.1 \leq x_2 \leq 0.9$.

(2) For a mixture approaching the L.G.M. limits.

(3) For a mixture approaching the Quasi L.G.M. limit.

We observe that the contribution of this term is important for mixtures approaching the L.G.M. limit. Also we find that for the $(\lambda^{(2)}_{mix} / \lambda^{(1)}_{mix})$ ratio, the limits $(M_1 >> M_2$, $\sigma_{11} >> \sigma_{22})$ and $(M_1 >> M_2$, $x_1 >> x_2)$ are not equivalent.

For the Ar-Ne system, the contributions of the diffusive part along with that of λ'_{mix} are given in table 12 for x_2 varying between 0.1 to 0.9 for the first two orders. It is clear that the contributions of the diffusive term is less than 1.3%. This is, probably, the range of x_2 and mass-ratio on which earlier conclusion (M.C-58) was based.

TABLE 12

Diffusive part of thermal conductivity is compared with λ'_{mix} for the first two orders for various concentrations for the Ar-Ne system (Rigid sphere : M_1 = 39 .44gms., M_2 = 20 .18gms., σ_{11} = 3.64A , σ_{22} = 2.58A)

x_2	First order		Second order	
	Diffusive term ($x10^{-1}$)	λ'_{mix} $x(10^{-3})$	Diffusive term $x(10^{-1})$	λ'_{mix} $x(10^{-3})$
0.9	1.5365	4.0751	1.7096	4.1756
0.8	2.3304	3.6335	2.6128	3.7284
0.7	2.6426	3.2565	2.9834	3.3449
0.6	2.6381	2.9313	2.9967	3.0124
0.5	2.4234	2.6481	2.7682	2.7217
0.4	2.0687	2.3995	2.3749	2.4656
0.3	1.6215	2.1798	1.8699	2.2384
0.2	1.1139	1.9844	1.2898	2.0357
0.1	.5683	1.8096	.6605	1.8539

APPROACH TO L.G.M. AND QUASI - L.G.M. LIMITS

In table 13, the contribution of the diffusive part is compared with that of the λ'_{mix} for $M_1/M_2 = 10^3$ and 10^4 and $x_1/x_2 = 1$ to 2×10^5 for the first and second orders. It is seen that for both the mass-ratios, the contribution of the diffusive term is 5% of λ'_{mix} for both the orders for the values of $x_1/x_2 = 1$ and goes on decreasing with increasing x_2. For increasing x_1/x_2, the value of $\lambda^{(2)}_{mix}/\lambda^{(1)}_{mix}$ approaches the simple gas limit as given in fig. 10.

In table 14, the contributions of the diffusive term and the λ_{mix} term are compared for $M_1/M_2 = 10^3$ and 10^4 and for $\sigma_{11}/\sigma_{22} = 1.0$ to 1.0×10^5 ($\sigma_{22} = 1.0$ A, $x_1 = x_2 = 0.5$). The contribution of the diffusive term is prominent for all σ_{11}/σ_{22} ratios. Furthermore, a limiting value for $\lambda^{(2)}_{mix}/\lambda^{(1)}_{mix}$ is reached for ($M_1 \gg M_2$; $\sigma_{11} \gg \sigma_{22}$). This limiting value is 1.117 and is different from the limiting values in table 13 and

TABLE 13

Diffusive part of thermal conductivity is compared with λ'_{mix} for the first two orders for various mass - and concentration - ratios (Rigid sphere ; M_2 = 1.0gm , $\sigma_{11} = \sigma_{22}$ = 1.0Å)

M_1/M_2	n_1/n_2	First Order		Second Order	
		λ'_{mix} x10^{-5}	Diffusive part	λ'_{mix} x10^{-5}	Diffusive part
10^3	1	0.4783	2.360x10^3	0.5133	2.955x10^3
	19	1.248	1.024x10^3	1.282	1.135x10^3
	2x10^2	1.362	1.192x10^2	1.394	1.305x10^2
	2x10^3	1.374	12.099	1.405	13.228
	2x10^4	1.375	1.2115	1.406	1.3239
	2x10^5	1.375	0.12116	1.406	0.13237
10^4	1	0.4537	2.361x10^3	0.4884	2.912x10^3
	19	1.244	1.024x10^3	1.279	1.077x10^3
	2x10^2	1.362	1.194x10^2	1.394	1.166x10^2
	2x10^3	1.374	12.096	1.405	13.072
	2x10^4	1.375	1.218	1.406	1.336
	2x10^5	1.375	0.1216	1.406	0.1328

TABLE 14

Diffusive part of thermal conductivity is compared with λ'_{mix} for the first two orders for various mass- and σ - ratios

(Rigid sphere ; M_2 = 1.0gm, x_1 = x_2 = 0.5, σ_{22}-1.0A)

M_1/M_2	σ_{11}/σ_{22}	First Order		Second Order	
		λ'_{mix}	Diffusive part	λ'_{mix}	Diffusive part
10^3	1.0	4.783×10^4	2.360×10^3	5.133×10^4	2.955×10^3
	10.0	2.154×10^3	159.87	2.413×10^3	219.44
	100.0	25.86	1.938	29.047	2.695
	1.0×10^3	0.2633	1.968×10^{-2}	0.2957	2.744×10^{-2}
	1.0×10^4	2.637×10^{-3}	1.971×10^{-4}	2.962×10^{-3}	2.748×10^{-4}
	1.0×10^5	2.638×10^{-5}	1.976×10^{-6}	2.963×10^{-5}	2.749×10^{-6}
10^4	1.0	4.537×10^4	2.361×10^3	4.884×10^4	2.912×10^3
	10.0	2.124×10^3	159.89	2.382×10^2	219.53
	100.0	25.55	1.851	28.73	2.696
	1.0×10^3	0.2602	1.892	0.2925	2.743×10^{-2}
	1.0×10^4	2.606×10^{-3}	1.898	2.931×10^{-3}	2.747×10^{-4}
	1.0×10^5		1.901	2.931×10^{-5}	2.748×10^{-4}

the corresponding limiting value for $\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix}$. It is to be noticed that the present limit is the same as the L.G.M. limit of Chapman and Cowling (C.C.-52) and is not identical with ($M_1 \gg M_2$; $x_1 \gg x_2$). Moreover the absolute values in tables 13 and 14 are entirely different.

A similar set of tables 15 and 16 are made for mass-and σ -ratios and for mass-and σ_{22}/σ_{11} - ratios respectively. In these tables, the contribution of the diffusive term is much smaller than that in tables 13 and 14 and is slightly larger than that in table 12. In tables 15 and 16, we also approach a limiting value for $\lambda^{(2)}_{mix} / \lambda^{(1)}_{mix}$ but, in contrast to the previous cases, these limiting values are different. This shows that for $\lambda^{(2)}_{mix} / \lambda^{(1)}_{mix}$, the limiting values for the limits ($M_1 \gg M_2$; $\varkappa_2 \gg \varkappa_1$) and ($M_1 \gg M_2$; $\sigma_{22} \gg \sigma_{11}$) are not equivalent. Thus we observe that for the absolute values of $\lambda^{(1)}_{mix}$ and $\lambda^{(2)}_{mix}$ the diffusive term is most important for systems approaching the L.G.M. limit.

iv) <u>Diffusion</u> (Tables 17 to 23, Figs. 15 to 19)

Algebraic expressions for the first and second orders

TABLE 15

Diffusive part of thermal conductivity is compared with λ'_{mix} for the first two orders for various mass- and concentration - ratios (Rigid sphere ; M_2 = 1.0gm, $\sigma_{11} = \sigma_{22}$ = 1.0 A)

M_1/M_2	n_2/n_1	First Order		Second Order	
		$\lambda'_{mix} \times 10^{-4}$	Diffusive part	$\lambda'_{mix} \times 10^{-4}$	Diffusive part
10^3	1	4.783	2.360×10^3	5.133	2.955×10^3
	19	0.7645	2.504×10^2	0.8143	3.426×10^2
	2×10^2	0.4670	24.946	0.4809	34.38
	2×10^3	0.4381	2.494	0.4483	3.438
	2×10^4	0.4352	0.2494	0.4451	0.3440
	2×10^5	0.4349	0.02494	0.4448	0.03440
10^4	1	4.537	2.361×10^3	4.884	2.912×10^3
	19	0.4701	2.504×10^2	0.5134	3.360×10^2
	2×10^2	0.1700	24.943	0.1772	33.54
	2×10^3	0.1408	2.493	0.1432	3.341
	2×10^4	0.1378	0.2493	0.1410	0.3377
	2×10^5	0.1375	0.02493	0.1407	0.03377

TABLE 16

Diffusive part of thermal conductivity is compared with λ'_{mix} for the first two orders for various mass- and σ- ratios

(Rigid sphere ; M_2 = 1.0gm., x_1 = x_2 = 0.5, σ_{11} = 1.0 A)

M_1/M_2	σ_{22}/σ_{11}	First order		Second order	
		λ'_{mix}	Diffusive part	λ'_{mix}	Diffusive part
10^3	1.0	4.783×10^4	2.360×10^3	5.133×10^4	2.955×10^3
	10.0	1.556×10^3	26.36	1.598×10^3	30.826
	100.0	19.107	0.2529	19.51	0.2934
	1.0×10^3	0.1937	2.516×10^{-3}	0.1978	2.917×10^{-3}
	1.0×10^4	1.940×10^{-3}	2.514×10^{-5}	1.980×10^{-3}	2.916×10^{-5}
	1.0×10^5	1.940×10^{-5}	2.514×10^{-7}	1.980×10^{-3}	2.915×10^{-3}
10^4	1.0	4.537×10^4	2.361×10^3	4.884×10^4	2.912×10^3
	10.0	1.366×10^3	26.40	1.408×10^3	30.88
	100.0	19.020	0.2534	19.43	0.2940
	1.0×10^3	0.1933	2.520×10^{-3}	0.1974	2.923×10^{-3}
	1.0×10^4	1.936×10^{-3}	2.519×10^{-5}	1.976×10^{-3}	2.921×10^{-5}
	1.0×10^5	1.936×10^{-5}	2.519×10^{-7}	1.977×10^{-5}	2.920×10^{-7}

are given by Chapman and Cowling (C.C.-52). The third and fourth order expressions are written by Mason and Devoto (Ma-57, De-66). The numerical calculations for the L.G.M. case up to the fourth order have been given by Chapman and Cowling and Devoto (C.C.-52, De-66). Part of the analytical structure of the second order expression has been discussed by Chapman and Cowling (Ch. 14, C.C.-52).

The results of the present calculations are placed in tables 17 to 23 and in figures 15 to 19.

CONVERGENCE OF THE FIRST FIVE ORDERS

In fig. 15 and table 17, the absolute values of D_{12} for the first five orders for the Ar-Ne mixture for various concentrations are given. This table and figure gives an idea of the variation of these quantities. This variation was not previously available in the literature. Also the experimental values were not extensive enough regarding the variation with different concentrations. We observe that the absolute values for orders higher than the first increase continuously with decreasing x_2. Also in fig. 15 and table 18, the ratios of the second, third, fourth and fifth orders to the first order for various concentrations are given. It is clear from the table and figure that for the ratio of a particular order the

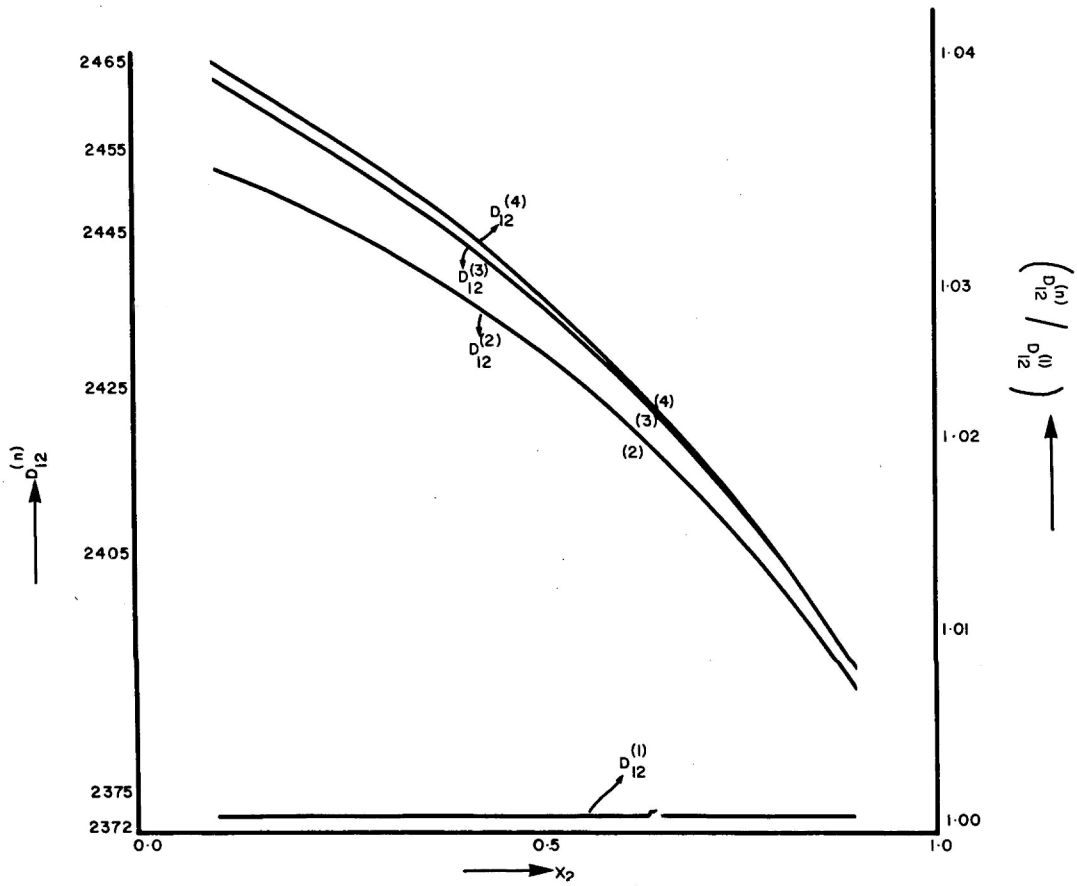

Fig. 15 .. For Ar-Ne , the absolute values of first four orders of diffusion have been compared for various concentrations of the lighter component. Also we have plotted the ratios of second, third and fourth orders to the first for diffusion for various concentration of the lighter component. (Rigid sphere; M_1=39.44 gms , M_2=20.18 gms , σ_{11}=3.64·A, σ_{22}=2.58·A).

Table 17.

Values of the first five orders of diffusion (D_{12}) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms. σ_{11}=3.64 Å, σ_{22}=2.58 Å).

$$(D_{12})_1 = \cdot 2372.$$

x_2	$(D_{12})_2$	$(D_{12})_3$	$(D_{12})_4$	$(D_{12})_5$
.9	0.2388	0.2390	0.2390	0.2390
.8	0.2402	0.2405	0.2405	0.2405
.7	0.2413	0.2417	0.2418	0.2418
.6	0.2423	0.2428	0.2429	0.2429
.5	0.2431	0.2437	0.2438	0.2439
.4	0.2438	0.2445	0.2447	0.2447
.3	0.2444	0.2452	0.2454	0.2454
.2	0.2449	0.2458	0.2460	0.2461
.1	0.2453	0.2464	0.2466	0.2466

TABLE 18.

Ratios of the first five orders to the first order for diffusion (D_{12}) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A, σ_{22}=2.58·A).

x_2	$(D_{12}^{(2)})/(D_{12}^{(1)})$	$D_{12}^{(3)}/D_{12}^{(1)}$	$D_{12}^{(4)}/D_{12}^{(1)}$	$D_{12}^{(5)}/D_{12}^{(1)}$
0.9	1.00696	1.00754	1.00764	1.00765
0.8	1.01266	1.01382	1.01400	1.01404
0.7	1.01742	1.01913	1.01942	1.01949
0.6	1.02143	1.02367	1.02407	1.02417
0.5	1.02483	1.02758	1.02809	1.02821
0.4	1.02774	1.03095	1.03157	1.03173
0.3	1.03022	1.03388	1.03461	1.03480
0.2	1.03234	1.03864	1.03726	1.03749
0.1	1.03417	1.03642	1.03959	1.03985

contribution to D_{12} increases as X_2 decreases. The difference between corresponding values of the consecutive orders increases with decreasing X_2. Moreover it is clear that the rate of decrement for different orders is greater for the higher values of X_2 than for the smaller values.

In fig. 16 and table 19, the ratios $(D_{12}^{(n)}/D_{12}^{(1)})$ for n=2, 3, 4, 5 for different $(\sigma_{11}/\sigma_{22})$ ratios are given. In this case, $\sigma_{22} = 1$ A and $M_1 = 10.0$ $M_2 = 10.0$ gms. It is seen from the table that the limit is reached when $\sigma_{11}/\sigma_{22} = 10^3$ but for all practical purposes, the limit value is reached between $\sigma_{11}/\sigma_{22} = 10$ to 100 as is clear in fig. 16.

VARIATION WITH MASS-RATIO

In fig. 17, the variation of mass-ratios with concentration ratios for $(D_{12}^{(n)}/D_{12}^{(1)})$ (n = 2,3) is shown. It is clear that for all mass-ratios the contribution for a particular order increases for decreasing values of X_2. The separation among curves of different mass-ratios is a minimum for large values of X_2. This separation decreases continuously for decreasing values of X_2.

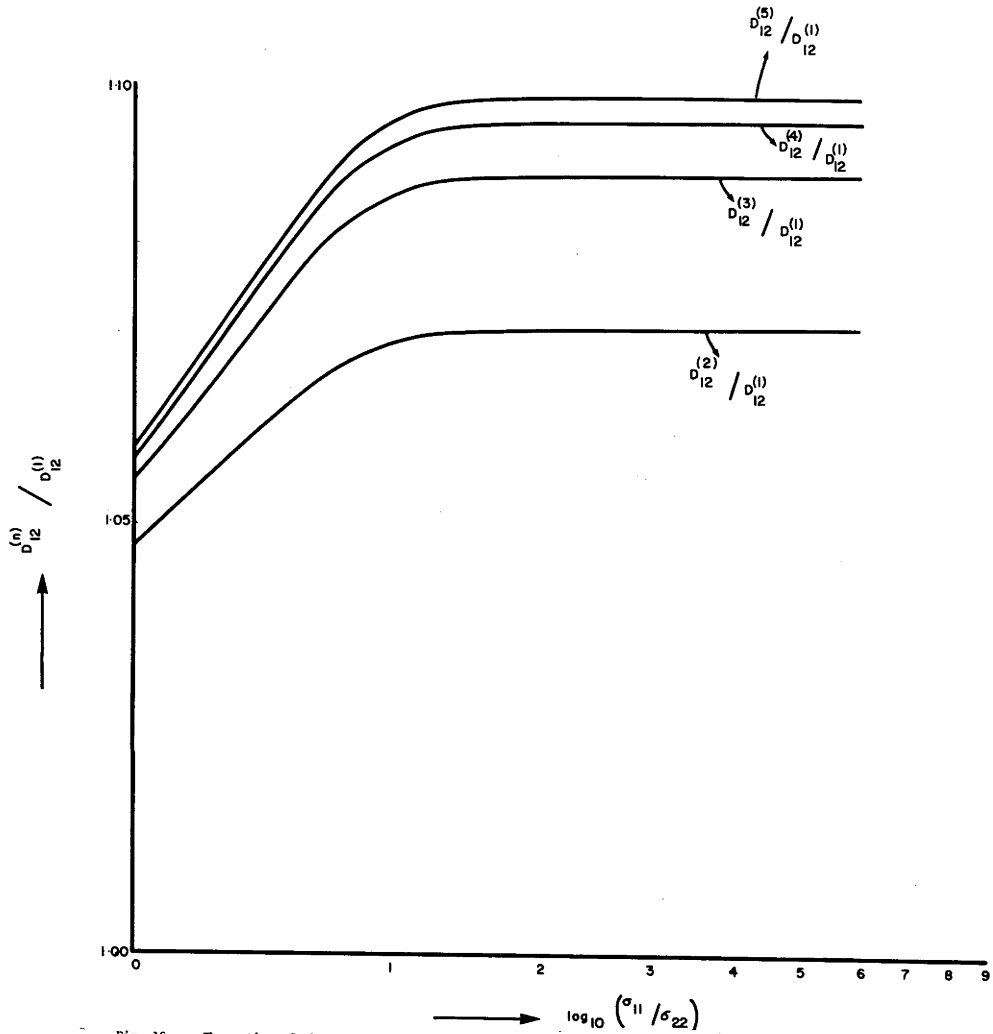

Fig. 16 .. The ratios of the second, third, fourth and fifth orders to the first order of diffusion have been compared for various σ_{11}/σ_{22} ratios. (Rigid sphere; M_1=10 M_2=10.0 gms, σ_{22}=1.0°A, X_1=X_2=0.5).

Table 19.

Ratios of the first five orders to the first order for diffusion (D_{12}) for a binary mixture for different (σ_{11}/σ_{22}) ratios. (Rigid sphere; M_1=10 M_2=1o.0 gms, σ_{22}=1·A, ~~$X_1=X_2=0.5$~~)
$X_1=X_2=0.5$)

σ_{11}/σ_{22}	$D_{12}^{(2)}/D_{12}^{(1)}$	$D_{12}^{(3)}/D_{12}^{(1)}$	$D_{12}^{(4)}/D_{12}^{(1)}$	$D_{12}^{(5)}/D_{12}^{(1)}$
1	1.04757	1.05550	1.05775	1.05848
10	1.07096	1.08776	1.09368	1.09623
10^2	1.07215	1.08953	1.09575	1.09847
10^3	1.07216	1.08955	1.09577	1.09850
10^4	1.07216	1.08955	1.09577	1.09850
10^5	1.07216	1.08955	1.09577	1.09850
10^6	1.07216	1.08955	1.09577	1.08950

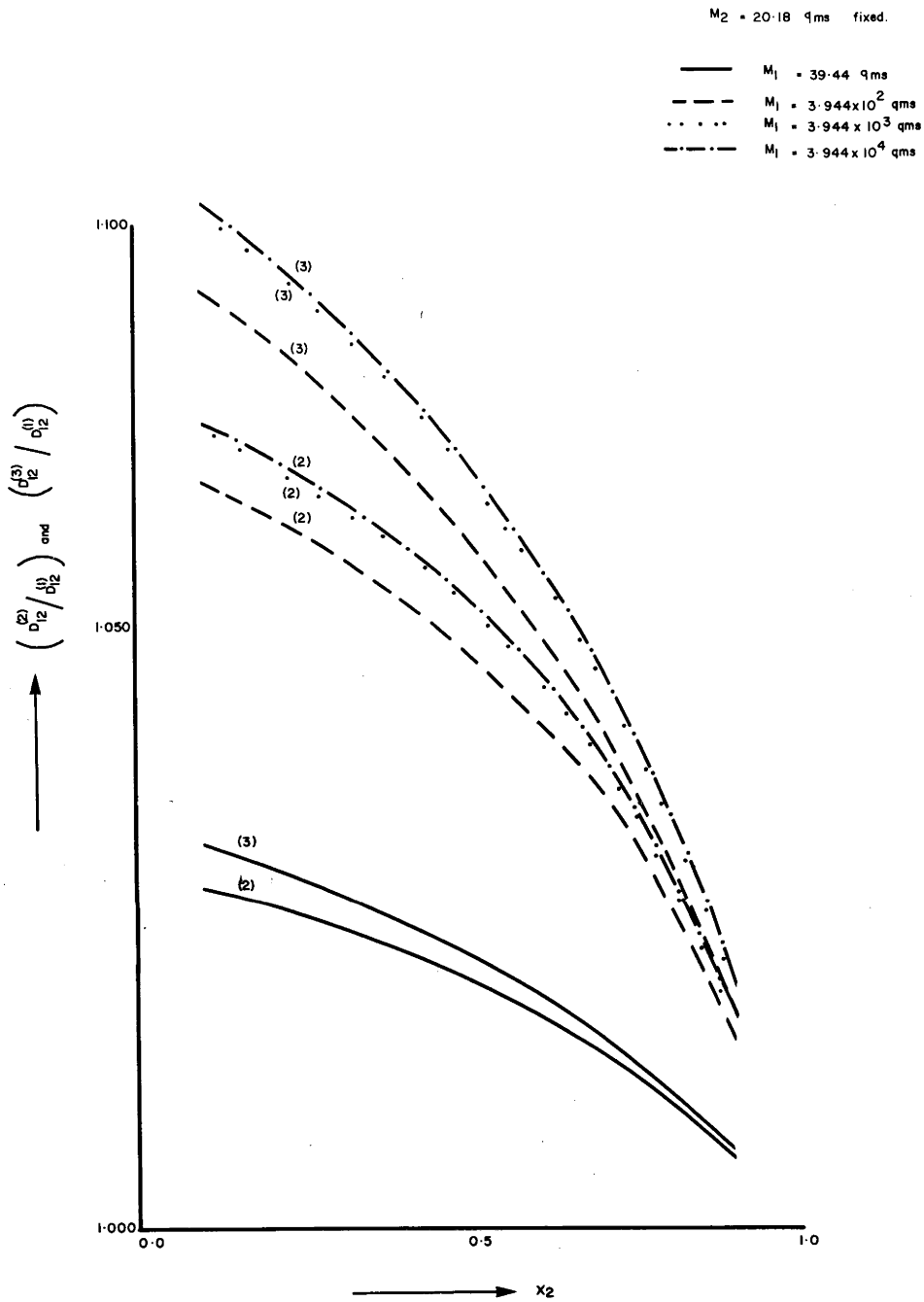

Fig. 17 .. The ratios of the second and third orders to the first order of Diffusion have been plotted versus concentration of the lighter component for different mass ratios. Number (2) and (3) on different curves showing the corresponding orders involved. (Rigid sphere; M_2=20.18 gms, σ_{11}=3.64·A , σ_{22}=2.58·A).

APPROACH TO THE ($M_1 \gg M_2$; $x_1 \gg x_2$) AND ($M_1 \gg M_2$ $\sigma_{11} \gg \sigma_{22}$) LIMITS

In figs. 18 and 19, an equivalence of the ($M_1 \gg M_2$; $x_1 \gg x_2$) and ($M_1 \gg M_2$; $\sigma_{11} \gg \sigma_{22}$) limits for the ($D_{12}^{(2)}/D_{12}^{(1)}$) is shown. The limiting value in these figures is the same as for the Lorentzian gas (C.C.-52, De-66). This limit is reached, for all practical purposes, for M_1/M_2 10^3 and σ_{11}/σ_{22} = 10 to 100 or $x_1/x_2 \simeq 200$. The value of the mass-ratio can occur in ionised gases.

We observe that the Lorentzian gas limit is reached only for the $D_{12}^{(2)}/D_{12}^{(1)}$ ratio and not for the absolute values of D_{12}. For a comparative idea of the values involved, we give, in tables 20 and 21, the values of the ratio for different values of M_1/M_2 , $\frac{x_1}{x_2}$ and M_1/M_2 ; σ_{11}/σ_{22} and in tables 22 and 23, the absolute values of $D_{12}^{(2)}$ for different mass, concentration and σ - ratios.

APPROACH TO THE ($M_1 \gg M_2$; $x_2 \gg x_1$) AND THE ($M_1 \gg M_2$, $\sigma_{22} \gg \sigma_{11}$) LIMITS

The variation of $D_{12}^{(2)}/D_{12}^{(1)}$ with the M_1/M_2 and x_2/x_1

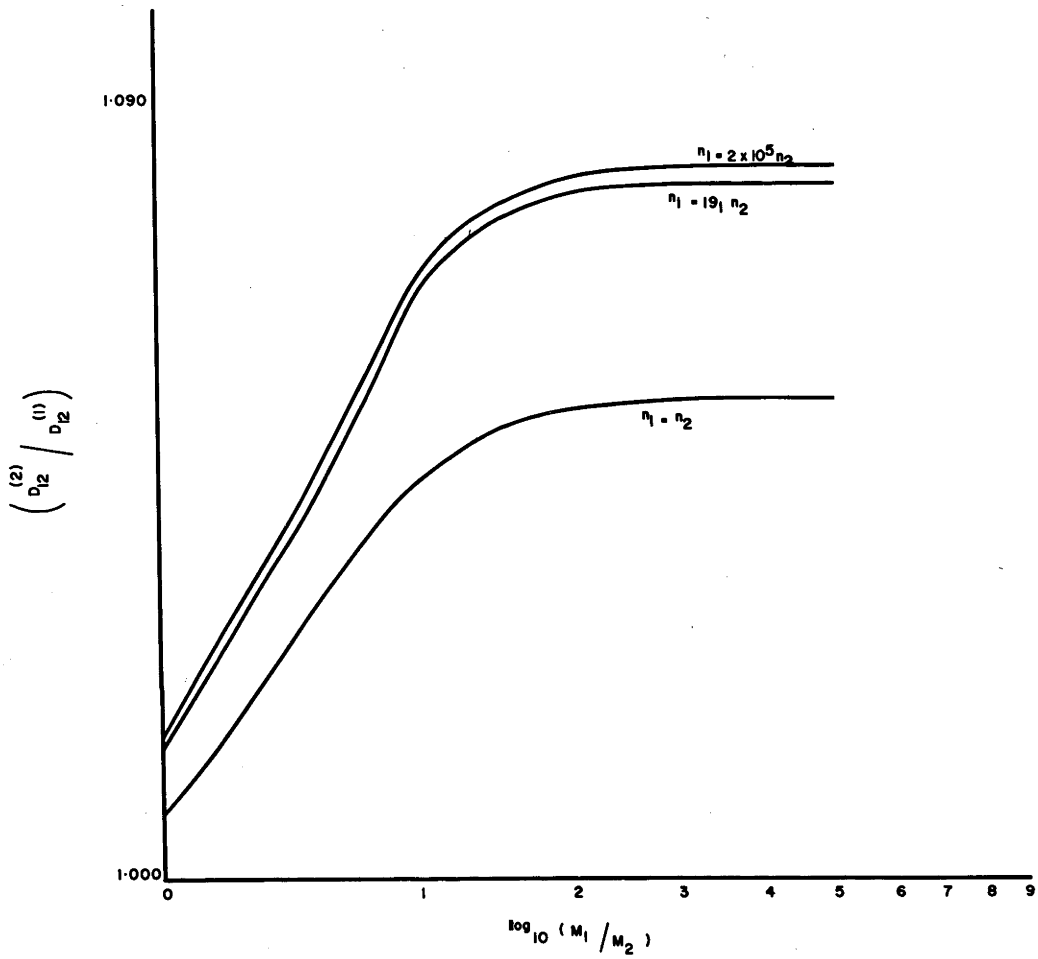

Fig. 18 .. The ratio of the second order to the first order of Diffusion has been plotted versus mass ratios for different concentration ratios. (Rigid sphere; M_2=1.0 gm, $\sigma_{11}=\sigma_{22}$=1.0°A).

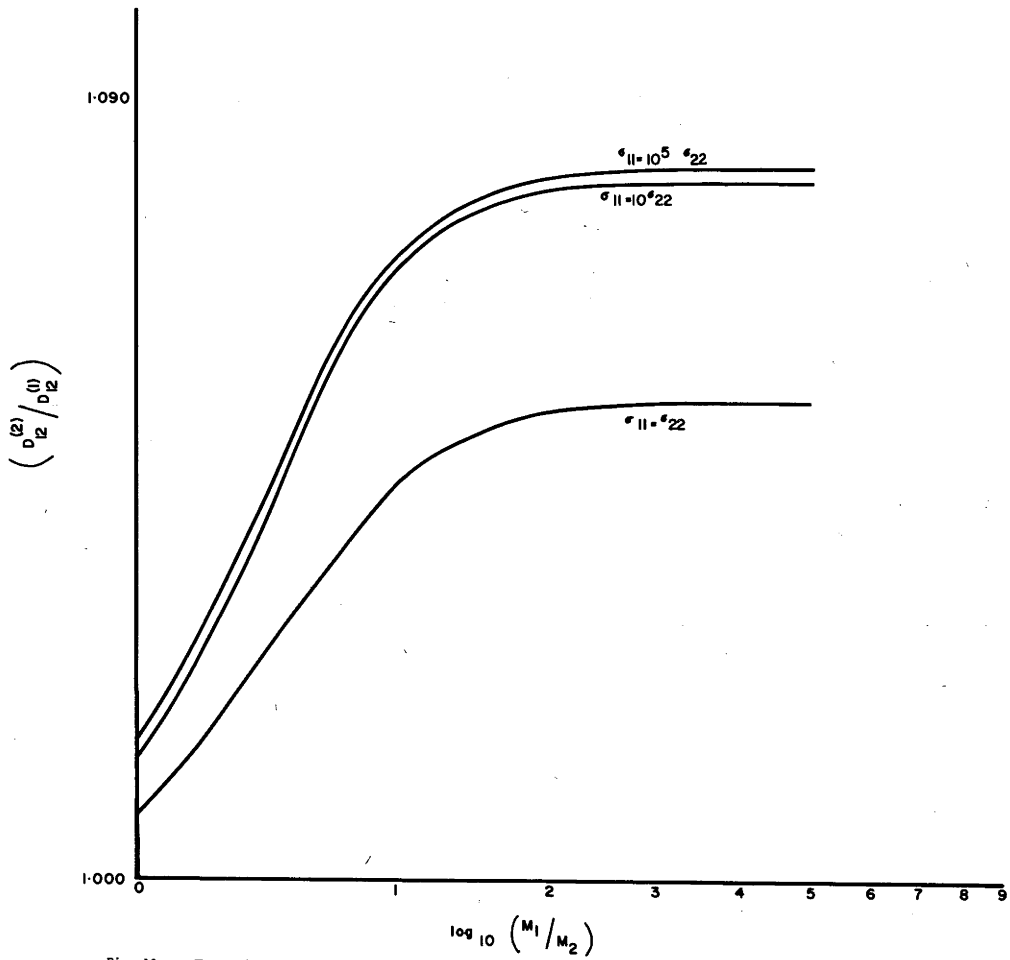

Fig. 19 .. The ratio of the second order to the first order of Diffusion has been plotted versus mass ratios for different $(\sigma_{11}/\sigma_{22})$ ratios. (Rigid sphere; M_2=1.0 gm, for $\sigma_{11}/\sigma_{22} > 1$, σ_{22}=1.0·A, for $\sigma_{22}/\sigma_{11} > 1$, σ_{11}=1.0·A , X_1=X_2=0.5).

TABLE 20

Ratios of the second order to the first for diffusion (D_{12}) for various mass and concentration ratios (Rigid sphere ; $\sigma_{22} = \sigma_{11} = 1.0\text{Å}$, $M_2 = 1.0\text{gm}$)

$(D_{12}^{(2)}/D_{12}^{(1)})$

M_1/M_2 ; x_1/x_2	1	10	10^2	10^3	10^4	10^5
1	1.00743	1.04636	1.05456	1.05504	1.05546	1.05548
19	1.01524	1.06892	1.07906	1.08010	1.08010	1.08013
199	1.01602	1.07060	1.08088	1.08192	1.08192	1.08195
1.99×10^3	1.01610	1.07077	1.08105	1.08210	1.08210	1.08211
1.99×10^4	1.01611	1.07081	1.08107	1.09212	1.08212	1.08212
1.99×10^5	1.01611	1.07081	1.08107	1.08212	1.08212	1.08212

TABLE 21

Ratios of the second order to the first for diffusion (D_{12}) for various mass and σ ratios (Rigid sphere : σ_{22} = 1A , $x_1 = x_2 = 0.5$, M_2 = 1.0gm)

$(D_{12}^{(2)}/D_{12}^{(1)})$

σ_{11}/σ_{22} \ M_1/M_2	1	10	10^2	10^3	10^4	10^5
1	1.00743	1.04636	1.05456	1.05504	1.05546	1.05548
10	1.01414	1.07096	1.07980	1.08047	1.08085	1.08087
10^2	1.01464	1.07096	1.08109	1.08214	1.08211	1.08211
10^3	1.01465	1.07216	1.08109	1.08214	1.08212	1.08212
10^4	1.01465	1.07216	1.08109	1.08214	1.08212	1.08212
10^5	1.01465	1.07216	1.08109	1.08214	1.08212	1.08212

TABLE 22

Absolute values of the second order for diffusion (D_{12}) for various mass and concentration ratios (Rigid sphere ; $\sigma_{11} = \sigma_{22} = 1\text{Å}$, $M_2 = 1.0\text{gm}$)

$(D_{12}^{(2)})$

x_1/x_2 \ M_1/M_2	10	10^2	10^3	10^4	10^5
1	9.209	8.893	8.861	8.858	8.857
19	9.408	9.100	9.068	9.065	9.064
2×10^2	9.423	9.115	9.083	9.080	9.080
2×10^3	9.424	9.117	9.085	9.081	9.081
2×10^4	9.424	9.117	9.085	9.082	9.081

TABLE 23

Absolute values of the second order for diffusion (D_{12}) for various mass-and σ - ratios (Rigid sphere ; $x_1 = x_2 = 0.5$, $M_2 = 1.0\,gm$)

$D_{12}^{(2)}$

M_1/M_2 \ σ_{11}/σ_{22}	10	10^2	10^3	10^4	10^5
1	9.209	8.894	8.861	8.858	8.857
10	0.3112	0.3010	0.3000	0.3000	0.2998
10^2	3.696×10^{-3}	3.575×10^{-3}	3.562×10^{-3}	3.561×10^{-3}	3.561×10^{-3}
10^3	3.763×10^{-5}	3.640×10^{-5}	3.627×10^{-5}	3.625×10^{-5}	3.625×10^{-5}
10^4	3.769×10^{-7}	3.646×10^{-7}	3.633×10^{-7}	3.632×10^{-7}	3.632×10^{-7}

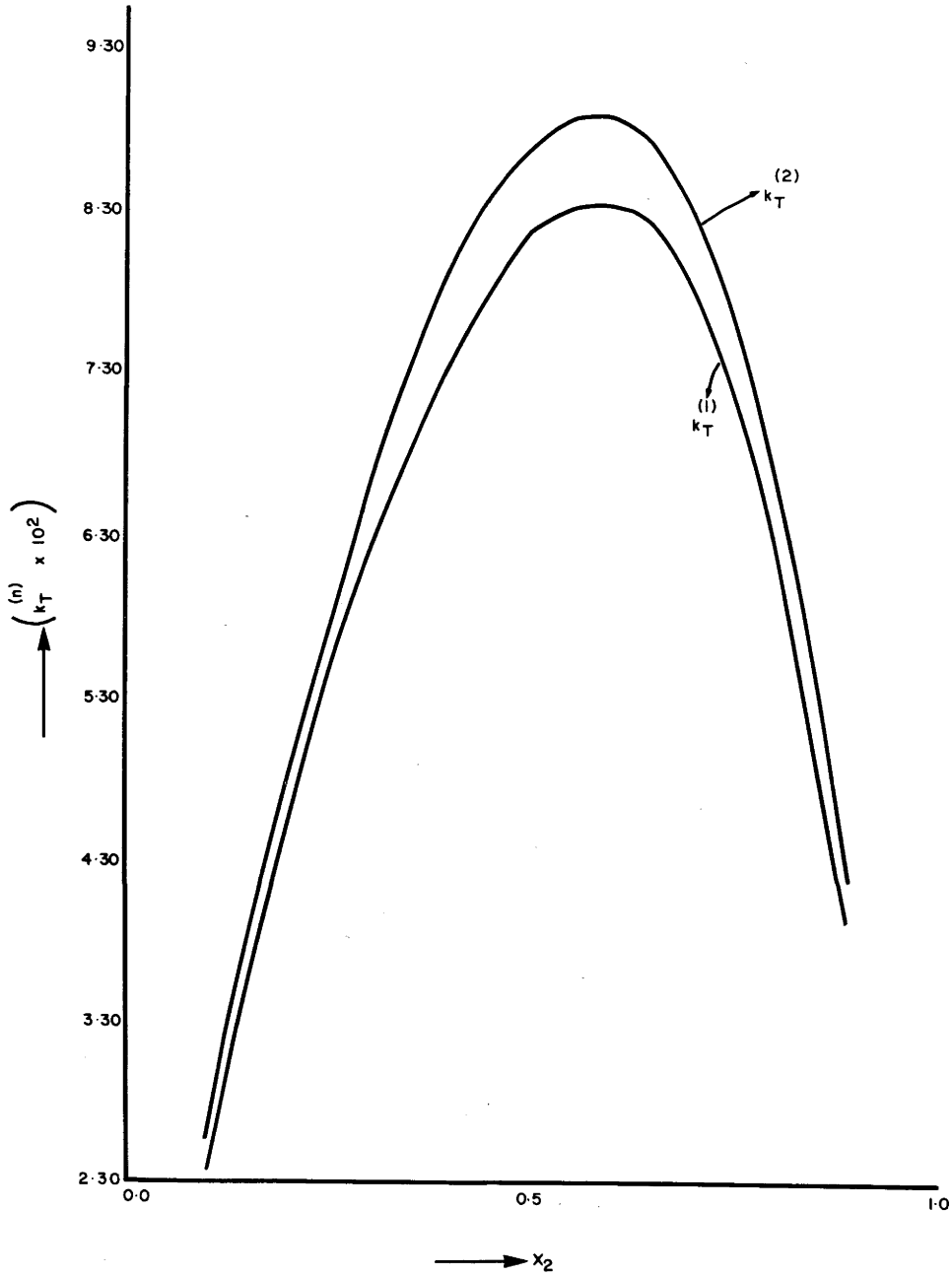

Fig. 20 .. For Ar-Ne , the absolute values for first two orders of thermal-diffusion ratio have been plotted for various concentrations of the lighter component. (Rigid sphere; M_1=39.44 gms, M_2=20.17 gms, σ_{11}=3.64·A , σ_{22}=2.58·A).

the actual variation of k_T with x_2 for different x_2. Previously no theoretical plot for orders higher than the first was available. This plot shows a maximum at $x_2 \simeq 0.5$.

In fig. 21 and table 25, $k_T^{(n)}/k_T^{(1)}$ for n=2, 3, 4 is given for the Ar-Ne mixture for different values of x_2. The contributions to the orders higher than the first increase with decreasing x_2. Also the contribution to corresponding values of different orders increases with decreasing x_2. Moreover it is clear from the figure that the rate of decrement for different orders is greater for larger values of x_2 than for smaller value. It, also, follows from the table that the value of $k_T^{(n)}/k_T^{(1)}$ for the L.G.M. limit is very high as compared to the value for this ratio for $0.1 \leq x_2 \leq 0.9$ (compare table 25 with table 7, p. 196, C.C.-52). Previously our concept about the convergence was based on the values of the ratio for the L.G.M. limit.

In fig. 22 and table 26, we study the variation of $(k_T^{(n)}/k_T^{(1)})$ for n=2, 3, 4 for various σ_{11}/σ_{22} ratios $\sigma_{22} = 1$ Å), for $M_1 = 10\ M_2$ ($M_2 = 1$ gm) and for $x_1 = x_2 = 0.5$. For all practical purpose, the limit is reached for $\sigma_{11}/\sigma_{22} \simeq 10$ to 10^2.

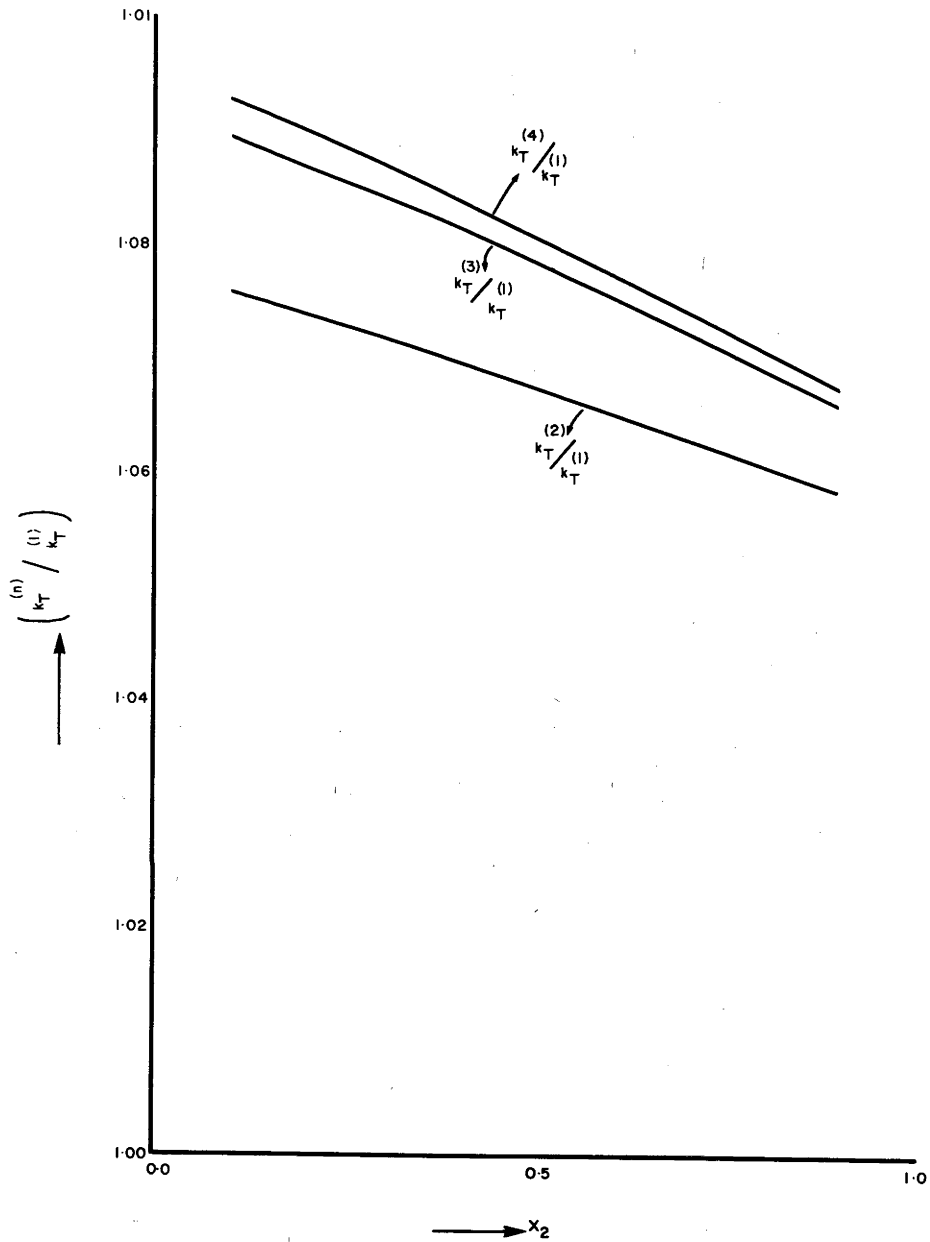

Fig. 21 .. For Ar-Ne , the ratios of the second, third and fourth orders to the first order of thermal-diffusion ratio have been plotted for various concentrations of the lighter components. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A, σ_{22}=2.58·A).

Table 25.

Ratios of the first four orders to the first order for thermal-diffusion ratio (k_T) for the Ar-Ne mixture for different values of x_2. (Rigid sphere; M_1=39.44 gms, M_2=20.18 gms, σ_{11}=3.64·A , σ_{22}=2.58·A)

x_2	$k_T^{(2)}/k_T^{(1)}$	$k_T^{(3)}/k_T^{(1)}$	$k_T^{(4)}/k_T^{(1)}$
0.9	1.05877	1.06614	1.06755
0.8	1.06094	1.06928	1.07096
0.7	1.06326	1.07250	1.07446
0.6	1.06559	1.07568	1.07790
0.5	1.06786	1.07874	1.08122
0.4	1.07002	1.08166	1.08439
0.3	1.07206	1.08440	1.08737
0.2	1.07397	1.08697	1.09017
0.1	1.07575	1.08936	1.09279

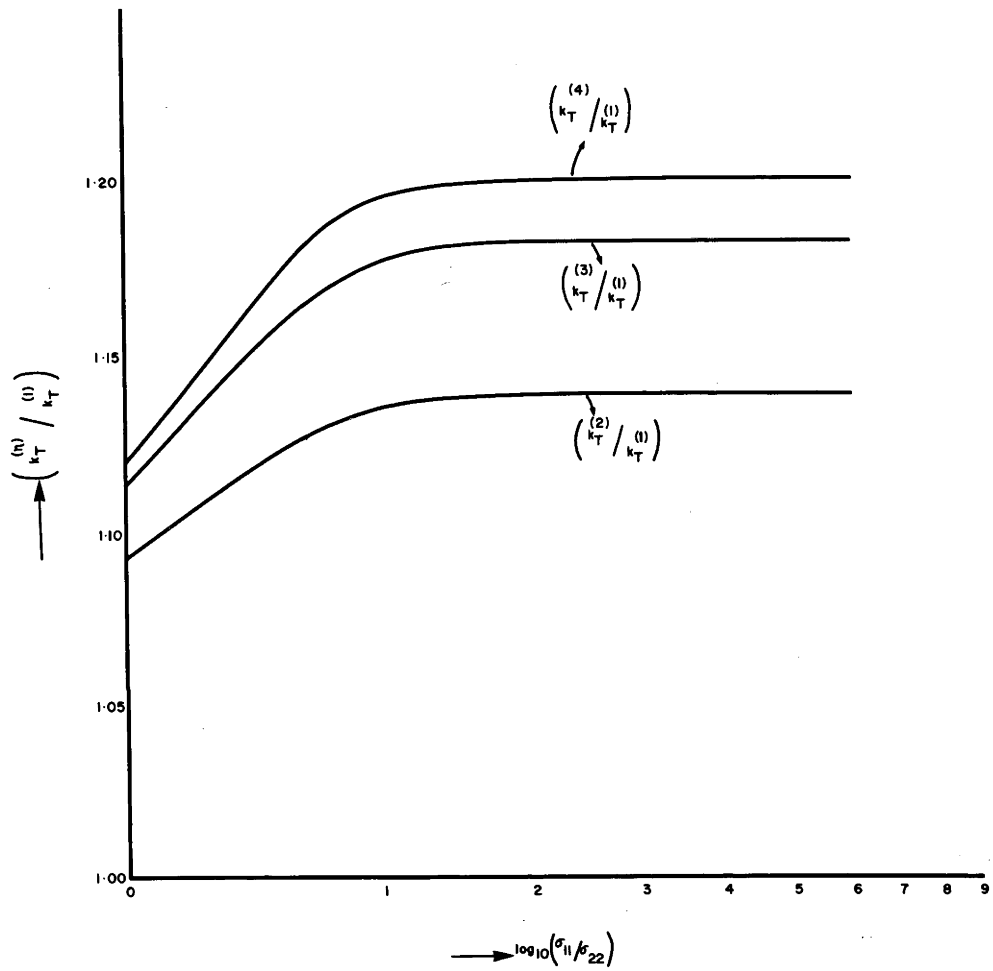

Fig. 22 .. The ratios of the second, third and fourth orders to the first order of thermal-diffusion ratio have been compared for various σ_{11}/σ_{22} ratios. (Rigid sphere; M_1=10 M_2=10.0 gms, σ_{22}=1.0°A, X_1=X_2=0.5).

Table 26.

Ratios of the first four orders to the first order for thermal-diffusion ratio (k_T) for a binary mixture for different (σ_{11}/σ_{22}) ratios. (Rigid sphere; M_1=10 M_2=10.0 gms, σ_{22}=1·A, ~~$X_1=X_2=0.5$~~).
$x_1=x_2=0.5$).

σ_{11}/σ_{22}	$k_T^{(2)}/k_T^{(1)}$	$k_T^{(3)}/k_T^{(1)}$	$k_T^{(4)}/k_T^{(1)}$
1	1.09352	1.11429	1.12070
10	1.13685	1.178446	1.19526
10^2	1.13977	1.18302	1.20077
10^3	1.13986	1.18312	1.20090
10^4	1.13990	1.18314	1.20093
10^5	1.13991	1.18314	1.20093

VARIATION WITH MASS-RATIOS

In fig. 23, we have plotted $(k_T^{(n)}/k_T^{(1)})$ for $(n=2,3)$ for different mass-ratios and $\varkappa_2$. It is clear that the contribution to the ratio increases with decreasing $\varkappa_2$. Also the higher values of $\varkappa_2$ show a greater rate of decrement for different mass-ratios than the lower values of $\varkappa_2$.

APPROACH TO THE $(M_1 \gg M_2 ; \varkappa_1 \gg {}_2)$, $(M_1 \gg M_2 ; \varkappa_2 \gg \varkappa_1)$, $(M_1 \gg M_2 ; \sigma_{11} \gg \sigma_{22})$ AND $(M_1 \gg M_2 ; \sigma_{22} \gg \sigma_{11})$ LIMITS

In figs. 24 and 25, we study the approach to the following types of limiting cases and compare the limiting values for $k_T^{(2)}/k_T^{(1)}$.

(1) (a) $M_1 \gg M_2 ; \varkappa_1 \gg \varkappa_2$

(b) $M_1 \gg M_2 ; \sigma_{11} \gg \sigma_{22}$

(2) (a) $M_1 \gg M_2 ; \varkappa_2 \gg \varkappa_1$

(b) $M_1 \gg M_2 ; \sigma_{22} \gg \sigma_{11}$

It is clear from the figures that the limiting value for the former type of limits $(M_1 \gg M_2 ; \varkappa_1 \gg \varkappa_2$ and $M_1 \gg M_2 ; \sigma_{11} \gg \sigma_{22})$ is the same while for the latter

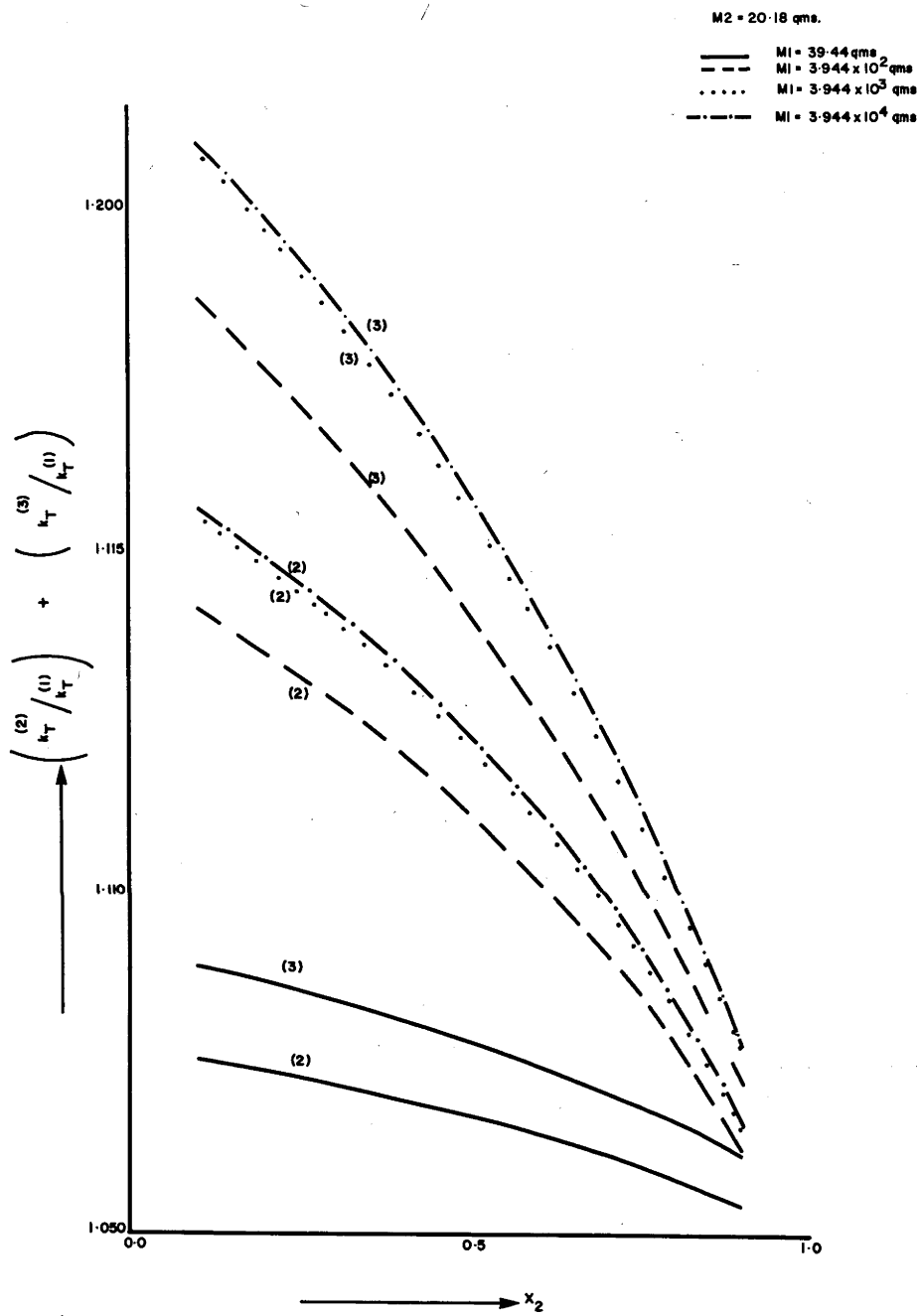

Fig. 23 .. The ratios of the second and third orders to the first order of thermal-diffusion ratio have been plotted versus concentration of the lighter component for various mass-ratios. Numbers on different curves indicate the corresponding orders considered. (Rigid sphere; M_2=20.18 gms, σ_{11}=3.64·A , σ_{22}=2.58·A).

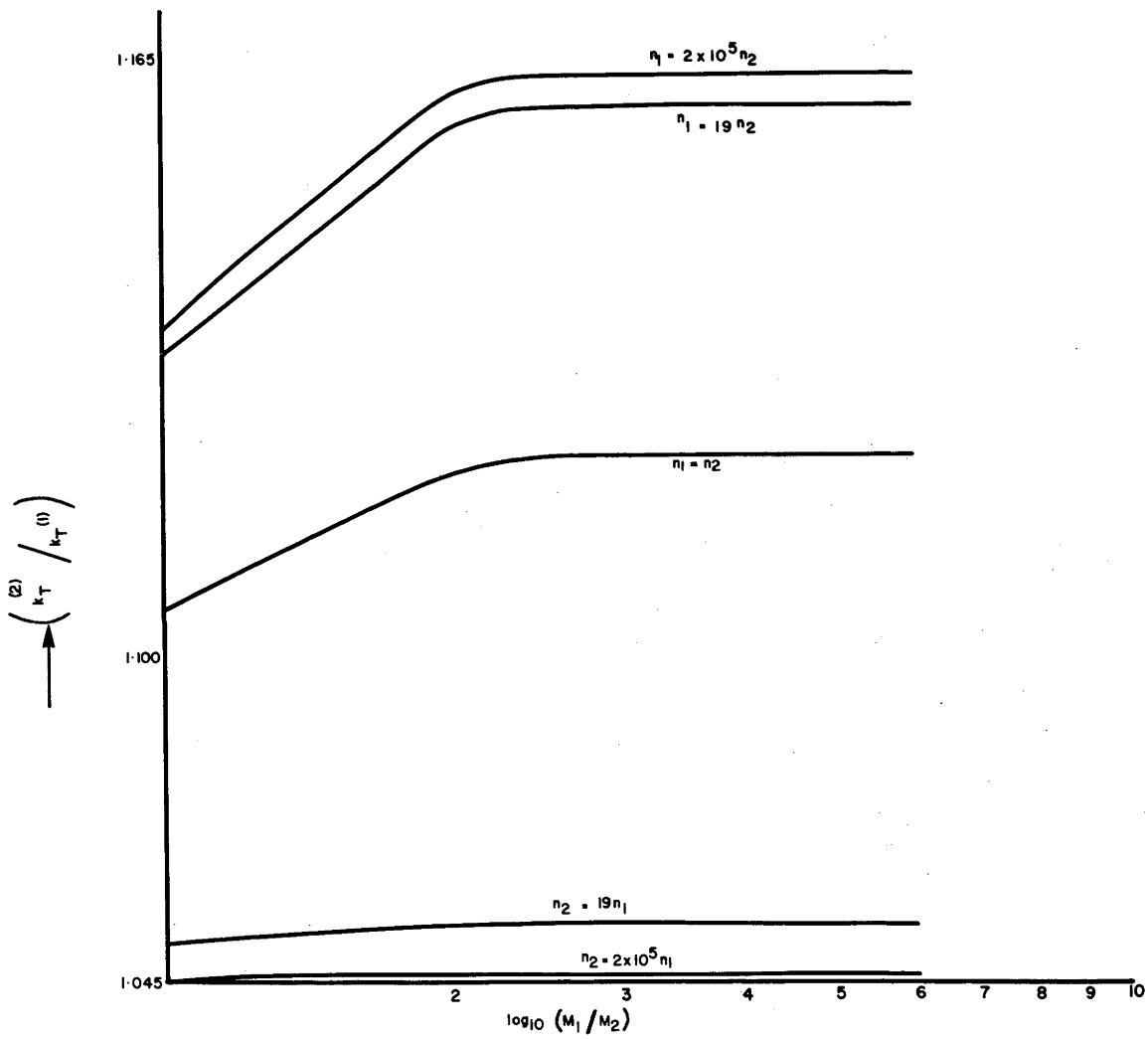

Fig. 24 .. The ratio of the second order to the first order of thermal-diffusion ratio has been plotted versus mass ratios for different concentration ratios. (Rigid sphere; M_2=1.0 gms, $\sigma_{11}=\sigma_{22}$=1.0 Å).

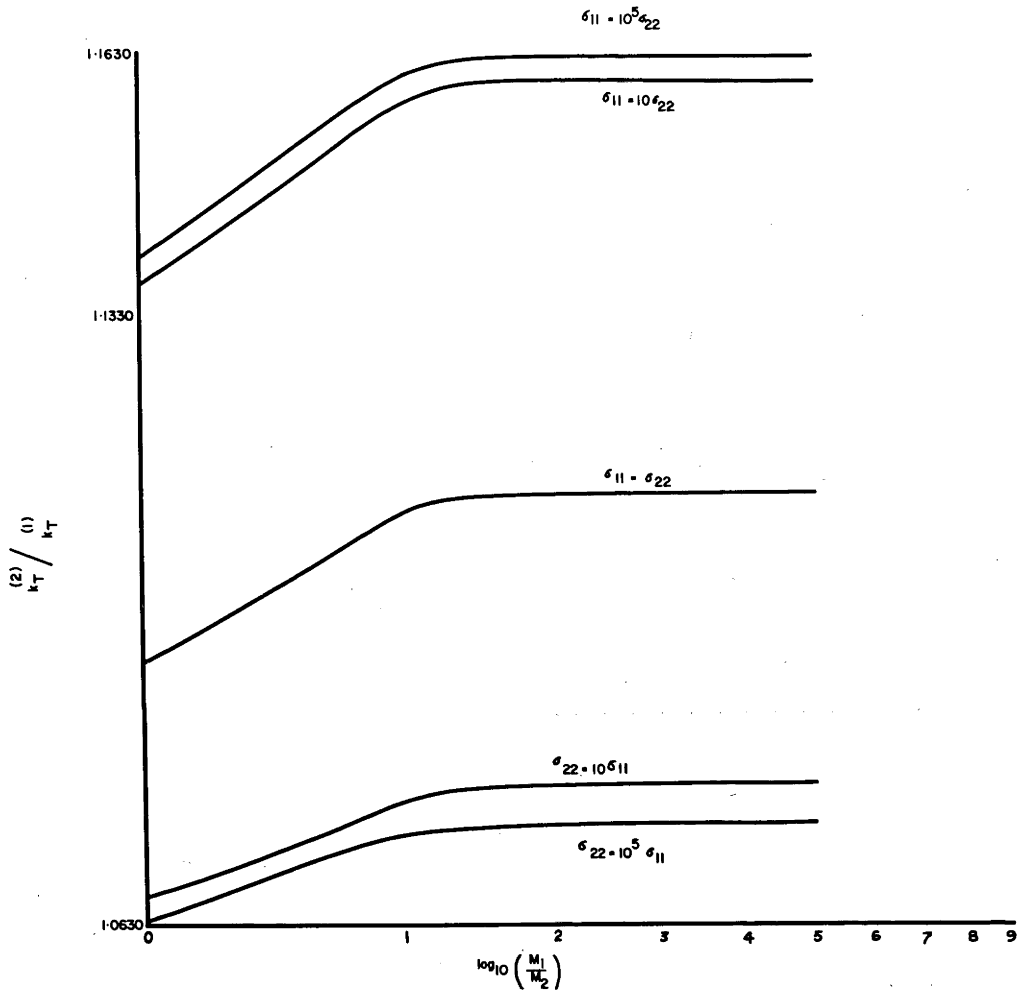

Fig. 25 .. The ratio of the second order to the first order of thermal-diffusion ratio has been plotted versus mass ratios for different $(\sigma_{11}/\sigma_{22})$ ratios. (Rigid sphere; M_2=1.o gm, for $\sigma_{11}/\sigma_{22} > 1$, σ_{22}=1.0·A , for $(\sigma_{22}/\sigma_{11}) > 1$, σ_{11}=1 A fixed).

case ($M_1 \gg M_2$; $x_2 \gg x_1$ and $M_1 \gg M_2$; $\sigma_{22} \gg \sigma_{11}$) the limits are reached in both cases but the limiting values are different. Thus we see that for the ($M_1 \gg M_2$; $x_1 \gg x_2$) and ($M_1 \gg M_2$; $\sigma_{11} \gg \sigma_{22}$) limits ($k_T^{(2)}/k_T^{(1)}$) values are the same. This limiting value for ($k_T^{(2)}/k_T^{(1)}$) corresponds to the ($k_T^{(2)}/k_T^{(1)}$) value for the L.G.M. case in Chapman and Cowling's and Devoto's works (C.C.-52, De-66). For all practical purposes, the limiting value for ($k_T^{(2)}/k_T^{(1)}$) is reached at $M_1/M_2 \simeq 10^3$ and $\frac{x_1}{x_2} \simeq 200$ or $\sigma_{11}/\sigma_{22} \simeq 10$ to 100. This mass, concentration and σ - ratios can occur in ionised gases. In tables 27 and 25 the variations of ($k_T^{(2)}/k_T^{(1)}$) with (M_1/M_2) (σ_{11}/σ_{22}) and (x_1/x_2) are given. By comparing the corresponding values of this table with that of table 25, we see that the values of ($k_T^{(2)}/k_T^{(1)}$) for $0.1 \leq x_2 \leq 0.9$ are much lower than the corresponding values at the L.G.M. limit.

As far as the absolute values of $k_T^{(2)}$ or $k_T^{(1)}$ for the $\left(\frac{M_1}{M_2} ; \frac{x_1}{x_2}\right)$ and (M_1/M_2 , σ_{11}/σ_{22}) variation concerned they are very different as is clear from tables 29 and 30.

TABLE 27

Ratios of the second order to the first for thermal diffusion ratio (k_T) for various mass and σ ratios. (Rigid sphere; σ_{22} = 1 Å, $x_1 = x_2 = 0.5$ M_2 = 1.0gm)

$(k_T^{(2)} / k_T^{(1)})$

M_1/M_2 \ σ_{11}/σ_{22}	10	10^2	10^3	10^4	10^5
1	1.09352	1.11097	1.11275	1.11291	1.11293
10	1.13686	1.15759	1.15944	1.15962	1.15963
10^2	1.13978	1.16031	1.16213	1.16230	1.16231
10^3	1.13986	1.16040	1.16216	1.16234	1.16235
10^4	1.1398	1.16041	1.16216	1.16234	1.16235
10^5	1.1398	1.16041	1.16216	1.16234	1.16235

TABLE 28

Ratios of the second order to the first for thermal diffusion ratio (k_T) for various mass and concentration ratios (Rigid sphere ; $\sigma_{22} = \sigma_{11} = 1.0\text{Å}$, $M_2 = 1.0\text{gm}$)

$(k_T^{(2)}/k_T^{(1)})$

n_1/n_2 \ M_1/M_2	10	10^2	10^3	10^4	10^5
1	1.09353	1.11097	1.11275	1.11291	1.11293
19	1.12621	1.15552	1.15788	1.15806	1.15808
1.99×10^2	1.12898	1.15934	1.16172	1.161913	1.16193
1.999×10^3	1.12925	1.15972	1.16210	1.16229	1.16231
1.99×10^4	1.12928	1.115976	1.16214	1.16233	1.16235
1.99×10^5	1.12928	1.115976	1.16215	1.16233	1.16235

TABLE 29

Absolute values of the first order for thermal diffusion ratio (k_T) for various mass and concentration ratios (Rigid sphere : $\sigma_{22} = \sigma_{11} = 1.0\dot{A}$, $M_2 = 1.0gm$)

($k_T^{(1)} \times 10^2$)

M_1/M_2 \ x_1/x_2	10	10^2	10^3	10^4	10^5
1	12.58	13.33	13.39	13.40	13.40
19	1.887	1.879	1.880	1.880	1.880
199	0.1938	0.1918	0.1919	0.1919	0.1919
2×10^3	.01943	0.1922	0.01923	0.01923	0.01923
2×10^4	.001944	.001923	.001923	0.001923	0.00192

Also we conclude from figs.24 and 25 that the limiting value of $(k_T^{(2)}/k_T^{(1)})$ for the limits $(M_1 \gg M_2 ; \varkappa_2 \gg \varkappa_1)$ and $(M_1 \gg M_2 ; \sigma_{22} \gg \sigma_{11})$ is not the same. The former limit corresponds to the quasi L.G.M. limit in Devoto's work (De-66). While the latter limit is different and higher than the former. For $(k_T^{(2)}/k_T^{(1)})$ the quasi L.G.M. limit for all practical purpose is reached for $M_1/M_2 \simeq 10^3$ and $\varkappa_2/\varkappa_1 \simeq 200$ while the $(M_1 \gg M_2 ; \sigma_{22} \gg \sigma_{11})$ limit is reached when $M_1/M_2 \simeq 10^3$ and $\sigma_{22}/\sigma_{11} \simeq 10$ to 10^3. Both the sets of values, again, can occur for slightly dusty or foggy gases.

vi) <u>COMPARISON OF DIFFERENT COEFFICINETS:</u>

(1) Behaviour of $\eta_{mix}^{(n)} / \eta_{mix}^{(1)}$ and $\lambda'^{(n)}_{mix} / \lambda'^{(1)}_{mix}$ for different values of X_2 is similar and that of $(D_{12}^{(n)}/D_{12}^{(1)})$ and $(k_T^{(n)}/k_T^{(1)})$ is similar. This is clear from tables 7, 10, 18 and 25. Also this is shown in figs 1, 5, 15 and 21. The difference in the two sets is that in the former set we get maxima for various ratios at $X_2 = 0.5$ and for the latter set there is no maximum. Also in the former set the rate of decrement is only slightly dependant upon X_2 while in the latter set the rate of decrement is greatest for large values of X_2.

(2) By comparing tables 7, 10, 18 and 25 we note that the rate of decrement is large for all coefficients but it is

greatest in the case of viscosity. Also the details of the dependence of convergence upon the parameters are different for different coefficients, as discussed earlier.

(3) The absolute values of $\eta^{(n)}_{mix}$ and $\lambda'^{(n)}_{mix}$ (Tables 6 and 9) increase with increasing x_2 for the Ar-Ne mixture while for $D^{(n)}_{12}$ (Table 17) they decrease with increasing x_2. In the case of $k^{(n)}_T$ (Table 24), these values show a maxima at $x_2 \simeq 0.5$.

(4) For D_{12} and k_T, the limits ($M_1 \gg M_2$, $x_1 \gg x_2$) and ($M_1 \gg M_2$, $\sigma_{11} \gg \sigma_{22}$) are equivalent while the limits ($M_1 \gg M_2$, x_1, x_2) and ($M_1 \gg M_2$, $\sigma_{22} \gg \sigma_{11}$) are not equivalent for λ_{mix}.

(5) The L.G.M. limit ($M_1 \gg M_2$, $x_1 \gg x_2$ or $\sigma_{11} \gg \sigma_{22}$) for $(k^{(n)}_T/k^{(1)}_T)$, $\lambda^{(n)}_{mix}/\lambda^{(1)}_{mix}$ and $(D^{(n)}_{12}/D^{(1)}_{12})$ are much higher than the corresponding values for $0.1 \leq x_2 \leq 0.9$ which are commonly encountered in the laboratory (see tables 25 and 27, table 12 and 13, table 18 and 20). For $\lambda^{(2)}_{mix}/\lambda^{(1)}_{mix}$, the value for L.G.M. is 11.7% while the corresponding value for mixture of λ'_{mix} $0.1 \leq x_1 \leq 0.9$ is 2.3 to 3.0%. For $(D^{(2)}_{12}/D^{(1)}_{12})$, the L.G.M. limit is 8.21% while the corresponding value for mixture of $0.1 \leq x_1 \leq 0.9$ is 0.6 to 3.0%. For $(k^{(2)}_T/k^{(1)}_T)$ the L.G.M. limit is 16.2% while the corresponding value of mixture of $0.1 \leq x_1 \leq 0.9$ is 5.3 to 7.3%. If one is worried about accuracies only higher than the accuracies of L.G.M. gas, the previous conclusions are very much valid but if one is interested in higher accuracies than the L.G.M. gas, the previous studies seem to be relatively inaccurate (see for example, Ma.-57a, S.M.-66).

C. Lennard-Jones potential.

In the last section, the convergence of the first four orders for the expressions of the transport coefficients, both for the case of the simple gas and for a binary gas-mixture, for various sets of parameters, has been discussed for the rigid sphere potential. A similar type of study will be presented in this section for the Lennard-Jones potential which is more realistic in nature and results in a better agreement between theory and experiment.

The major difficulty in working with the Lennard-Jones potential lies in writing the computer programme for the interaction integrals ($V^{\ell}_{nn'}$) . The interaction integrals were computed by first computing the collision integrals $\Omega^{(\ell,s)}$ following the method of Smith and Munn (S.M.-64). For each temperature T^* ($T^* = k\,T/\epsilon$, where k is the Boltzmann constant, T is the absolute temperature and ϵ is the depth of the potential well) all the interaction integrals needed for a calculation upto particular order were stored on the disc and, later on, these values were used for computing various transport coefficients for that order. A brief outline for writing the computer programme for the interaction integrals ($V^{\ell}_{nn'}$) is given in appendix A.

In the present computation no attempt was made to compute the interaction integrals ($V^{\ell}_{nn'}$) directly. It was thought that in this first calculation it would be better to have the intermediate $\Omega^{(\ell,s)}$ for purposes of checking with earlier work. In future work the values of $V^{\ell}_{nn'}$ obtained here may be used for checking the output of programs for directly computing the $V^{\ell}_{nn'}$. The computer time becomes an important factor when an extensive calculation for the coefficients is to be done. A direct computation of $V^{\ell}_{nn'}$, from eqn. (2.41) could then be more economical for computer time.

All the calculations in this section were done to the seventh decimal place but the results given in the tables have been rounded off to the fourth decimal place. As mentioned earlier, in the discussion of the computational errors in the introduction of this chapter, the accuracy of the calculations of $\Omega^{(\ell,s)}$ and therefore of $V^{\ell}_{nn'}$ is only 1 to 2 in 10^3. The question therefore arises whether we can place any reliance on the differences between the values of the coefficients in, say, third and fourth orders which is also of the same magnitude. Our reasons for thinking that these comparisons are valid are several. Firstly, it appears that although the absolute values of the transport coefficients are sensitive to the errors in the

$V^{\ell}_{nn'}$ (so that the comparisons with the experimental data will not be meaningful beyond those errors) the difference between calculations upto different orders may not be sensitive to errors in $V^{\ell}_{nn'}$. Secondly, the pattern of these differences in case of Lennard-Jones potential is quite similar to that in the case of rigid sphere potential where the accuracy is manifestly sufficient. The continuous and orderly behaviour of these differences lends further support to the view that they are significant. Finally, we note that in recent tabulations (M.M-61) the values of $\Omega^{(\ell,s)}$ themselves are quoted upto sixth decimal place. Our values agree with these values and it appears that these calculations are perhaps more reliable than the limits quoted above from the previous estimations.

The outline of this section is similar to that of the last section (rigid sphere potential) i.e. first the simple gas and, then, binary gas mixtures are discussed. It may be pointed out here that, in the literature, a lot of interest has been shown to study experimentally the temperature dependence on the values of the binary gas-coefficients. (K.K.W-66, [illegible], G.M-61). A systematic study for the temperature dependence on the theoretical values for the four orders has been done for the simple gas and for the Ar-Ne gas-mixtures.

(a) SIMPLE GAS

For the Lennard-Jones potential, the only case in which systematic calculations have been done for higher orders is that of a simple gas where Hirschfelder et al have given a table of the ratios ($\eta^{(3)}/\eta^{(1)}$) and ($\lambda^{(3)}/\lambda^{(1)}$) for various values of the parameter T (H.C.B.-64, Table I-A, p. 1110.) These values are independent of the range parameter σ as can be seen from eqns. (5.1) and (5.3) , $T^{*} = (kT/\epsilon)$, therefore, serves as a universal parameter for all gases. (It will be noted that in case of a binary gas-mixture three values of ϵ and are involved and hence no single universal parameter can be formed. Therefore, in that case we shall present the results in terms of T itself.)

As a first check for our calculations, we computed the values of ($\eta^{(n)}/\eta^{(1)}$) and ($\lambda^{(n)}/\lambda^{(1)}$) for n= 2.3.4 for different values of T . These values are placed in tables 31 and 32 and in figs. 26 and 27, these ratios for n = 2 and n = 3 against T^{*} are shown. The crosses in these figures represent the values taken from Hirschfelder et al (H.C.B.-64, Table I-P, p. 1130). This shows a good agreement between our set of values for n = 3 and the Hirschfelder et al's values.

TABLE 31.

Ratios of the first four orders to the first of viscotity (η) for a simple gas for different values of T^* for the L.J. potential.

T^*	$\eta^{(2)}/\eta^{(1)}$	$\eta^{(3)}/\eta^{(1)}$	$\eta^{(4)}/\eta^{(1)}$
0.4032	1.00033	1.00049	1.00052
1.6128	1.00050	1.00053	1.000538
3.2256	1.0037	1.00373	1.00373
4.8384	1.0055	1.00565	1.00566
6.4512	1.00637	1.00661	1.00663
8.0640	1.0068	1.00709	1.00711
16.128	1.00748	1.00786	1.00790
24.192	1.00757	1.00796	1.0080
32.256	1.00761	1.0080	1.00804
40.32	1.00762	1.0080	1.00805

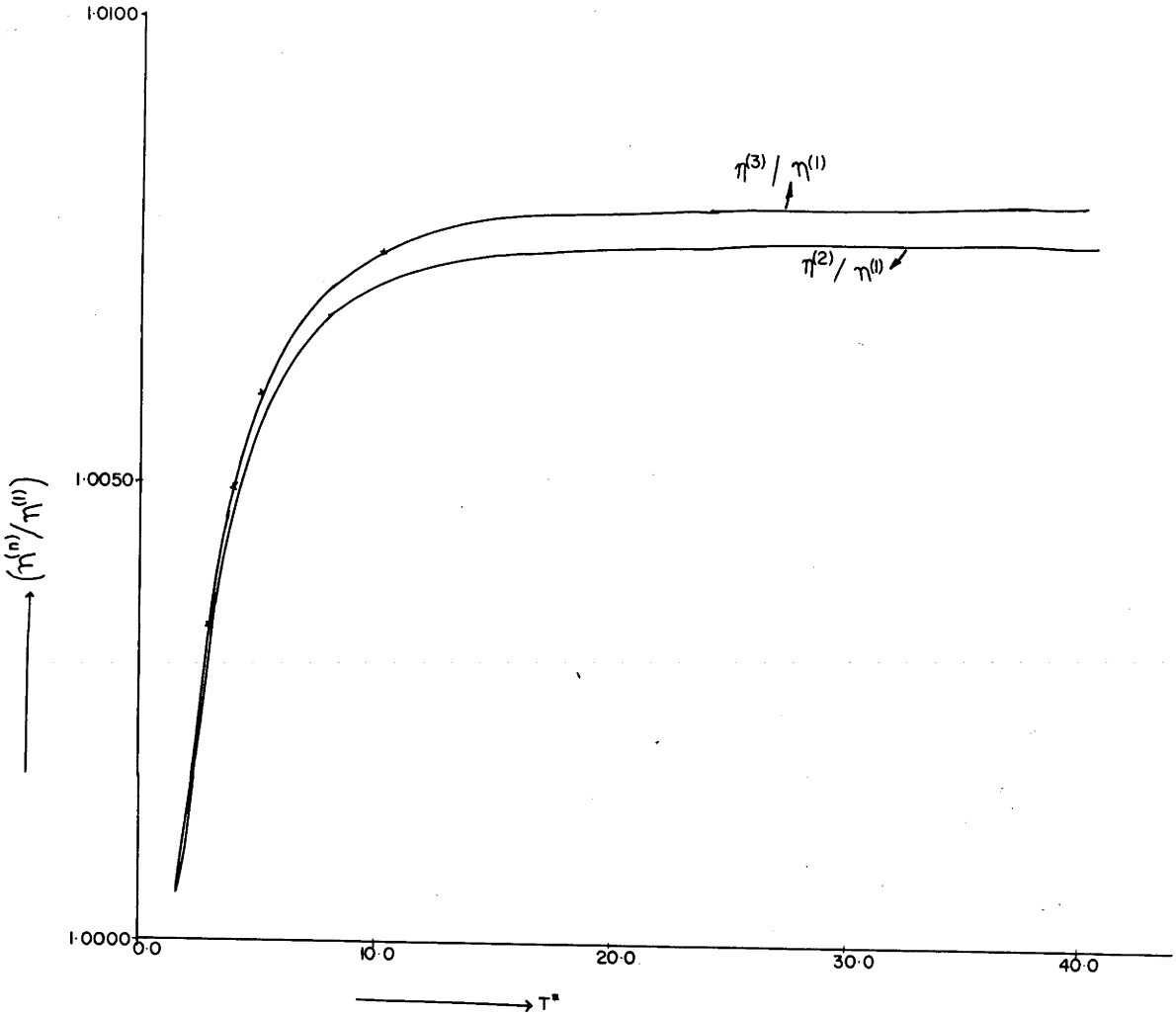

Fig. 26 .. Ratios of the second and third orders to the first of viscosity (η) for the simple gas vs. T* for the L.J. potential. Crosses indicate the values taken from Hirschfelder et al (H.C.B-64, Table I-P) for $(\eta^{(3)}/\eta^{(1)})$. The curve corresponding to $(\eta^{(4)}/\eta^{(1)})$ is not shown but it lies very close and above $(\eta^{(3)}/\eta^{(1)})$ curve.

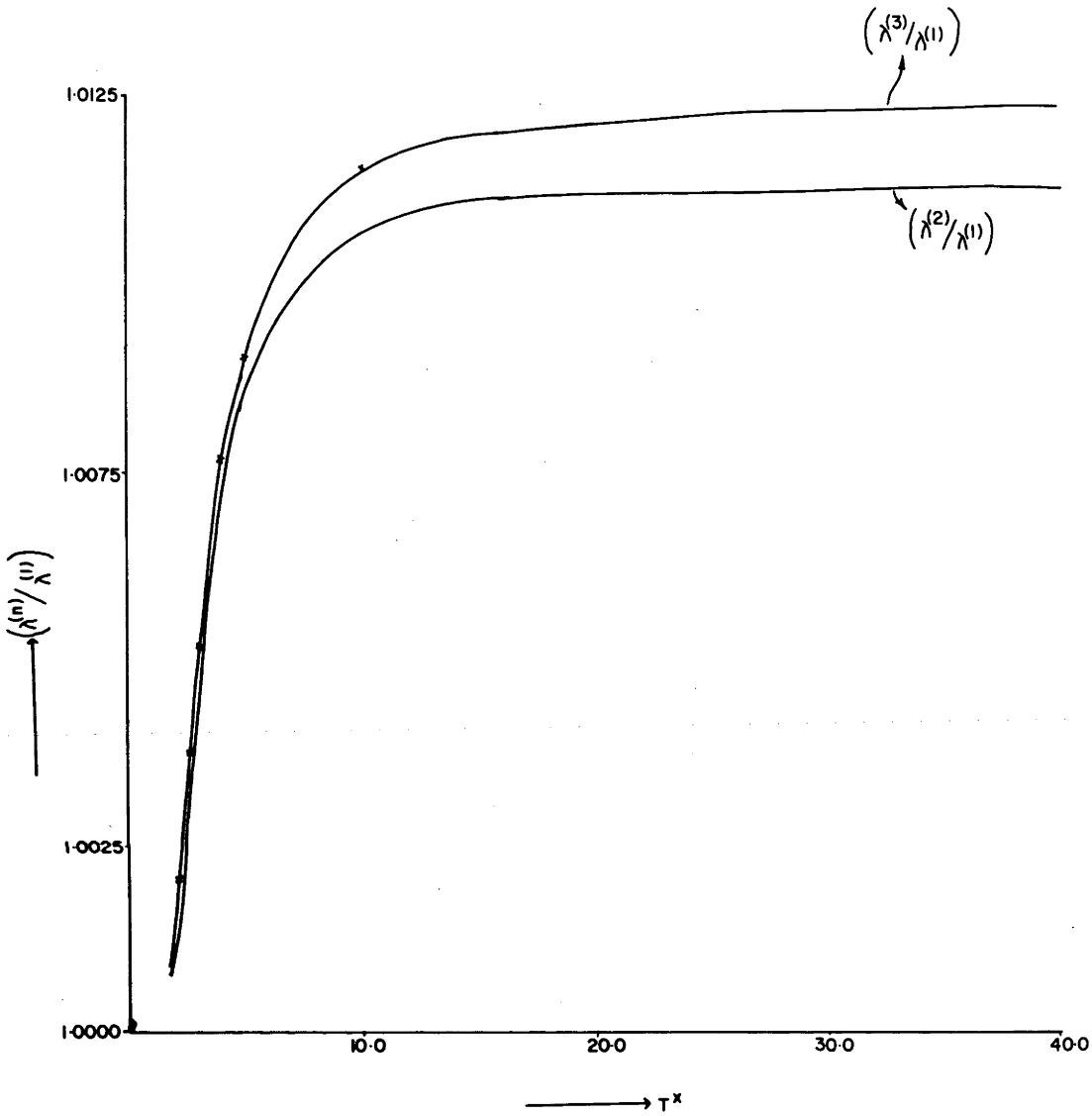

Fig. 27 .. Ratios of the second and third orders to the first of thermal-conductivity (λ) for the simple gas vs. T^* for the L.J. potential. Crosses indicate the values taken from the Hirschfelder et al values (H.C.B-64, Table I-P) for $(\lambda^{(3)}/\lambda^{(1)})$. The curve corresponding to $(\lambda^{(4)}/\lambda^{(1)})$ is not shown but it lies very close and above $(\lambda^{(3)}/\lambda^{(1)})$ curve.

The ratios for the two coefficients are universal functions of T^*, thus, these figures and tables can be used for calculating $\eta^{(n)}$ and $\lambda^{(n)}$ (n = 2,3,4) once, $\eta^{(1)}$ and $\lambda^{(1)}$ have been calculated.

Comparing the corresponding values of these tables with those of table 5 for rigid sphere potential, we notice that for all T, the rate of decrement for the first four orders is more rapid in the present case. As for the rigid sphere here also the rate of decrement for the first four orders is more rapid for η than for λ (Compare these tables 31 and 32).

Since it may be of some interest to show the absolute magnitude we give, in figure 28 and 29, the values of η and λ plotted against T for the case of Ar-gas. The force constants are given in table 34 and the values of $\eta^{(1)}$ and $\lambda^{(1)}$ are given in table 33. It is to be noted from the figures that the contributions from the orders higher than the first are appreciably different only at high temperatures.

(b) BINARY GAS-MIXTURES

In this section, the rate of decrement of the first four orders of all the coefficients with concentration and temperature is

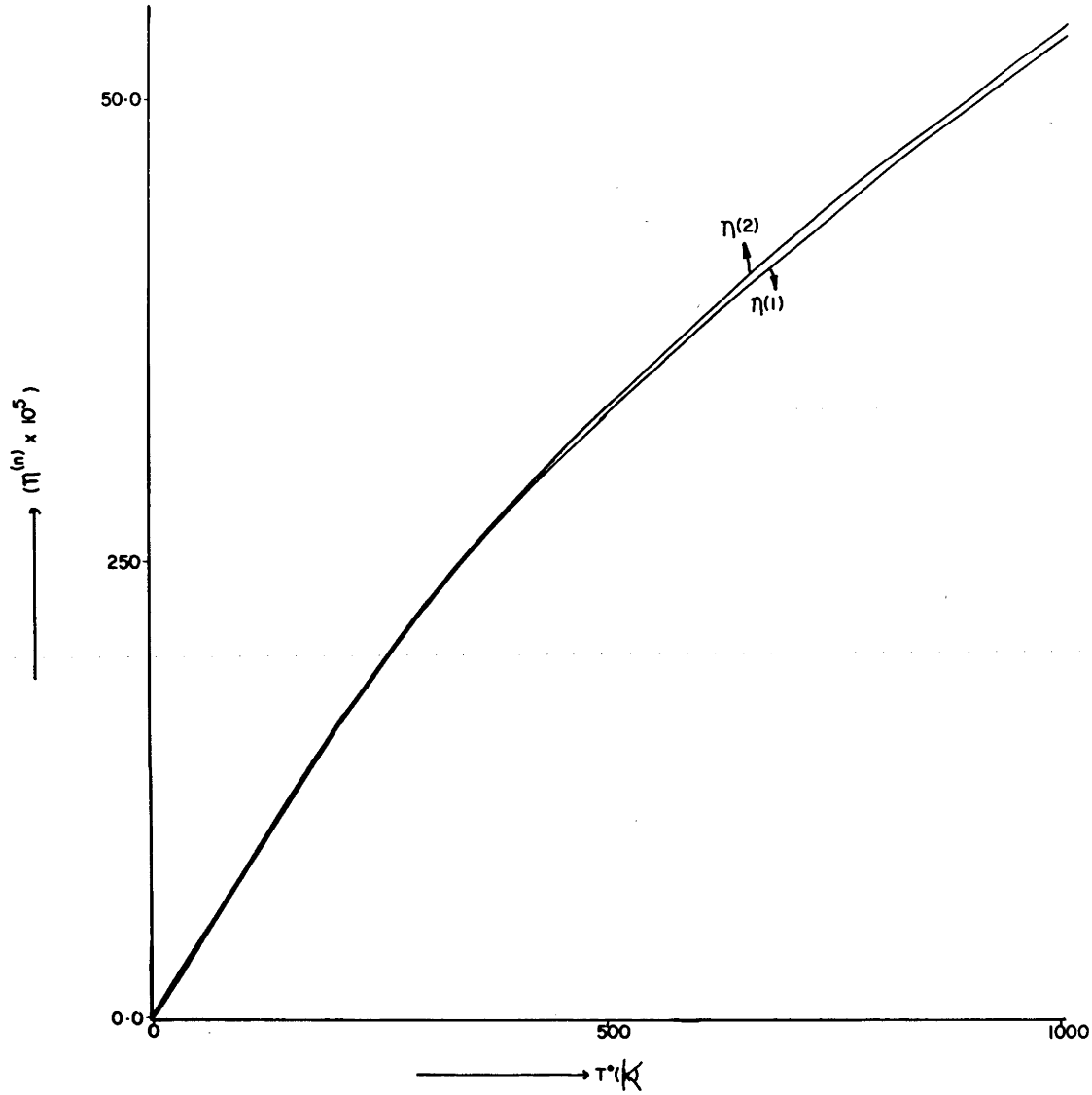

Fig. 28 .. Theoretical values of the first and fourth orders of viscosity (η) for Ar vs. T for the L.J. potential. Curves corresponding to $\eta^{(2)}$ and $\eta^{(3)}$ are not shown. These curves lie very close and below $\eta^{(4)}$ curve.

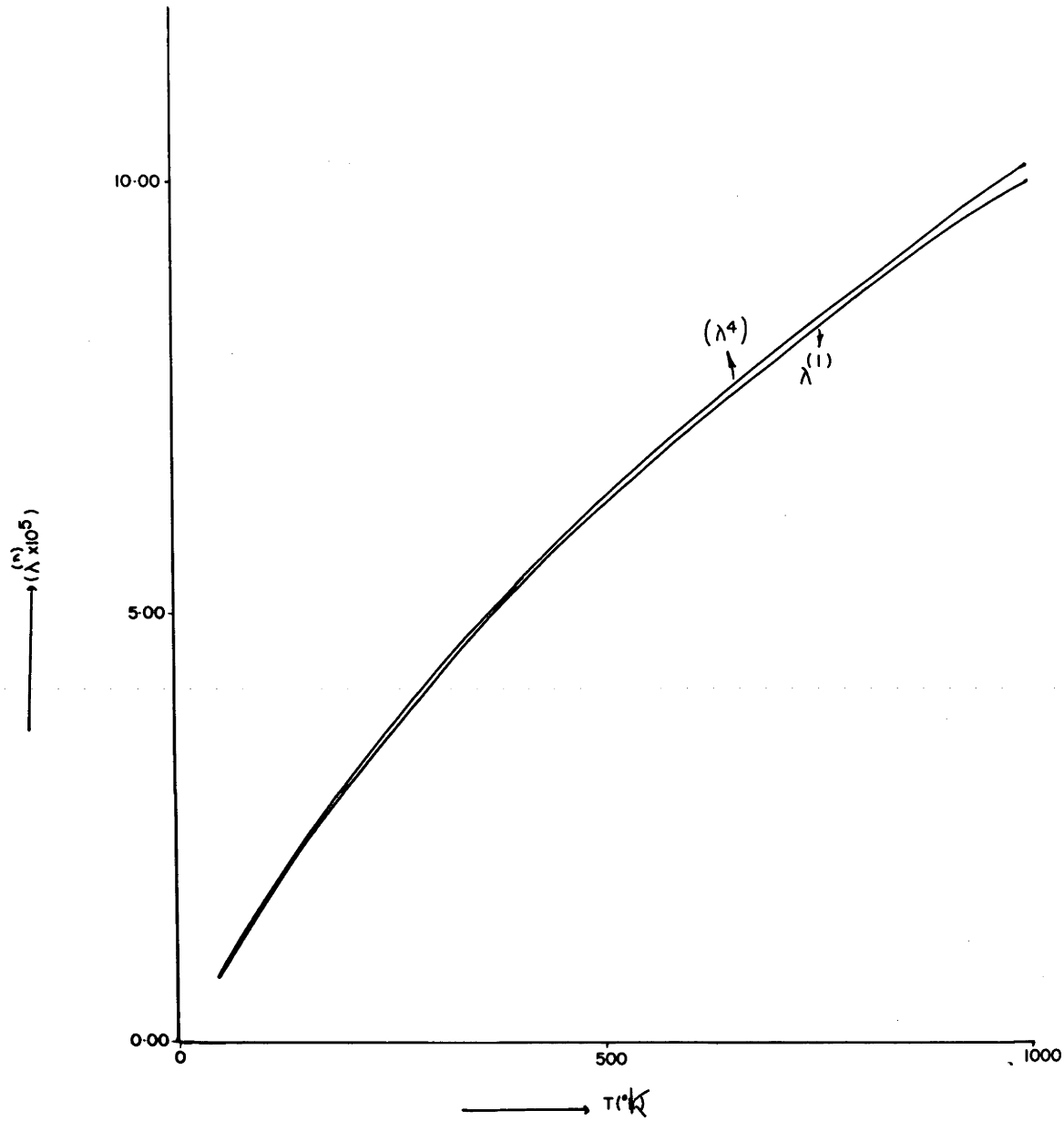

Fig. 29 .. Theoretical values of the first and fourth orders of thermal-conductivity (λ) for Ar vs. T for the L.J. potential. Curves corresponding to $\lambda^{(2)}$ and $\lambda^{(3)}$ are not shown. They lie very close and below $\lambda^{(4)}$ curve.

TABLE 33.

Theoretical values of the first order of viscosity (η) and thermal-conductivity (λ) for Ar for different temperatures for the L.J. potential.

$T^{o}(K)$	$\eta^{(1)}$ $(\times 10^{5})$	$\lambda^{(1)}$ $(\times 10^{5})$
50	4.065	0.7582
200	15.971	2.979
400	28.312	5.280
600	37.927	7.073
800	46.187	8.614
1000	53.587	9.994

TABLE 34.

Force constants used in this work for the different gas-systems for the Lennard-Jones potential. These values have been taken from Hirschfelder et al's book (H.C.B.-4, Table I-A).

Gas	ϵ/k (°K)	σ (°A)
Xe	229.	4.055
Kr	190.	3.61
A	124.	3.418
Ne	35.7	2.789
He	10.22	2.576

studied. Again subscript (1) refers to the heavier component and (2) to the lighter.

Concentration dependence studies have been done for four gas-mixtures which are Ar-Ne , Kr-Ne , Kr-He and Xe-Kr . The force constants for individual gas systems are given in table 34 and have been taken from Hirschfelder et al (H.C.B.-64), Table I-A, p. 1110). Only these sets of constants are used in the work of this section and the next chapter. The force constants for interaction between unlike molecules are obtained by using the combination rules

$$\epsilon_{12} = (\epsilon_1 \epsilon_2)^{1/2} \text{ and } \sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) .$$

All the subsequent calculations in this section and the next chapter are based on these combination rules.

The results of the concentration dependence studies may be grouped in two parts.

(1) For viscosity (η_{mix}) and thermal-conductivity (λ'_{mix}) experimental values (Th-60, Th.-61, T.B.-62) and the absolute values of the first four orders are given in tables (35-38) and (42-45) and also in figs. (30, 46-48, 34, 49-51). The ratios of the first four orders are given only for Ar-Ne system

(Tables 39, 42, Figs. 31, 35). Inferences about the rate of decrement are similar for the other gas-systems. The reason for the apparently unsystematic choice for the values of $x_2 (= n_2/(n_1 + n_2))$ in these calculations is that in the next chapter we shall be interested in making some comparison with the experimental data which are available only for these values of x_2. This is also the reason for the choice of the four particular gas-mixtures to be studied here.

(2) For diffusion $(\mathcal{D}_{12})$ as in the case of rigid sphere, we had to calculate first five orders of $\mathcal{D}_{12}$ in order to calculate the first four orders of k_T. For $\mathcal{D}_{12}$, the values for the first five orders and for k_T the values for the first four orders are given for the Ar-Ne and Kr-Ne mixtures in tables (49, 50, 54 and 55) and in figs. 38 and 42. The ratios of the first five (four) orders to the first for $\mathcal{D}_{12}$ (k_T) are given for the Ar-Ne mixture alone (Tables 51, 56, Figs. 39, 43). The behaviour of the Kr-Ne system is similar. The other system Kr-He and Xe-Kr were also studied but the results will not be presented here because they are similar to those for the Ar-Ne case in most details and no experimental data are available for these cases.

For the temperature dependence studies, only the Ar-Ne system was studied for all the coefficients. The temperature range was 50°-1000° K and $x_1 = x_2 = 0.5$. The absolute values of the first four order (five orders in case of D_{12}) are placed in figs. (32, 36, 40 and 44) and in tables (40, 47, 52 and 57). The ratios of the first four (five for D_{12}) orders to the first of all the coefficients are placed in figs. (33, 37, 41 and 45) and in tables (41, 48, 53 and 58). The behaviour of the other systems with temperature is expected to follow the same pattern.

The results obtained from these tables and graphs have been grouped together for each coefficient and are discussed below. Finally a comparison is made among the behaviour of all these coefficients in section (V-C. b-v).

i) Viscosity (Tables 35-41, Figs. 30-33, 46-48).

In the literature the only higher order calculation for the Lennard-Jones potential is for the second order in case of N_2-He mixture (K.K.W-66) for which it is stated that for $0.5 \leq x_2 \leq 1.0$, there is an overlap between the first and second order of the theory.

Our results for various gas-mixtures are placed in figs. (30-33, 46-48) and in tables (35-41).

Convergence of the first four orders.

1) With concentration.

The absolute values of the first four orders for various mixtures are given in table (35-38) and in figs. (30, 46-48) for different values of x_2 while the ratios of the first four orders to the first for Ar-Ne system is given in table 39. These ratios for other gas systems are similar to those for the Ar-Ne system and vary only in the third decimal place. The table for the ratios for the Ar-Ne system shows that the rate of decrement of the second, third and fourth orders is very rapid. The $(\eta^{(3)}_{mix} / \eta^{(1)}_{mix})$ ratio differs from the $(\eta^{(4)}_{mix} / \eta^{(1)}_{mix})$ ratio only in the fifth decimal place. These ratios are plotted in fig. 31 for different values of x_2. This figure shows that the contribution to the orders higher than the first goes on increasing when x_2 is increasing (or x_1 is decreasing). It means that when the heavier component is in a minority, the contribution of the second and higher order to η_{mix} reaches a maximum value. This supports the comment of Storvick and Mason (S.M.-66) that for viscosity of a binary gas-mixture, since

TABLE 35.

Theoretical values of the first four orders of viscosity (η_{mix}) for the Ar-Ne mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	(η_{mix}) x 10^6 exp	$\eta_{mix}^{(1)}$ (x 10^6)	$\eta_{mix}^{(1)}$ (x 10^6)	$\eta_{mix}^{(3)}$ (x 10^6)	$\eta_{mix}^{(4)}$ (x 10^6)
0.10	228	227.4	228.0	228.0	228.0
0.197	236	234.4	235.1	235.1	235.1
0.274	239	240.2	241.0	241.1	241.1
0.362	247	247.1	248.1	248.2	248.2
0.459	255	255.2	256.4	256.4	256.4
0.564	267	264.5	265.8	265.9	265.9
0.692	278	274.6	276.2	276.2	276.2
0.779	285	285.3	287.0	287.1	287.1
0.843	290	292.0	293.8	293.9	293.9

TABLE 36.

Theoretical values of the first four orders of viscosity (η_{mix}) for the Xe-Kr mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\eta_{mix})_{exp}$ $\times 10^6$	$\eta_{mix}^{(1)}$ $\times 10^6$	$\eta_{mix}^{(2)}$ $\times 10^6$	$\eta_{mix}^{(3)}$ $\times 10^6$	$\eta_{mix}^{(4)}$ $\times 10^6$
0.104	228	225.1	225.1	225.1	225.1
0.214	229	227.3	227.3	227.3	227.3
0.307	233	229.2	229.2	229.2	229.2
0.405	233	231.3	231.3	231.3	231.3
0.509	237	233.5	233.5	233.5	233.6
0.603	238	235.6	235.6	235.6	235.6
0.704	240	237.9	237.9	237.9	237.9
0.799	243	240.1	240.2	240.2	240.2
0.885	245	242.2	242.2	242.2	242.2

TABLE 37.

Theoretical values of the first four orders of viscosity (η_{mix}) for the Kr-Ne mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\eta_{mix})_{exp}$ (x 10^6)	$\eta_{mix}^{(1)}$ (x 10^6)	$\eta_{mix}^{(2)}$ (x 10^6)	$\eta_{mix}^{(3)}$ (x 10^6)	$\eta_{mix}^{(4)}$ (x 10^6)
0.111	255	252.0	252.3	252.3	252.3
0.203	264	258.2	258.6	258.6	258.6
0.357	275	269.0	269.7	269.7	269.7
0.467	280	277.3	278.2	278.2	278.2
0.562	287	284.5	285.6	285.6	285.6
0.661	294	291.9	293.2	293.2	293.2
0.771	303	299.6	301.1	301.2	301.2
0.889	310	306.2	308.1	308.2	308.2
0.935	312	308.0	310.0	310.1	310.1

TABLE 38.

Theoretical values of hthe first four orders of viscosity (η_{mix}) for the Kr-He mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\eta_{mix})_{exp}$ x 10^6	$\eta_{mix}^{(1)}$ x 10^6	$\eta_{mix}^{(2)}$ x 10^6	$\eta_{mix}^{(3)}$ x 10^6	$\eta_{mix}^{(4)}$ x 10^6
0.109	252	248.7	249.0	249.0	249.0
0.203	254	252.1	252.5	252.6	252.6
0.302	259	255.6	256.3	256.3	256.4
0.400	260	259.1	259.9	259.9	260.0
0.561	263	263.5	264.6	264.7	264.7
0.647	264	264.2	265.5	265.6	265.6
0.728	262	262.7	264.1	264.2	264.2
0.849	249	251.7	253.2	253.3	253.3
0.931	229	231.0	232.5	232.5	232.6

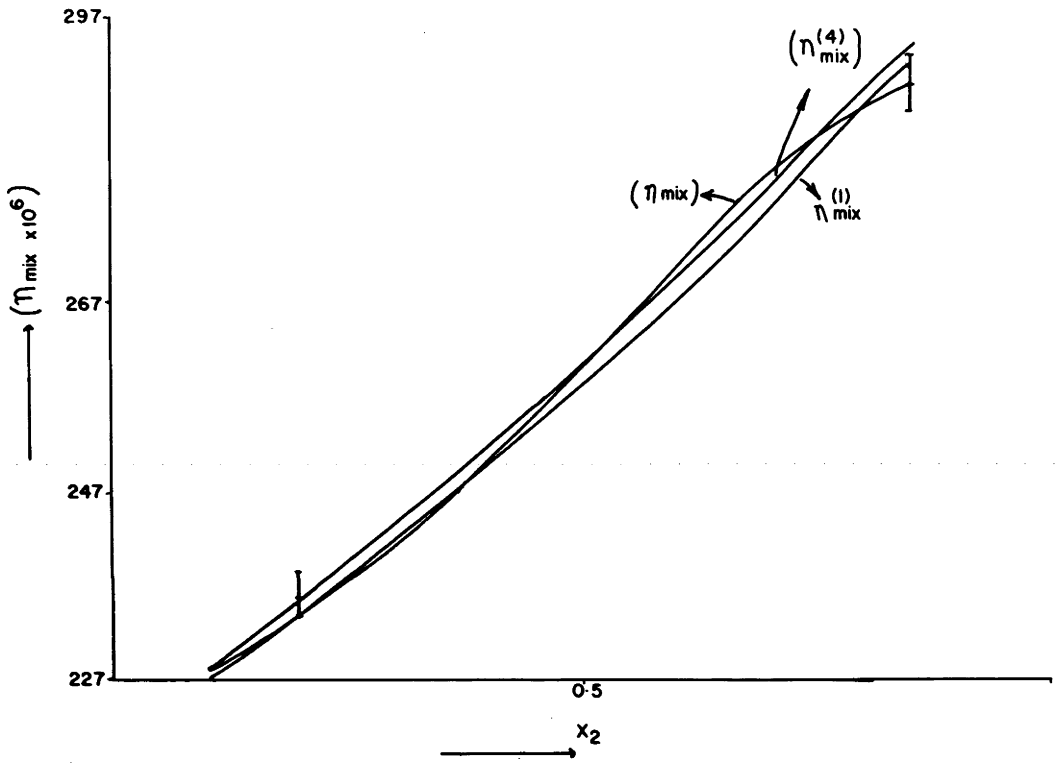

Fig. 30 .. Theoretical values of the first and fourth orders of viscosity (η_{mix}) for the Ar-Ne mixture vs. x_2 for the L.J. potential. Experimental curve with the errors indicated is also drawn. Curves corresponding to $\eta^{(2)}_{mix}$ and $\eta^{(3)}_{mix}$ are not drawn but they lie very close and below $\eta^{(4)}_{mix}$ curve.

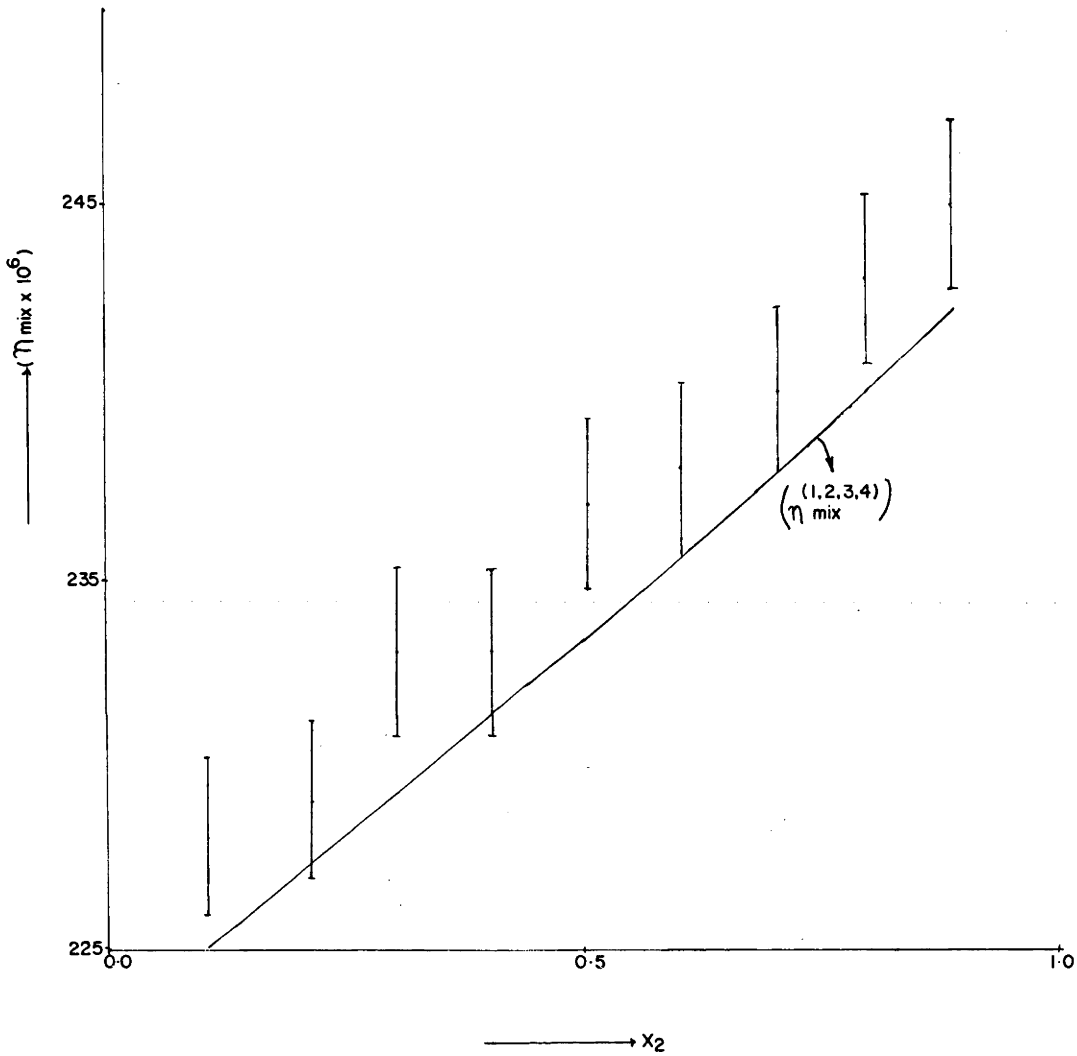

Fig. 46 .. Theoretical values of the first four orders of viscosity (η_{mix}) for the Xe-Kr mixture vs. x_2 for the L.J. potential. All the four curves overlap. Also the experimental points with errors are shown.

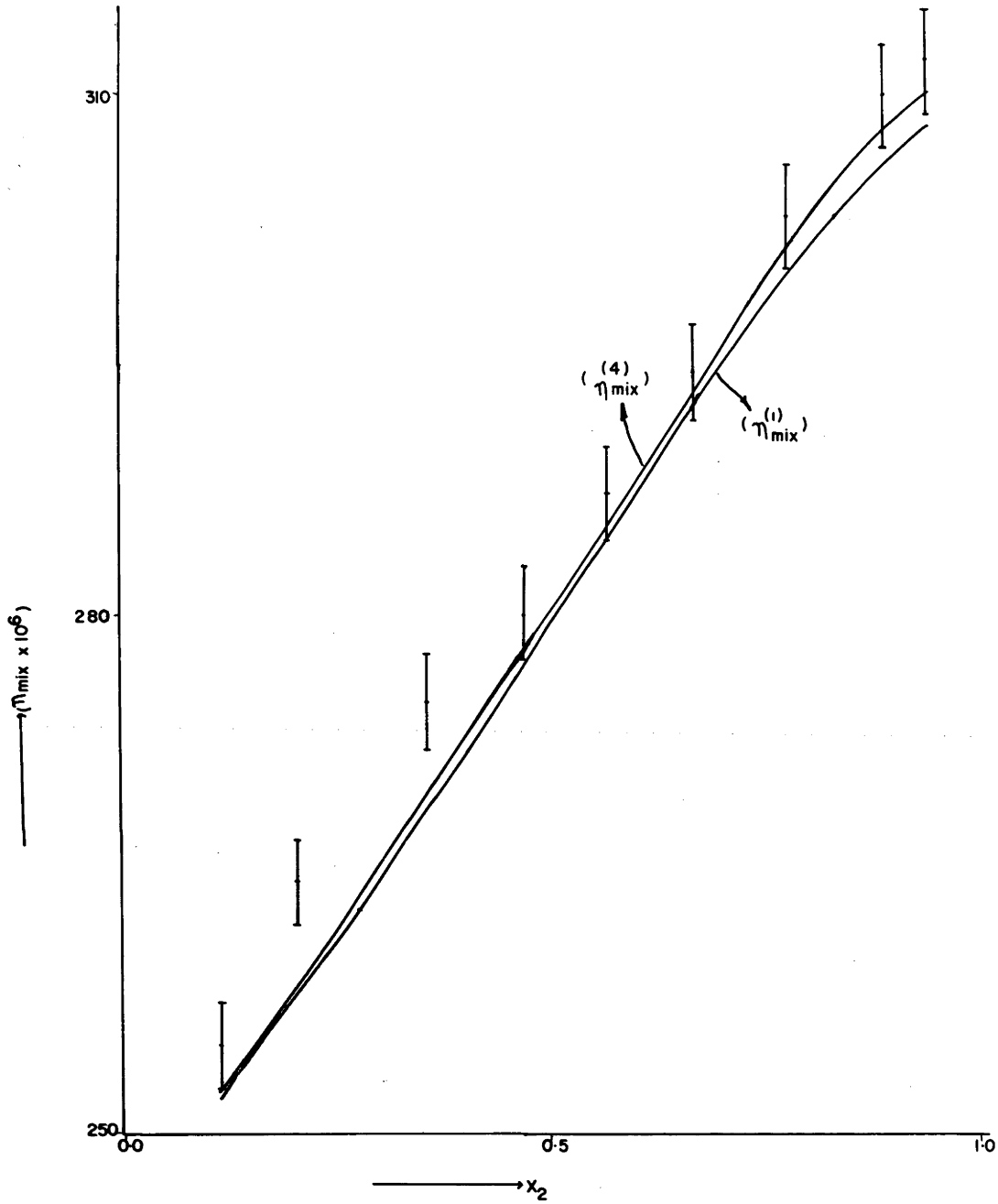

Fig. 47 .. Theoretical values of the first and fourth orders of viscosity (η_{mix}) for the Kr-Ne mixture vs. x_2 for the L.J. potential. Curves corresponding to ($\eta^{(2)}_{mix}$) and ($\eta^{(3)}_{mix}$) are not drawn. These curves lie very close and below ($\eta^{(4)}_{mix}$) curve. Also the experimental points with errors are shown.

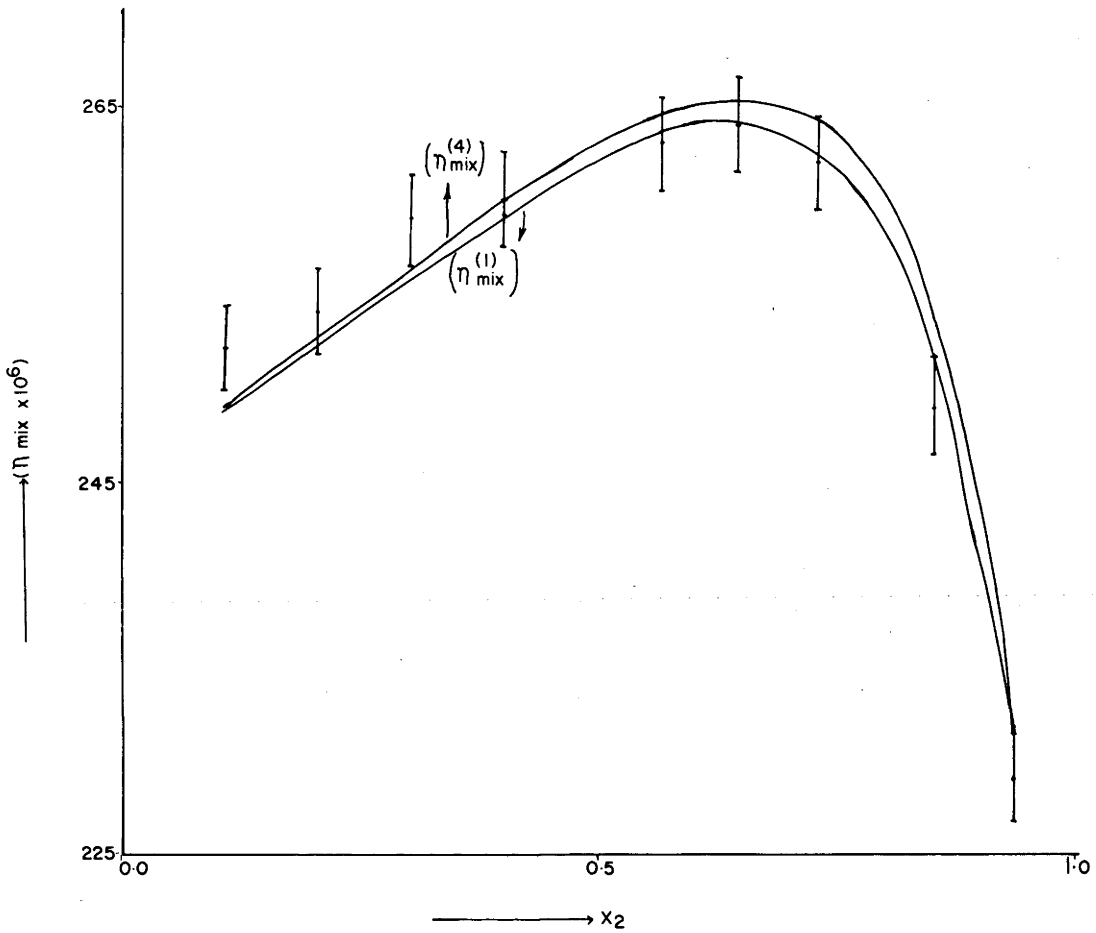

Fig. 48 .. Theoretical values of the first and fourth orders of viscosity (η_{mix}) for the Kr-He mixture vs. x_2 for the L.J. potential. Curves corresponding to $(\eta^{(2)}_{mix})$ and $(\eta^{(3)}_{mix})$ are not drawn. These curves lie very close and below $(\eta^{(4)}_{mix})$ curve. Also the experimental points with errors are shown.

TABLE 39.

Ratios of the first four orders to the first viscosity (η_{mix}) for the Ar-Ne mixture for different values of x_2 for the L.J. potential.

x_2	$\eta^{(2)}_{mix} / \eta^{(1)}_{mix}$	$\eta^{(3)}_{mix} / \eta^{(1)}_{mix}$	$\eta^{(4)}_{mix} / \eta^{(1)}_{mix}$
0.10	1.00261	1.00264	1.00264
0.197	1.00317	1.00323	1.00324
0.274	1.00360	1.00369	1.00369
0.362	1.00408	1.00419	1.00420
0.459	1.00459	1.00473	1.00473
0.564	1.00510	1.00528	1.00528
0.672	1.00560	1.00580	1.00581
0.779	1.00605	1.00628	1.00630
0.843	1.00630	1.00655	1.00656

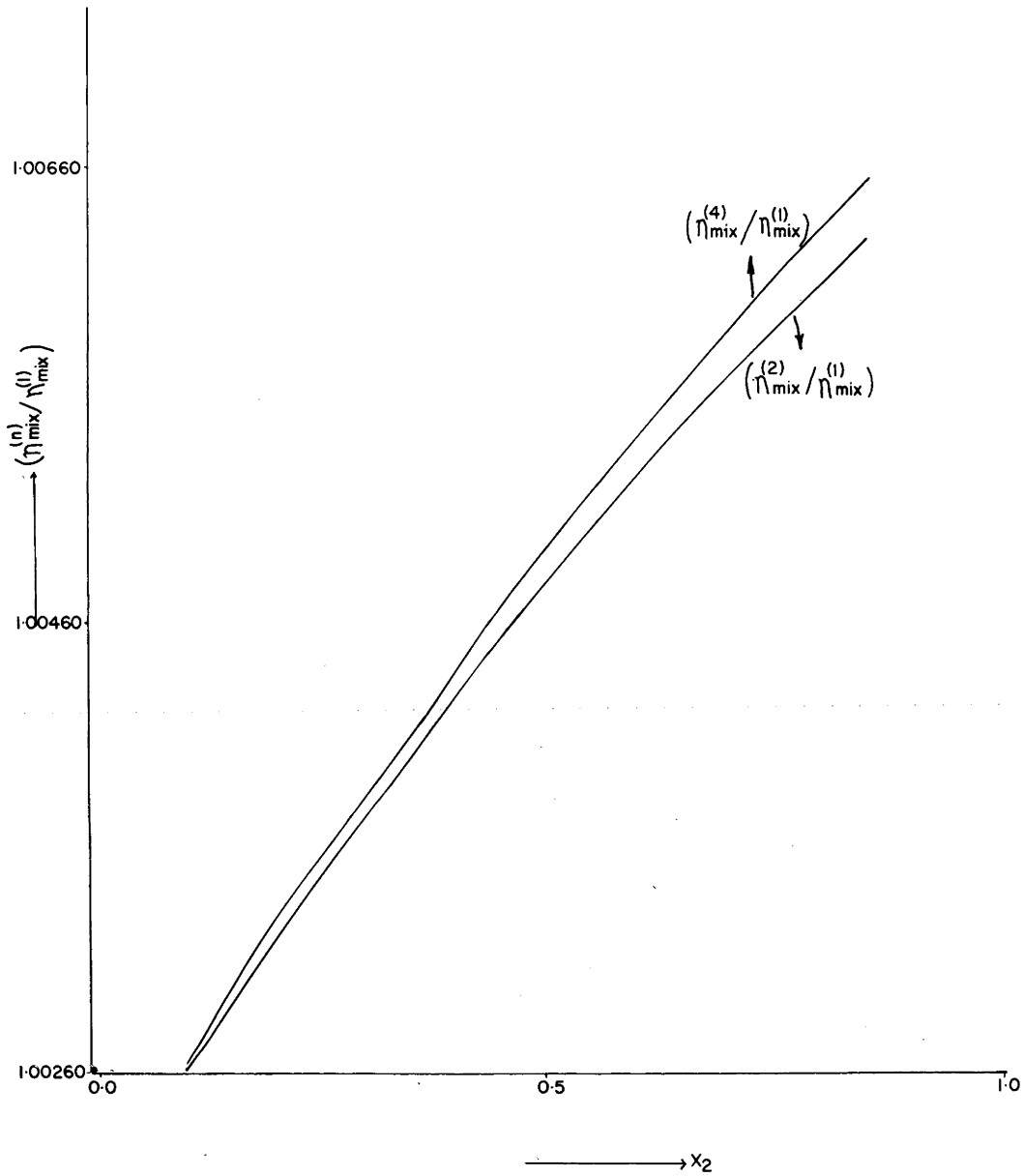

Fig. 31 .. Ratios of the second and fourth orders to the first of viscosity (η_{mix}) for the Ar-Ne mixture vs. x_2 for the L.J. potential. Curve corresponding to $(\eta^{(3)}_{mix}/\eta^{(1)}_{mix})$ is not drawn but it lies very close and below $(\eta^{(4)}_{mix}/\eta^{(1)}_{mix})$ curve.

the heavier component is the momentum carrier, a contribution to the second order of η_{mix} should attain a maximum value when the heavier component is in a minority. This behaviour is valid for all the gas-mixtures. It may be remarked here that unlike the case of rigid sphere, we do not need any restrictions on the mass and concentration ratios (See Fig. 4) for the Lennard-Jones potential. However as we shall see later, the present calculations of λ'_{mix} do not confirm the corresponding comments of Storvick and Mason (S.M.-66) for thermal-conductivity.

1) <u>With Temperature.</u>

The absolute values for the first four orders for various temperatures for $x_1 = x_2 = 0.5$ are given in table 40 for the Ar-Ne system. These values show that there is a continuous increase in $_{mix}$ with temperature for all the orders. This behaviour may be seen in fig. 32. Again as in case of the simple gas, the higher-order contribution are important only at high temperatures.

The ratios of the second, third and fourth orders to the first of η_{mix} are given in table 41 for various temperatures for the Ar-Ne system. It is clear that the rate of decrement for the first four orders is very rapid. This point is clearer in

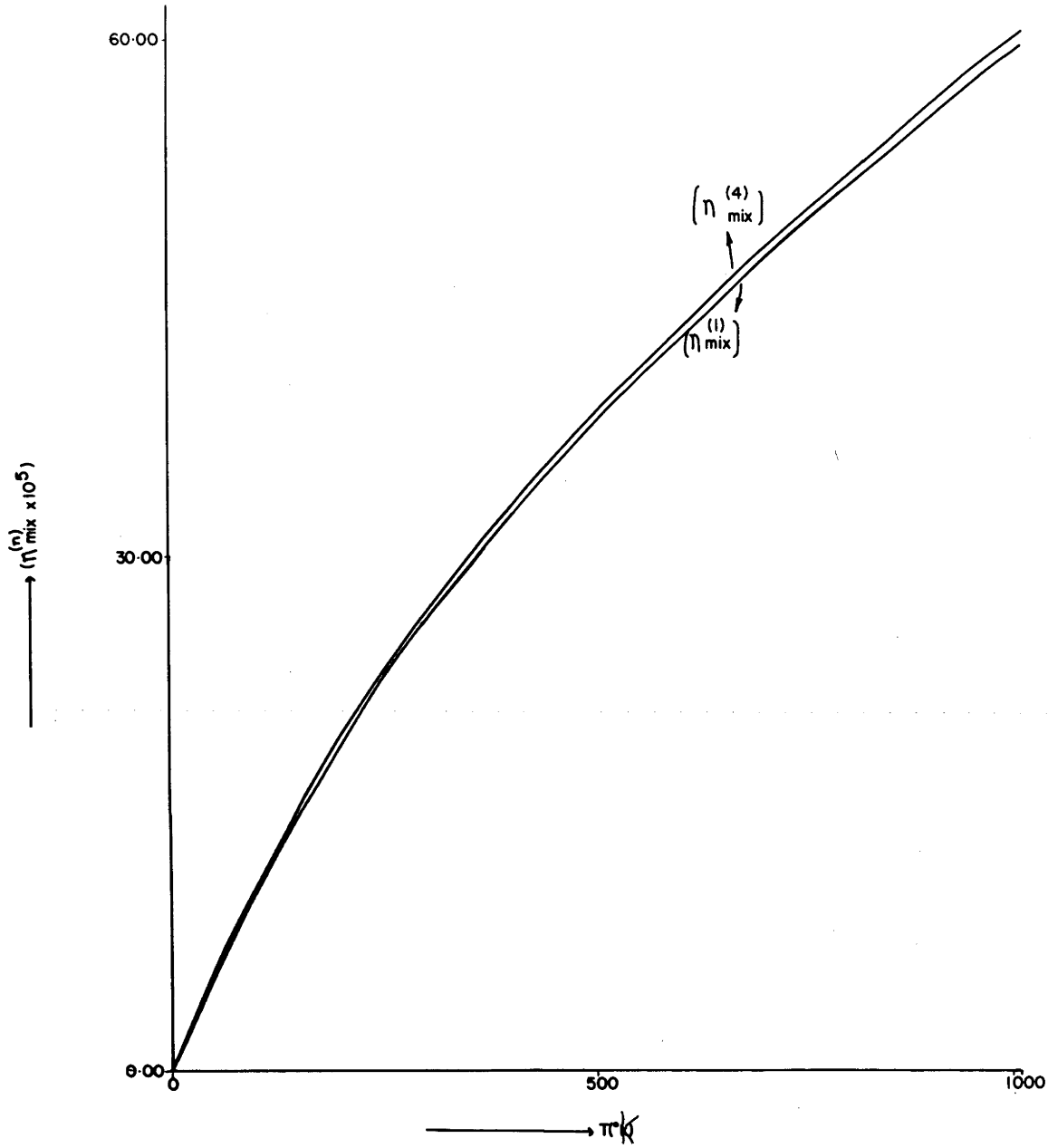

Fig. 32 .. Theoretical values of the first and fourth orders of viscosity (η_{mix}) for the Ar-Ne mixture vs. T for the L.J. potential. Curves corresponding to $\eta^{(2)}_{mix}$ and $\eta^{(3)}_{mix}$ are not drawn but they lie very close and below $\eta^{(4)}_{mix}$ curve.

TABLE 41.

Ratios of the first four orders to the first of viscosity (η_{mix}) for the Ar-Ne mixture for different temperatures for the L.J. potential.

T^{o}(K)	$\eta^{(2)}_{mix} / \eta^{(1)}_{mix}$	$\eta^{(3)}_{mix} / \eta^{(1)}_{mix}$	$\eta^{(4)}_{mix} / \eta^{(1)}_{mix}$
50	1.000047	1.000081	1.000090
200	1.00312	1.00317	1.00318
400	1.00594	1.00619	1.00621
600	1.00695	1.00730	1.00734
800	1.00737	1.00778	1.00782
1000	1.00761	1.00804	1.00809

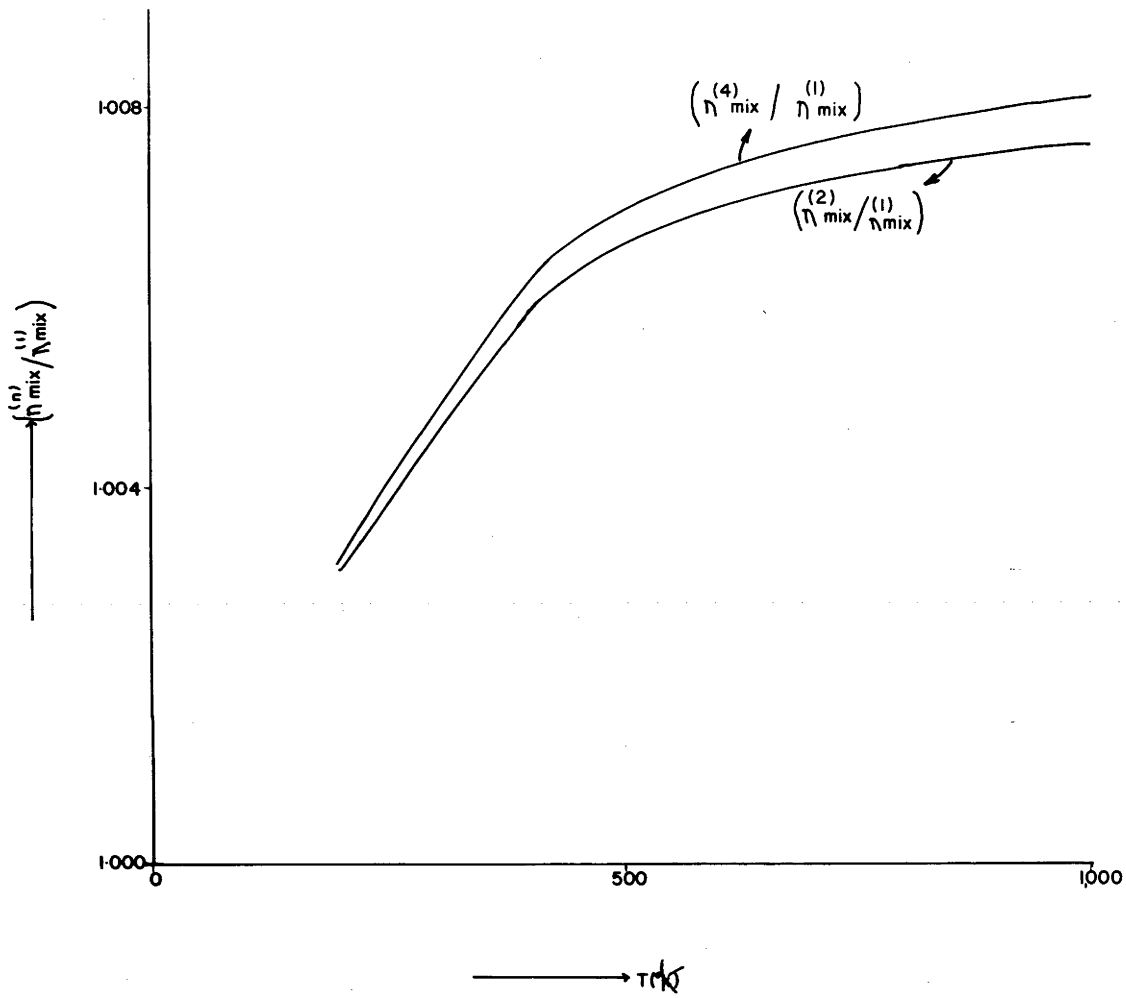

Fig. 33 .. Ratios of the second and fourth orders to the first of viscosity (η_{mix}) for the Ar-Ne mixture vs. T for the L.J. potential. Curve corresponding to $(\eta^{(3)}_{mix}/\eta^{(1)}_{mix})$ is not drawn but it lies very close and below $(\eta^{(4)}_{mix}/\eta^{(1)}_{mix})$ curve.

fig. 33 where these ratios have been plotted for various temperatures. This is to be contrasted with the rigid sphere potential where the rate of decrement of different orders of η_{mix} is independent of temperature.

ii) Thermal-Conductivity (Tables 42-48, Figs. 34-37, 49-51).

In the literature, no higher order calculations for the Lennard-Jones (L.J.) potential is available.

Only the λ'_{mix} part of the general expression of λ'_{mix} (3.122) is considered here. The contribution of the diffusive term was also calculated in all cases and was never found to exceed 0.5% of λ'_{mix}.

The results of the present fourth order calculations are placed in figs. (34-37, 49-51) and in tables (42-48).

<u>Convergence of the first four orders.</u>

i) <u>With Concentration.</u>

The results of the calculations for the four gas-mixtures for different values of x_2 for the λ'_{mix} part are given in tables (42-46) and in figs. (34, 35, 49-51). The discussion of the inferences from these tables and figure is very similar to

TABLE 42.

Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Ar-Ne mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\lambda_{mix})_{exp}$ x 10^7	$\lambda'^{(1)}_{mix}$ (x 10^7)	$\lambda'^{(2)}_{mix}$ (x 10^7)	$\lambda'^{(3)}_{mix}$ (x 10^7)	$\lambda'^{(4)}_{mix}$ (x 10^7)
0.10	470	455.8	458.0	458.1	458.1
0.197	520	502.8	505.9	506.0	506.0
0.274	570	543.2	547.0	547.1	547.1
0.362	620	593.0	597.7	597.9	597.9
0.459	680	653.2	658.9	659.1	659.2
0.564	760	725.5	732.3	732.7	732.7
0.672	840	809.0	817.1	817.5	817.6
0.729	930	902.8	912.1	912.6	912.6
0.843	990	965.0	975.1	975.6	975.7

TABLE 43.

Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Xe-Kr mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\lambda_{mix})_{exp}$ x 10^7	$\lambda'^{(1)}_{mix}$ x 10^7	$\lambda'^{(2)}_{mix}$ x 10^7	$\lambda'^{(3)}_{mix}$ x 10^7	$\lambda'^{(4)}_{mix}$ x 10^7
0.104	138	133.6	133.6	133.6	133.6
0.214	145	141.5	141.6	141.6	141.6
0.307	152	148.6	148.7	148.7	148.7
0.405	160	156.6	156.7	156.7	156.7
0.509	168	165.6	165.7	165.7	165.7
0.603	178	174.3	174.4	174.4	174.4
0.703	187	184.2	184.3	184.3	184.3
0.799	197	194.2	194.3	194.4	194.4
0.885	207	203.9	204.0	204.0	204.0

TABLE 44.

Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Kr-Ne mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\lambda_{mix})_{exp}$ x 10^7	$\lambda'^{(1)}_{mix}$ x 10^7	$\lambda'^{(2)}_{mix}$ x 10^7	$\lambda'^{(3)}_{mix}$ x 10^7	$\lambda'^{(3)}_{mix}$ x 10^7
0.111	257	264.5	265.7	265.7	265.7
0.203	305	308.4	310.5	310.6	310.6
0.357	400	394.1	398.0	398.2	398.2
0.467	482	469.8	475.0	475.3	475.3
0.562	568	545.6	552.0	552.3	552.3
0.661	650	638.7	646.4	646.8	646.8
0.771	780	764.1	773.2	773.7	773.8
0.889	960	933.9	944.6	945.2	945.3
0.935	1030	1013.2	1024.5	1025.1	1025.2

TABLE 45.

Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Kr-He mixture for different values of x_2 for the L.J. potential. The experimental values are also given.

x_2	$(\lambda_{mix})_{exp}$ x 10^7	$\lambda'^{(1)}_{mix}$ x 10^7	$\lambda'^{(2)}_{mix}$ x 10^7	$\lambda'^{(3)}_{mix}$ x 10^7	$\lambda'^{(4)}_{mix}$ x 10^7
0.109	343	344.3	350.2	351.2	351.4
0.203	480	471.0	482.2	484.1	484.5
0.302	642	626.8	643.8	646.5	647.0
0.400	825	809.5	832.5	836.0	836.7
0.561	1210	1196.1	1229.1	1233.6	1234.5
0.647	1530	1465.2	1503.3	1508.1	1509.0
0.728	1850	1776.3	1818.7	1823.6	1824.4
0.849	2500	2393.9	2440.5	2445.0	2445.8
0.931	3050	2972.1	3018.7	3022.5	3023.1

TABLE 46.

Ratios of the first four orders to the first of thermal-conductivity (λ'_{mix}) for the Ar-Ne mixture for different values of x_2 for the L.J. potential.

x_2	$\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix}$	$\lambda'^{(3)}_{mix} / \lambda'^{(1)}_{mix}$	$\lambda'^{(4)}_{mix} / \lambda'^{(1)}_{mix}$
0.10	1.00472	1.00483	1.00485
0.197	1.00607	1.00627	1.00629
0.274	1.00699	1.00726	1.00728
0.362	1.00789	1.00823	1.00825
0.459	1.00872	1.00913	1.00915
0.564	1.00943	1.00990	1.00993
0.672	1.00997	1.01049	1.01052
0.729	1.01033	1.01093	1.01096
0.843	1.01045	1.01103	1.01107

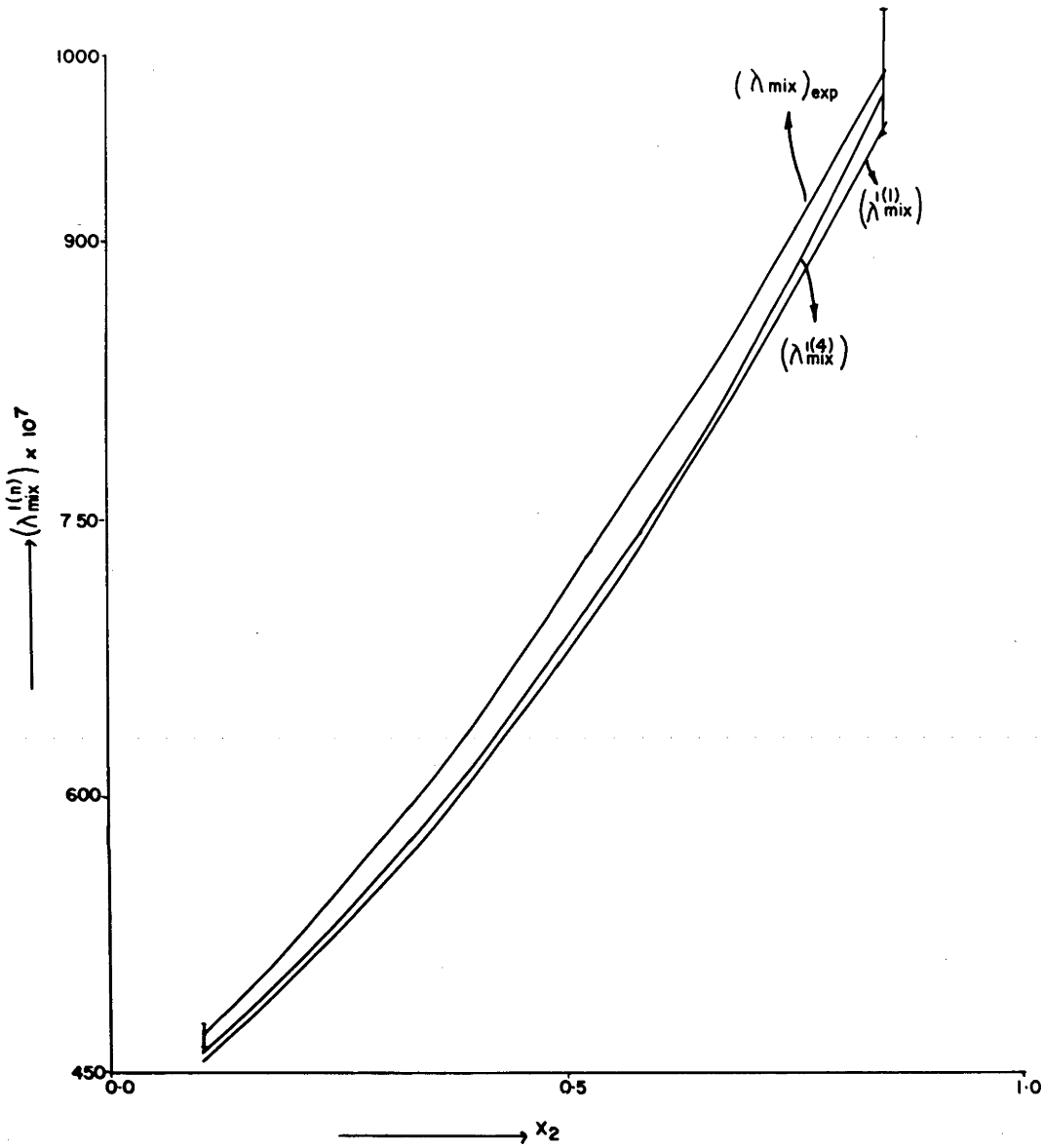

Fig. 34 .. Theoretical values for the first and fourth orders of thermal conductivity (λ'_{mix}) for the Ar-He mixture vs. x_2 for the L.J. potential. Experimental curve with the errors indicated is also drawn. Curves corresponding $(\lambda'^{(2)}_{mix})$ and $(\lambda'^{(3)}_{mix})$ are not drawn but they lie very close and above $(\lambda'^{(1)}_{mix})$ curve.

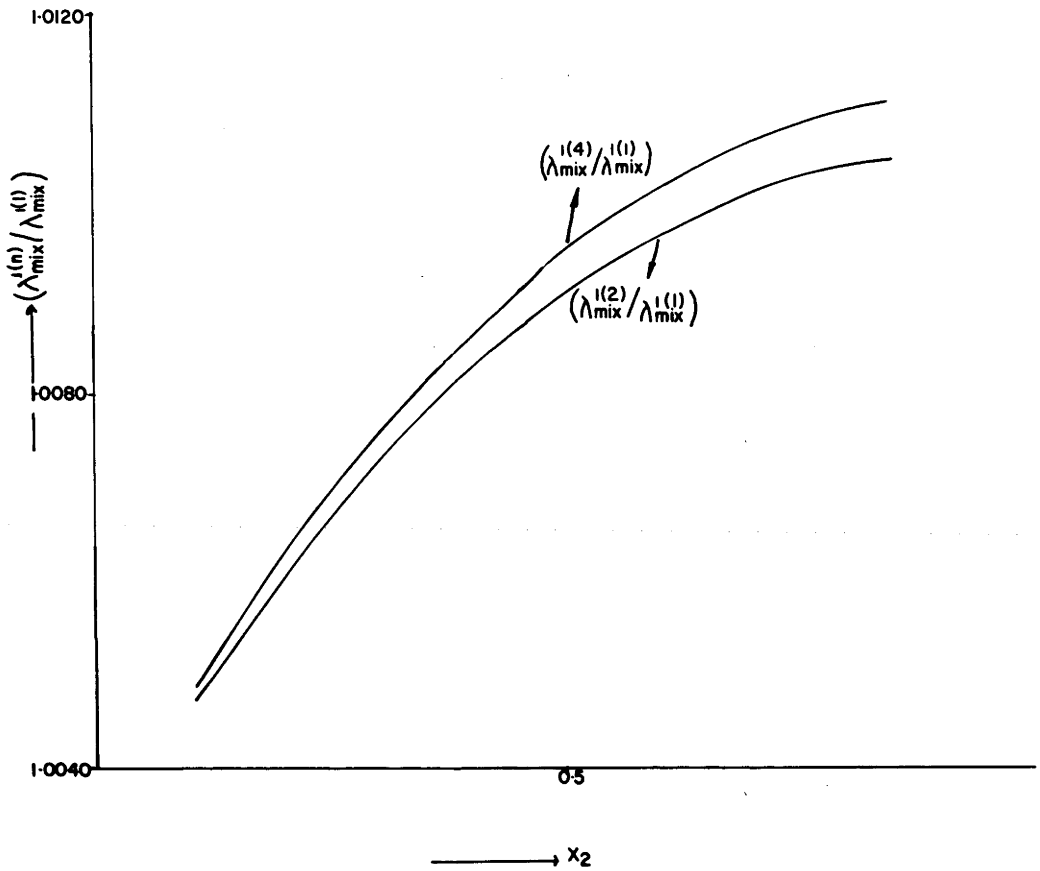

Fig. 35 .. Ratios of the second and fourth orders to the first of thermal-conductivity (λ'_{mix}) for the Ar-Ne mixture vs. x_2 for the L.J. potential curve corresponding $(\lambda'^{(3)}_{mix}/\lambda'^{(1)}_{mix})$ is not drawn but it lies very close and below $(\lambda'^{(4)}_{mix}/\lambda'^{(1)}_{mix})$ curve.

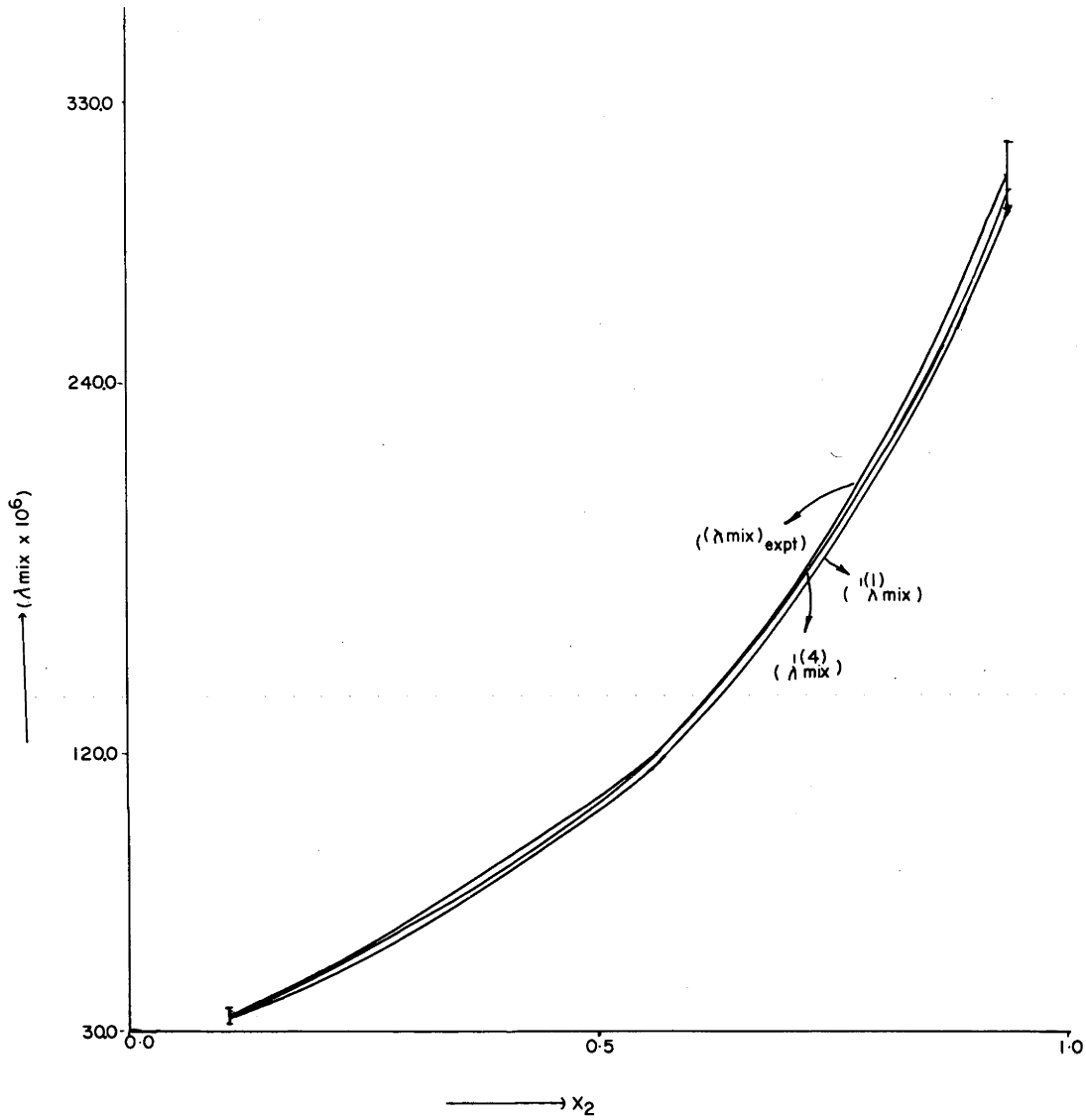

Fig. 49 .. Theoretical values of the first and fourth orders of thermal-conductivity (λ'_{mix}) for the Kr-He mixture vs. x_2 for the L.J. potential. Curves corresponding to $(\lambda'^{(2)}_{mix})$ and $(\lambda'^{(3)}_{mix})$ are not drawn. These curves lie very close and below $(\lambda'^{(4)}_{mix})$ curve. Also the experimental curve with errors is drawn.

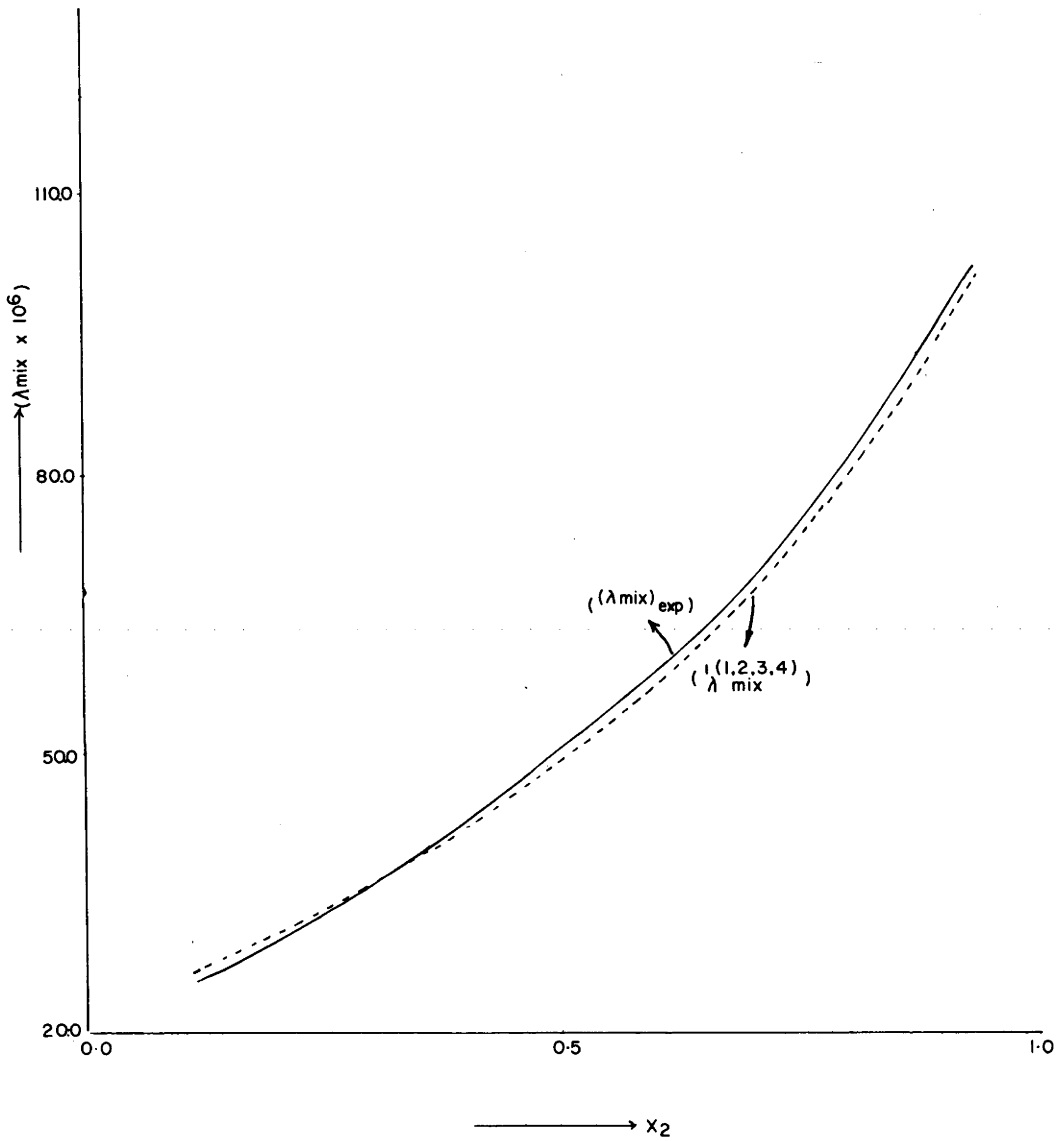

Fig. 50 .. Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Kr-Ne mixture vs. x_2 for the L.J. potential. All the four curves overlap. Also the experimental curve with error is drawn.

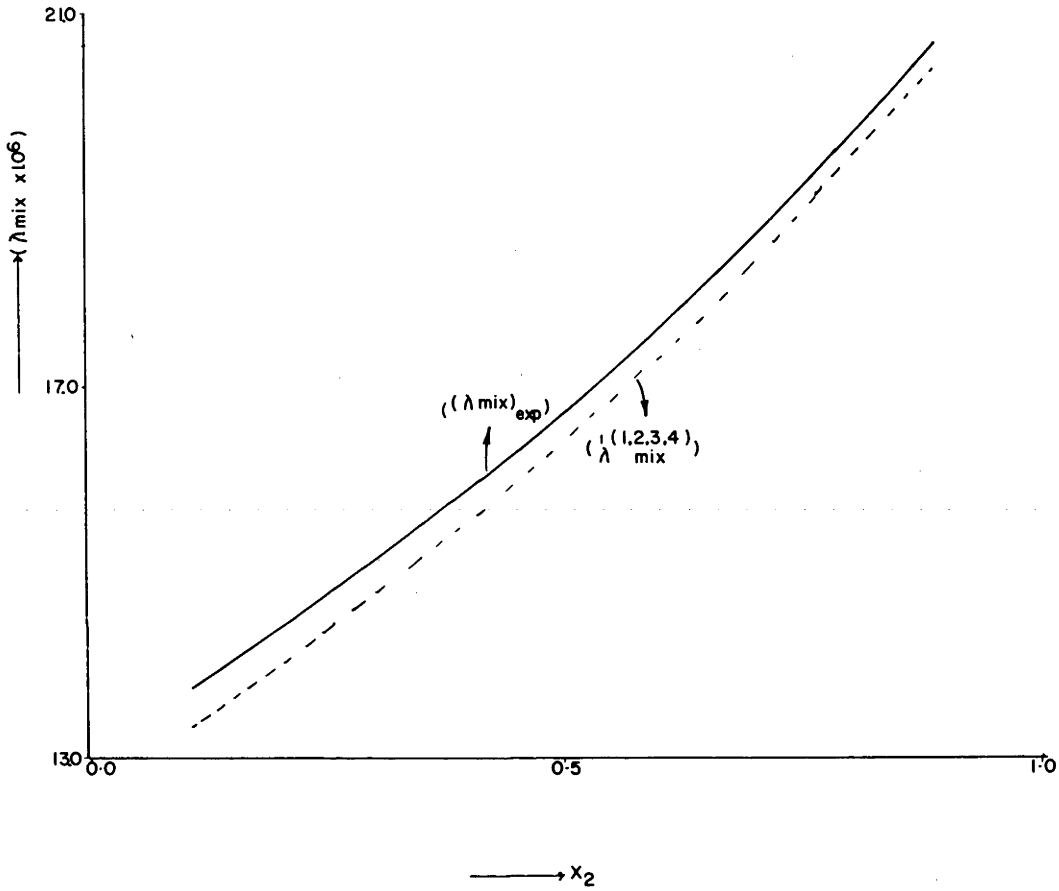

Fig. 51 .. Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Xe-Kr mixture vs. x_2 for the L.J. potential. All the four curves overlap. Also the experimental curve with error is drawn.

that in case of η_{mix}. The points of additional interest are given below.

a) Like rigid sphere case, comparing tables 46 and 39., we notice that the rate of decrement for the first four orders is slower for λ'_{mix} than for η_{mix}.

b) The contribution for the second and higher order to λ'_{mix} reaches a maximum value when x_2 is large (see Table 4.6, Fig. 35). This means that the contribution of the second and higher orders goes to a maximum only when the heavier component is in a minority. This, as mentioned before, is contrary to the statement of Storvick and Mason, (S.M.-66) that the contribution of the second order to λ'_{mix} is the largest only when the lighter component is in a minority. It may be pointed out here that in the case of rigid sphere, this contribution reaches a maximum only for certain mass and concentration ratios (see Fig. 8).

2) <u>With Temperature</u>

The discussion is similar to that for η_{mix}. The results of the present calculations for the Ar-Ne mixture for the λ'_{mix} part are given in tables (47,48) and in figs. (36, 37).

TABLE 47.

Theoretical values of the first four orders of thermal-conductivity (λ'_{mix}) for the Ar-Ne mixture for different temperatures for the L.J. potential.

T^{o} (K)	(1) λ'_{mix} x 10^5	(2) λ'_{mix} x 10^5	(3) λ'_{mix} x 10^5	(4) λ'_{mix} x 10^5
50	1.488	1.488	1.488	1.488
200	5.1369	5.1692	5.170	5.170
400	8.521	8.614	8.620	8.621
600	11.218	11.358	11.369	11.370
800	13.567	13.745	13.760	13.762
1000	15.695	15.908	15.926	15.928

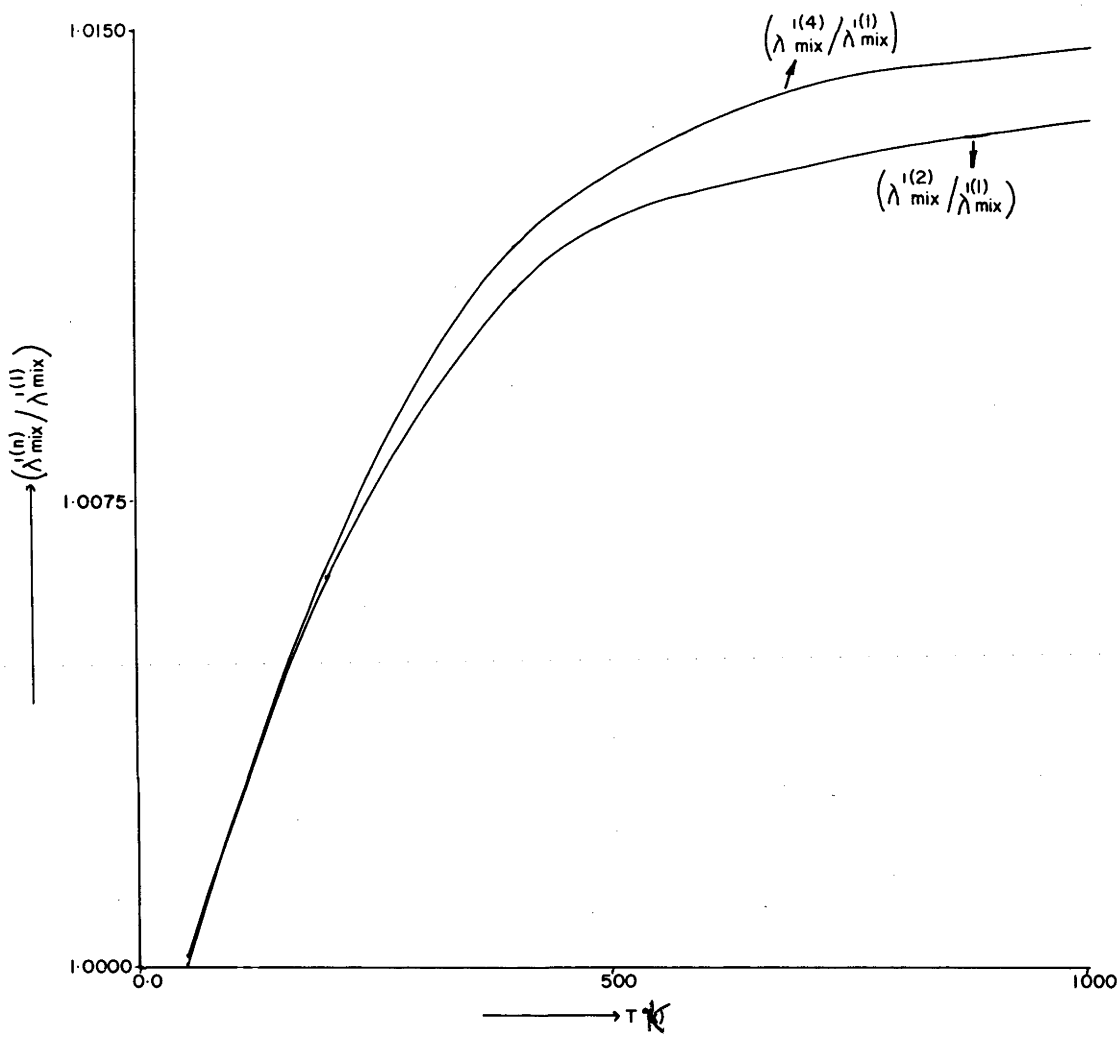

Fig. 37 .. Ratios of the second and fourth orders to the first of thermal-conductivity (λ'_{mix}) for the Ar-Ne mixture vs. T for the L.J. potential. Curve corresponding to $(\lambda'^{(3)}_{mix}/\lambda'^{(1)}_{mix})$ is not drawn but it lies very close and below $(\lambda'^{(4)}_{mix}/\lambda'^{(1)}_{mix})$ curve.

iii) Diffusion (Tables 49-53, Figs. 38-41).

In the literature, only higher order calculations of diffusion for the L.J. potential is for the second order (Jo .-60). These calculations are done for two or three values of concentrations for each of the gas-mixture.

The results of the present computations for the first five orders are given in tables (49-54) and in figs. (38-41).

Convergence of the first four orders.

1) With Concentration.

The results for the first five orders for different values of x_2 for the Ar-Ne and Kr-Ne mixtures are placed in figs. (38-39) and in tables (49-51). Again the discussion of the inferences is the same as in the case of η_{mix}. Some points of particular interest are listed below.

a) The rate of decrement for the first four orders is slower for diffusion than for η_{mix} and λ'_{mix} for all values of x_2 except for very large values of x_2 (compare Tables 51, 46 and 39).

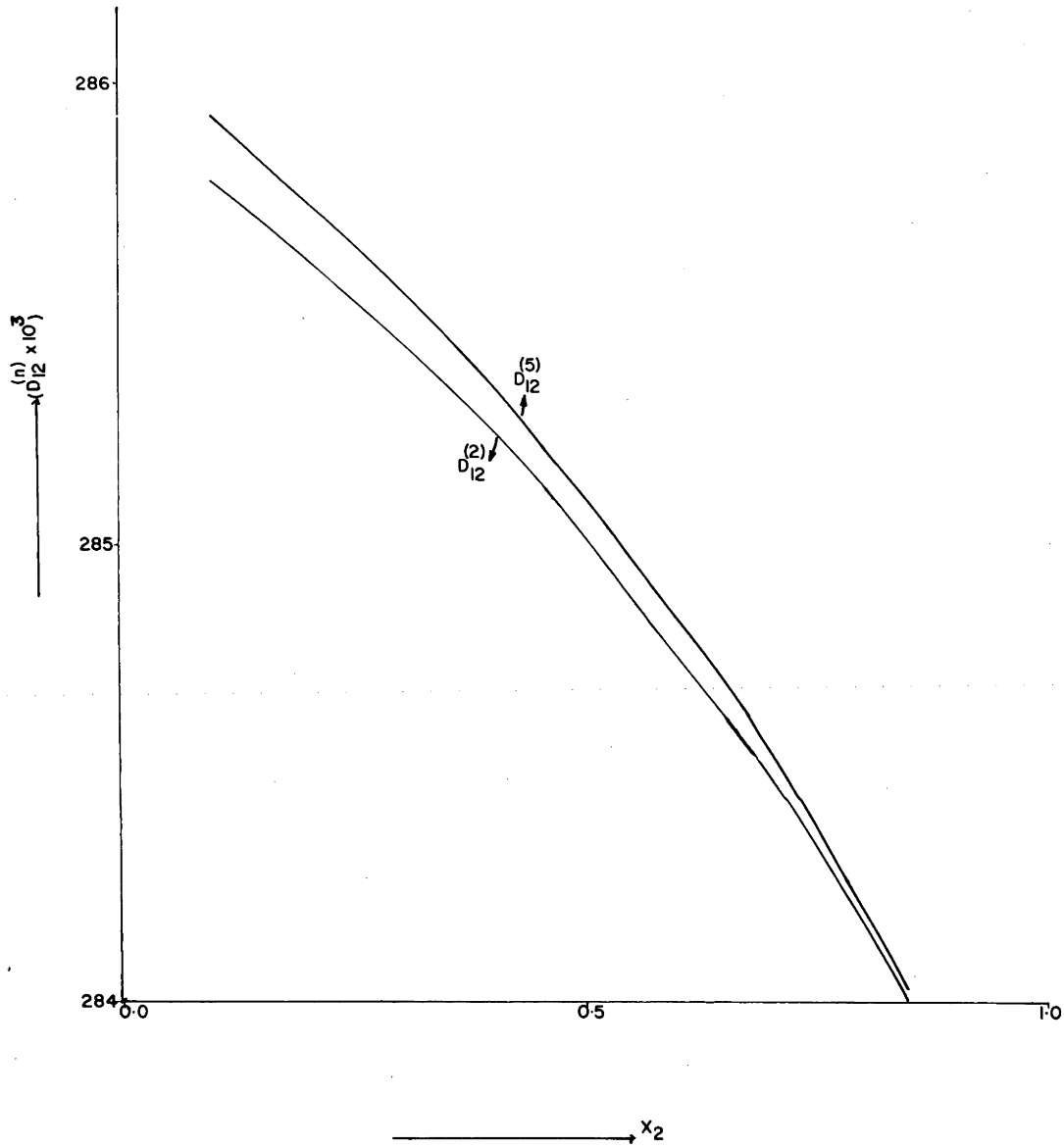

Fig. 38 .. Theoretical values of the second and fifth orders to the first of diffusion (D_{12}) for the Ar-Ne mixture vs. x_2 for the L.J. potential. Curves corresponding to $(D_{12}^{(3)})$ and $(D_{12}^{(4)})$ are not drawn but they lie close and below $(D_{12}^{(5)})$ curve.

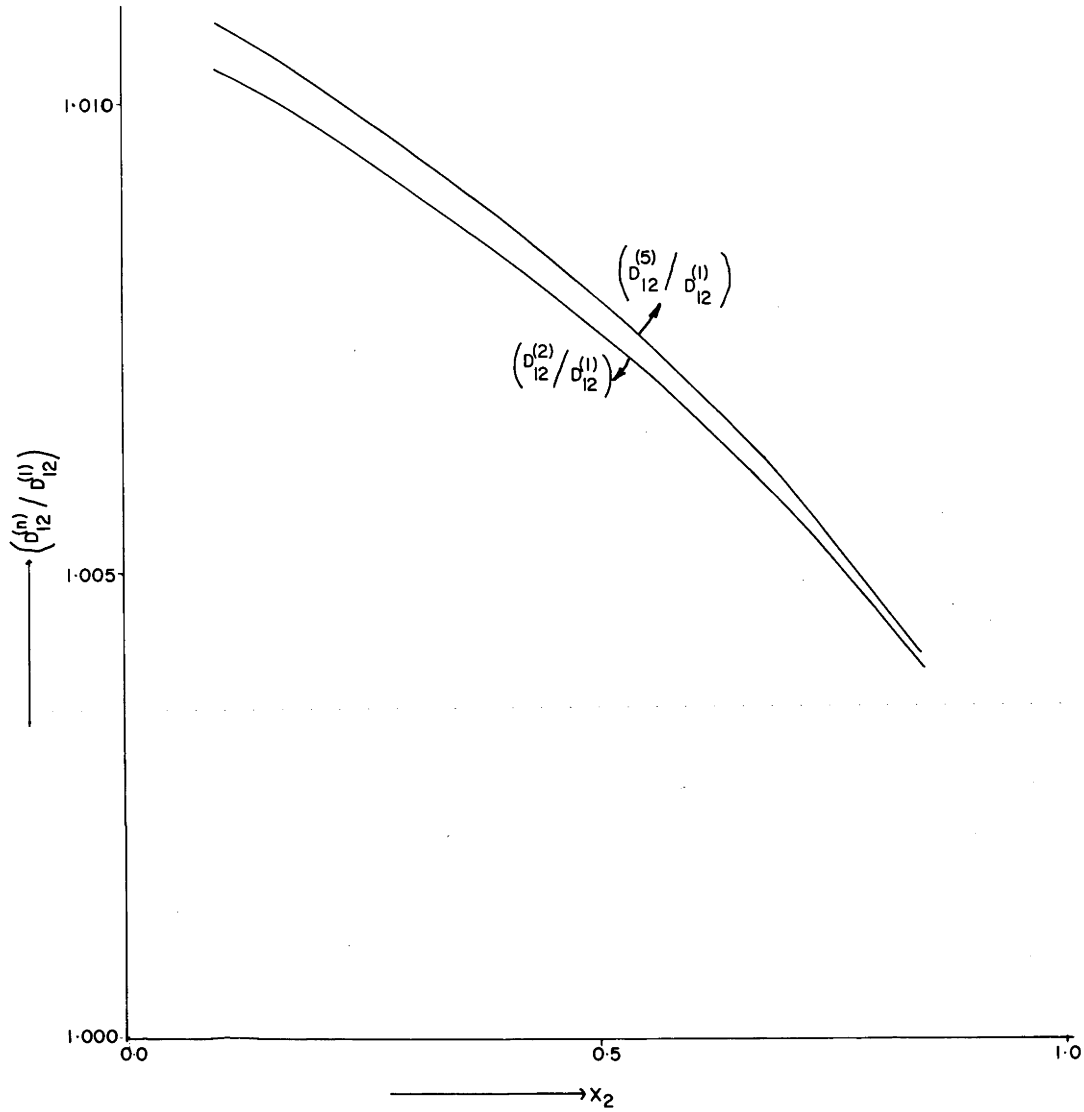

Fig. 39 .. Ratios of the second and fifth orders to the first of diffusion (D_{12}) for the Ar-Ne mixture vs. x_2 for the L.J. potential. Curves corresponding to $(D_{12}^{(3)}/D_{12}^{(1)})$ and $(D_{12}^{(4)}/D_{12}^{(1)})$ are not drawn, but they lie very close and below $(D_{12}^{(5)}/D_{12}^{(1)})$ curve.

TABLE 49.

Theoretical values of the first five orders of diffusion ($\mathcal{D}_{12}$) for the Ar-Ne mixture for different values of x_2 for the L.J. potential.

x_2	($\mathcal{D}_{12}^{(2)}$) x 10	($\mathcal{D}_{12}^{(3)}$) x 10	($\mathcal{D}_{12}^{(4)}$) x 10	($\mathcal{D}_{12}^{(5)}$) x 10
0.10	2.858	2.859	2.859	2.859
0.197	2.856	2.858	2.858	2.858
0.274	2.855	2.856	2.856	2.856
0.362	2.853	2.854	2.854	2.854
0.459	2.851	2.852	2.852	2.852
0.564	2.849	2.849	2.849	2.849
0.672	2.846	2.846	2.846	2.846
0.779	2.842	2.843	2.843	2.843
0.843	2.840	2.840	2.840	2.840

TABLE 50.

Theoretical values of the first four orders of diffusion ($\mathcal{D}_{12}$) of the Kr-Ne mixture for different values of x_2 for the L.J. potential.

x_2	$\mathcal{D}_{12}^{(2)}$ (x 10)	$\mathcal{D}_{12}^{(3)}$ (x 10)	$\mathcal{D}_{12}^{(4)}$ (x 10)	$\mathcal{D}_{12}^{(5)}$ (x 10)
0.111	2.334	2.336	2.336	2.336
0.203	2.333	2.334	2.334	2.334
0.357	2.330	2.331	2.331	2.331
0.467	2.327	2.328	2.328	2.328
0.562	2.325	2.326	2.326	2.326
0.661	2.321	2.322	2.322	2.322
0.771	2.317	2.317	2.317	2.317
0.889	2.310	2.310	2.310	2.310
0.935	2.308	2.308	2.308	2.308

TABLE 51.

Ratios of the first five orders to the first of diffusion ($\mathcal{D}_{12}$) for the Ar-Ne mixture for different values of x_2 for the L.J. potential.

x_2	$\mathcal{D}_{12}^{(2)} / \mathcal{D}_{12}^{(1)}$	$\mathcal{D}_{12}^{(3)} / \mathcal{D}_{12}^{(1)}$	$\mathcal{D}_{12}^{(4)} / \mathcal{D}_{12}^{(1)}$	$\mathcal{D}_{12}^{(5)} / \mathcal{D}_{12}^{(1)}$
0.10	1.01032	1.01080	1.01082	1.01082
0.197	1.00977	1.01022	1.01024	1.01024
0.274	1.00929	1.00971	1.00972	1.00972
0.362	1.00869	1.00907	1.00908	1.00908
0.459	1.00795	1.00829	1.00830	1.00830
0.564	1.00706	1.00734	1.00735	1.00735
0.672	1.00600	1.00623	1.00624	1.00624
0.779	1.00480	1.00497n	1.00498	1.00498
0.843	1.00400	1.00413	1.00413	1.00413

b) $\mathcal{D}_{12}$ varies much less with x_2 than do η_{mix} and λ'_{mix} (Table 49 and 50 and compare with Tables (35-38) and (42-45)).

c) The contribution to the second and higher-orders of $\mathcal{D}_{12}$ goes on increasing when the lighter component is decreasing (see Fig. 39).

2) <u>With Temperature.</u>

The discussion is again similar to that for η_{mix}. The results of the present calculations for the Ar-Ne mixture for the first five orders for different temperatures are given in tables (52, 53) and in figs. (40, 41).

iv) Thermal-diffusion ratio (Tables 54-58, Figs. 42-45).

In the literature no calculation has been reported for the second and higher orders for the Lennard-Jones potential.

The results of the present calculations for the first four orders are given in tables (54-58) and in figs. (42-45).

<u>Convergence of the first four orders.</u>

1) <u>With Concentration.</u>

TABLE 52.

Theoretical values of the first five order of diffusion ($\mathcal{D}_{12}$) for the Ar-Ne mixture for different temperatures for the L.J. potential.

$T^{o}(K)$	$\mathcal{D}_{12}^{(1)}$ (x 10)	$\mathcal{D}_{12}^{(2)}$ (x 10)	$\mathcal{D}_{12}^{(3)}$ (x 10)	$\mathcal{D}_{12}^{(4)}$ (x 10)	$\mathcal{D}_{12}^{(5)}$ (x 10)
50	0.6130	0.6130	0.6131	0.6131	0.6131
200	2.1453	2.1553	2.1555	2.1555	2.1555
400	3.5410	3.5735	3.5755	3.5756	3.5756
600	4.6692	4.7185	4.7223	4.7727	4.7228
800	5.6563	5.7189	5.7240	5.7247	5.7249
1000	6.5562	6.6305	6.6368	6.6378	6.6379

TABLE 53.

Ratios of the first five orders to the first of diffusion ($\mathcal{D}_{12}$) for the Ar-Ne mixture for different temperatures for the L.J. potential.

T^{o} (K)	$\mathcal{D}_{12}^{(2)} / \mathcal{D}_{12}^{(1)}$	$\mathcal{D}_{12}^{(3)} / \mathcal{D}_{12}^{(1)}$	$\mathcal{D}_{12}^{(4)} / \mathcal{D}_{12}^{(1)}$	$\mathcal{D}_{12}^{(5)} / \mathcal{D}_{12}^{(1)}$
50	1.0000	1.0001	1.0001	1.0001
200	1.00466	1.00474	1.00474	1.00474
400	1.00919	1.00974	1.00982	1.00983
600	1.01056	1.01137	1.01147	1.01149
800	1.01111	1.01195	1.01208	1.01210
1000	1.01135	1.01232	1.01246	1.01248

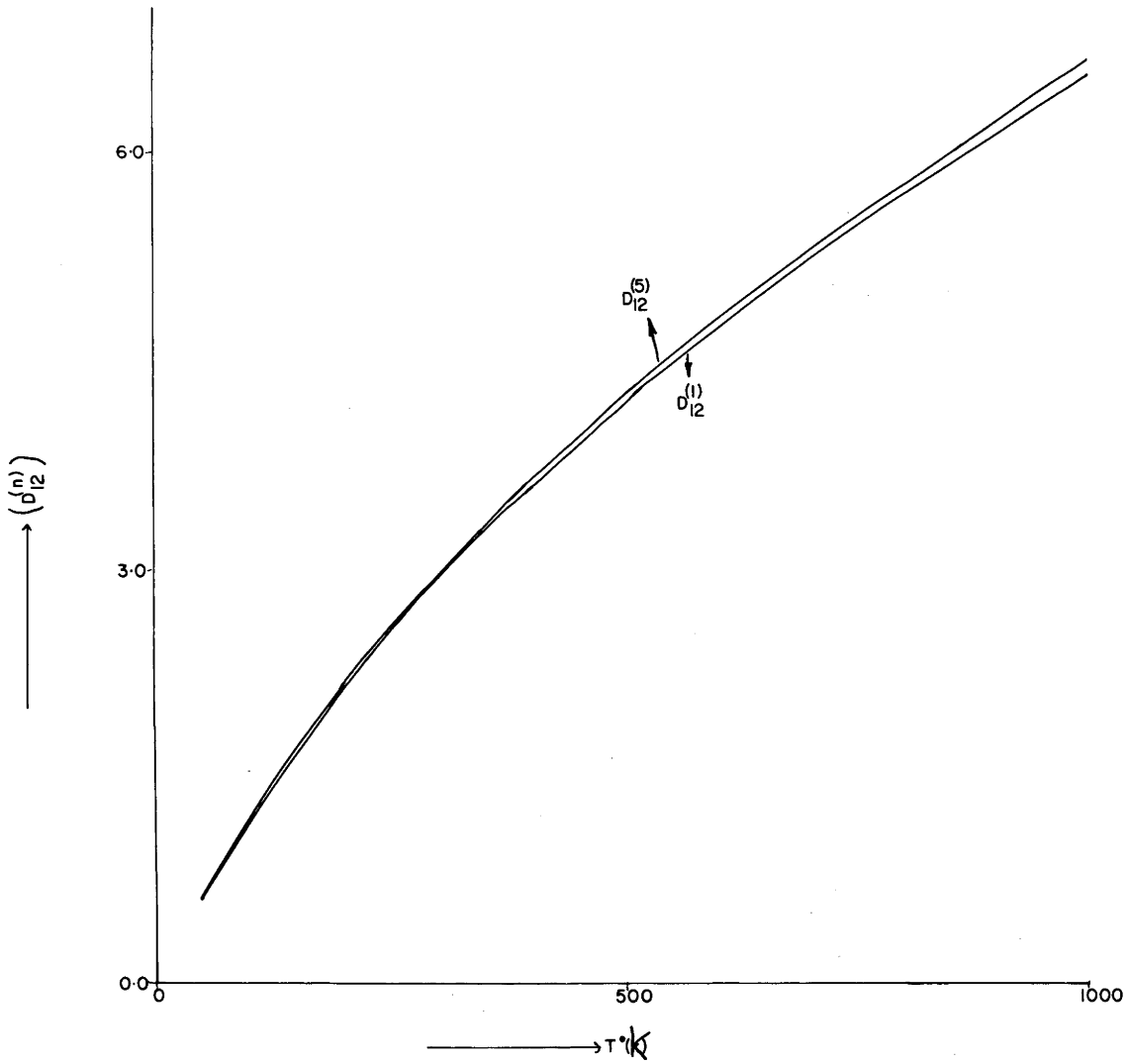

Fig. 40 .. Theoretical values of the first and fifth orders to the first of diffusion (D_{12}) for the Ar-Ne mixture vs. T for the L.J. potential. Curves corresponding to $(D_{12}^{(2)})$, $(D_{12}^{(3)})$ and $(D_{12}^{(4)})$ are not drawn but they lie close and below $(D_{12}^{(5)})$ curve.

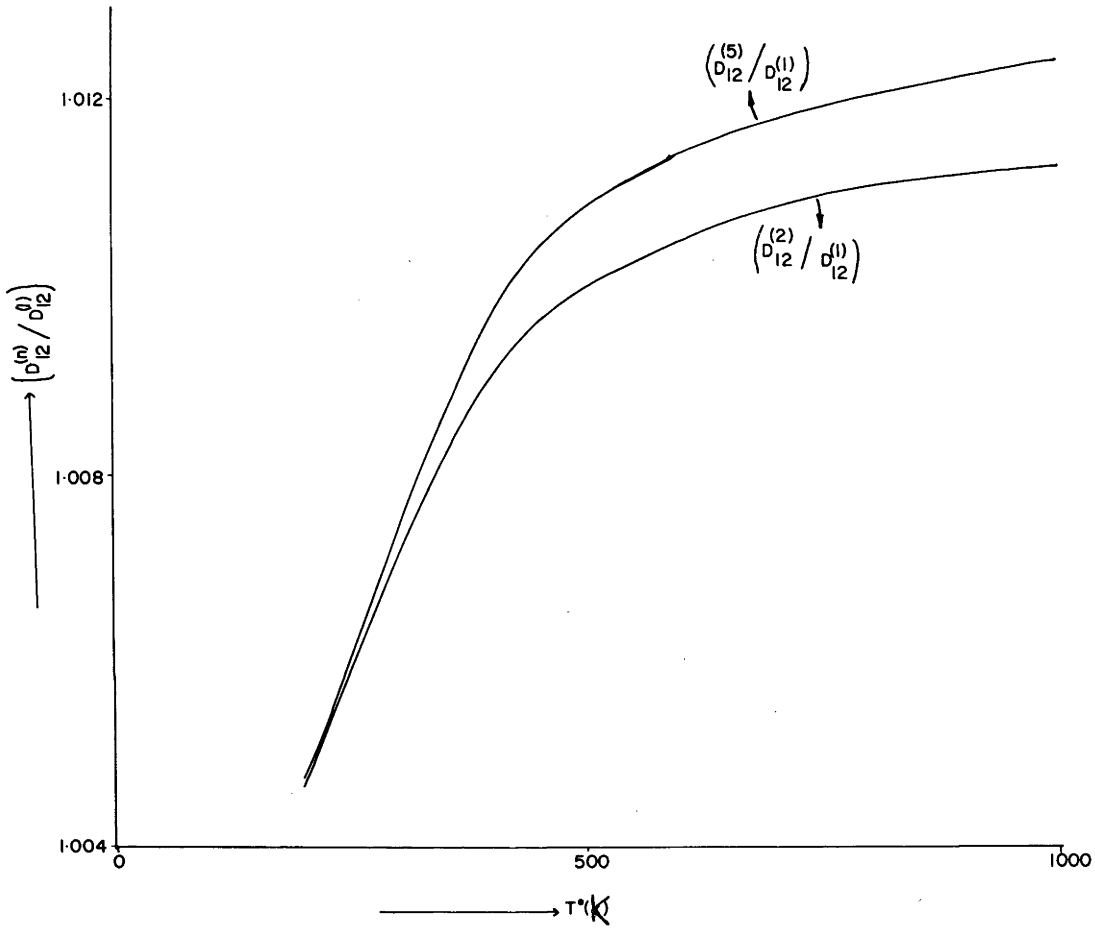

Fig. 41 .. Ratios of the second and fifth orders to the first of diffusion (D_{12}) for the Ar-Ne mixture vs. T for the L.J. potential. Curves corresponding to $(D_{12}^{(3)}/D_{12}^{(1)})$ and $(D_{12}^{(4)}/D_{12}^{(1)})$ are not drawn but they lie very close and below $(D_{12}^{(5)}/D_{12}^{(1)})$ curve.

The results of the calculations for the first four orders for the Ar-Ne and Kr-Ne mixtures are placed in figs. (42, 43) and in tables (54-56). The discussion is, again, similar to that for η_{mix}. Additional comments specific to this coefficient are as follows.

a) Unlike previous coefficients, the value of k_T approaches zero when $x_2 = 0$ or 1 and has a maximum at $x_2 \simeq 0.5$ for each order. (Compare Figs. (42, 38, 34 and 30), Tables (54, 49, 42 and 35)).

b) Like D_{12}, the contributions of the higher orders to k_T goes to a maximum value when the lighter component is in minority (See Figs. 43, 39).

c) The rate of decrement is slower even as compared to diffusion (Compare Tables 56 and 51).

2) <u>With Temperature.</u>

The results for the first four orders of calculation are given in tables (57, 58) and in figs. (44, 45). The discussion of the results is, again, similar to that for η_{mix}. Some additional remarks specific to this case are given below.

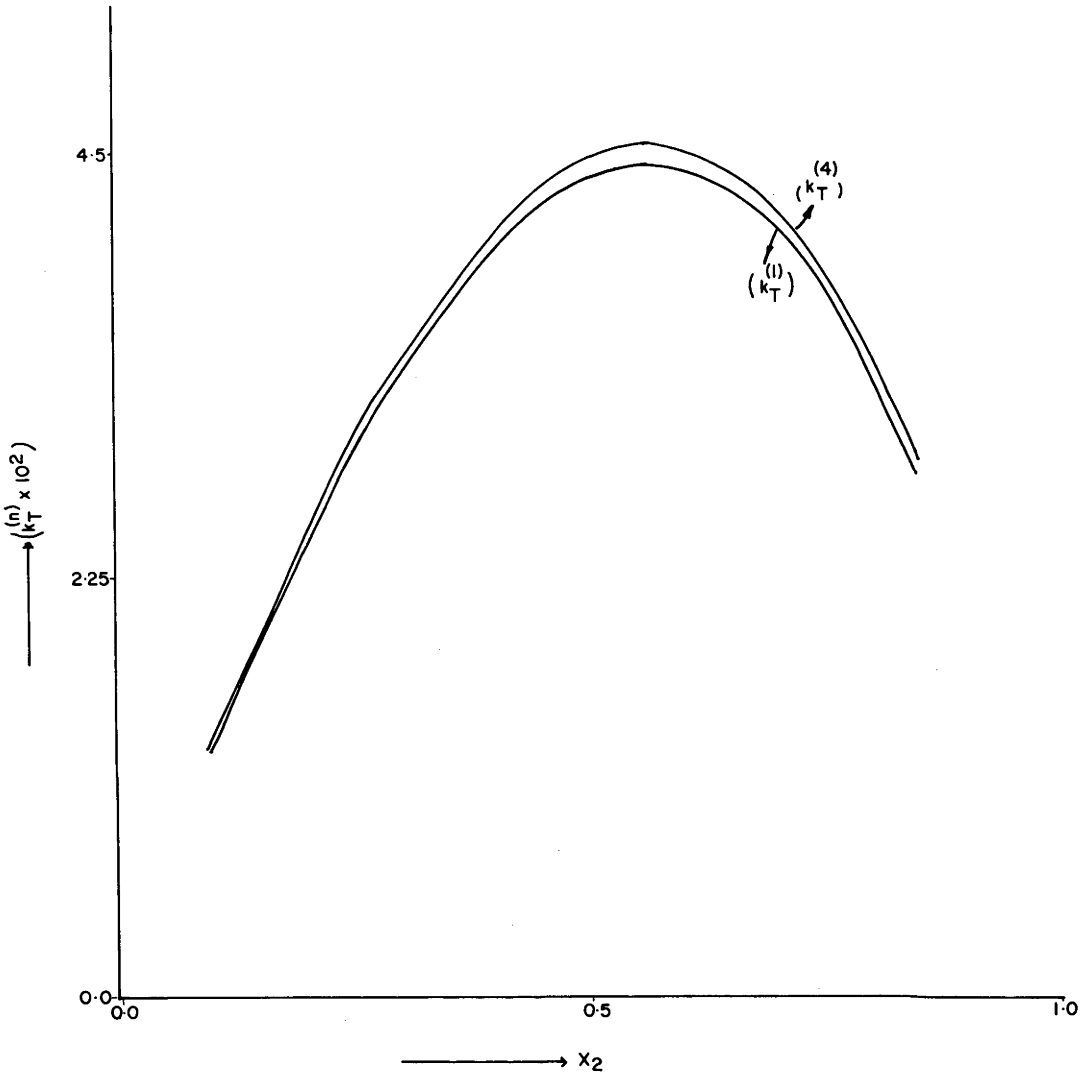

Fig. 42 .. Theoretical values of the first and fourth orders to the first of thermal-diffusion ratio (k_T) for the Ar-Ne mixture vs. x_2 for the L.J. potential. Curves corresponding to $(k_T^{(3)})$ and $(k_T^{(2)})$ are not drawn. They lie close and below $(k_T^{(4)})$ curve.

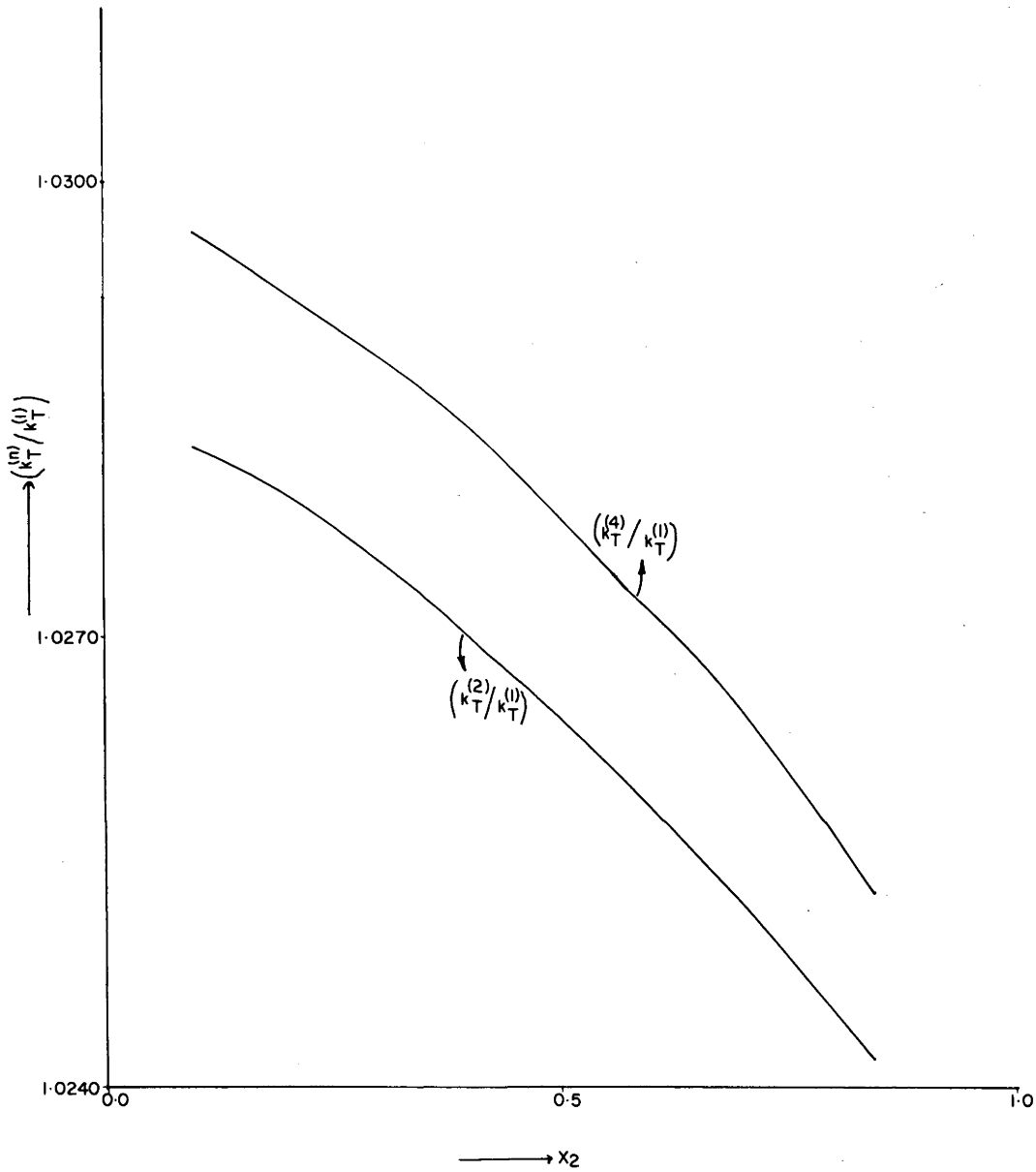

Fig. 43 .. Ratios of the second and fourth orders to the first of thermal-diffusion ratio (R_T) for the Ar-Ne mixture vs. x_2 for the L.J. potential. Curve corresponding to $(k_T^{(3)}/k_T^{(1)})$ is not drawn. It lies very close and below $(k_T^{(4)}/k_T^{(1)})$ curve.

TABLE 54.

Theoretical values of the first four orders of thermal-diffusion ratio (k_T) for the Ar-Ne mixture for different values of x_2 for the L.J. potential.

x_2	(1) k_T ($\times 10^2$)	(2) k_T ($\times 10^2$)	(3) k_T ($\times 10^2$)	(4) k_T ($\times 10^2$)
0.10	1.303	1.340	1.342	1.342
0.197	2.389	2.456	2.459	2.459
0.274	3.111	3.196	3.201	3.201
0.362	3.765	3.867	3.872	3.872
0.459	4.247	4.360	4.366	4.366
0.564	4.442	4.558	4.564	4.564
0.672	4.227	4.335	4.340	4.340
0.779	3.517	3.604	3.609	3.609
0.843	2.814	2.882	2.886	2.886

TABLE 55.

Theoretical values of the first four orders of thermal-diffusion ratio (k_T) of the Kr-Ne mixture for different values of x_2 for the L.J. potential.

x_2	$k_T^{(1)}$ ($\times 10^2$)	$k_T^{(2)}$ ($\times 10^2$)	$k_{tT}^{(3)}$ ($\times 10^2$)	$k_T^{(4)}$ ($\times 10^2$)
0.111	1.956	2.012	2.014	2.014
0.203	3.390	3.484	3.487	3.487
0.357	5.323	5.465	5.469	5.469
0.467	6.238	6.398	6.402	6.402
0.562	6.642	6.806	6.809	6.809
0.661	6.574	6.728	6.732	6.732
0.771	5.740	5.865	5.868	5.868
0.889	3.631	3.704	3.705	3.705
0.935	2.358	2.404	2.405	2.405

TABLE 56.

Ratios of the first four orders to the first of thermal-diffusion ratio (k_T) for the Ar-Ne mixture for different values of x_2 for the L.J. potential.

x_2	$(k_T^{(2)}/k_T^{(1)})$	$(k_T^{(3)}/k_T^{(1)})$	$(k_T^{(4)}/k_T^{(1)})$
0.10	1.0283	1.0297	1.0297
0.197	1.0280	1.0293	1.0293
0.274	1.0276	1.0290	1.0290
0.362	1.0272	1.0286	1.0286
0.459	1.0267	1.0281	1.0281
0.564	1.0261	1.0274	1.0274
0.672	1.0254	1.0267	1.0268
0.779	1.0247	1.0259	1.0259
0.843	1.0242	1.0253	1.0253

TABLE 57.

Theoretical values of the first four orders of thermal-diffusion ratio (k_T) for the Ar-Ne mixture for different temperatures for the L.J. potential.

T^o (K)	$k_T^{(1)}$ ($\times 10^2$)	$k_T^{(2)}$ ($\times 10^2$)	$k_T^{(3)}$ ($\times 10^2$)	$k_T^{(4)}$ ($\times 10^2$)
50	-0.3528	-0.3557	-0.3561	-0.3556
200	3.712	3.769	3.769	3.769
400	4.758	4.919	4.933	4.934
600	5.048	5.248	5.270	5.273
800	5.146	5.361	5.386	5.391
1000	5.192	5.416	5.443	5.448

TABLE 58.

Ratios of the first four orders to the first of thermal-diffusion ratio (k_T) for the Ar-Ne mixture for different temperatures for the L.J. potential.

T^{o}(K)	$k_T^{(2)}/k_T^{(1)}$	$k_T^{(3)}/k_T^{(1)}$	$k_T^{(4)}/k_T^{(1)}$
50	1.0081	1.0094	1.0080
200	1.0155	1.0154	1.0154
400	1.0339	1.0368	1.0370
600	1.0396	1.0440	1.0447
800	1.0418	1.0468	1.0476
1000	1.0431	1.0484	1.0494

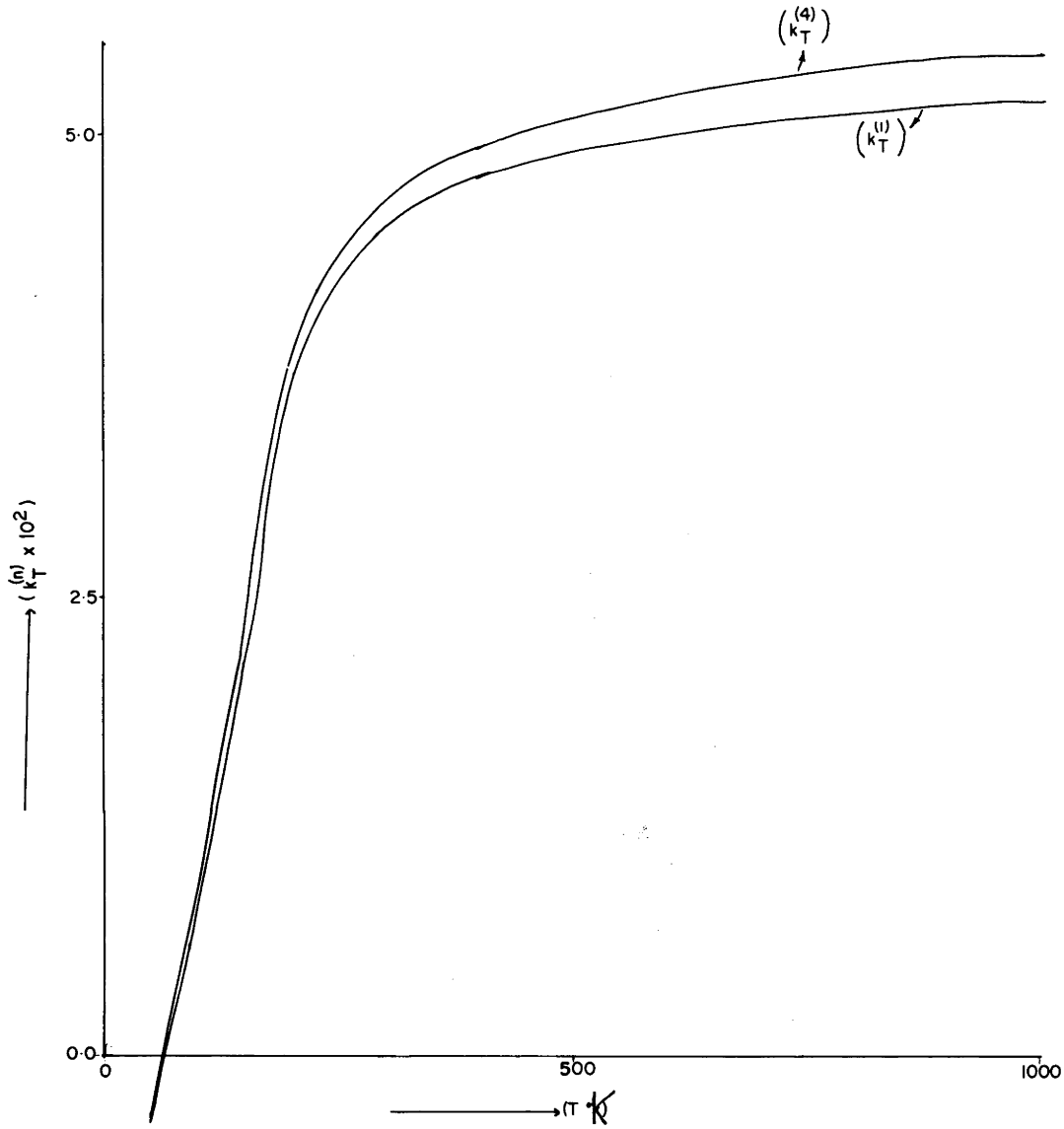

Fig. 44 .. Theoretical values of the first and fourth orders of thermal-diffusion ratio (k_T) for the Ar-Ne mixture vs. T for the L.J. potential. Curves corresponding to $(k_T^{(2)})$ and $(k_T^{(3)})$ are not drawn. These curves lie verv close and below $(k_T^{(4)})$ curve.

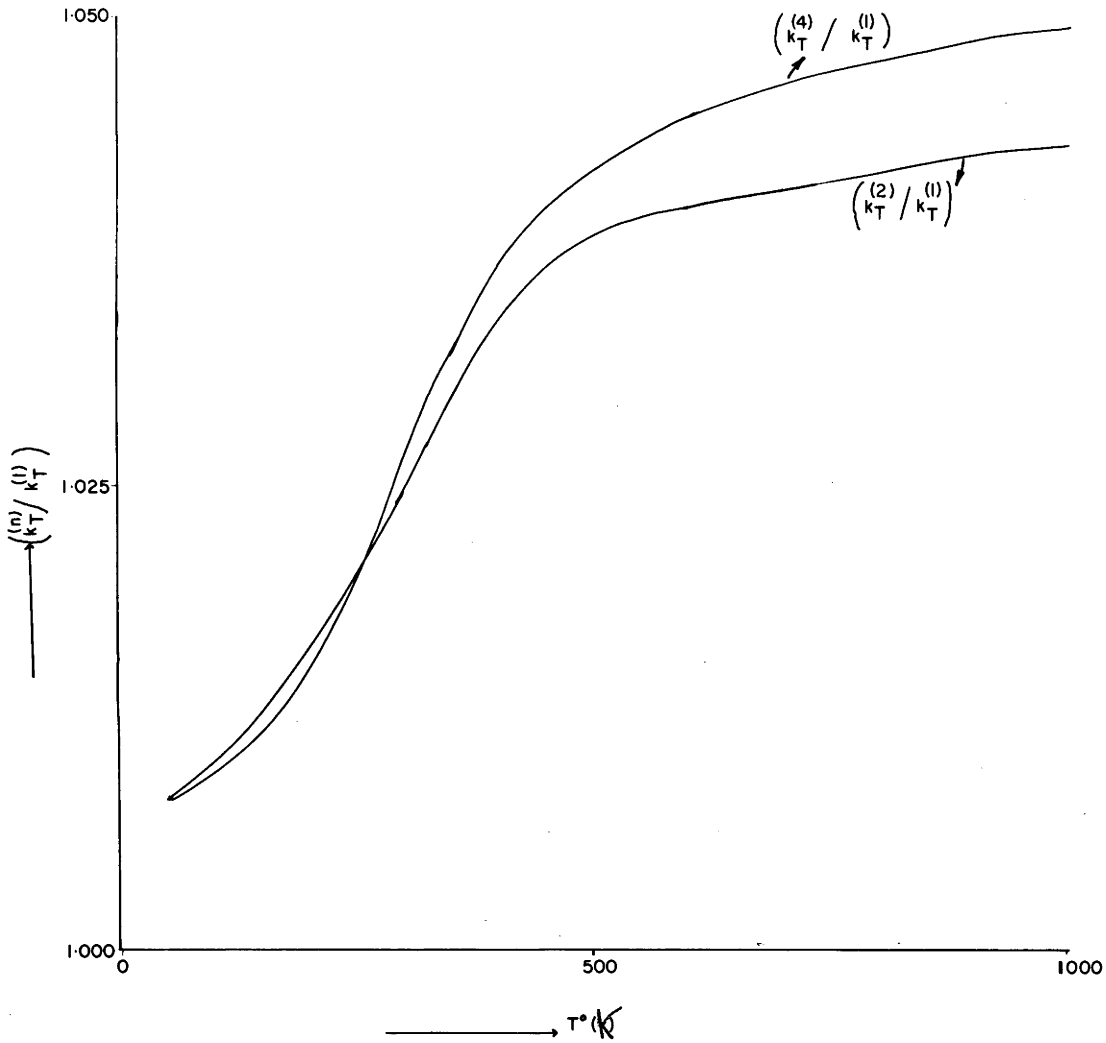

Fig. 45 .. Ratios of the second and fourth orders to the first of thermal-diffusion ratio (k_T) for the Ar-Ne mixture vs. T for the L.J. potential. Curve corresponding to $(k_T^{(3)}/k_T^{(1)})$ is not drawn. It lies very close and below $(k_T^{(4)}/k_T^{(1)})$ curve.

a) The higher order contributions are less than the first order contribution for temperatures less than or equal to 200° K. (See Table 58).

b) The value of k_T is negative below 100°K (See Fig. 44). This should not be very surprising as the experimental studies of the temperature dependence on k_T for Kr-Ar and Xe-Kr mixture (G.M.-61) have shown that for Kr-Ar , the value of k_T passes through a positive minimum while the Xe-Kr case it is negative for very low temperatures. It may therefore be of interest to study the temperature dependence on k_T for all orders below 200°K more systematically for more mixtures. In the present work, we have calculated only one value of k_T for the Ar-Ne mixture below 200°K.

v) Comparison of Different Coefficients.

a) Like rigid-sphere potential the rate of decrement is rapid for all the coefficients, the sequence of rapidity being k_T (slowest), D_{12}, λ'_{mix}, n η_{mix}. For example from table 56, we notice that $k_T^{(2)}/k_T^{(1)}$ for the Ar-Ne system for $x_2 = 0.1$ is 2.83%, while for $D_{12}^{(2)} / D_{12}^{(1)}$ is 1.03% (Table 51), for $(\lambda'^{(2)}_{mix} / \lambda'^{(1)}_{mix})$ is 0.472% (Table 46) and for

($\eta^{(2)}_{mix}$ / $\eta^{(1)}_{mix}$) is 0.261% (Table 39).

b) For each coefficient, the contributions for higher orders increase with temperature but, as remarked earlier, these contributions are not affected with temperature for the rigid sphere potential.

c) For η_{mix} and λ'_{mix}, the second and higher order contributions are maximum when the lighter component is in majority while for $\mathcal{D}_{12}$ and k_T, these contributions are maximum when the lighter component is in minority.

In the case of rigid sphere potential, the behaviour observed for $\mathcal{D}_{12}$ and k_T is the same while for η_{mix} and λ'_{mix} it differs in as much as the latter have a maximum at $x_2 \simeq 0.5$.

CHAPTER VI

FORCE CONSTANTS AND EXPERIMENTAL DATA

Introduction

The force constants for interaction between like molecules for the Lennard-Jones potential (Table 34) used in the last chapter, have been obtained by fitting the viscosity data of the simple gases and are taken from the Hirschfelder et al's work (H.C.B.-64, Table I-A, p. 1110). The (12-6) Lennard-Jones interaction potential gives better results for the coefficients of the simple gases and for the virial coefficients than the other known two-parameter potentials (For extensive comparison, see Chs. 3 and 8, H.C.B. 64). Even a three-parameter potential like the 'Modified Expo-6', although more complicated to handle, does not give results different from those of the Lennard-Jones potential (Ma-54). It appears that for the simple gases, there is no possibility of varying the form of interaction potential.

In the binary gas mixture calculations we have followed the approach of previous workers (e.g. Th-60, Th-61) and used the same form of potential for the unlike molecules as for the like molecules and obtained the force constants for unlike molecules by the usual combination rules. In the literature extensive comparisons of the first order theory and the experimental data for various gas-mixtures and for different concentrations have been made (Th-60, Th-61,

T.B.-62, H.C.B.-64 Ch.8, Gu-67). These comparisons show that the discrepancy between the first order theory and the experimental data is sometimes as large as 20% which is outside the range of the experimental error of about 4% (Gu-67). Hopes have been expressed in the literature (S.J.-63, S.M.-65, M.M.S.-65) that the higher order contributions based on the present set of potential parameters will resolve these discrepencies.

With the facility of computing the higher orders developed in the last four chapters, we are in a position to test this conjecture. It may be recalled that this was one of the aims of studying the four gas-mixtures in the last chapter. For such a comparison, the calculations are restricted to the fourth order because it has been established in the previous chapter that the rate of decrement of the first four orders is very rapid and the contributions from the orders higher than the fourth order would only make negligible contributions. In section A of this chapter, the comparisons of the higher orders of the theory and the experimental data for the four mixtures are given. The outcome of these comparisons is that the higher order contributions, alone, fail to resolve the discrepency between theoretical values and the experimental data. Thus

in order to have a better agreement between the theory and experiment (which is sometimes as large as 20%), we have two alternatives, one is to change the form of the potential and the other is to abandon the combination rules and find new and better sets of force constants for unlike molecules by free adjustment. It appears that the latter is to be preferred. The reasons for this are discussed in section A. They are convincing but not conclusive.

If we accept the latter alternative (i.e. to find a new set of force constants for unlike molecules) different and more efficient ways for finding these constants are needed. In the literature, two methods of calculation are available. One is due to Hirschfelder et al (Ch.8, H.C.B. 64) and is based on using the data of viscosity and the other is due to Srivastva and Madan (S.M.-53) which uses the first order theoretical expressions and the experimental data for k_T and D_{12}. The former method was not practical at that time due to the lack of availability of extensive and accurate data. In a recent paper (Gu-67), we have presented a modified method based on Hirschfelder et al's suggestion. By carrying out the first order comparisons we have discussed the advantages of working with the modified method over the method based on k_T and D_{12}. In section B this discussion has been brought up to date by including the contributions of the higher orders of the theory.

A. DISCUSSION OF COMBINATION RULES

As a first step for the discussion of these rules for the Lennard-Jones potential, an extensive comparison of the fourth order of the theory and the experimental data is made for Ar-Ne, Kr-Ne, Kr-He and Xe-Kr.

For all these mixtures, the experimental data for η_{mix} and λ_{mix} has been taken from the papers of Thoronton and Baker (Th.-60, Th.-61, T.B.-62). Recently Saxena et al (G.S.-66, G.S.-67) have published some more accurate data for λ_{mix} for these mixtures but we have not used this data for the present comparison because it is not extensive enough. For k_T, the experimental data is available only for Ar-Ne while for D_{12}, the experimental data is not extensive enough to carry out any comparison. The comparisons have been shown in figs. (30, 34, 46-51) and in tables (34-37, 42-45). The results have been grouped for each of the coefficients separately.

(a) <u>Viscosity</u> -

The results of different gas-mixtures are given separately.

(1) <u>Ar-Ne</u> - The discrepency between the first order theory and the experimental data varies between -1.1% to +0.7%. Taking the fourth order contributions into account, we observe no discrepency for lower values of x_2 while some discrepency can

be seen for higher values of x_2 (See Fig. 30).

(2) Kr-Ne - The discrepency between the first order theory and the experimental data varies between -2.2% to -0.8%. Taking the contributions of the first four orders into account, we observe that there is a general improvement in the agreement between the theory and the experiment, but still, the higher order contributions are not large enough to resolve the discrepency (See Fig. 46).

(3) Kr-He - The discrepency between the first order theory and the data lies between -1.3% to +1.3%. The fourth order contributions lie within the experimental range for some values of x_2 while they lie outside the range for other values of x_2 (See Fig. 47).

(4) Xe-Kr - The discrepency between the first order theory and the data is -1.2% to 0.0%. The higher order contributions overlap the first order contributions and the discrepency is not removed (See Fig. 48).

Thus we observe that for η_{mix}, the higher order contributions, alone, fail to resolve the deviations between the experimental data and the theoretical values.

(b) Thermal Conductivity

Again the results for each mixture have been discussed separately.

(1) Ar-Ne - The deviation between the theory and the experimental data is in between -4.9% to -2.7%. The higher order contributions give a better agreement of the theory and the data but some of the calculated values still fall outside the range of experimental error range. (See Fig. 34).

(2) Kr-Ar, Kr-He and Xe-Kr - For these mixtures a similar conclusion to that for Ar-Ne mixture follows (See Fig. 49-51).

(c) Thermal diffusion ratio

For this coefficient the only mixture for which the experimental data are available is Ar-Ne (Ch. 8, H.C.B.-64). These values are obtained at 324°K, while our calculations are done for 291°K (See Fig. 42 and Table 55). Comparison of the first order theory and the data are given by Hirschfelder et al (Ch. 8, H.C.B.-64) and it shows that the theoretical values are always higher than the experimental values. From Table 55, it follows that the higher order theoretical values would be still higher than the first order values by about 3% which means that the discrepency would be worse.

(d) Diffusion

There is no mixture for which enough experimental data is available to carry out a comparison.

Thus we conclude that the higher order contributions, based on the present sets of force constants, widely accepted in the literature, except for Kr, do give us a better agreement

but these agreements are accurate up to 1.6% in case of η_{mix} and up to 4.4% in case of λ_{mix} while the corresponding experimental accuracies are respectively 1.0% and 2.5%. In order to resolve the discrepancies completely within the framework of the Lennard-Jones potential, we are left with two alternatives. Firstly, the combination rules are true but the force constants for interaction between like molecules are in error. Secondly, the combination rules are not strictly valid. The force constants for simple gases are calculated mainly by fitting crystal data, second order virial coefficients and viscosity data. For a particular gas, there is a certain amount of variation in the values of the force constants when they are calculated from the different data (See Table I-A, pages 1110, 1212, H.C.B.-64). This variation is particularly noticeable for Krypton. The reasons for this are given by Fender (Fe-61). It has been noticed (Ma-61) that, except for Krypton, for all the other gas-systems force constants determined from one of these data (say viscosity) reproduce the theoretical data from other studies (crystal and second order virial coefficients) very satisfactorily.

Without going into the questions which may be involved in these comparisons we believe that for our purposes the force constants determined from the viscosity data on the pure gas are the relevant ones, because these data are sufficiently

accurate (K.L.-59) and more importantly the same theory is involved in considering the transport properties of simple gases and mixtures.

If this is accepted then the only choice left for getting a better agreement between the theoretical and experimental values is to abandon the combination rules and to find new sets of force constants for unlike molecules. Such a suggestion has been made by Saxena (Sa-57) for the Lennard-Jones potential but he could not show conclusively that the combination rules are not strictly valid because of the non-availability of the higher order contributions.

B. FORCE CONSTANTS FOR UNLIKE MOLECULES*

In the literature, one of the alternative ways for determining force constants is by fitting the experimental data of k_T and D_{12} with the first order expressions of k_T and D_{12}. We have shown in the last chapter that for k_T and D_{12}, the contributions of the higher orders is much larger than for η_{mix} and λ_{mix}. So such a calculation is likely to introduce a substantial error. The other alternative based on the first order expressions of η_{mix} and λ_{mix} is discussed below.

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* A preliminary account of this work based on the first order theoretical values has already been published (Gu-67).

In the present work, we wish to point out the importance of separating the contributions of interaction between like and unlike molecules to the expressions of η_{mix} and λ_{mix}. Since accurate estimates of the parts depending upon the interactions between like molecules can be obtained from the experimental data of corresponding simple gases, they can be subtracted off. The resulting quantities depend upon the interactions between unlike molecules and can be used for a study of the parameters for these interactions. As the data for these coefficients is more accurate (I.K.N.-64, K.K.W.-66) and extensive (Th.-60, Th.-61, T.B.-62) than for D_{12} and k_T, it would be more profitable to use these data directly for this study. (A suggestion for calculating potential parameters for interaction between unlike molecules has already been made by Hirschfelder et al (Ch. 8 H.C.B.-64), but it was not practical at that time due to the lack of accurate and extensive data).

This approach is to be contrasted with that of Weissmann et al (W.M.-62, We-65, G.S.-66a) who have determined the diffusion coefficients from the measured values of η_{mix} and λ_{mix} using some appropriate formulae and estimates for certain ratios of the collision integrals. Even if one disregards the discrepancy between these calculations and the

first order theory which is sometimes as high as 25%, This only shows what is obvious in principle that all the transport coefficients are related as can be seen from the simple gas theory. Further, it has been observed by Storvick and Mason (S.M.-66) that even taking effects of the second order into account, the values of calculated D_{12} would have errors ten times as large as that of η_{mix} data from which they have been obtained.

Except as a test of consistency of the different data, such calculation of diffusion coefficients seems irrelevant, especially since the data on η_{mix} and λ_{mix} can be directly used to calculate the force constants for interaction between unlike molecules.

Let the first order expression of a transport coefficient of a binary gas mixture be written as

$$T^{(1)} = T_o^{(1)} + T_{int.}^{(1)} \qquad (6.1)$$

where $T_{int.}^{(1)}$ depends upon the force constants of interaction between like and unlike molecules and the composition of the mixture. It is zero when the interaction between the two gas-systems is absent. $T_o^{(1)}$ depends only on the force constants of the individual gas components. It is zero for diffusion ($D_{12}^{(1)}$) and thermal diffusion ratio ($k_T^{(1)}$) as can be shown

from eqns. (3-102, 3-103, C-1, -2, -5, -11, -12, -15, -21, -22, -15) by putting interactions between unlike molecules zero. For η_{mix} and λ_{mix}, we have

$$\eta_o^{(1)} = \eta_1^{(1)} + \eta_2^{(1)} \qquad (6.2)$$

$$\lambda_o^{(1)} = \lambda_1^{(1)} + \lambda_2^{(1)} \qquad (6.3)$$

where subscript (1) refers to the heavier component and (2) to the lighter. Eqns. (6.2) and (6.3) are obtained by putting interactions between (1) and (2) zero in the first order expressions of η_{mix} and λ_{mix} by combining eqns (3.82, 3.124, C-1, -2, -5, -11, -12, -15, -21, -22, -25, -31, -41, -51). When 2 goes to 1, $\lambda_o^{(1)} = \lambda_1^{(1)}$ and $\eta_o^{(1)} = \lambda_o^{(1)}$ because $T_{int}^{(1)} = -\eta_1^{(1)}$ and $-\lambda_1^{(1)}$ respectively.

For the simple gas, we have shown in the last chapter that the convergence of the first order is very rapid. So the contribution of the first order can be put equal to the experimental value i.e. $T_1^{(1)} = (T_1)_{expt.}$ Using these approximations, eqns. (6.2) and (6.3) become

$$\eta_{o\ E}^{(1)} = \eta_{1\ expt} + \eta_{2\ expt} \qquad (6.4)$$

$$\lambda_{o\ E}^{(1)} = \lambda_{1\ expt} + \lambda_{2\ expt} \qquad (6.5)$$

An experimental value for the contribution to the transport coefficient due to the interaction between unlike molecules can now be obtained as follows :

$$(T_{int})_E = T_{expt} - T_o^{(1)}{}_{expt} \qquad (6.6)$$

The first important point we wish to make is that the values of $(T_{int})_E$ for viscosity $((\eta_{int})_E)$ and thermal conductivity $((\lambda_{int})E))$ are always negative and are comparable with η_{mix} and λ_{mix} in magnitude. As an example, we plot, in figs. 52 and 53 these quantities for an Ar-He mixture as a function of the concentration ratio x_1 $(= n_1/(n_1 + n_2))$. Other mixtures show similar behaviour. This shows in contrast to some remarks in previous literature (Ma-57a, Ch.-62) that the contribution of interactions between unlike molecules to η_{mix} and λ_{mix} is quite significant. Also we note that $(\eta_{int}^{(1)})$ and $(\lambda_{int}^{(1)})$ are the theoretical counterparts of $(D_{12}^{(1)})$ and $(k_T^{(1)})$ in the sense that all of them vanish when there are no interactions between unlike molecules.

From eqn. (6.1), the first order approximation to eqn. (6.6) is $T_{int}^{(1)}$. The values of $T^{(1)}$ needed for $T_{int}^{(1)}$ for a Lennard-Jones potential have been computed in the literature (Th.-60, Th.-61, T.B.-62) with the set of potential parameters for interaction between unlike molecules obtained by the usual combination rules (Table 34).

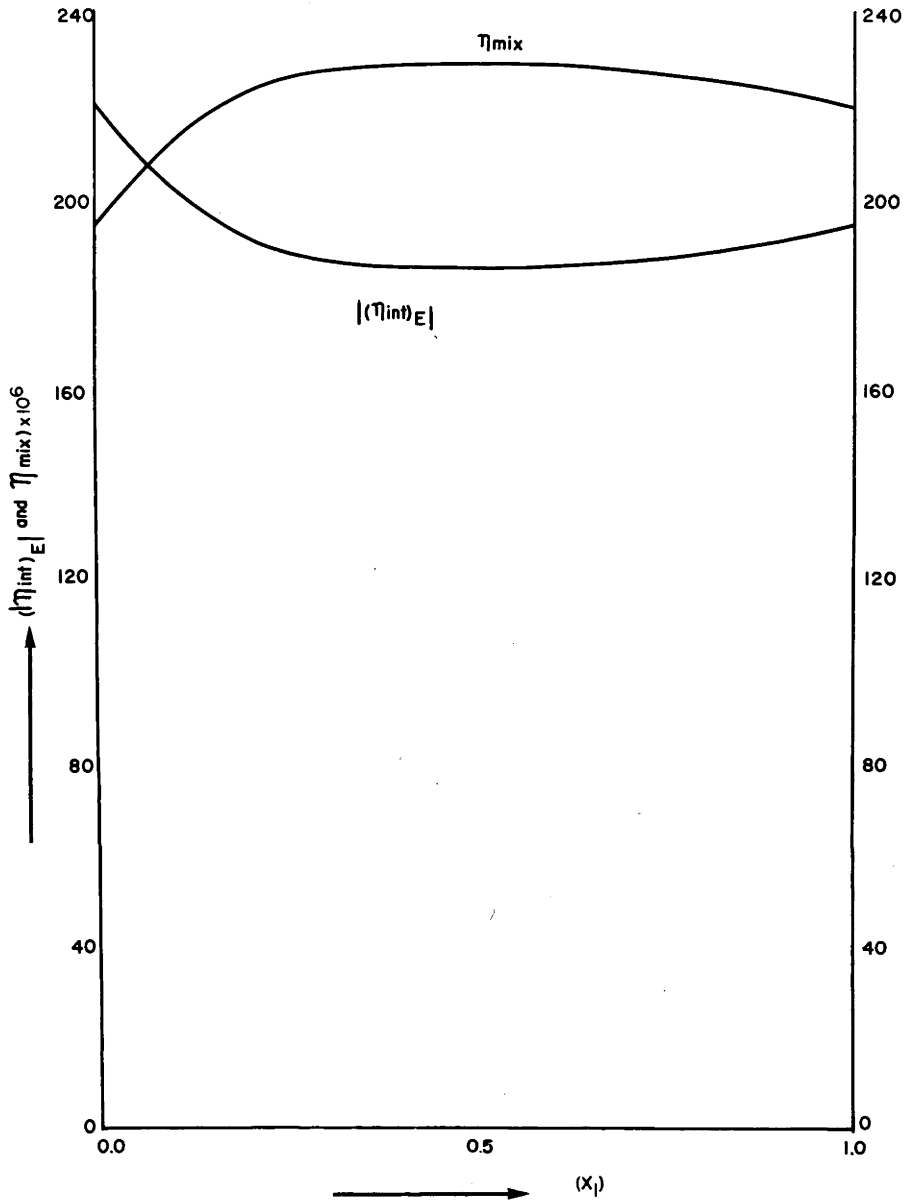

Fig. 52 .. For Ar-He, the experimental values for viscosity (η_{mix}) and for the part of viscosity depending upon the interactions between unlike molecules ($(\eta_{int})_E$) have been compared for various concentrations of the heavier component.

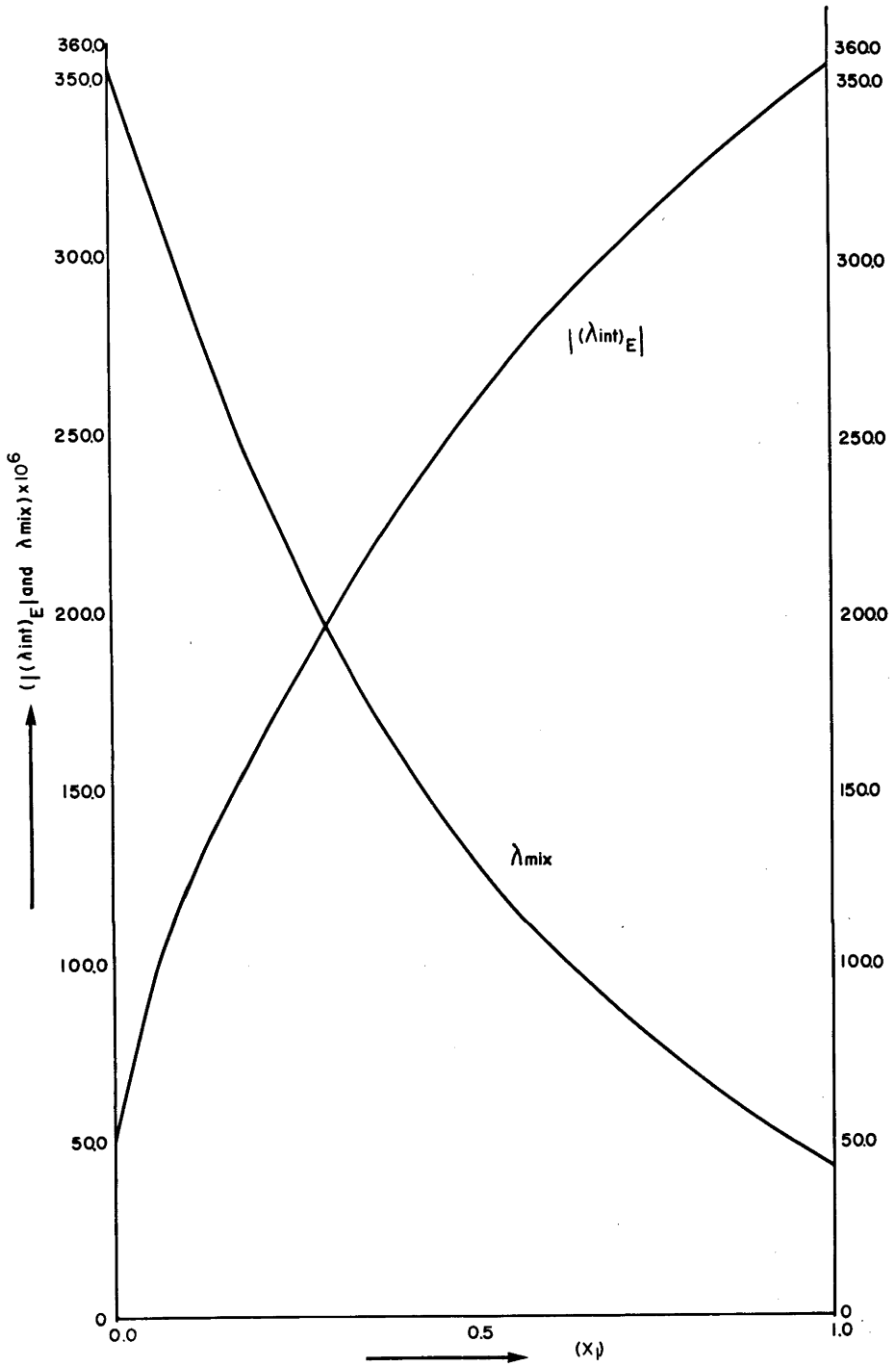

Fig. 53 .. For Ar-He, the magnitudes of experimental values for thermal-conductivity (λ_{mix}) and for the part of thermal-conductivity depending upon interactions between unlike molecules ($(\lambda_{int})_E$) have been compared for various concentrations of the heavier component.

We shall now state the results of comparing $(T_{int})_E$ with the corresponding theoretical values.

$T_{int}^{(1)}$, for various values of X_1 in figs. 54 to 58 for various gas mixtures (Xe-Kr, Xe-Ar, Xe-Ne, Xe-He, Kr-Ne, Kr-He, Ar-Ne, Ar-He).

<u>Viscosity</u> - Xe-Kr, Xe-Ar, Xe-Ne and Ar-He, the deviation is within the experimental error 1.5%.

Xe-He, Kr-Ne, Kr-He and Ar-Ne, the deviation is up to 3.0% from the experimental values which are accurate up to 1.5%.

<u>Thermal Conductivity</u> - Xe-Kr, Xe-Ar, Xe-Ne, Xe-He and Ar-Ne, the deviation is within the experimental error of 3.2% to 5.3%.

Kr-Ne, Kr-He and Ar-He, the deviation is up to 10% from the experimental values which are accurate up to 3.2%to 5.3%.

The above comparison with the first order theory shows that the assumed potential parameters are quite suitable for these cases. Still in view of the accuracy of the experimental data, one has a discrepancy as high as 5% (in some cases) to explain. Using the theoretical values given in Tables (35-38, 42-45) we can show that the discrepancies for the Ar-Ne, Kr-He and Kr-Ne cannot

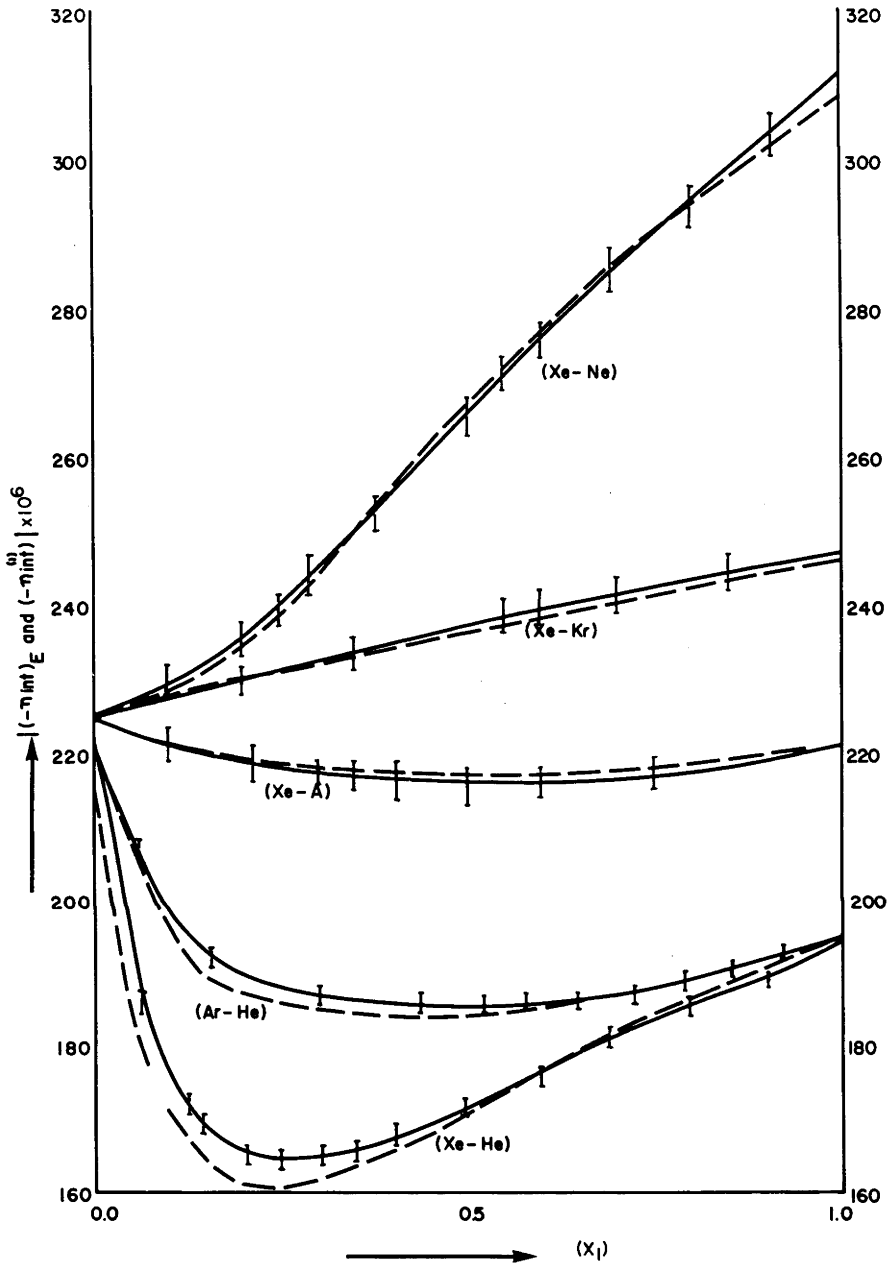

Fig. 54 .. For (Xe-Kr, Xe-Ar, Xe-He), the experimental and the first order theoretical values for the part of viscosity depending upon interaction between unlike molecules have been compared for various concentrations of the heavier component. Solid lines for experimental and dotted for theoretical values.

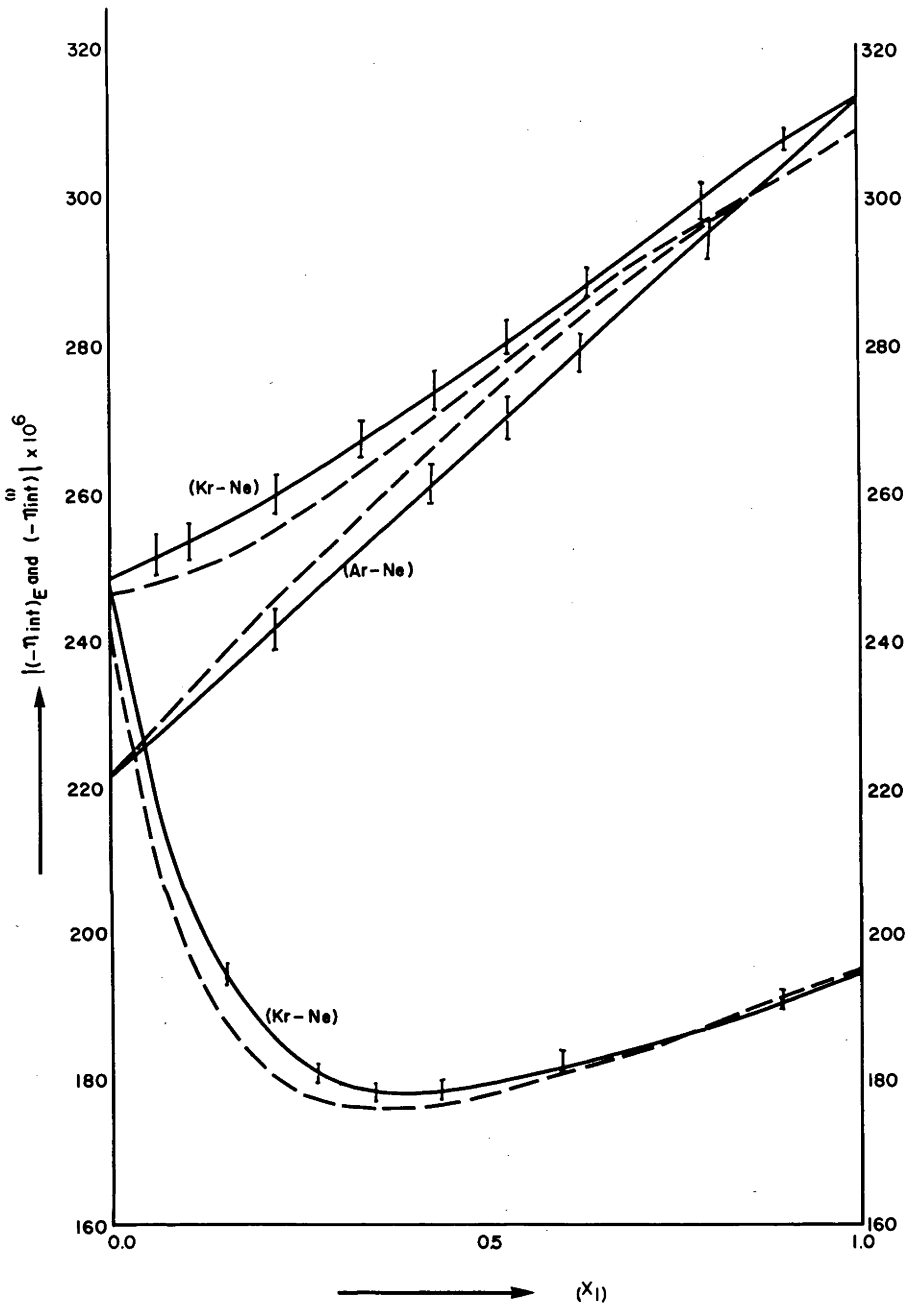

Fig. 55 .. For (Kr-Ne, Kr-He, Ar-Ne, Ar-He), the experimental and the first order theoretical values for the part of viscosity depending upon interactions between unlike molecules have been compared for various concentrations of the heavier components. Solid lines for experimental and dotted for theoretical values.

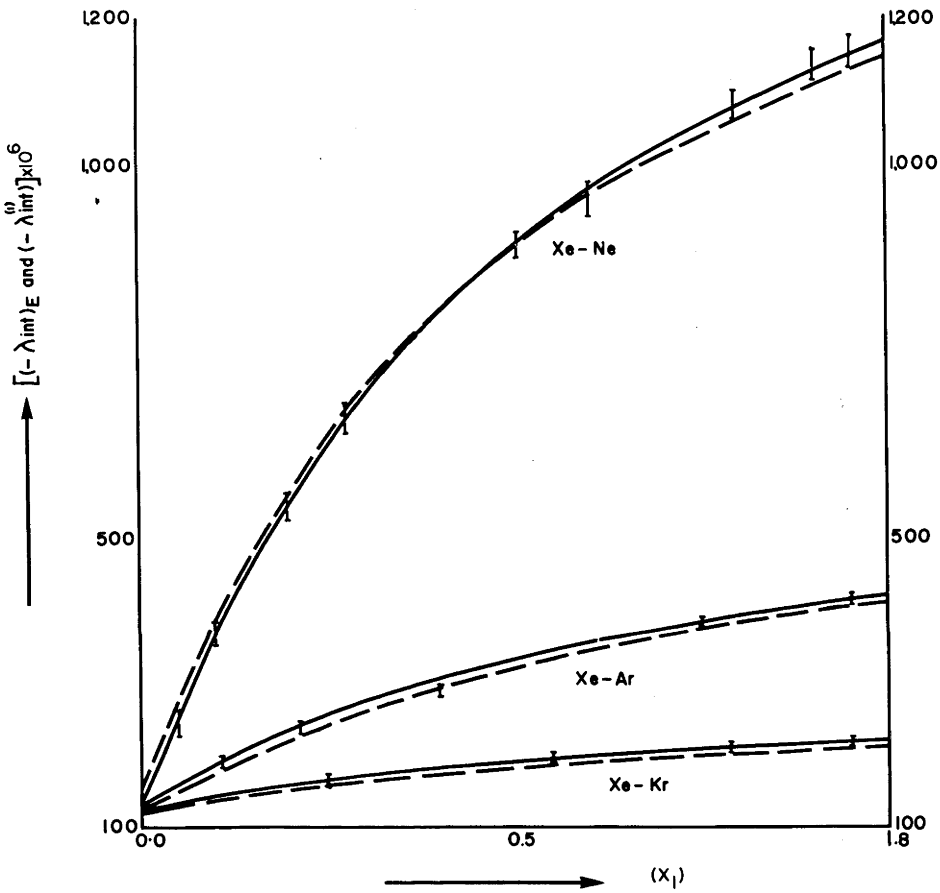

Fig. 56 .. For (Xe-Kr, Xe-A, Xe-Ne) cases, the experimental and the first order theoretical values for the part of thermal conductivity depending upon interaction between unlike molecules have been compared for various concentrations of the heavier component. Solid lines for experimental and dotted for theoretical values.

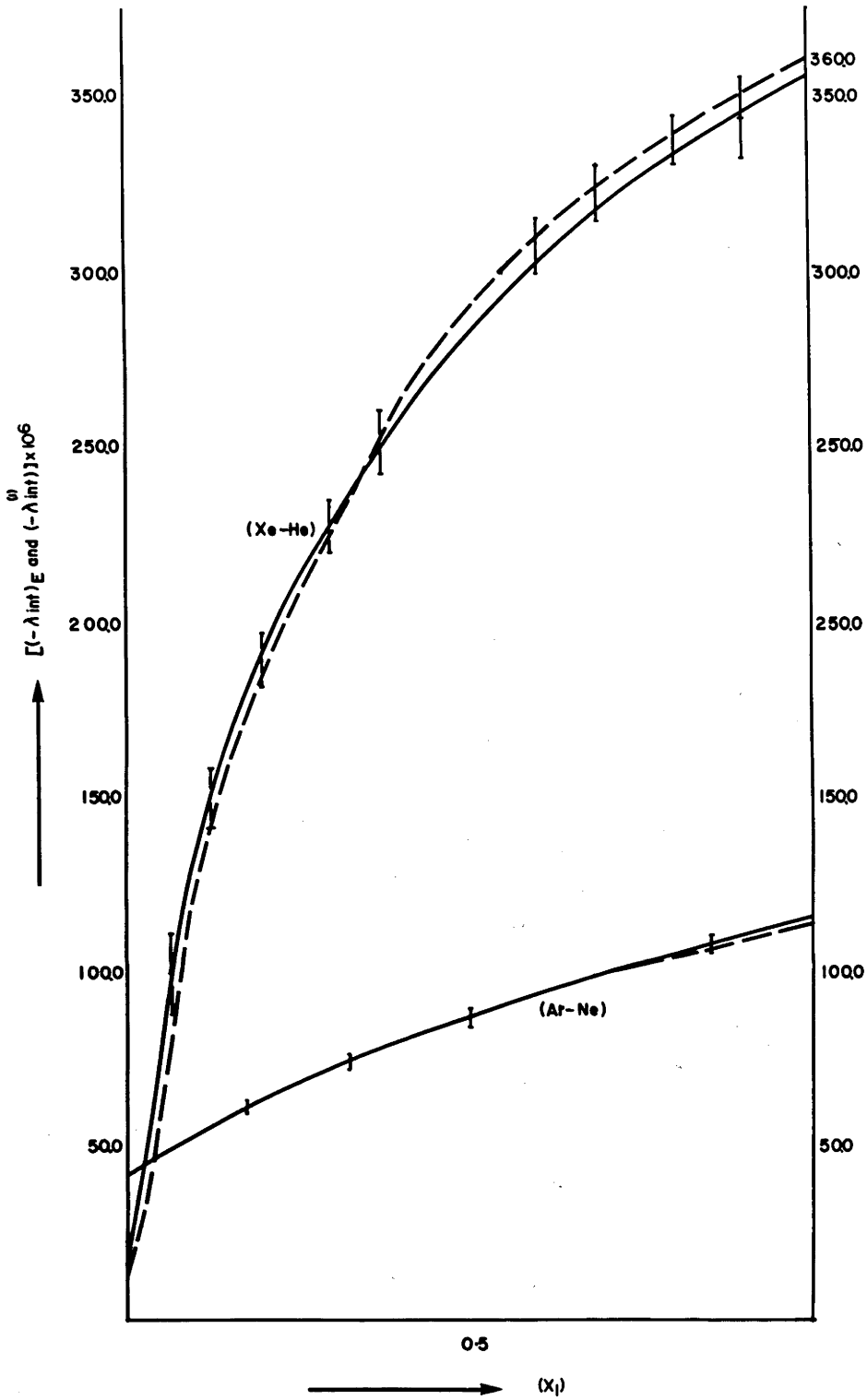

Fig. 57 .. For (Xe-He, Ar-Ne), the experimental and the first order theoretical values for the part of thermal conductivity depending upon interactions between unlike molecules have been compared for various concentrations of the heavier component. Solid lines for experimental and dotted for theoretical values.

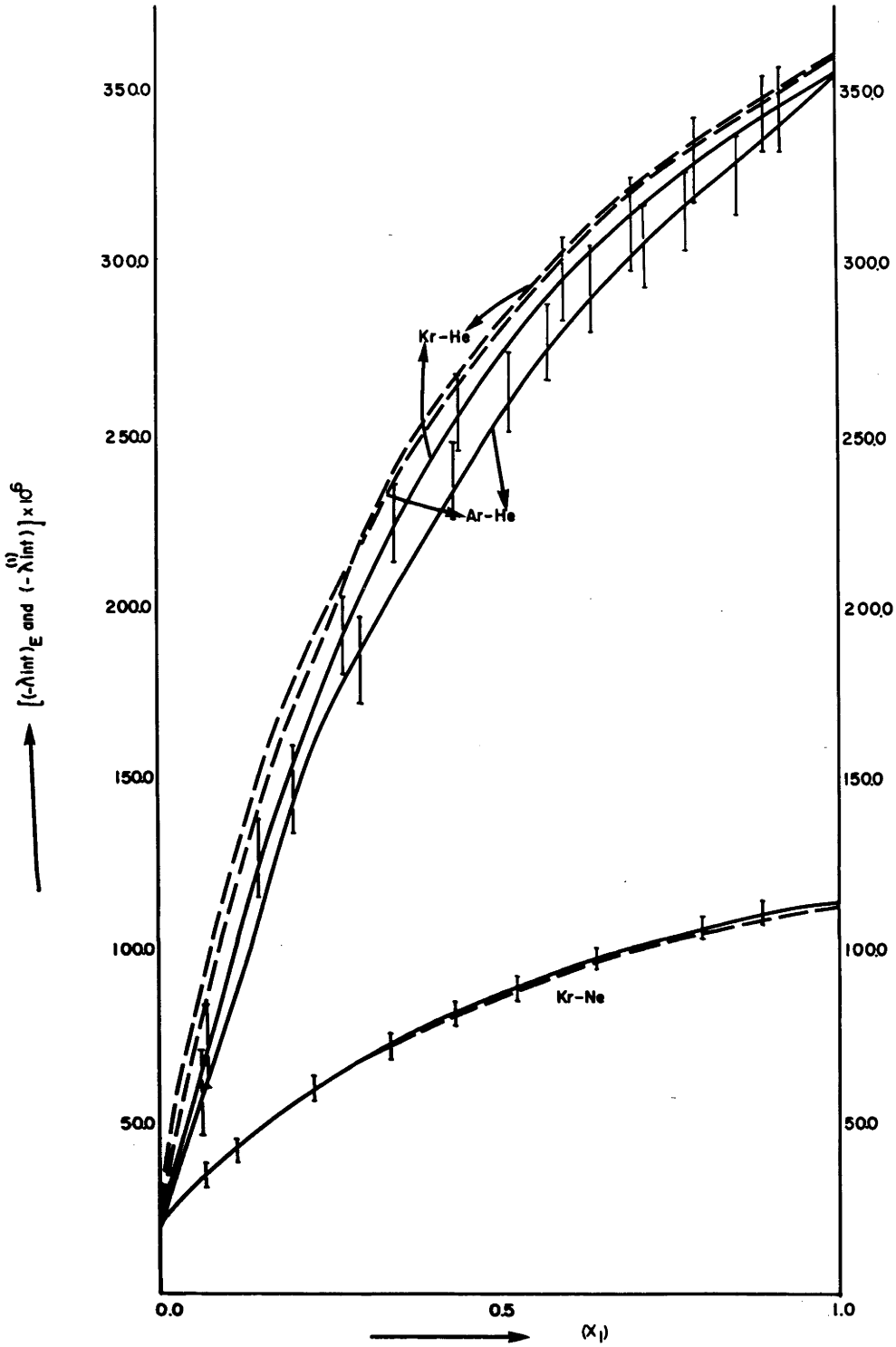

Fig. 58 .. For (Kr-Ne, Kr-He, Ar-He), the experimental and the first order theoretical values for the part of thermal conductivity depending upon interactions between unlike molecules have been compared for various concentrations of the heavier component. Solid lines for experimental and dotted for theoretical values.

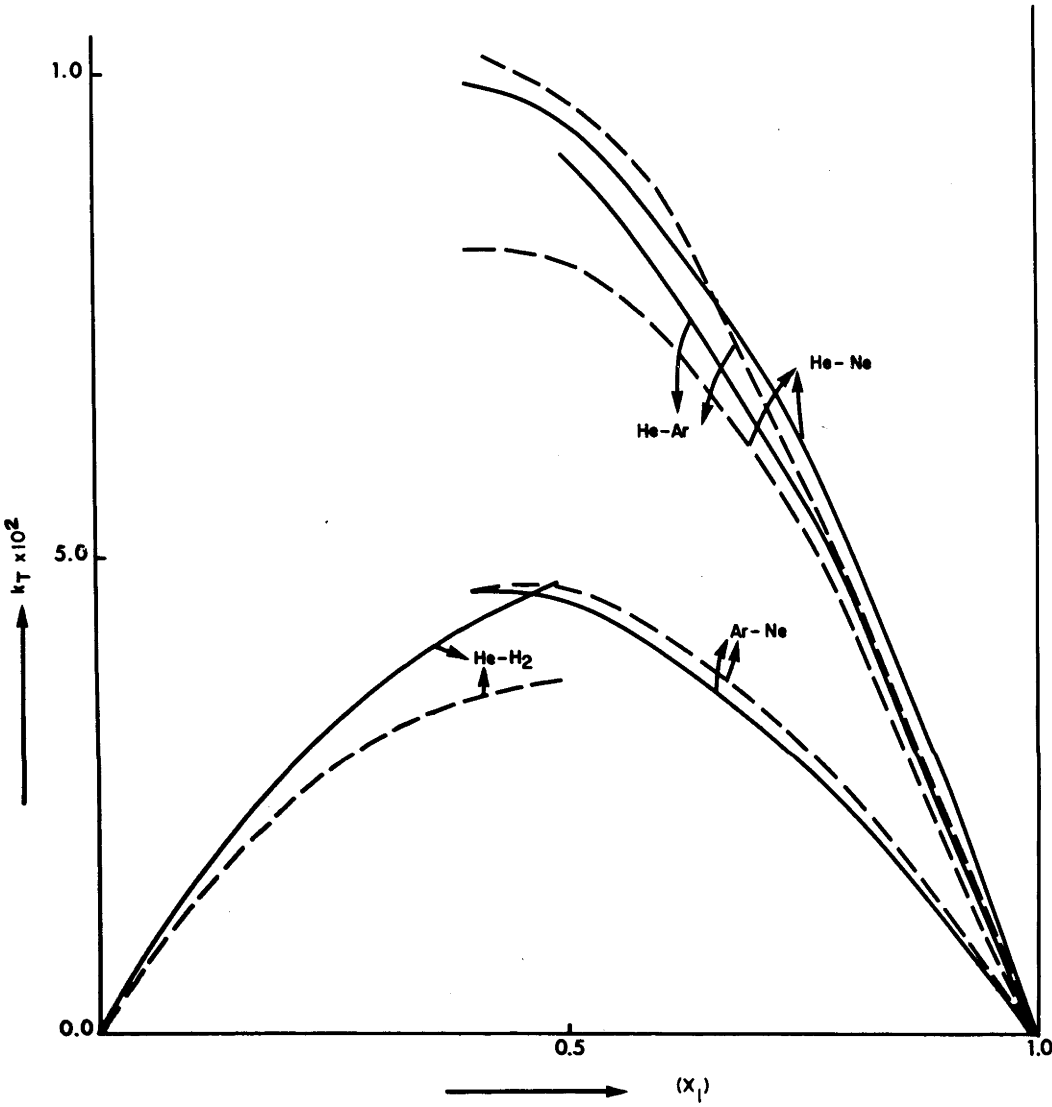

Fig. 59 .. For (Ar-Ne, He-H_2, Ar-He, Ne-He), the experimental and the first order theoretical values for thermal-diffusion ratio have been compared. Solid lines for experimental and dotted for theoretical values.

be removed by including even the fourth order contribution. For example, for the Ar-Ne mixture, in case of η_{mix}, by including the first four order contributions, the discrepancy is 2.2% while for Kr-He, in case of λ_{mix}, it is about 7%.

A comparison of the experimental values and the first order theory for the Lennard-Jones potential for k_T is plotted in Fig. 59 for He-H_2, Ar-Ne, Ne-He and Ar-He mixture (Ch. 8, H.C.B.-64). It depicts that the deviation of the experimental data from $k_T^{(1)}$ is as high as 20.0% though the experimental error is up to 3%. The higher order contributions are much smaller than the deviations.

From these cases it would, then, appear more profitable to compare $((\eta_{int})_E)$ and $((\lambda_{int})_E)$ with the corresponding theoretical expressions instead of studying k_T for the following reasons :

(1) More accurate and extensive data are available for η_{mix} and λ_{mix} than for k_T and D_{12}.

(2) Better agreement between $(\eta_{int}^{(1)})$ and $(\eta_{int})_E$, $(\lambda_{int}^{(1)})$ and $(\lambda_{int})_E$ as compared with $k_T^{(1)}$ and $(k_T)_{expt}$.

(3) As shown in the previous chapter, the rate of decrement of the first four orders is faster for η_{mix} and λ_{mix} than for D_{12} and k_T.

APPENDIX A

CALCULATION OF THE INTERACTION INTEGRALS

From eqn. (2.42)

$$V^{\ell}_{nn'}(12) = \int_0^{\infty} \bar{w}(\gamma g)\, R_{n\ell}(\gamma g)\; R_{n\ell}(\gamma g)\; (\sigma_0 - \sigma_{\ell}(g))\, g^3\, dg \qquad \text{(A-1)}$$

Where $R_{n\ell}(\gamma g)$ from eqn. (2.7) is

$$R_{n\ell}(\gamma g) = N_{n\ell}\left(\frac{\gamma g}{\sqrt{2}}\right)^{\ell} S^{n}_{\ell+\frac{1}{2}}\left(\tfrac{1}{2}\gamma^2 g^2\right) \qquad \text{(A-2)}$$

$$S^{(n)}_{\ell+\frac{1}{2}}(x) = \sum_{p=0}^{n} a_p (x)^p$$

$$= \sum_{p=0}^{n} \frac{1}{p!\,(n-p)!} \frac{(n+\ell+3/2)}{(p+\ell+3/2)} (-x)^p \qquad \text{(A-3)}$$

and $\sigma_{\ell}(g)$ from eqn. (2.40) is

$$\sigma_{\ell}(g) = 2\pi \int_{-\pi}^{\pi} \sigma(g,\chi)\; P_{\ell}(\cos\chi)\, d(\cos\chi)\,. \qquad \text{(A-4)}$$

χ by definition is

$$\chi(b\quad g) = \pi - 2b \int_{rm}^{\infty} \frac{dr/r^2}{\sqrt{1 - \frac{b^2}{r^2} - \frac{\varphi(r)kT}{\frac{1}{2}\gamma^2 g^2}}} \qquad \text{(A-5)}$$

where all the symbols have the usual meanings.

A RIGID SPHERE POTENTIAL

$$\left.\begin{aligned} \varphi(r) &= \infty \text{ for } r \leq \sigma \\ &= 0 \quad \text{for } r > \sigma \end{aligned}\right\} \tag{A-6}$$

Now substituting (Υ) in eqn (A-5) and putting $r_m = \sigma$ if $b \leq \sigma$ and $r_m = b$ for $b > \sigma$ we get

$$\left.\begin{aligned} \chi &= 2 \cos^{-1} (b/\sigma) \quad \text{for } b \leq \sigma \\ &= 0 \qquad\qquad\qquad \text{for } b > \sigma \end{aligned}\right\} \tag{A-7}$$

Substituting this value of χ in eqn. (A-4) we get

$$\sigma_\ell(g) = \pi \sigma^2 \quad \delta_{\ell 1} \tag{A-8}$$

Substituting (A-2), (A-3) and (A-8) and integrating (A-1), we get

$$V^{\ell}_{nn'}(12) = 2\pi \frac{\sigma^2_{12}}{\gamma} N_{n\ell} N_{n\ell} \sum_{p\,p'} a_p a_{p'} (\ell + p + p' + 1)! \tag{A-9}$$

It is convenient to introduce a quantity $Z^{\ell}_{nn'}$

which is independant of the nature of the gas and temperature.

$$V^{\ell}_{nn'} = \frac{\sigma^2_{12}}{\gamma} Z^{\ell}_{nn'} \tag{A-10}$$

Then by eqn (A-9)

$$Z^{\ell}_{nn'} = 2\pi N_{n\ell} N_{n'\ell} \sum_{p\,p'} a_p a_{p'} (\ell + p + p' + 1)! \tag{A-11}$$

The coefficients a_p can be computed from the following recursion relation (p = n)

$$\frac{a_p}{a_{p+1}} = \frac{(-)\ (p+1)\ (p+\ell+3/2)}{(n-p)} \qquad \text{(A-12)}$$

with the initial value

$$a_n = \frac{(-)^n}{n\,!} \qquad \text{(A-13)}$$

The values of $Z^{\ell}_{nn'}$ for = 1 to 5 and n = 0 to 3 and n' = 0 to 3 are given in table 3.

B LENNARD-JONES POTENTIAL

The general form of the potential is

$$\Phi(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \qquad \text{(A-14)}$$

Where ϵ is the depth of the potential will and σ is the range parameter. The calculations of the interaction integrals ($V^{\ell}_{nn'}$) for this potential are much more difficult than for the rigid sphere case. The associated difficulties ~~associated~~ are the same as those in the calculation of the collision integrals ($\Omega^{(\ell, s)}$). The latter calculations have been considered in detail by many workers (H.B.S.-48, D.S.-62, Sm-64, S.M.-64, I.G.S.-61). Without going into

Table 3

VALUES OF $Z^{\ell}_{nn'}$ $\left(= \dfrac{\gamma \; V^{\ell}_{nn'}(12)}{\sigma_{12}^{2}}\right)$ FOR A RIGID SPHERE POTENTIAL

	n = 0	n = 1	n = 2	n = 3	n = 4	
n′ = 0	6.68434	-2.11377	-0.399466	-0.163061	-8.68546	
= 1	-2.11377	8.68964	-2.90541	-0.567292	-0.236745	
= 2	-0.399466	-2.90541	10.3369	-3.49880	-0.692832	$\ell = 1$
= 3	-0.163061	-0.567292	-3.49880	11.7650	-3.99051	
= 4	-0.0868546	-0.236724	-0.692832	-3.99327	13.0460	
n′ = 0	8.02121	-2.14376	-0.357293	-0.131955	-0.0646253	
= 1	-2.14376	9.74004	-2.96021	-0.528933	-0.204007	
= 2	-0.357293	-2.96021	11.2201	-3.56727	-0.660814	$\ell = 2$
= 3	-0.131955	-0.528933	-3.56745	12.5371	-4.06665	
= 4	-0.0646253	-0.204403	-0.661582	-4.06835	13.7186	
n′ = 0	9.16710	-2.16070	-0.325738	-0.110630	-0.0503063	
= 1	-2.16070	10.6949	-2.99431	-0.495519	-0.178656	
= 2	-0.325738	-2.99431	12.0492	-3.61315	-0.628816	
= 3	-0.110630	-0.495655	-3.61315	13.2734	-4.11526	$\ell = 3$
= 4	-0.0503063	-0.178656	-0.628816	-4.11591	14.3962	

TABLE 3 (Cont'd.)

$n' = 0$	10.1857	-2.17159	-0.301145	-0.0952801	-0.0404555
$= 1$	-2.17159	11.5746	-3.01761	-0.466657	-0.158546
$= 2$	-0.301145	-3.01761	12.8300	-3.64557	-0.601583
$= 3$	-0.0952801	-0.467058	-3.64557	13.9798	-4.16176 $\ell = 4$
$= 4$	-0.0404555	-0.158546	-0.599651	-4.16306	-6650.04

$n' = 0$	11.1116	-2.17917	-0.281329	-0.0836543	-0.0338157
$= 1$	-2.17917	12.3937	-3.03453	-0.442182	-0.142266
$= 2$	-0.281329	-3.03453	13.5688	-3.67114	-0.579429
$= 3$	-0.0836543	-0.442592	-3.67114	14.6580	4320.61 $\ell = 5$
$= 4$	-0.0338157	-0.142266	-0.582114	4320.61	39304.0

details, we will just mention the nature of major difficulties (For details, see S.M.-64). The collision integral $\Omega^{(\ell,s)}$ is given by

$$\Omega^{(\ell,s)} = \frac{1}{2\pi\gamma}\int_0^\infty e^{-x^2}\, x^{2s+3}\, Q^{\ell}(kT\,x)\,dx \qquad \text{(A-15)}$$

where

$$Q^{\ell}(E) = 2\pi\int_0^\infty (1-\cos^{\ell}\chi)\, b\, db \qquad \text{(A-16)}$$

and

$$\chi(E,b) = \pi - 2b\int_{r_m}^{\infty}\frac{dr/r^2}{\sqrt{\left(1-\frac{\phi(r)}{E}-\frac{b^2}{r^2}\right)}} \qquad \text{(A-17)}$$

All the symbols have their usual meanings.

The main difficulties are: Firstly, the potential has a minimum so that we have to distinguish between orbitting and non-orbitting energies. There is a critical energy, E_C, for this potential only below which the orbitting takes place. Secondly, there is a singularity in the integrand of $\chi(b,E)$. Thirdly, since all the above integrals are to be evaluated numerically, the knowledge about the behaviour of two integrands is very important in neglecting the contributions beyond a certain value of r, b and x.

Because of the above difficulties, a lot of computor

time is taken by the preliminary calculations of α and limits for i and j in eqns. (A-19 to A-22) below, before the final programme can be written. To give an idea of the complications of working with the present potential, in terms of computor time, the final programme for the $V_{nn'}^{\ell}$, for a fourth order calculation of the coefficients, as discussed later, took 4.12 minutes on the I.B.M. - 360 for a given gas-mixture and temperature. A similar calculation in the case of rigid sphere potential takes only 0.45 minutes. Moreover, the time needed for calculating V's for 12 temperatures for a given mixture and for the fourth order calculation was 20.2 minutes while for the rigid sphere case, only one calculation is sufficient for all temperature so the time is still 0.45 minutes.

For a binary mixture, we have three values of ϵ and σ parameters denoted by ϵ_{11}, ϵ_{12}, ϵ_{22}, σ_{11}, σ_{12} and σ_{22}, corresponding to like and unlike molecules. A calculation of the coefficient for a particular temperature involves three sets of V's to be known. For each such set, for a fourth order calculation, we need 75 V's corresponding to the variation in ℓ from 1 to 5, n from 0 to 4 and n' from zero to n. For these V's we need 45 Ω's because ℓ will vary from 1 to 5 and s varies from ℓ to $\ell + n + n'$. Thus for 12 temperatures we need 36 sets of V's and Ω's where each of such sets contains 75 V's and 45 Ω's.

Due to the numerical approximations of the integrals, the accuracy of calculated Ω's is always quoted to be 1 to 3 in 10^3 by different workers (S.M.-64, H.B.S.-48). In the recently published tabulations for this potential for different values of T^* (= kT/ϵ) the values are given up to the sixth decimal place (M.M.-61), which suggests that the values may be more accurate than the ones quoted.

In the present work, we have calculated the interaction integrals $V_{nn'}^{\ell}$ by first calculating the collision integrals $\Omega^{(\ell, s)}$ and then using eqn. (4.46). The collision integrals have been calculated by the method of Smith and Munn (S.M.-64). Following their notation, we made several modifications :

(1) Following the same method, we work with reduced quantities which are denoted by a star (For explicit relationships between the reduced and ordinary quantities, see Ch. 8, H.C.B.-64). Eqn. (A-15) becomes

$$\phi^* (r^*) = 4\left[\left(\frac{1}{r^*}\right)^{12} - \left(\frac{1}{r^*}\right)^{6}\right] \qquad \text{(A-18)}$$

Writing the numerical values of the integrals (A-15 to A-17) by using gaussian quadratures, eqns. (14), (17), (18) and (19) of Smith and Munn in this notation become

$$\chi (E^*, b^*) = \pi - \frac{\pi b^*}{N r_m^*} \sum_{j=1}^{N/2} \frac{a_{(N/2) - j + 1}}{F(r^*_m/a_j)} \qquad \text{(A-19)}$$

$$\int_0^{b_0^*} b^* (1 - \cos^{\ell}\chi)\, b^*\, db^* = \frac{\left[1 - \frac{1}{2}\frac{1 + (-)^{\ell}}{(1+\ell)}\right]}{4} b_0^* \sum_{i=1}^{N} W_i\, b_i^* (1 - \cos^{\ell}\chi_i) \qquad \text{(A-20)}$$

$$\int_{b_0^*}^{\infty} b^* (1 - \cos^{\ell}\chi)\, b^*\, db^* = \frac{\left[1 - \frac{1}{2}\frac{1 + (-)^{\ell}}{(1+\ell)}\right]}{2} \sum_{j=1}^{N} (W_j \exp y_j) b_j^* (1 - \cos^{\ell}\chi_j) \qquad \text{(A-21)}$$

$$\Omega^{(\ell,S)*}(T^*) = \frac{1}{(S+1)!} \sum_{j=1}^{N} W_j\, y_j^{S+1}\, Q^{(\ell)*}(kT\, y_i) \qquad \text{(A-22)}$$

All the symbols have their usual meanings.

In eqns. (A-19 to A-22), we have corrected some misprints in eqns. (14), (17) and (19) of Smith and Munn's paper (S.M.-64).

(2) Instead of following the complicated way of Smith and Munn, we calculated E_C^* the critical energy by the following conditions

$$\varphi_{eff}^{*\prime}(r^*) = \varphi_{eff}^{*\prime\prime}(r^*) = 0 \qquad \text{(A-23)}$$

where

$$\varphi_{eff}^*(r^*) = \varphi^*(r^*) + \frac{b^{*2}\, E^*}{r^{*2}} \qquad \text{(A-24)}$$

(3) For calculating turning points, instead of using five point Aitkin's interpolation formula as suggested in Smith and Munn, we found that even the three point Aitkin's interpolation formula is good enough.

Finally, the values of $V^{\ell}_{nn'}$ were obtained from eqn (4.46) using the values of $\Omega^{(\ell,s)*}$ as obtained above and the values of brackets $(B(n\ell, n'\ell ; p))$ given by eqn. (3.4) of Bordy and Moshinsky tables (B.M.-60). These values for given values of Ω's, temperature and order were stored on the disc. We have given a specimen set of values for $V^{\ell}_{nn'}$ or $Z^{\ell}_{nn'}$ (eqn. (A-10)) for $\ell = 1$ to 5, $n = 0$ to 4 and $n' = 0$ to 4 in table 4 for $T^* = 1.613$.

Our values of $\Omega^{(\ell,s)*}$ are in good agreement with those of other existing tabulations which are available up to third-order calculations (total number of Ω's tabulated for each T^* are 16 e.g. Table I - M, p.1126 H.C.B.-64, Ma - 57a). The agreement is up to 1 to 3 in 10^3 for values up to $T^* = 30$.

The stored values were used for calculating transport coefficients. It was found that the first order values for Kr-He mixture obtained from this work (Table 45) agree with those of Thoronton (Th.-61) who calculated the coefficients using $\Omega^{(\ell,s)*}$ values of Hirschfelder et al (Table I - M, p. 1126, H.C.B.-64), within a few parts in a thousand. The calculations, in both cases, are done for 291° K. The discrepancy between the two sets when Krypton is in majority (corresponding to low T^*) is minimum (1 to 10^3) and is maximum, as large as 5 to 10^3, when Helium is in majority (corresponding to high T^*).* Meanwhile the corresponding

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* The reason for discussing this case was that the discrepancy of few parts in a thousand was the maximum.

TABLE 4

VALUES OF $Z^{\ell}_{nn'}$ FOR THE LENNARD-JONES POTENTIAL FOR $T^* = 1.613$

	n = 0	n = 1	n = 2	n = 3	n = 4	
n′ = 0	7.792470	-0.5252469	.2381303	.2170962	.1400837	
= 1	-0.5252469	8.855278	-0.9767417	.1445013	.1967291	
= 2	.2381303	-0.9767417	9.652292	-1.353868	.02753864	$\ell = 1$
= 3	.2170962	.1445013	-1.353868	10.32118	-1.663027	
= 4	.1400837	.1968056	.02753864	-1.663639	10.93284	
n′ = 0	10.25641	-0.5008545	.3102875	.2140808	.08970642	
= 1	-0.5008545	11.28944	-1.001923	.2326965	.2012177	
= 2	.3102875	-1.001923	12.07803	-1.457764	.1101074	$\ell = 2$
= 3	.2140808	.2325745	-1.458008	12.76489	-1.847900	
= 4	.090C1160	.1999969	.1130371	-1.847900	13.39551	
n′ = 0	12.07783	-0.4420142	.3936495	.2656904	.1292595	
= 1	-0.4420142	13.10988	-0.8799549	.3987174	.3185302	
= 2	.3936495	-0.8799549	13.91772	-1.305636	.3163883	$\ell = 3$
= 3	.2656904	.3987174	-1.305636	14.61751	-1.677714	
= 4	.1292595	.3185302	.3114926	-1.687506	15.19642	

TABLE 4 (Cont'd.)

$n' = 0$	13.57472	-0.4302979	.4026031	.2510986	.1103516	
$= 1$	-0.4302979	14.56091	-0.8425293	.4411621	.3110352	
$= 2$	.4026031	-0.8425293	15.34619	-1.246826	.4658203	$\ell = 4$
$= 3$	.2510986	.4431152	-1.246826	16.09375	-1.429687	
$= 4$	.1103516	.3168945	.4345703	-1.425781	17.25781	

$n' = 0$	14.89482	-0.4136915	.4072085	.2405232	.08950049	
$= 1$	-0.4136915	15.83917	-0.7918882	.4956955	.2707966	
$= 2$	.4072085	-0.7918882	16.62965	-1.200684	.4464319	$\ell = 5$
$= 3$	.2405232	.4914117	-1.205580	17.31506	-1.659661	
$= 4$	.08858258	.3099626	.4562234	-1.659661	14.28581	

discrepencies of the values of $\Omega^{(\ell, s)*}$ in that range is at the most, 3 to 10^3. The reason for the increase in discrepency is not hard to seek.

In the present work, to start off, we calculate and store $Q^{(\ell)*}$ for different ℓ's and for forty energies (For the method of choosing energies and other details, see S.M.-64). Then we compute $\Omega^{(\ell, s)*}$ for which we need different $Q^{(\ell)*}$ corresponding to different abscissa (See eqn. A-22). The latter $Q^{(\ell)*}$s are obtained from the already tabulated ones by carrying suitable interpolations. The interpolations are linear for $0.8 \leqslant E^* \leq 1.6$ while for other energies, interpolations between $\log E^*$ and $\log Q^{(\ell)*}$ are linear. Thoronton calculates a particular $\Omega^{(\ell, s)*}$ for a given T^* by linear interpolation throughout and therefore, does not fully take into account the logarithmic behaviour of the interpolations so., that our calculations are more likely to be accurate.

APPENDIX B

Relation between interaction integrals and collision integrals.

The relationship between $V^{\ell}_{nn'}$ and $\Omega^{(\ell,s)*}$ is given by eqn. (4.45). Here we will consider the following specific cases.

$\ell = 1$; $n = 0,1,2,3$; $n' = 0,1,2,3$.

$\ell = 2$; $n = 0,1,2$; $n' = 0,1,2$.

$\ell = 3$; $n = 0,1$; $n' = 0,1$.

$\ell = 4$; $n = 0$; $n' = 0$.

Since $V^{\ell}_{nn'}(12)$ is symmetric (eqn. (2.42)) in (n,n'), the corresponding relations for $V^{\ell}_{n'n}$ are not given.

In the following cases, the exact fraction part is from $A(\lambda,p,p)$ (eqn. (4.47)) and the other numerical part is from Moshinsky brackets $B(n\lambda,n'\lambda;p)$ (eqn. (4.46); B.M-60). Denoting A as $\sqrt{2\pi}\,\frac{\sigma^2_{12}}{\gamma}$, $V^{\ell}_{nn'}$ as $V^{\ell}_{nn'}(12)$ and $\Omega^{(\ell,s)*}$ as $\Omega^{(\ell,s)*}_{12}$, we get the following relations.

$$V^1_{00} = A \left[{}^8/_3 \, \Omega^{(1,1)*} \right] \tag{B-1}$$

$$V^1_{01} = A \left[1.581 \left(\frac{8}{3} \Omega^{(1,1)*} - \frac{16}{5} \Omega^{(1,2)*} \right) \right] . \tag{B-2}$$

$$V^1_{02} = A \left[2.0916 \left(\frac{8}{3} \Omega^{(1,1)*} - \frac{32}{5} \Omega^{(1,2)*} + \frac{128}{35} \Omega^{(1,3)*} \right) \right] . \tag{B-3}$$

$$V^1_{03} = A \left[2.562 \left(\frac{8}{3} \Omega^{(1,1)*} - \frac{48}{5} \Omega^{(1,2)*} + \frac{384}{35} \Omega^{(1,3)*} - \frac{256}{63} \Omega^{(1,4)*} \right) \right] . \tag{B-4}$$

$$V^1_{11} = A \left[2.500 \left(\frac{8}{3} \Omega^{(1,1)*} - \frac{32}{5} \Omega^{(1,2)*} + \frac{128}{25} \Omega^{(1,2)*} \right) \right] . \tag{B-5}$$

$$V^1_{12} = A \left[3.307 \left(\frac{8}{3} \Omega^{(1,1)*} - \frac{48}{5} \Omega^{(1,2)*} \right) + 12.5673 \left(\frac{96}{35} \Omega^{(1,3)*} \right) - 5.953 \left(\frac{256}{63} \Omega^{(1,4)*} \right) \right] . \tag{B-6}$$

$$V_{13}^{1} = A \left[4.050 \left(\frac{8}{3}\,\Omega^{(1,1)*} - \frac{64}{5}\Omega^{(1,2)*}\right) + 29.16 \left(\frac{128}{35}\,\Omega^{(1,3)*}\right) - 25.92 \left(\frac{256}{63}\right)\Omega^{(1,4)*}\right) + 8.911 \left(\frac{1024}{231}\right)\Omega^{(115)*} \right] . \qquad \text{(B-7)}$$

$$V_{22}^{1} = A \left[4.375 \left(\frac{8}{3}\,\Omega^{(1,1)*} - \frac{64}{5}\,\Omega^{(1,2)*}\right) + 33.25 \left(\frac{96}{35}\right)\Omega^{(1,3)*} - 31.50 \left(\frac{256}{63}\right)\Omega^{(1,4)*} + 12.375 \left(\frac{1024}{231}\right)\Omega^{(1,5)*} \right] . \qquad \text{(B-8)}$$

$$V_{23}^{1} = A \left[5.360 \left(\frac{8}{3}\,\Omega^{(1,1)*} - 16\,\Omega^{(1,2)*}\right) + 66.44 \left(\frac{128}{35}\right)\Omega^{(1,3)*} - 92.16 \left(\frac{256}{63}\right)\Omega^{(1,4)*} + 69.04 \left(\frac{1024}{231}\right)\Omega^{(1,5)*} - 21.89 \left(\frac{4096}{1001}\right)\Omega^{(1,6)*} \right] . \qquad \text{(B-9)}$$

$$V_{33}^{1} = A \left[5.562 \left(\frac{8}{3}\,\Omega^{(1,1)*} - \frac{96}{5}\,\Omega^{(1,2)*}\right) + 122.062 \left(\frac{128}{35}\right)\Omega^{(1,3)*} - 225.75 \left(\frac{256}{63}\right)\Omega^{(1,4)*} + 253.688 \left(\frac{1024}{231}\right)\Omega^{(1,5)*} - 160.875 \left(\frac{4096}{1001}\right)\Omega^{(1,6)*} - 44.688 \left(\frac{8192}{2145}\right)\Omega^{(1,7)*} \right] . \qquad \text{(B-10)}$$

$$V_{00}^{2} = A \left(\frac{16}{5} \Omega^{(2,2)*} \right) \quad . \tag{B-11}$$

$$V_{01}^{2} = A \left[1.870 \left(\frac{16}{5} \Omega^{(2,2)*} - \frac{128}{35} \Omega^{(2,3*} \right) \right] \quad . \tag{B-12}$$

$$V_{02}^{2} = A \left[2.806 \left(\frac{16}{5} \Omega^{(2,2)*} - \frac{256}{35} \Omega^{(2,3)*} + \frac{256}{63} \Omega^{(2,4)*} \right] \right. \quad . \tag{B-13}$$

$$V_{11}^{2} = A \left[3.500 \left(\frac{16}{5} \Omega^{(2,2)*} - \frac{256}{35} \Omega^{(2,3)*} + \frac{256}{49} \Omega^{(2,4)*} \right) \right] \quad . \tag{B-14}$$

$$V_{12}^{2} = A \left[5.25 \left(\frac{16}{5} \Omega^{(2,2)*} - \frac{384}{35} \Omega^{(2,3)*} \right) + 18.75 \left(\frac{256}{63}\right) \Omega^{(2,4)*} - 8.25 \left(\frac{1024}{231}\right) \Omega^{(2,5)*} \right] \quad . \tag{B-15}$$

$$V_{22}^{2} = A \left[7.875 \left(\frac{16}{5} \Omega^{(2,2)*} - \frac{512}{35} \Omega^{(2,3)*} + 56.25 \left(\frac{256}{63}\right) \Omega^{(2,4)*} - 49.5 \left(\frac{1024}{231}\right) \Omega^{(2,5)*} + 17.875 \left(\frac{2048}{429}\right) \Omega^{(2,6)*} \right] \right. \quad . \tag{B-16}$$

$$V^3_{00} = A \left[\frac{64}{7} \Omega^{(3,3)*} - \frac{192}{35} \Omega^{(1,3)*} \right] , \tag{B-17}$$

$$V^3_{01} = A \left[2.12 \left(\frac{64}{7} \Omega^{(3,3)*} - \frac{192}{35} \Omega^{(1,3)*} \right) - \frac{640}{63} \Omega^{(3,4)*} + \frac{128}{21} \Omega^{(1,4)*} \right] . \tag{B-18}$$

$$V^3_{11} = A \left[4.50 \left(\frac{64}{7} \Omega^{(3,3)*} - \frac{192}{35} \Omega^{(1,3)*} \right) - \frac{1280}{63} \Omega^{(3,4)*} + \frac{256}{21} \Omega^{(1,4)*} + \frac{2560}{189} \Omega^{(3,5)*} - \frac{512}{63} \Omega^{(1,5)*} \right] . \tag{B-19}$$

$$V^4_{00} = A \left(\frac{128}{9} \Omega^{(4,4)*} - \frac{640}{63} \Omega^{(2,4)*} \right) . \tag{B-20}$$

The consistency of these relations can be checked by putting $\Omega^{(\ell,s)*} = 1$ (rigid sphere case) and finding the specific values of $V^{\ell}_{nn'}$ and comparing it with the values of $Z^{\ell}_{nn'}$ in table 3.

APPENDIX C

Algebraic Expressions for the Collision Matrices

We denote $V^{\ell}_{nn'}$ (12) by $V^{\ell}_{nn'}$ in all the following expressions. Also it is to be remembered that M_1 and M_2 are as defined by eqns. (4.49) and (4.50).

(a) VECTOR PART

(i) Matrix Elements of $J^1_{\nu_1\nu_2}$ (12)

Since from eqn. (4.5)

$$\mathcal{J}^1_{\nu_1\nu_2}(12) = J^1_{\nu_1\nu_2}(12) \quad ,$$

the corresponding matrix elements are not given.

$$J^1_{00}(12) = M_2 V^1_{00} \tag{C-1}$$

$$J^1_{01}(12) = M_2^2 V^1_{01} \tag{C-2}$$

$$J^1_{02}(12) = M_2^3 V^1_{02} \tag{C-3}$$

$$J^1_{03}(12) = M_2^4 V^1_{03} \tag{C-4}$$

$$J^1_{11}(12) = 3.0\, M_1^2\, M_2\, V^1_{00} + M_2^3\, V^1_{11} + 1.33\, M_1\, M_2^2\, V^2_{00} \quad . \tag{C-5}$$

$$J^1_{12}(12) = 5.02\, M_1^2\, M_2^2\, V^1_{01} + M_2^4\, V^1_{12} + 1.885\, M_1\, M_2^3\, V^2_{01} \quad . \tag{C-6}$$

$$J^1_{13}(12) = 6.971\, M_1^2\, M_2^3\, V^1_{02} + M_2^5\, V^1_{13} + 2.31\, M_1\, M_2^4\, V^2_{02} \quad . \tag{C-7}$$

$$J^1_{22}(12) = 5.0\, M_1^4\, M_2\, V^1_{00} + 3.73\, M_1^2\, M_2^3\, V^1_{11} + M_2^5\, V^1_{22} + 5.33\, M_1^3\, M_2^2\, V^2_{00} + 2.667\, M_1\, M_2^4\, V^2_{11} + 1.60\, M_1^2\, M_2^3\, V^3_{00} \quad . \tag{C-8}$$

$$J^1_{23}(12) = 11.62\, M_1^4\, M_2^2\, V^1_{01} + 5.185\, M_1^2\, M_2^4\, V^1_{12} + M_2^6\, V^1_{23} + 10.471\, M_1^3\, M_2^3\, V^2_{01} + 3.277\, M_1\, M_2^5\, V^2_{12} + 2.77\, M_1^2\, M_2^4\, V^3_{01} \quad . \tag{C-9}$$

$$J^1_{33}(12) = 7.0\, M_1^6\, M_2\, V^1_{00} + 27.0\, M_1^4\, M_2^3\, V^1_{11}$$

$$+ 16.2\, M_1^2\, M_2^5\, V^1_{22} + M_2^7\, V^1_{33} + M_2^7\, V^1_{33}$$

$$+ 12.0\, M_1^5\, M_2^2\, V^2_{00} + 20.57\, M_1^3\, M_2^4\, V^2_{11}$$

$$+ 4.0\, M_1\, M_2^6\, V^2_{22} + 8.0\, M_1^4\, M_2^3\, V^3_{00}$$

$$+ 4.80\, M_1^2\, M_2^5\, V^3_{11} + 1.829\, M_1^3\, M_2^4\, V^4_{00} \qquad \text{(C-10)}$$

(ii) <u>Matrix elements of</u> $J^1_{\underline{\nu}_1\nu_2}(12)$ and $J^1_{\nu_1\nu_2}(21)$

Since from eqns. (4.6) and (4.48)

$$\tilde{J}^1_{\underline{\nu}_1\nu_2}(12) = J^1_{\nu_1\nu_2}(21)$$

and

$$J^1_{\nu_1\nu_2}(21) = \left(\frac{M_1}{M_2}\right)^{\nu_2-\nu_1} J^1_{\nu_2\nu_1}(21) \quad ,$$

the corresponding matrix elements are not given.

$$J^1_{00}(21) = -\,(M_1\, M_2)^{1/2}\, V^1_{00} \qquad \text{(C-11)}$$

$$J^1_{01}(21) = -\, M_1^{1/2}\, M_2^{3/2}\, V^1_{01} \qquad \text{(C-12)}$$

$$J^1_{02}\,(21) = -\ M_1^{1/2}\ M_2^{5/2}\ V^1_{02}\ . \tag{C-13}$$

$$J^1_{03}\,(21) = -\ M_1^{1/2}\ M_2^{7/2}\ V^1_{03}\ . \tag{C-14}$$

$$J^1_{11}\,(21) = M_1^{3/2}\ M_2^{3/2}\ (-3.0\ V^1_{00} - V^1_{11} + 1.33\ V^2_{00})\ . \tag{C-15}$$

$$J^1_{12}\,(21) = M_1^{3/2}\ M_2^{5/2}\ (-5.02\ V^1_{01} - V^1_{12} + 1.885\ V^2_{01})\ . \tag{C-16}$$

$$J^1_{13}\,(21) = M_1^{3/2}\ M_2^{7/2}\ (-6.971\ V^1_{02} - V^1_{13} + 2.31\ V^2_{02})\ . \tag{C-17}$$

$$J^1_{22}\,(21) = M_1^{5/2}\ M_2^{5/2}\ (-5.0\ V^1_{00} - 3.73\ V^1_{11} - V^1_{22} + 5.33\ V^2_{00} + 2.667\ V^2_{11} - 1.60\ V^3_{00})\ . \tag{C-18}$$

$$J^1_{23}\,(21) = M_1^{5/2}\ M_2^{7/2}\ (-11.62\ V^1_{01} - 5.185\ V^1_{12} - V^1_{23} + 10.471\ V^2_{01} + 3.277\ V^2_{12} - 2.77\ V^3_{01})\ . \tag{C-19}$$

$$J^1_{33}(21) = M_1^{7/2} \; M_2^{7/2} \; (-7.0\, V^1_{00} - 27.0\, V^1_{11} -$$

$$- 16.2\, V^1_{22} - V^1_{33} + 12.0\, V^2_{00} + 20.57\, V^2_{11}$$

$$+ 4.0\, V^2_{22} - 8.0\, V^3_{00} - 4.80\, V^3_{11}$$

$$+ 1.829\, V^4_{00}) \quad . \qquad \text{(C-20)}$$

(iii) <u>Matrix element of</u> $\underset{\sim}{J}^1_{\nu_1\nu_2}(21)$

Since from eqn. (4.8)

$$\tilde{\underset{\sim}{J}}^1_{\nu_1\nu_2}(21) = \underset{\sim}{J}^1_{\nu_1\nu_2}(21) \quad ,$$

the corresponding matrix elements are not given.

$$\underset{\sim}{J}^1_{00}(21) = M_1\, V^1_{00} \quad . \qquad \text{(C-21)}$$

$$\underset{\sim}{J}^1_{01}(21) = M_1^2\, V^1_{01} \quad . \qquad \text{(C-22)}$$

$$\underset{\sim}{J}^1_{02}(21) = M_1^3\, V^1_{02} \quad . \qquad \text{(C-23)}$$

$$\underset{\sim}{J}^1_{03}(21) = M_1^4\, V^1_{03} \quad . \qquad \text{(C-24)}$$

$$\underset{\sim}{J}^1_{11}(21) = 3.0\, M_1\, M_2^2\, V^1_{00} + M_1^3\, V^1_{11} + 1.33\, M_1^2\, M_2\, V^2_{00} . \qquad \text{(C.25)}$$

$$\underline{J}^1_{12}\,(21) = 5.02\, M_1^2\, M_2^2\, V^1_{01} + M_1^4\, V^1_{11}$$

$$+ 1.885\, M_1^3\, M_2\, V^2_{01} \quad . \qquad \text{(C-26)}$$

$$\underline{J}^1_{13}\,(21) = 6.971\, M_1^3\, M_2^2\, V^1_{02} + M_1^5\, V^1_{13}$$

$$+ 2.31\, M_1^4\, M_2\, V^2_{02} \quad . \qquad \text{(C-27)}$$

$$\underline{J}^1_{22}\,(21) = 5.0\, M_1\, M_2^4\, V^1_{00} + 3.73\, M_1^3\, M_2^2\, V^1_{11} + M_1^5\, V^1_{22}$$

$$+ 5.33\, M_1^2\, M_2^3\, V^2_{00} + 2.667\, M_1^4\, M_2\, V^2_{11}$$

$$+ 1.60\, M_1^3\, M_2^2\, V^3_{00} \quad . \qquad \text{(C-28)}$$

$$\underline{J}^1_{23}\,(21) = 11.62\, M_1^2\, M_2^4\, V^1_{01} + 5.185\, M_1^4\, M_2^2\, V^1_{12} + M_1^6\, V^1_{23}$$

$$+ 10.471\, M_1^3\, M_2^3\, V^2_{01} + 3.277\, M_1^5\, M_2\, V^2_{11}$$

$$+ 2.77\, M_1^4\, M_2^2\, V^3_{00} \quad . \qquad \text{(C-29)}$$

$$\underset{\sim}{J}^1_{33}(21) = 700\, M_1\, M_2^6\, V^1_{00} + 27.0\, M_1^3\, M_2^4\, V^1_{11}$$

$$+ 16.2\, M_1^5\, M_2^2\, V^1_{22} + M_1^7\, V^1_{33} + 12.00\, M_1^2\, M_2^5\, V^2_{00}$$

$$+ 20.57\, M_1^4\, M_2^3\, V^2_{11} + 4.0\, M_1^6\, M_2\, V^2_{22}$$

$$+ 8.0\, M_1^3\, M_2^4\, V^3_{00} + 4.80\, M_1^5\, M_2^2\, V^3_{11}$$

$$+ 1.829\, M_1^4\, M_2^3\, V^4_{00} \quad . \qquad \text{(C-30)}$$

(b) TENSOR PART

(i) <u>Matrix elements of</u> $J^2_{\nu_1\nu_2}(12)$

Since from eqn. (4.5)

$$\tilde{J}^2_{\nu_1\nu_2}(12) = J^2_{\nu_1\nu_2}(12) \quad ,$$

the corresponding matrix elements are not given.

$$J^2_{00}(12) = 2.0\, M_1\, M_2\, V^1_{00} + M_2^2\, V^2_{00} \quad . \qquad \text{(C-31)}$$

$$J^2_{01}(12) = 2.366\, M_1\, M_2^2\, V^1_{01} + M_2^3\, V^2_{01} \quad . \qquad \text{(C-32)}$$

$$J^2_{02}(12) = 2.683\, M_1\, M_2^3\, V^1_{02} + M_2^4\, V^2_{02} \quad . \qquad \text{(C-33)}$$

$$J^2_{03}\ (12) = 2.966\ M_1\ M_2^4\ V^1_{03} + M_2^5\ V^2_{03} \quad . \tag{C-34}$$

$$J^2_{11}\ (12) = 4.00\ M_1^3\ M_2\ V^1_{00} + 2.8\ M_1\ M_2^3\ V^1_{11}$$

$$+ 3.666\ M_1^2\ M_2^2\ V^2_{00} + M_2^4\ V^2_{11}$$

$$+ 1.2\ M_1\ M_2^3\ V^3_{00} \quad . \tag{C-35}$$

$$J^2_{12}\ (12) = 7.688\ M_1^3\ M_2^2\ V^1_{01} + 3.175\ M_1\ M_2^4\ V^1_{12}$$

$$+ 5.879\ M_1^2\ M_2^3\ V^2_{01} + M_2^5\ V^2_{12}$$

$$+ 1.697\ M_1\ M_2^4\ V^3_{01} \quad . \tag{C-36}$$

$$J^2_{13}\ (12) = 11.651\ M_1^3\ M_2^3\ V^1_{02} + 3.510\ M_1\ M_2^5\ V^1_{13}$$

$$+ 7.961\ M_1^2\ M_2^4\ V^2_{02} + M_2^6\ V^2_{13} +$$

$$+ 2.078\ M_1\ M_2^5\ V^3_{02} \quad . \tag{C-37}$$

$$J_{22}^{2}(12) = 6.00\, M_1^5\, M_2\, V_{00}^{1} + 5.32\, M_1^3\, M_2^3\, V_{11}^{1}$$

$$+ 3.6\, M_1\, M_2^5\, V_{22}^{1} + 8.99\, M_1^4\, M_2^2\, V_{00}^{2}$$

$$+ 9.42\, M_1^2\, M_2^4\, V_{11}^{2} + M_2^6\, V_{22}^{2} + 5.60\, M_1^3\, M_2^3\, V_{00}^{3}$$

$$+ 2.4\, M_1\, M_2^5\, V_{11}^{3} + 1.371\, M_1^2\, M_2^4\, V_{00}^{4} \quad . \qquad \text{(C-38)}$$

$$J_{23}^{2}(12) = 15.415\, M_1^5\, M_2^2\, V_{01}^{1} + 8.18\, M_1^3\, M_2^4\, V_{12}^{1}$$

$$+ 3.979\, M_1\, M_2^6\, V_{23}^{1} + 19.54\, M_1^4\, M_2^3\, V_{01}^{2}$$

$$+ 12.766\, M_1^2\, M_2^5\, V_{12}^{2} + M_2^7\, V_{32}^{2}$$

$$+ 10.723\, M_1^3\, M_2^4\, V_{01}^{3} + 2.939\, M_1\, M_2^6\, V_{12}^{3}$$

$$+ 2.375\, M_1^2\, M_2^5\, V_{01}^{4} \quad . \qquad \text{(C-39)}$$

$$J_{33}^{2}(12) = 8.0\, M_1^7\, M_2\, V_{00}^{1} + 39.60\, M_1^5\, M_2^3\, V_{11}^{1} + 33.94\, M_1^3\, M_2^5\, V_{22}^{1}$$

$$+ 4.40\, M_1\, M_2^7\, V_{33}^{1} + 17.0\, M_1^6\, M_2^2\, V_{00}^{2} + 42.428\, M_1^4$$

$$+ 42.428\, M_1^4\, M_2^4\, V_{11}^{2} + 11.286\, M_1^2\, M_2^6\, V_{22}^{2} + M_2^8\, V_{33}^{2}$$

$$+ 16.4\ M_1^5\ M_2^3\ V_{00}^3 + 6.277\ M_1^3\ M_2^5\ V_{11}^3$$

$$+ 3.60\ M_1\ M_2^7\ V_{22}^3 + 7.771\ M_1^4\ M_2^4\ V_{00}^4$$

$$+ 4.114\ M_1^2\ M_2^6\ V_{11}^4 + 1.524\ M_1^3\ M_2^5\ V_{00}^5 \quad . \qquad \text{(C-40)}$$

(ii) <u>Matrix elements for</u> $J^2_{-\nu_1\nu_2}(12)$ <u>and</u> $J^2_{\nu_1\nu_2}(21)$

Since from eqns. (4.6)and (4.48)

$$\tilde{J}^2_{-\nu_1\nu_2}(12) = J^2_{\nu_1\nu_2}(21)$$

and

$$J^2_{\nu_2\nu_1}(21) = \left(\frac{M_1}{M_2}\right)^{\nu_1-\nu_2} J^2_{\nu_1\nu_2}(21) \quad .$$

So the corresponding matrix elements are not given.

$$J^2_{00}(21) = M_1\ M_2\ (V^2_{00} - 2.0\ V^1_{00}) \quad . \qquad \text{(C-41)}$$

$$J^2_{01}(21) = M_1\ M_2^2\ (V^2_{01} - 2.366\ V^1_{01}) \quad . \qquad \text{(C-42)}$$

$$J^2_{02}(21) = M_1\ M_2^3\ (V^2_{02} - 2.863\ V^1_{02}) \quad . \qquad \text{(C-43)}$$

$$J^2_{03}(21) = M_1\ M_2^4\ (V^2_{03} - 2.966\ V^1_{03}) \quad . \qquad \text{(C-44)}$$

$$J^2_{11}(21) = M^2_1 M^2_2 (-4.00\, V^1_{00} - 2.8\, V^1_{11} + 3.66\, V^2_{00} + V^2_{11} - 1.2\, V^3_{00}) \quad . \qquad \text{(C-45)}$$

$$J^2_{12}(21) = M^2_1 M^3_2 (-7.588\, V^1_{01} - 3.175\, V^1_{12} + 5.879\, V^2_{01} + V^2_{12} - 1.697\, V^3_{01}) \quad . \qquad \text{(C-46)}$$

$$J^2_{13}(21) = M^2_1 M^4_2 (-11.651\, V^1_{02} - 3.510\, V^1_{13} + 7.961\, V^2_{02} + V^2_{13} - 2.078\, V^3_{02}) \quad . \qquad \text{(C-47)}$$

$$J^2_{22}(21) = M^3_1 M^3_2 (-6.00\, V^1_{00} - 5.32\, V^1_{11} - 3.6\, V^1_{22} + 8.99\, V^2_{00} + 9.42\, V^2_{11} + V^2_{22} - 5.60\, V^3_{00} - 2.4\, V^3_{11} + 1.371\, V^4_{00}) \quad . \qquad \text{(C-48)}$$

$$J^2_{23}(21) = M^2_1 M^4_2 (-15.415\, V^1_{01} - 8.18\, V^1_{12} - 3.979\, V^1_{23} + 19.54\, V^2_{01} + 12.766\, V^2_{12} + V^2_{23} - 10.723\, V^3_{01} - 2.939\, V^3_{12} + 2.375\, V^4_{01}). \qquad \text{(C-49)}$$

$$J^2_{33}\,(21) = M_1^4\, M_2^4\,(-8.0\, V^1_{00} - 39.60\, V^1_{11} - 33.94\, V^1_{22}$$

$$- 4.40\, V^1_{33} + 17.0\, V^2_{00} + 42.428\, V^2_{11}$$

$$+ 11.286\, V^2_{22} + V^2_{33} - 16.4\, V^3_{00} - 6.277\, V^3_{11}$$

$$- 3.66\, V^3_{22} + 7.771\, V^4_{00} + 4.114\, V^4_{11}$$

$$- 1.524\, V^5_{00}) \quad . \qquad \text{(C-50)}$$

(iii) <u>Matrix elements for</u> $\underline{J}^2_{\nu_1\nu_2}\,(21)$

Since from eqn. (4.8)

$$\underline{\tilde{J}}^2_{\nu_1\nu_2}\,(21) = \underline{J}^2_{\nu_1\nu_2}\,(21) \quad ,$$

the corresponding matrix elements are not given.

$$\underline{J}^2_{00}\,(21) = 2.0\, M_1\, M_2\, V^1_{00} + M_1^2\, V^2_{00} \quad . \qquad \text{(C-51)}$$

$$\underline{J}^2_{01}\,(21) = 2.366\, M_1^2\, M_2\, V^1_{01} + M_1^3\, V^2_{01} \quad . \qquad \text{(C-52)}$$

$$\underline{J}^2_{02}\,(21) = 2.683\, M_1^3\, M_2\, V^1_{02} + M_1^4\, V^2_{02} \quad . \qquad \text{(C-53)}$$

$$\underset{\sim}{J}^2_{03}\,(21) = 2.966\ M_1^4\ M_2\ V_{03}^1 + M_1^4\ V_{03}^2 \quad . \tag{C-54}$$

$$\begin{aligned}\underset{\sim}{J}^2_{11}\,(21) = {} & 4.00\ M_1\ M_2^3\ V_{00}^1 + 2.8\ M_1^3\ M_2\ V_{11}^1 \\ & + 3.666\ M_1^2\ M_2^2\ V_{00}^2 + M_1^4\ V_{11}^2 \\ & + 1.2\ M_1^3\ M_2\ V_{00}^3 \quad .\end{aligned} \tag{C-55}$$

$$\begin{aligned}\underset{\sim}{J}^2_{12}\,(21) = {} & 7.588\ M_1^2\ M_2^3\ V_{01}^1 + 3.175\ M_1^4\ M_2\ V_{12}^1 \\ & + 5.879\ M_1^3\ M_2^2\ V_{01}^2 + M_1^5\ V_{12}^2 \\ & + 1.697\ M_1^4\ M_2\ V_{01}^3 \quad .\end{aligned} \tag{C-56}$$

$$\begin{aligned}\underset{\sim}{J}^2_{13}\,(21) = {} & 11.651\ M_1^3\ M_2^3\ V_{02}^1 + 3.510\ M_1^5\ M_2\ V_{13}^1 \\ & + 7.961\ M_1^4\ M_2^2\ V_{02}^2 + M_1^6\ V_{13}^2 \\ & + 2.078\ M_1^5\ M_2\ V_{02}^3 \quad .\end{aligned} \tag{C-57}$$

$$\underset{\sim}{J}^2_{22}\,(21) = 6.00\, M_1\, M_2^5\, V_{00}^1 + 5.32\, M_1^3\, M_2^3\, V_{11}^1$$

$$+ 3.60\, M_1^5\, M_2\, V_{22}^1 + 8.99\, M_1^2\, M_2^4\, V_{00}^2$$

$$+ 9.42\, M_1^4\, M_2^2\, V_{11}^2 + M_1^6\, V_{22}^2$$

$$+ 5.60\, M_1^3\, M_2^3\, V_{00}^3 + 2.4\, M_1^5\, M_2\, V_{11}^3$$

$$+ 1.371\, M_1^4\, M_2^2\, V_{00}^4 \quad . \qquad \text{(C-58)}$$

$$\underset{\sim}{J}^2_{23}\,(21) = 15.415\, M_1^2\, M_2^5\, V_{01}^1 + 8.18\, M_1^4\, M_2^3\, V_{12}^1$$

$$+ 3.979\, M_1^6\, M_2\, V_{23}^1 + 19.54\, M_1^3\, M_2^4\, V_{01}^2$$

$$+ 12.755\, M_1^5\, M_2^2\, V_{12}^2 + M_1^7\, V_{23}^2$$

$$+ 10.723\, M_1^4\, M_2^3\, V_{01}^3 + 2.939\, M_1^6\, M_2\, V_{12}^3$$

$$+ 2.375\, M_1^5\, M_2^2\, V_{01}^4 \quad . \qquad \text{(C-59)}$$

$$
\begin{aligned}
J^2_{33}(21) = {} & 8.0\, M_1\, M_2^7\, V^1_{00} + 39.60\, M_1^3\, M_2^5\, V^1_{11} \\
& + 33.94\, M_1^5\, M_2^3\, V^1_{22} + 4.40\, M_1^7\, M_2\, V^1_{33} \\
& + 17.0\, M_1^2\, M_2^6\, V^2_{00} + 42.428\, M_1^4\, M_2^4\, V^2_{11} \\
& + 11.286\, M_1^6\, M_2^2\, V^2_{22} + M_1^8\, V^2_{33} \\
& + 16.4\, M_1^3\, M_2^5\, V^3_{00} + 6.277\, M_1^5\, M_2^3\, V^3_{11} \\
& + 3.60\, M_1^7\, M_2\, V^3_{22} + 7.771\, M_1^4\, M_2^4\, V^3_{22} \\
& + 4.114\, M_1^6\, M_2^2\, V^4_{11} + 1.524\, M_1^5\, M_2^2\, V^5_{00} \,. \qquad \text{(C-60)}
\end{aligned}
$$

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