General Introduction

It is well-known that the transport properties of gases i.e. viscosity, thermal conductivity and diffusion arise due to the transport of some physical quantity viz., momentum, thermal energy and mass respectively. They are referred to as the first-order effects. The second-order effects, thermal diffusion (or the Soret effect in liquid) and diffusion-thermo effect or Dufour effect involve the transport of mass due to temperature gradient and transport of thermal energy due to concentration gradient, respectively. Among all these properties, in the present thesis we are concerned only with thermal diffusion and thermal conductivity. Both the phenomena are affected by inelastic collisions.

When a temperature gradient exists in a uniform mixture, thermal diffusion occurs resulting in a concentration gradient which in turn produces ordinary diffusion that tends to neutralise the effect. These two opposite effects cause a dynamic equilibrium in the steady state. The mixture which becomes partially separated, usually contains higher concentration of the heavier component in the cooler region and the lighter component in the hotter region.

The thermal diffusion phenomenon in gases has wide application such as in the separation of isotopes, flames, planetary atmosphere, steller interiors, nebulae etc. On the theoretical side it is a convenient and dependable tool for the study of intermolecular forces and effects of inelastic collisions.
The Kinetic Theory in Brief

The simple kinetic theory does not throw light on inter-molecular force and remains silent regarding the second-order effects. Moreover the theory gives an approximate pressure and temperature dependence of the transport properties. The rigorous kinetic theory was put forward by Enskog (1911) and Chapman (1912) independently and almost simultaneously. The theory shows that the properties of dilute gases can be completely described by the distribution function $f_i(\mathbf{r}_i, \mathbf{v}_i, t)$. This function represents the number of molecules of the $i$th species which at time $t$ lies in a unit volume element about the point $\mathbf{r}_i$ and which have velocities within a unit range about $\mathbf{v}_i$. This distribution function is the solution of the Boltzmann integro-differential equation.

$$\frac{\partial f_i}{\partial t} + \mathbf{v}_i \cdot \frac{\partial f_i}{\partial \mathbf{v}_i} + \frac{1}{m_i} \left( \mathbf{X}_i \cdot \frac{\partial f_i}{\partial \mathbf{v}_i} \right) = 2\pi \sum_j \int \left( f_j' f_j f_i f_i - f_i f_i f_j f_j' \right) g_{ij} \frac{db}{db} db db' db'' \ldots \ldots (1)$$

In the above equation, "$b$" is the impact parameter which characterises a collision, "$\frac{\partial f_i}{\partial \mathbf{v}_i}$" is the initial relative velocity and $f_i', f_j'$ represent $f' (\mathbf{r}_i', \mathbf{v}_i', t)$ and $f' (\mathbf{r}_j', \mathbf{v}_j', t)$ respectively, $\mathbf{v}_i'$ and $\mathbf{v}_j'$ being the velocities after collision, $\mathbf{X}_i = X_i (\mathbf{r}; t)$ is the external force on the $i$th species.

Equation (1) forms the basis for the discussion on the transport properties and is applicable to gases at sufficiently low densities. The expression for the transport coefficient are
obtained in terms of set of collision integrals \( \mathcal{L} \) which involve the intermolecular potential function.

**Flux Vectors**

Transport properties can be calculated by computing the 'flux vectors' of the appropriate mechanical property, such as momentum, energy or mass, across a reference plane. Any flux in turn can be calculated by integrating the appropriate molecular property over the distribution function. Since the mechanism of each of these molecular properties can be treated in a similar way we designate them collectively by \( \Psi_j \). Now, a flux vector \( \Psi_j \) associated with the property \( \Psi_j \) can be defined by

\[
\Psi_j = \int \psi_j f_j \bar{v}_j d\bar{v}_j
\]

The physical significance of this vector lies in the fact that the component of the vectors in any direction \( n \) is the flux of the associated property across a surface normal to \( n \). The expression for the flux vectors related to the transport of mass, momentum and energy can be written in the following way:

(i) Transport of mass

Mass flux vector

\[
\vec{\Psi}_d = \vec{m}_d \int \vec{f}_j \bar{v}_j d\bar{v}_j
\]

\[
= \vec{n}_j \vec{m}_j \vec{v}_j = \vec{J}_j
\]

(3)
(ii) Transport of momentum: \( \Psi_j = m_j v_j \)

\[ \Psi_j = m_j \int \vec{v}_j \times \vec{v}_j \; d\vec{v}_j = \eta_j m_j (\vec{v}_j \times \vec{v}_j) \quad \cdots \quad (4) \]

(iii) Transport of kinetic energy: \( \psi_j = \frac{1}{2} m_j v_j^2 \)

The primary task is to find out the distribution function by solving the equation (1). For a system in equilibrium, where there are no gradients in the composition, velocity and temperature, the zero-order solution of equation (1) is known as the Maxwell-Boltzmann distribution function and is given by

\[ f_i \left( \vec{v}_i \right) = n_i \left( \frac{m_i}{2\pi kT} \right)^{3/2} \exp \left( -\frac{m_i v_i^2}{2kT} \right) \quad \cdots \quad (5) \]

where \( m_i \) is the mass and \( n_i \) is the number density of molecules of the \( i \)th species and \( \vec{v}_i \) is the peculiar velocity defined as the velocity of the molecules with respect to co-ordinates moving with mass average velocity.

For a non-equilibrium system, the Boltzmann equation (1) can be solved by perturbation method developed by Enskog.
Equation (1) can be written as,
\[
\frac{\partial f_i}{\partial t} + (\vec{v}_i \cdot \frac{\partial f_i}{\partial \vec{r}}) + \frac{1}{m_i} (\vec{x}_i \cdot \frac{\partial f_i}{\partial \vec{v}_i}) = \frac{1}{\varepsilon} \sum_j J(f_i, f_j) \quad \ldots \quad (6)
\]
where \( J(f_i, f_j) \) is bilinear form
\[
J(f_i, f_j) = \iiint (f'_i f'_j - f_i f_j) g d b d v_j \quad \ldots \quad (7)
\]
and \( \varepsilon \) is a perturbation parameter introduced into Boltzmann equation in such a way that frequency of collision can be changed in an arbitrary manner without affecting the relative number of collision of a particular kind. The distribution function is expanded in a series in \( \varepsilon \),
\[
f_i = f_i^{[0]} + \varepsilon f_i^{[1]} + \varepsilon^2 f_i^{[2]} + \ldots \quad (8)
\]
Substituting this series in equation (6) and equating the coefficient of equal power in \( \varepsilon \) we obtain the following set of equations for the function \( f_i^{[0]}, f_i^{[1]}, f_i^{[2]} \)
\[
\sum_j J(f_i^{[0]}, f_j^{[0]}) = 0 \quad \ldots \quad (8a)
\]
\[
\frac{\partial f_i^{[0]}}{\partial t} \left( \vec{V}_i \cdot \frac{\partial f_i^{[0]}}{\partial \vec{r}} \right) + \frac{1}{m_i} (\vec{x}_i \cdot \frac{\partial f_i^{[0]}}{\partial \vec{v}_i}) = \sum_j \left[ J(f_i^{[0]}, f_j^{[0]}) + J(f_i^{[0]}, f_j^{[0]}) \right] \quad (8b)
\]
\[
\frac{\partial f_i^{[0]}}{\partial t} \left( \vec{V}_i \cdot \frac{\partial f_i^{[0]}}{\partial \vec{r}} \right) + \frac{1}{m_i} (\vec{x}_i \cdot \frac{\partial f_i^{[0]}}{\partial \vec{v}_i}) = \sum_j \left[ J(f_i^{[0]}, f_j^{[0]}) + J(f_i^{[0]}, f_j^{[0]}) \right] + J(f_i^{[0]}, f_j^{[0]}) \quad (8c)
\]
The zero-order solution, which is represented by equation (8a) has the most general solution
\[ f_i^{[0]} = n_i \left( \frac{m_i}{2\pi k T} \right)^{3/2} \exp \left\{ -\frac{m_i (V_i - V_o)^2}{2 k T} \right\} \] ... (9)

The quantities
\[ n_i = n_i (\vec{r}, t) \quad \text{and} \quad V_o = V_o (\vec{r}, t) \quad T = T (\vec{r}, t) \]

are arbitrary functions of space and time in so far as this set of equation is concerned. In order for these functions to represent the local values of the physical quantities, number density, mass average velocity, and temperature it is necessary for the solutions of the remaining equations to be such that
\[ \int f_i \, dV_i = n_i \] ... (10)
\[ \sum_i m_i \int V_i f_i \, dV_i = \rho V_o \] ... (11)
\[ \frac{1}{2} \sum_i m_i \int (V_i - V_o)^2 f_i \, dV_i = \frac{3}{2} n k T \] ... (12)

Chapman and Cowling have shown that each of the remaining integral equations (8a), (8b), (8c) along with the auxiliary conditions
\[ \int f_i^{[0]} \, dV_i = 0 \quad \tau = 1, 2, 3. \] ... (13)
\[ \sum_i m_i \int V_i f_i^{[0]} \, dV_i = 0 \quad \tau = 1, 2, 3. \] ... (14)
\[ \frac{1}{2} \sum_i m_i \int (V_i - V_o)^2 f_i^{[0]} \, dV_i = 0 \quad \tau = 1, 2, 3. \] ... (15)
specify uniquely a set of functions \[ f_i^{[0]} \] since the set of distribution functions so defined satisfies the conditions of
of equations (10), (11) and (12), it is used as the solution of the Boltzmann equation.

The equation for the $f_i^{[3]}$ may be written in terms of a perturbation function $\phi_i$ defined thus

$$\int f_i^{[3]} (\vec{\nu}, \vec{V}_i, t) = f_i^{[5]} (\vec{\nu}, \vec{V}_i, t) \varphi_i (\vec{\nu}, \vec{V}_i, t) \quad \therefore \quad (16)$$

In terms of this function the equation (8b) becomes

$$\frac{\delta f_i^{[3]}}{\delta t} + (V_i \cdot \nabla f_i^{[3]}) + \frac{1}{m_i} (\nabla_i \cdot \nabla_V f_i^{[3]}) = \sum \int \int \int_{x_v} f_i^{[3]} f_j^{[3]} (\phi_i' + \phi_j' - \phi_i - \phi_j) g_{ij} \delta b \delta b \delta \vec{V}_j \, dt \quad (17)$$

The preceding auxiliary conditions, in terms of $\phi_i$ are

$$\int f_i^{[3]} \phi_i \, d\vec{V}_i = 0 \quad \therefore \quad (18)$$

$$\sum_i m_i \int \vec{V}_i f_i^{[3]} \phi_i \, d\vec{V}_i = 0 \quad \therefore \quad (19)$$

$$\frac{1}{2} \sum_i m_i \int (\vec{V}_i - \vec{V}_o)^2 f_i^{[3]} \phi_i \, d\vec{V}_i = 0 \quad \therefore \quad (20)$$

As stated above, this set of equations is just sufficient to define the perturbation functions $\phi_i$ uniquely. The differentiations of the functions $f_i^{[3]}$ indicated in equation (17) may be carried out. The resulting expressions involve space and time derivatives of the functions $\varphi_i (\vec{\nu}, t); \varphi_j (\vec{\nu}, t)$ and $T (\vec{\nu}, t)$. The time derivatives are eliminated by means of equations
of change given by

\[ \frac{\partial n_i}{\partial t} + \{ \nabla \cdot \bar{n}_i (\bar{V}_o + \bar{V}_i) \} = 0 \quad \ldots \quad (21) \]

\[ \frac{\partial \bar{V}_o}{\partial t} + (\bar{V}_o \cdot \nabla \bar{V}_o) = -\frac{1}{\rho} (\nabla p) + \frac{1}{\rho} \sum n_i \bar{x}_i \quad \ldots \quad (22) \]

\[ \frac{3}{2} n k \left[ \frac{\partial T}{\partial t} + (\bar{V}_o \cdot \nabla T) \right] = -(\nabla q_i) - (p: \bar{V}_o) + \sum n_i (\bar{x}_i \cdot \bar{V}_i) + \frac{3}{2} k T \left( \nabla \cdot \sum n_i \bar{V}_i \right) \quad \ldots \quad (23) \]

It is consistent with this approximation to replace \( f_i \) by \( f_i^{[q]} \) in the integrals for the flux vectors which occur in the equations of change. The resulting equation for the perturbation function

\[ \Phi_i \]

is

\[ f_i^{[q]} \left[ \frac{n_a}{n_i} (\bar{V}_i \cdot \bar{d}_i) + (b_i \cdot \nabla \bar{V}_o) - (\frac{5}{2} - \omega_i) (\bar{V}_i \cdot \nabla \ln T) \right] \]

\[ = \sum_j \sum_j \sum f_i^{[q]} f_j^{[q]} (\Phi'_i + \Phi'_j - \Phi_i - \Phi_j) b_{ij} b_{kl} d_{ij} d_{kl} \quad \ldots \quad (24) \]

The quantity \( \bar{d}_i \) and \( b_i \) are defined by

\[ \bar{d}_i = \nabla \left( \frac{n_i}{n} \right) + \left( \frac{n_i}{n} - \frac{n_i m_i}{\rho} \right) \nabla \ln \rho - \left( \frac{n_i m_i}{\rho} \right) \left[ \frac{p_i}{m_i \bar{x}_i} - \sum \frac{m_j}{d} \bar{x}_j \right] \]

\[ b_i = 2 \bar{W}_i \cdot \bar{V}_i - \frac{1}{2} \bar{W}^2_i \quad \ldots \quad \ldots \quad (25) \]

The dimensionless velocity \( \bar{W}_i \) is defined by

\[ \bar{W}_i = 2 \frac{m_i}{2 k T} \bar{V}_i \quad \ldots \quad \ldots \quad (27) \]

The perturbation function \( \Phi_i \) depends upon space and time only through the quantities \( n_i, V_0 \) and \( T \) and their space derivatives.
It is clear from the form of the integral equation for $\varphi_i$ that this quantity is linear in the derivatives and has the form

$$
\varphi_i = - \left( \vec{A}_i \cdot \nabla \ln T \right) - (\vec{B}_i : \nabla \nu) + \eta \sum_j \vec{C}_i^j \cdot \vec{a}_j \ldots \ldots (28)
$$

where $\vec{A}_i$, $\vec{B}_i$ and $\vec{C}_i^j$ are functions of the dimensionless velocity $\vec{W}_i$, the local composition and the local temperature. When the expression for $\varphi_i$ in equation (28) is inserted into equation (24) and the coefficients of similar gradients are equated, separate integral equations result for the functions $\vec{C}_i^j$, $\vec{B}_i$ and $\vec{A}_i$. It has been shown that $\vec{A}_i$ and $\vec{C}_i^j$ are of the form

$$
\vec{C}_i^j = \vec{W}_i \vec{C}_i^j (\nu_i) \ldots \ldots \ldots \ldots \ldots \ldots (29)
$$

$$
\vec{A}_i = \vec{W}_i \vec{A}_i (\nu_i) \ldots \ldots \ldots \ldots \ldots \ldots (30)
$$

where $\vec{C}_i^j$ and $\vec{A}_i$ are functions of $\nu_i$ which depend parametrically on $T$ and all the $\eta_j$. It has been shown that the tensor $\vec{B}_i$ is of the form

$$
\vec{B}_i = \left[ \frac{\vec{W}_i \cdot \vec{W}_i}{2} - \frac{1}{2} \vec{W}_i \cdot \vec{U} \right] \vec{B}_i (\nu_i) \ldots \ldots \ldots \ldots (31)
$$

Solutions of these integral equations have been obtained by two equivalent methods, that of Chapman and Cowling and a variational method of Curtiss and Hirschfelder (1949). In both the methods the scaler functions $\vec{C}_i (\nu_i)$, $\vec{B}_i (\nu_i)$ and $\vec{A}_i (\nu_i)$ are expanded in a series of Sonine polynomials. Chapman and Cowling used an infinite series of these polynomials, with the result that the
transport coefficient are expressed in terms of ratios of infinite
determinants. To get numerical values it is necessary to consider
only a few elements of these determinants since the convergence of
the ratios of determinants is quite rapid as additional rows and
columns are included.

The formulation of transport coefficients

If the expression for $\Phi_i$ given by equation (28) is used
in the integrals for flux vectors, we obtain expressions for the
diffusion velocity, the pressure tensor, and the heat flux
vectors in terms of integrals of the functions $A_i(W_i)$, $B_i(W_i)$
and $C_i^{(j)}(W_i)$. These relations for the flux vectors are
given below.

Diffusion and thermal diffusion coefficient in terms of
Sonine polynomeal expansion coefficients

The integrals for the diffusion velocity written in terms
of $\Phi_i$ is

$$\overrightarrow{V_i} = \frac{1}{\eta_i} \int \overrightarrow{V_i'} f_i d\overrightarrow{V_i'} = \frac{1}{\eta_i} \int \overrightarrow{V_i'} \Phi_i^{(S)} f_i d\overrightarrow{V_i'} \ldots \ (32)$$

Using equation (28) and the form of the functions $A_i$ and $C_i^{(j)}$
indicated in equation (29) and (30) we obtain

$$\overrightarrow{V_i} = \left(\frac{n_i^2}{\eta_i \rho}\right) \sum_j m_i D_j \overrightarrow{d_j} - \frac{1}{\eta_i m_i} D_i^T \overrightarrow{\nabla \ln T} \ldots \ (33)$$
in this expression \( \tilde{d}_j \) is defined as in equation (35) and \( D_{ij} \) and \( D^T_i \) are

\[
D_{ij} = \frac{\rho}{3nm_j} \sqrt{\frac{2kT}{m_i}} \int c_i(w_i) w_i f_i^{B3} d\vec{V}_i \quad \ldots \quad (34)
\]

\[
D^T_i = \frac{m_i}{3} \sqrt{\frac{2kT}{m_i}} \int a_i(w_i) w_i f_i^{B3} d\vec{V}_i \quad \ldots \quad (35)
\]

There are the expressions for the multicomponent diffusion coefficients and the multicomponent thermal diffusion coefficient respectively.

Thus we see that the diffusion velocity \( \vec{v} \) contains a term proportional to the concentration gradient, the pressure gradient, the difference in the external forces acting on the various species of molecules, and the gradient in the temperature.

By means of Sonine polynomial expansion the expression for the diffusion coefficients becomes

\[
D_{ij}(\xi) = \left( \frac{\rho}{3nm_j} \right) \sqrt{\frac{m_i}{2kT}} \sum_{m=0}^{\xi-1} \left( \begin{array}{c} \xi \\ m \end{array} \right) C_{ijm}(\xi) \int V_i^2 S_{ij}^{(m)}(w_i) f_i^{B3} d\vec{V}_i \quad \ldots \quad (36)
\]

\[
D^T_i(\xi) = \frac{m_i}{3} \sqrt{\frac{m_i}{2kT}} \sum_{m=0}^{\xi-1} A_{im}(\xi) \int V_i^2 S_{ij}^{(m)}(w_i) f_i^{B3} d\vec{V}_i \quad \ldots \quad (37)
\]

The argument \( \xi \) of \( D_{ij}(\xi) \) and \( D^T_i(\xi) \) being the number of terms used in the Sonine expansion. These integrals when evaluated yield the following expression for \( D_{ij}(\xi) \) and \( D^T_i(\xi) \).
To obtain the coefficient of thermal diffusion at least two terms are required in the Sonine Polynomial expansion, use of one term results in zero thermal diffusion. For this reason thermal diffusion is frequently referred to as a "second-order effect".

The integrals

The transport co-efficients have been expressed in terms of the Sonine polynomial expansion coefficients. These coefficients are complicated combinations of the bracket integrals Chapman and Cowling have shown that these integrals may be written as linear combinations of a set of integrals \( \Omega^{(L_0)} \). For collisions between molecules of type \( i \) and \( j \), these integrals are defined by

\[
\Omega^{(L_0)}_{ij} = \left( \frac{2 \pi kT}{\mu_{ij}} \right)^{1/2} \int_0^\infty \int_0^\infty \exp(-\gamma_{ij}^2) \gamma_{ij}^{2s+3} (1 - \cos \chi) b d b d \gamma_{ij}
\]

where \( \mu_{ij} = \) reduced mass of the colliding molecules \( i \) and \( j \)
\( \gamma_{ij} = \) reduced initial relative speed of the colliding molecule.
\[ \chi = \text{angle by which the molecules are deflected in the centre of gravity co-ordinate system} \]
\[ \mathbf{v} = \text{relative velocity of the colliding molecules at infinite separation} \]
\[ b = \text{impact parameter} \]

The expression for \( \chi \) is given by
\[
\chi = \pi - 2b \int_{r_m}^{\infty} \frac{r^2 dr}{\left(1 - \frac{1}{2} \mu q^2 - \frac{b^2}{r^2}\right)^2} \ldots \ldots \ldots (41)
\]

Here \( r_m \) is the distance of closest approach of the two colliding molecules and \( \Phi(r) \) is the intermolecular potential field which should be symmetrical for the above definition to be valid. We shall discuss the different representation of the potential energy function in the succeeding section.

The final step in finding expression for the transport coefficient is to solve an infinite set of coupled algebraic equation whose coefficients are given in terms of collision integrals. This solution involves some approximations which systematically truncates the infinite set. This truncation is related to different order of approximation.

To a first approximation the expression for the thermal diffusion factor in a binary gas mixture is given by
\[
(\alpha_T)^1_1 = \frac{1}{6\lambda_{12}} \frac{S(x_4 - S^{(2)}x_2)}{x_\lambda + \gamma_\lambda} \left(6C_{12}^x - 5\right) \ldots \ldots (42)
\]
where,

\[
S^{(2)} = \frac{M_1 + M_2}{2M_2} \left[ \frac{1}{\lambda_{12}} \right] - \frac{15}{4 A_{12}^\alpha} \frac{(M_1 - M_2)}{2M_1} - 1
\]

\[
S^{(2)} = \frac{M_2 + M_1}{2M_1} \left[ \frac{1}{\lambda_{12}} \right] - \frac{15}{4 A_{12}^\alpha} \frac{(M_1 - M_2)}{2M_2} - 1
\]

\[
X_{\lambda} = \frac{x_1^2}{[\lambda_1]} + \frac{x_2^2}{[\lambda_2]}, \quad Y_{\lambda} = \frac{x_1^2}{[\lambda_1]} - \frac{x_2^2}{[\lambda_2]}, \quad U^{(2)} = \frac{x_1^2}{[\lambda_1]} + \frac{x_2^2}{[\lambda_2]}
\]

\[
U^{(2)} = \frac{4}{15} A_{12}^\alpha - \frac{1}{12} \left( \frac{12}{5} B_{12}^\alpha + 1 \right) \frac{M_1}{M_2} + \frac{1}{2} \frac{(M_1 - M_2)^2}{M_1 M_2}
\]

\[
U^{(2)} = \frac{4}{15} A_{12}^\alpha - \frac{1}{12} \left( \frac{12}{5} B_{12}^\alpha + 1 \right) \frac{M_2}{M_1} + \frac{1}{2} \frac{(M_2 - M_1)^2}{M_1 M_2}
\]

\[
U^{(2)} = \frac{4}{15} A_{12}^\alpha \left[ \frac{(M_1 + M_2)^2}{4M_1 M_2} \right] \frac{[\lambda_{12}]}{[\lambda_1]} \frac{[\lambda_{12}]}{[\lambda_2]} - \frac{1}{12} \left( \frac{12}{5} B_{12}^\alpha + 1 \right) - \frac{5}{32} \frac{1}{A_{12}^\alpha} \left( \frac{12}{5} B_{12}^\alpha - 5 \right) \frac{(M_1 - M_2)^2}{M_1 M_2}
\]

in which \( x_1, M_1 \) are respectively the mole fraction and the molecular weight of the species 1 and \([\lambda_{12}]\), is the thermal conductivity of the same species calculated up to first approximation from the relation

\[
[\lambda_{12}] = \frac{1989.1 \left( T_1 M_1 \right)^{1/2}}{\left( T_1 \right)^{\alpha/2} \left( T_2 \right)^{\beta/2}} \times 10^{-7} \quad \ldots \quad (43)
\]

\( \lambda_{12} \) is the thermal conductivity of a hypothetical species whose potential parameters and mass are given by \( \epsilon_{12}/R, \sigma_{12} \) and \( M_{12} \) respectively and are defined as

\[
\epsilon_{12}/R = \left\{ \left( \frac{\epsilon_1}{R} \right)^{1/2} \left( \frac{\epsilon_2}{R} \right)^{1/2} \right\}^{1/2}; \quad \sigma_{12} = \frac{\sigma_1 + \sigma_2}{2}, \quad M_{12} = \frac{2M_1 M_2}{M_1 + M_2}
\]

\[
\left\{ \begin{array}{c}
\frac{\epsilon_1}{R} = \frac{2M_1 M_2}{M_1 + M_2}
\end{array} \right\} \quad \ldots \quad (44)
\]
The remaining quantities are defined as,

\[ T^* = \text{reduced temperature} = \frac{kT}{\epsilon} \]

\[ \xi = \text{depth of the potential minima for the species 1} \]

\[ \sigma_1 = \text{collision diameter of the species 1} \]

\[ A^{*}_{12} = \frac{\Omega^{(2,2)*}_{12}}{\Omega^{(1,1)*}_{12}} \quad ; \quad B^{*}_{12} = \frac{5\Omega^{(1,2)*}_{12} - 4\Omega^{(1,3)*}_{12}}{\Omega^{(1,1)*}_{12}} \quad ; \quad C^{*}_{12} = \frac{\Omega^{(1,2)*}_{12}}{\Omega^{(1,1)*}_{12}} \]

where

\[ \Omega^{(L,S)}_{p,q} = \frac{\Omega^{(L,S)}_{p,q}}{\Omega^{(L,S)}_{r,s}} \quad \text{rigid sphere} \]

For higher approximations, the equation (42) can be written as

\[ \alpha_T = (\alpha_T)_1 \left[ 1 + K_{12} \right] \quad \ldots \quad \ldots (46) \]

where the higher approximations are all contained in \( K_{12} \). From equation (42) it appears that thermal diffusion factor is a function of concentration, temperature, molecular weights and potential parameters. However, the main composition dependence is governed by \[ \left[ S^{(1)} x_1 - S^{(2)} x_2 \right] \], the main mass dependence is given by \( S^{(1)} \) and \( S^{(2)} \) and the temperature dependence is controlled by the quantity \( 6C_{12}^* - 5 \).

For the binary mixture, higher approximation for the thermal diffusion factor was considered by Mason. It was pointed out that the error involved in the calculation of thermal diffusion factor from the first approximation formula is sometimes greater than the experimental uncertainty. The general formula given for the higher approximations are very complicated and have been calculated numerically by Mason and Saxena et al.
considered three extreme cases, viz. (1) \( \frac{m_1}{m_2} \gg 1, \frac{\chi_1}{\chi_2} \) (Lorenzian mixture) (2) \( \frac{m_1}{m_2} \gg 1, \frac{\chi_1}{\chi_2} \ll 1 \) (quasi Lorenzian mixture) and (3) \( m_1 \approx m_2 \) (isotopic mixture). The result shows that for these cases, the second approximation to the thermal diffusion factor should usually be sufficiently accurate, with Kihara's approximation\(^2\) preferred over Chapman and Cowling\(^4\) for both accuracy and simplicity.

**Limitation of the Chapman – Enskog Theory**

The Chapman – Enskog theory is based upon several assumptions which limit the applicability of the final results. The assumptions together with the condition under which each is important are enumerated below.

(1) The theory assumes only binary collisions which means that it is applicable to fairly dilute gases

(2) The Chapman – Enskog theory of gases applies only to monoatomic gases (molecules with no internal degrees of freedom) for which the interaction potential is spherically symmetric. Inelastic collision occurs between molecules with internal degrees of freedom. In these collisions the kinetic energy is no longer conserved although mass and momentum are conserved. Consequently the viscosity and diffusion are not significantly affected by the presence of internal degrees of freedom and for these properties, the Chapman – Enskog theory can be applied to polyatomic molecules with considerable success.
(3) The use of classical mechanics to describe the molecular collisions limits the applicability of the theory for the lighter gases at low temperature where the de Broglie wavelength becomes comparable to molecular dimension. The de Broglie wavelength corresponding to mean molecular velocity is \( \lambda = \frac{2\pi}{\sqrt{MT}} \) Å where \( M \) is the molecular weight. At low temperature the average molecular velocity is small and the associated wavelength is large. When the de Broglie wavelength is of the order of molecular dimension quantum mechanical "diffraction effect" occurs. At still lower temperature when the de Broglie wavelength is of the order of magnitude of the average distance between molecules, "Statistical effect" related to Pauli's exclusion principle becomes important.

(4) The theory assumes that local equilibrium is established everywhere. At very low densities, the molecules collide more frequently with the walls of the containing vessel than with each other, hence there is little mechanism for the establishment of local equilibrium within the gas and the concept of local density, temperature, velocity loses meaning.

(5) By assuming the perturbation term to be small only small deviations from the equilibrium are postulated.

**Subsequent developments**

(1) The quantal effects and non-central force field effects can be introduced into the Boltzmann equation and the Chapman-Enskog solution. This is done by replacing an integration over the impact parameter by that over deflection angles involving the quantal differential cross-section\(^1,4,5\).

\[ 2907 \]
The introduction of the effect of inelastic collision in the kinetic theory of gases is a very difficult job for the number of parameters characterising a collision between molecules increases rapidly as soon as the internal degrees of freedom are considered. As a result, it is difficult to obtain an explicit form of the collision integral.

The first attempt in the consideration of the kinetic theory of molecules having internal degrees of freedom was made by Wang Chang and Uhlenbeck. A similar treatment was given independently by de Boer. They considered translational degrees of freedom classically and internal degrees of freedom quantum mechanically. Also each internal molecular state is considered as a separate chemical species and inelastic collision as chemical reaction. Taxmann, approached in a different way by considering internal degrees of freedom classically.

However, the Wang Chang - Uhlenbeck - de Boer treatment is based on the assumption which is analogous to existence of inverse collision in classical mechanics. Since this assumption is valid only when the internal state is non-degenerate, the validity of their equation for most polyatomic molecules was in question. Mason and Monchick by applying the theory of Wang Chang - Uhlenbeck - de Boer derived expression for thermal conductivity of polyatomic and polar gases. The agreement between experiment and theory is quite satisfactory. The work of Waldmann and Dahler and Sather also verified the above mentioned fact. All these works show that
although there is a faulty assumption in Wang Chang - Uhlenbeck - de Boer treatment, the results are valid for all molecules provided their quantum - mechanical cross-section is replaced by corresponding degeneracy - averaged quantum-mechanical cross-section.

The work of Wang Chang - Uhlenbeck - de Boer has been extended by Waldmann and Trubenbacher\textsuperscript{11} and by Monchick, Munn and Mason\textsuperscript{12}.

However, it has been pointed out by Kagan and Afanas'ev\textsuperscript{13} that in a system of rotating molecules, the distribution function is dependent not only on the magnitude of the angular momentum vector (Pseudo vector, as called by them) but also on its polarisation caused by gradients of temperature, pressure and concentration. The partial polarisation of rotating molecules has been treated by Waldmann\textsuperscript{14} from a similar point of view. The quantum mechanical Boltzmann equation for a gas having rotating molecules was first derived by Waldmann\textsuperscript{15}. Snider\textsuperscript{16} also obtained the same expression from a different approach. Later McCourt and Snider\textsuperscript{17} used Wigner distribution function for the rotationally degenerate internal states. They solved the Boltzmann equation by Chapman - Enskog method to obtain an expression for thermal conductivity in terms of generalised quantum mechanical cross-section. But no numerical result can be obtained due to the generalised quantum mechanical cross-section values. Prior to the development of the general formal theory outlined, the transport phenomena had been studied for several molecular model with internal degrees of
freedom. Curtiss first considered classically the transport properties of molecules possessing rotational states in which angular momentum variables were explicitly considered. Assuming a sphero-cylindrical model Curtiss and Mukenfuss obtained expression for thermal conductivity and shear and bulk viscosities for pure components and mixture.

The two models for which calculation had been done to obtain numerical estimates of thermal diffusion factor are (1) Rough sphere model and (2) Loaded sphere model. In the rough sphere model suggested by Bryan the molecules are assumed to be impenetrable perfectly rough elastic sphere. The rough sphere model is such that the relative velocity of the point of contact is reversed on collision. The model permits exchange of rotational and translational energy between molecules on collision. The methods of Chapman - Enskog were extended by Pidduck. Numerical result for thermal diffusion factor in a rough sphere gas has been obtained by Trubenbacher.

The concept of loaded sphere molecules was proposed by Jeans in which molecules are assumed to be smooth sphere for which the centre of gravity lies at a short distance from the geometrical centre. Later Dahler and co-workers, Sandler and Mason developed the theory of gases consisting of loaded sphere molecules and have solved the kinetic equation for a loaded sphere - smooth sphere mixture. However the treatments have been confined to binary mixture of molecules of same masses.
Numerical estimates for the thermal diffusion have been tabulated as a function of composition and eccentricity of the loaded sphere molecules. Two sets of values have been obtained by using the approximation of Pidduck\textsuperscript{21}, which considers the distribution of spin to be isotropic and that of Kagan and Afanas'ev, which take into account spin polarisation. It has been shown that when the eccentricity of the loaded sphere is high, thermal diffusion factor is considerably affected by the choice of the above approximation. A comparison of the experimental values\textsuperscript{28-31} of the thermal diffusion factors for the systems $D_2$ - HT, $He^3$ - HD and $He^4$ - HT shows that the loaded - sphere values are in much better agreement with the experimental data than the Chapman - Enskog theory.

Monchick, Pereira and Mason\textsuperscript{32} presented a theory for the calculation of heat conductivity of polyatomic molecules. Their approach was based on the Wang Chang - Uhlenbeck - de Boer theory of polyatomic gases together with the assumption that (i) neglect of 'complex collision' and (ii) no correlation between internal energy states and relative velocities (or equal differential scattering cross-section for all scattering channels). Monchick, Munn and Mason\textsuperscript{33} extended the work of Monchick, Pereira and Mason\textsuperscript{32} in order to obtain the expression for thermal diffusion factor. They obtained the generalised Stefan - Maxwell diffusion equation for multicomponent mixtures of polyatomic gases carried to the second Chapman - Enskog approximation. The resulting expressions
take into account composition dependence of binary diffusion coefficients and correction term for the effect of inelastic collision on the diffusion and thermal diffusion coefficient. The final expression for the thermal diffusion factor is given by

\[ \chi_{ij} = \frac{1}{5R} \frac{M_i \left( \frac{6C_{ij} - 5}{\eta[D_{ij}],_j} \right)}{\eta[D_{ij}]}, \]

where \( \lambda_{ij} = \lambda_i = \lambda_{i,\infty} \approx 4\lambda_i \sum_{\alpha=1}^{N} \chi_{i,\alpha} \left[ \chi_{i,\alpha} + \sum_{\beta=1}^{N} \left( \Delta\lambda_{i,\alpha,\beta} \right) \left( \sum_{j=1}^{N} \chi_{j,\alpha} \cdot \lambda_{j,\beta} \right) \right] \}

\[ \Lambda_{ij} = \begin{bmatrix} L_{qq}^{10,10} & \delta_{q}^{q,\alpha} & L_{qq}^{10,10}^{-1} \\ \delta_{p}^{p,\alpha} & 0 & L_{qq}^{10,10}^{-1} \end{bmatrix} \]

The various terms used in equation (47) have been defined in Ref. (33).

Monchick, Sandler and Mason\(^{34}\) re-examined the problem by dropping the assumption used by Monchick et al.\(^{33}\) that the differential scattering cross-section is the same for all entrance and exit channels. When this assumption is excluded, additional terms involving the internal conductivity of the constituent species appear in the expression for \( \alpha_T \). Thus the final expression for \( \alpha_T \) can be written as
\[ \chi_T = \frac{(6\tilde{C}_{ji} - 5)}{5nK(D_{ij})} \left( \frac{\lambda_j^\text{trans}}{x_j m_j} - \frac{\lambda_i^\text{trans}}{x_i m_i} \right) + \left[ \frac{(6\tilde{C}_{ji} - 5)\lambda_j^\text{int}}{x_j} - \frac{(6\tilde{C}_{ij} - 5)\lambda_i^\text{int}}{x_i} \right] \] (48)

where

\[ (6\tilde{C}_{ji} - 5) = \left( \frac{5R}{C_{ji}^\text{int}} \right) \left\langle \frac{(\epsilon_{i,j} - \epsilon_j)(\gamma^2 - \gamma'\cos\chi)}{\left\langle \gamma^2 - \gamma'\cos\chi \right\rangle} \right\rangle_{ij} \] (49)

The various terms used in equation (48) and (49) are defined in Ref. (34). The collision integral ratio \((6\tilde{C}_{ji} - 5)\) differs from the well-known ratio \(C_{ji}^\text{int}\) in two aspects:

(i) \(\tilde{C}_{ji}\) is not symmetric with respect to the interchange of indices \(i\) and \(j\).

(ii) The numerical value of \(\tilde{C}_{ji}\) is quite sensitive to inelastic collision, it is zero if the \(j\)th species has no excitation internal energy.

At present, \(\tilde{C}_{ji}\) can only be evaluated for rigid body models. For the rough sphere model \((6\tilde{C}_{ji} - 5) = 0\). For eccentric loaded sphere model (Monchick et al.34)

\[ 6\tilde{C}_{ji} - 5 = \frac{5/2 (W_j^0 - W_j^{(3)})}{W_j^{(0)}} \] (50)
The function $w_j^{(l)}$ are related to the molecular eccentricity

$$e_j = \frac{m_j \hat{f}_j^2}{2I_j}$$

$$w_j^{(1)} = 2 e_j^{1/2} \sin^{-1} \left( \frac{e_j}{1+e_j} \right)^{1/2} \ldots \ldots \ldots \ldots \ldots (51)$$

$$w_j^{(3)} = \frac{2}{1+e_j} \ldots \ldots \ldots \ldots \ldots \ldots \ldots (52)$$

where $\hat{f}_j$ is the displacement of the centre of mass from the centre of symmetry and $I_j$ is the moment of inertia about the centre of mass.

It is clear from the above discussion that the recent theories of Monchick et al$^{33}$ and Monchick et al$^{34}$ for thermal diffusion phenomena require a critical analysis for different polyatomic system. With this end in view a large number of systems have been selected and thermal diffusion factor data have been measured and compared with the theory.

**Multicomponent Mixture**

The expression for transport properties of multicomponent mixtures were derived by Curtiss and Hirschfelder$^{35}$ by extending the work of Chapman and Cowling$^4$. Hellund$^{36}$ also obtained the equation for both ordinary and thermal diffusion, but his equations are more complicated than those of Curtiss and Hirschfelder$^{35}$, since he had taken the quantum correction into account. All these extremely complicated expressions suffer from the defect that they
fail to reduce to the proper form for a binary mixture. Monchick et al. point out that this defect arises due to the use of first-order approximation for diffusion coefficient in the formulation. Later Van der Valk following the suggestion of Waldmann, obtained an expression for thermal diffusion factor for any polynary mixture. The expressions are

\[
\lambda_{ij} = \begin{vmatrix}
   a_{11} & a_{12} & \cdots & a_{1n} & 1 \\
   a_{21} & a_{22} & \cdots & a_{2n} & 1 \\
   \vdots & \vdots & \ddots & \vdots & \vdots \\
   a_{n1} & a_{n2} & \cdots & a_{nn} & 1 \\
   b_{1,ij} & b_{2,ij} & \cdots & b_{n,ij} & 0
\end{vmatrix}^{-1}
\]

where

\[
a_{rs} = x_s M_{sr} M_{rs} (F_{rs}^*/E_{sr}) + \delta_{rs} \sum_s x_s (F_{sl}/E_{sl})
\]

\[
\delta_{rs} = 0 \text{ for } r \neq s
\]

\[
\delta_{rs} = 1 \text{ for } r = s
\]

\(x_s\) is the molefraction of the \(s\)-th component, and

\[
b_{1,ij} = -\left\{ (1 - \sum_k x_k) \frac{M_{ij}}{E_{ij}^*} + \sum_k x_k \frac{M_{ik}}{E_{ik}} \right\}
\]

\[
b_{2,ij} = \frac{2}{5} \left( 2/M_{ij} \right)^{1/2} \left( \sum_i \frac{M_{ij}}{E_{ij}^*} \right)
\]

\[
b_{n,ij} = \sum_k \frac{M_{ik}}{E_{ik}} \left( 6C_{ik}^* - 5/E_{ik} \right) - M_{jk} \left( 6C_{jk}^* - 5/E_{jk} \right)
\]

\[
F_{ij} = \frac{2}{5} \left( \Omega_{ii} \right)^{1/2} \left( \Omega_{ij} \right)^{1/2} \left( \sigma_{ij} \right)^{1/2}
\]

\[
F_{ij}^* = 6M_{ij}^2 + \left( 5 - \frac{12}{5} F_{ij}^* \right) M_{ij} M_{ij}^* \frac{16}{5} \frac{M_{ij}^*}{M_{ij}} A_{ij}^*
\]

\[
F_{ij}^* = \left( -11 \frac{12}{5} F_{ij}^* \right) \frac{16}{5} A_{ij}^*
\]
\[ M_{ij} = \frac{m_i}{m_i + m_j}, \quad M_{ji} = \frac{m_j}{m_i + m_j} \]

\( m_i \) is the mass of the \( i \)th molecule. \( A^*, B^* \) and \( C^* \) are given by,
\[
A_{ij}^* = \frac{\Omega_{ij}^{(2,2)}}{2 \Omega_{ij}^{(1,1)}}
\]
\[
B_{ij}^* = \frac{(\Sigma \Omega_{ij}^{(1,2)} - \Omega_{ij}^{(1,3)})}{3 \Omega_{ij}^{(1,0)}}
\]
\[
C_{ij}^* = \frac{\Omega_{ij}^{(1,2)}}{3 \Omega_{ij}^{(1,0)}}
\]
The remaining terms have their usual significance.

The formulation presented by Monchick et al.\(^ {24} \) are also valid for any polynary mixture and can be reduced to the form given by Van der Valk after a little manipulation. However, for polyatomic gases, Van der Valk's theory does not include any correction for inelastic collision.

**Effect of Magnetic and Electric Field on the Transport Properties of Gases**

An introduction to the transport phenomena in gases will be incomplete without a description of the effects of the magnetic and electric fields on the transport properties of polyatomic gases which is known as the Senftleben - Beenakker effect.
Effect of Magnetic Field

As early as 1930, Senftleben\textsuperscript{38} showed that the thermal conductivity of oxygen changes with the application of magnetic field. Thus effect was also observed in another diatomic gas possessing paramagnetism namely NO. In the thirties a whole series of experimental papers were published regarding this effect in $O_2$ \textsuperscript{39}. It was found simultaneously that the viscosities of a paramagnetic gas also depends on the magnetic field\textsuperscript{40}.

It was assumed that only for paramagnetic gases such effect exists. However a group of workers\textsuperscript{41} after a series of experiments concluded that it is a general property of polyatomic molecules. At present the data are available for a number of gases viz. $N_2$, $CO$, $CO_2$, para $H_2$, normal $H_2$, ortho $D_2$, normal $D_2$, HD, $CH_4$, $CD_4$.

In the presence of a magnetic field, the transport properties decrease. The effect is an even function of H. At constant temperature the approach to saturation is a unique function of $H/p$, where $p$ is the pressure. For mixture with a paramagnetic gas, the change is proportional to the concentration of paramagnetic component.

The first theoretical approach to consider this effect was made by Laue\textsuperscript{42}. He assumed that the free path depends on the angle between direction of molecular velocity and magnetic field and obtained a relation which explicitly contains the dependence of angle between $\vec{H}$ and $\nabla T$. 
Zernike and Van Lier, following the idea of Gorter, related this effect with the non-sphericity of the molecules. They considered the thermal conductivity in the mean free path approximation.

In 1961, Kagan and Maksimov first developed a kinetic equation for a paramagnetic gas in a magnetic field taking into account the rotational degrees of freedom, discretness of the magnetic moment and dependence of the scattering cross-section on the angle between direction of magnetic moment and the direction of the relative velocity. They solved the kinetic equation with reference to thermal conductivity and obtained an explicit expression for the thermal conductivity tensor.

The expression obtained by them shows that in the presence of magnetic field, the thermal conductivity is of tensor character, i.e. anisotropic. Thus it has different values when the field is parallel and perpendicular to the temperature gradient. Moreover when the gradient between $\mathbf{H}$ and $\nabla T$ lies between 0 and 90°, a heat flow component exists in a direction perpendicular to $\nabla T$. When $\mathbf{H}$ is parallel and perpendicular to $\nabla T$, the change for the thermal conductivity is given respectively by

$$\frac{\Delta \lambda_1}{\lambda_0} = \frac{\Psi}{2s+1} \sum_{\sigma} C, \quad \text{and} \quad \frac{\Delta \lambda_2}{\lambda_0} = \frac{\Psi}{2s+1} \sum_{\sigma} (C' + C'_2)$$

The meaning of the symbols are available in Ref. (45). At sufficiently large values of the magnetic field saturation sets in and both the quantities attain the following absolute
This value of \( \Delta \lambda \) is in agreement with the value obtained by experiment (Senftleben).

Knaap and Beenakker\(^4\) extended the work of Kagan and Maksimov for the heat conductivity of paramagnetic gases to the case of non-paramagnetic cases. They obtained the expression for heat conductivity and viscosity for a special case of linear molecule. The thermal conductivity tensor in the presence of a magnetic field shows that besides the change of thermal conductivity shown in the Kagan and Maksimov theory, there is flow of heat in a direction perpendicular to both magnetic field \( \mathbf{H} \) and \( \nabla T \), similar to Righi - Leduc effect in metals.

The starting point of Knaap and Beenakker's theory was Boltzmann equation

\[
\frac{\delta f}{\delta t} + \nabla \cdot \nabla f + \frac{\delta f}{\delta \mathbf{M}} \cdot (f \mathbf{\hat{M}}) = \left( \frac{\partial f}{\partial t} \right)_{\text{coll}} \quad \cdots (56)
\]

Here \( f = f(\mathbf{r}, \mathbf{v}, \mathbf{M}, t) \) is the distribution function, \( \nabla \) is the velocity and \( \mathbf{M} \) is the angular momentum, \( \mathbf{\hat{M}} = \mathbf{M} \wedge \mathbf{H} \quad \cdots (57) \)

\[
\mathbf{\hat{M}} = \frac{g}{2} \frac{\mathbf{M} \wedge \mathbf{H}}{\hbar} = \mathbf{\hat{M}} \quad \cdots \quad (58)
\]
\[ g = \text{Lande } g\text{-factor} \]
\[ \hbar = \text{Plank constant} \]

The expression for heat conductivity is given by the following scheme

<table>
<thead>
<tr>
<th>( q_x )</th>
<th>( \nabla_x T )</th>
<th>( q_y )</th>
<th>( \nabla_y T )</th>
<th>( q_z )</th>
<th>( \nabla_z T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>-( \lambda_0 (1 + \psi C'_1 + \psi C'_2) )</td>
<td>0</td>
<td>-( \lambda_0 (1 + \psi C'_1) )</td>
<td>-( \lambda_0 \psi C'_3 )</td>
<td>0</td>
<td>-( \lambda_0 (1 + \psi C'_1) )</td>
</tr>
</tbody>
</table>

which is in agreement with the expression given by De Groot and Mazur. The expression for the relative changes in heat conductivity in intermediate and infinite field are respectively given by

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)_H^{\|} = \psi (C'_1 + C'_2) = -\psi \frac{\Theta^2}{1+\Theta^2} \quad \cdots \quad (59)
\]

and

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)_H = -2 \psi \quad \cdots \quad (60)
\]

where

\[
\Theta = \frac{2M_N RT}{\hbar} \frac{\hbar}{p}
\]

while the changes with the gradients perpendicular to the field are

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)_H^{\perp} = \psi C'_1 = -\psi \left[ \frac{\Theta^2}{1+\Theta^2} + 2 \frac{4\Theta^2}{1+4\Theta^2} \right]
\]

and

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)_H = -3 \psi
\]
The meaning of the different symbols used can be obtained in Ref. (46). For the changes of trace we have,

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)^{\text{trace}} = \left( \frac{\Delta \lambda}{\lambda_0} \right)^{\|} + \left( \frac{\Delta \lambda}{\lambda_0} \right)^{\perp} = -\Psi 4 \left\{ \frac{\Theta}{1 + \Theta^2} + \frac{4 \Theta^2}{1 + 4 \Theta^2} \right\}
\]

and

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)^{\text{trace}}_{\gamma = \infty} = -8 \Psi
\]

The changes are all negative for all values of \( \Theta \). This was experimentally verified by Gorlick et al. The term \( C_3' \) determines the heat flow in a direction perpendicular to both \( H \) and \( \nabla T \)

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)^{\text{trans}} = \Psi C_3' = -\Psi \left\{ \frac{\Theta}{1 + \Theta^2} + 2 \frac{2 \Theta}{1 + 4 \Theta^2} \right\}
\]

and

\[
\left( \frac{\Delta \lambda}{\lambda_0} \right)^{\text{trans}}_{\gamma = \infty} = 0
\]

The heat flow is reversed when the direction of the field changes sign. Since \( C_3' \) is odd in \( \Theta \), this effect is odd in Lande's g-factor. This helps one to determine the sign of g-factor from heat conductivity experiment.

Knap and Beenakker considered the \( O_2 \) molecule and made a systematic comparison with the theory of Kagan and Muksimov. Since \( O_2 \) is a paramagnetic molecule in \( 3 \Sigma \) ground state, the electron spin angular momentum \( \hat{S} (S = 1) \) couple with the orbital angular momentum \( \hat{L} \) to give total angular momentum \( \hat{J} \). The spin angular momentum can have three orientations with respect to \( \hat{J} \). The component of \( S \) along \( \hat{J} \) being \( m_s = +1, 0, -1 \).
The molecules in the $m_s = 0$ state contribute to the diagonal element of the heat conductivity tensor. As this contribution occurs at a higher $H/p$ values, the change of transport property of $O_2$ in a magnetic field will be spread over a range of $H/p$ than in other cases e.g. $N_2$. This is in agreement with experiment.\(^{49}\)

Secondly, the $m_s = 0$ state will give rise to transverse effect which was verified experimentally by Korving et al.\(^{50}\). In the Kagan - Maksimov theory there is no such effect as the contribution of $m_s = +1$ and $m_s = -1$ cancel.

**Viscosity**

In the case of viscosity, the expression for five shear viscosities are given by

\[
\eta_1 = \eta_0 - \eta_0 \tilde{\varphi}\left\{2 \frac{\tilde{\Theta}^2}{1 + \tilde{\Theta}^2} + 8 \frac{4 \tilde{\Theta}^2}{1 + 4 \tilde{\Theta}^2}\right\}
\]

\[
\eta_2 = \eta_0 - \eta_0 \tilde{\varphi}\left\{4 \frac{\tilde{\Theta}^2}{1 + \tilde{\Theta}^2} + 6 \frac{4 \tilde{\Theta}^2}{1 + 4 \tilde{\Theta}^2}\right\}
\]

\[
\eta_3 = \eta_0 - \eta_0 \tilde{\varphi}\left\{7 \frac{\tilde{\Theta}^2}{1 + \tilde{\Theta}^2} + 6 \frac{4 \tilde{\Theta}^2}{1 + 4 \tilde{\Theta}^2}\right\}
\]

\[
\eta_4 = \eta_0 \tilde{\varphi}\left\{6 \frac{\tilde{\Theta}^2}{1 + \tilde{\Theta}^2} + 4 \frac{2 \tilde{\Theta}}{1 + 4 \tilde{\Theta}^2}\right\}
\]

\[
\eta_5 = \eta_0 \tilde{\varphi}\left\{5 \frac{\tilde{\Theta}}{1 + \tilde{\Theta}^2} - 6 \frac{2 \tilde{\Theta}}{1 + 4 \tilde{\Theta}^2}\right\}
\]
The meaning of the symbols is given in Ref. (46). If we call, the effect, which occurs when the field (in x direction) is parallel to the product of velocity and velocity gradient, the parallel effect and when the field is perpendicular to this vector product as perpendicular effect. Then we have

\[
2\eta_2 - \eta_1 = \eta_0 \tilde{\psi} \left\{ 6 \frac{\tilde{\Theta}^2}{1 + \tilde{\Theta}^2} + 4 \frac{4\tilde{\Theta}^2}{1 + 4\tilde{\Theta}^2} \right\}
\]

\[
\eta_1 - \eta_2 = -\eta_0 \tilde{\psi} \left\{ -2 \frac{\tilde{\Theta}^2}{1 + \tilde{\Theta}^2} + 2 \frac{4\tilde{\Theta}^2}{1 + 4\tilde{\Theta}^2} \right\}
\]

But no experimental data are as yet available to show the difference between the parallel and perpendicular effects. The transverse effect is given by

\[
\left( \frac{\Delta \eta}{\eta_0} \right)_{\text{trans}} = \tilde{\psi} \left\{ 5 \frac{\tilde{\Theta}}{1 + \tilde{\Theta}^2} - 6 \frac{2\tilde{\Theta}}{1 + 4\tilde{\Theta}^2} \right\}
\]
However, from the theory of Knaap and Beenakker it followed that thermal conductivity reaches saturation at a lower $H/p$ value than the viscosity which contradicts the experimental fact that the viscosity reaches saturation at lower $H/p$ value than heat conductivity. Further the ratio of saturation effect for heat conductivity and viscosity in high fields is found by

$$\frac{\Delta \gamma/\gamma_0}{\Delta \eta/\eta_0} \bigg|_{H=\infty} \approx 0 \Delta$$

which suggests a smaller effect for the heat conductivity than for the viscosity. But experimental$^{51}$ shows that the effect on heat conductivity is always a factor of 2 larger. They suggested that inelastic collision effects are responsible for this which would be more prominent for the heat conductivity.

A more refined theoretical expression for diamagnetic gases has been given by Levi and McCourt$^{52}$ in which they considered the most important angular momentum dependent expansion term. The result for the transverse flow of heat is given by

$$\frac{\lambda t_{\text{trans}}}{\lambda} = -\Psi \left\{ \frac{G}{1 + \omega^2} + \lambda \frac{\omega}{1 + 4\omega^2} \right\} + \Psi' \left\{ \frac{G}{1 + \omega^2} \right\}$$

So far the theoretical approach was limited to diamagnetic gases only. This is due to the fact that the description of the internal state for the paramagnetic molecule is very complicated. Again, too many assumptions lead to the fact that some effects such as double peaked thermal conductivity and a density dependence of the transverse effect are not obtained.
Morral and McCourt \cite{53} first considered the case of 2 molecule and obtained expression for the change in thermal conductivity. In their later publication \cite{54} they compared their theory with experiment for NO$_2$ and obtained a good agreement. Later \cite{55} they considered the diatomic molecule with the 2$\Sigma$ ground state having only a single unpaired electron which simplifies the internal state Hamiltonian. They obtained the change in the shear viscosity and the thermal conductivity. Cooper et al. \cite{56} studied theoretically the change in thermal conductivity and shear viscosity of a 2$\Pi$ molecule in a magnetic field. It was shown by them that the effect is due to two contribution corresponding to magnetic moment of 2$\Pi_{3/2}$ and 2$\Pi_{1/2}$ state respectively.

**Mixtures**

For dilute gas mixture consisting of linear molecules, the theory for the shear viscosity has been developed by Tip \cite{57}. Explicit expression for mixture of diamagnetic and noble gases were considered which is of particular interest for the measurement of angular momentum reorientation cross-section for molecule-noble gas collision. The expression for the five viscosity coefficients are given by

\[
\eta_1 = \eta_0 \\
\eta_2 = \eta_0 \left(1 - \frac{1}{2} k \frac{4 \Theta_i^2}{1 + 4 \Theta_i^2}\right)
\]
In capillary tube experiment with the field perpendicular to the capillary the actually measured quantity is
\[
\eta_3 = \eta_0 \left( 1 - K \frac{\Theta^2}{1 + \Theta^2} \right)
\]
\[
\eta_4 = \eta_0 \left( K \frac{2 \Theta_i}{1 + 4 \Theta_i^2} \right)
\]
\[
\eta_5 = -\eta_0 \left( K \frac{\Theta_i}{1 + \Theta_i^2} \right)
\]

The explicit expression for $K$ and $\Theta_i$, are given in Ref. (57).

Side by side, the model calculation for the change of transport properties under magnetic field has been developed by Dahler and co-workers\textsuperscript{58} who treated the phenomena in the case of rough sphere model which was first used by Bryan\textsuperscript{59} for studying the effect of inelastic collision on transport properties. But the results were not presented in the most desirable form. McCourt et al\textsuperscript{60} took up the problem and started with Boltzmann equation assuming that the system is slightly perturbed from equilibrium. They obtained the expression for the three components of $\Delta \lambda$, the change in thermal conductivity in magnetic field.
Klein et al.\textsuperscript{61} approached the problem by using sphere
cylinder model. Later Cooper and Hoffman\textsuperscript{62} generalised the
problem by considering three models (1) spherocylinder (2) the
ellipsoid of revolution and (3) distorted ellipsoid. They
computed the transport properties of diamagnetic, diatomic gases.
They found that odd terms in the angular momentum make only a
small contribution and in fact, is zero in the approximation of
Levi and McCourt. Moreover they found that viscosity served
a test of the model rather than thermal conductivity. Moraal
et al.\textsuperscript{63} derived the expression for change in shear and bulk
viscosities in external magnetic field. An external magnetic
field not only changes transport properties but also causes a
cross-coupling between the shear and bulk viscosities. They
determined the coefficient of cross-coupling for rough sphere
model. It was shown by them that the relative change in the
bulk viscosity and cross coefficient was thousand times smaller
than the corresponding change in the shear viscosity.

\textit{Effect of Magnetic Field on Thermal Diffusion}

Tip et al.\textsuperscript{64} studied thermal diffusion of Kr-85 in oxygen at
two different temperatures in presence of a magnetic field of
about 3000 gauss. It was found by them that there is no change
of the separation which help them to conclude that there is no
field influence on the thermal diffusion phenomena.
Effect of Electric Field

The effect of electric field on transport properties was studied by a number of workers. This effect is similar to the effect of magnetic field and this is a function of E/p and saturates at a higher E/p value. It was found that effect of electric field in some polar gases is to decrease the heat conductivity whereas in some strongly polar gases the heat conductivity increases.

The first theoretical approach to consider this effect was made by Borman et al. for linear molecules. Later Mikhailova and Maksimov presented a theory for polar molecules of the symmetric top type or diatomic polar molecules. The approach of Mikhailova et al. was based on classical mechanics. They first developed a kinetic equation and solved it by perturbation procedure. The expressions for thermal conductivity and viscosity were obtained by them. They also showed that when a temperature gradient exists one can obtain a change of the viscosity tensor and conversely.

Later Levi, McCourt and Tip considered the problem in a way different from that of Mikhailova and Maksimov. They started with quantum-mechanical Waldmann-Snider equation and used simpler variational procedure rather than the perturbation procedure introduced by Mikhailova and Maksimov. In presence of external field, the Waldmann-Snider equation can be written as

\[
\frac{\delta \ln f}{\delta t} + \nabla \cdot \nabla f = C(f,\rho_f) - i \frac{k}{\hbar} [H_{\text{int}}, f] \quad \cdots \quad \cdots \quad (64)
\]
f = one particle Wigner distribution function density matrix, $H_{\text{int}}$ is the Hamiltonian for internal state and $C$ is a bilinear super operator representing the effect of collision. They write

$$H_{\text{int}} = H' + H_{\text{Ficld}}$$  \hspace{1cm} (6.2)$$

$H'$ represents rotational Hamiltonian for one molecule. The function 'f' can no longer be assumed to be diagonal and can be split into diagonal and non-diagonal parts

$$f = f_d + f_{n_d}$$  \hspace{1cm} (6.3)$$

and the equation for distribution function can be split into two equations, one for $f_d$ and the other for $f_{n_d}$. They considered the two types of molecules (1) symmetric top molecules, (2) linear molecules having internal electronic ground state.

For symmetric top molecules the change in the shear viscosity and visco-thermal effect i.e. a velocity gradient gives rise not only to a stress tensor but also a heat flux vector and the expression of thermal conductivity and thermo viscous effect i.e. a stress tensor caused by a temperature gradient were also presented by them. They also showed that while viscosity is decreased by the presence of electric field, the change of thermal conductivity can be positive or negative.

In the case of linear molecule, they anticipated that no visco-thermal or thermo viscous effect will be possible. Further it was shown by them that in contrast to symmetric top molecule the
saturation values of viscosity and thermal conductivity of linear molecules in an electric field are very different from those in a magnetic field.

The anomalous behaviour of polar gases in an electric field has been reported in first paragraph of this chapter. Levi and McCourt\textsuperscript{73} related this phenomena theoretically to the non-self adjointness of the collision super operator in Waldmann - Snider equation. They showed that the condition of self adjointness of the super operator is equivalent to detailed balance i.e. all collisions have an inverse in classical picture. So they concluded that in strongly polar gases dipole-dipole interactions have no inverse. This conclusion has been contradicted by de Groot et al\textsuperscript{74} from experimental evidences.

\textbf{Intermolecular Forces and Potential Models}

The transport properties of gases as discussed above depend on the dynamics of collisions which in turn is determined by the relative kinetic energy of the colliding particles, impact parameter and intermolecular forces. We shall describe briefly the various types of intermolecular forces which come into play in molecular collisions.

The intermolecular forces may be divided into two broad types, viz. (1) Short-range forces and (2) Long-range forces. The short range forces which are in general, known as valence or
chemical forces originate by the overlapping of charge clouds of the colliding molecules when they come closer. The short-range interactions at very small intermolecular separations are strongly angle-dependent. It is difficult to determine the short-range interactions experimentally. Recently some progress has been made in this direction by high energy molecular beam scattering experiments and glory scattering. The short-range interactions for simple systems like H-He, H$_2$-He, He-He etc. have been determined from ab initio quantum mechanical calculations. Due to mathematical difficulties, this method has not yet been extended successfully, to more complicated systems.

The contributions to the long-range forces can be divided as follows: (1) the electrostatic contributions $\varphi^{(\delta)}$, (2) the induction contribution $\varphi^{(i\omega)}$, and (3) the dispersion contribution $\varphi^{(d\omega)}$. The general nature of these interactions is summarized below.

1. **Electrostatic Forces**

The electrostatic contributions to the intermolecular potential energy from the interactions of the various multipole moments in the molecules: charge (C), dipole moment (M), quadrupole moments (Q), etc. From the Coulombic law of electrostatic interaction the various types of interactions between molecules 'a' and 'b' are given by
\[ \Phi_{ab}^{(c,c)} = \frac{C_a C_b}{r} \]
\[ \Phi_{ab}^{(c,n)} = -\frac{C_a M_b}{r^2} \cos \theta_b \]
\[ \Phi_{ab}^{(c,q)} = -\frac{C_a Q_b}{4r^3} (3\cos^2 \theta_b - 1) \]
\[ \Phi_{ab}^{(n,n)} = -\frac{M_a M_b}{r^3} \left\{ 2\cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos \left( \phi_a - \phi_b \right) \right\} \]
\[ \Phi_{ab}^{(n,q)} = +\frac{3M_a Q_b}{4r^4} \left\{ \cos \theta_a (3\cos^2 \theta_b - 1) - 2\sin \theta_a \sin \theta_b \cos \theta_b \cos \left( \phi_a - \phi_b \right) \right\} \]
\[ \Phi_{ab}^{(q,q)} = +\frac{3Q_a Q_b}{16r^5} \left\{ -5\cos^3 \theta_a - 5\cos^2 \theta_b - 15\cos^2 \theta_a \cos \theta_b \right. \]
\[ \left.+ 2\left[ \sin \theta_a \sin \theta_b \cos \left( \phi_a - \phi_b \right) - 4\cos \theta_a \cos \theta_b \right] \right\} \]

The intermolecular distance is \( r \) and the angles \( \theta_a, \theta_b, \phi_a, \phi_b \) serve to define the orientations of the two molecules as shown in fig. (1).

The angle-dependence of the above expressions is complicated and there are several ways of averaging it so that the interaction potential becomes effectively spherically symmetric.
Fig. 1. Schematic diagram of the process of interaction between two molecules 'a' and 'b'. 
2. **Induction Forces**

When a charged particle interacts with a neutral molecule, the charged particle 'a' induces in the neutral molecule 'b' a dipole moment. If the polarizability of molecule 'b' is \( \chi_b \), the dipole moment induced in molecule 'b' is \( \frac{C_a \chi_b}{\gamma^2} \) and the energy of interaction between the charge and the induced moment is:

\[
\phi_{ab}^{( \text{c}, \text{ind}\mu)} = - \frac{C_a^2 \chi_b}{2\gamma^4}
\]

Similarly it may be shown that the potential energy of the interaction between a point dipole and an induced dipole produced in a neutral molecule is:

\[
\phi_{ab}^{( \text{p}, \text{ind}\mu)} = \frac{4 \alpha \chi_b}{2\gamma^6} \left( 3 \frac{C_a^2 \gamma + 1}{\gamma^6} \right)
\]

which is an important contribution to the potential of interaction between a polar and a non-polar molecule.

3. **Dispersion Forces**

When two non-polar molecules interacts, there are long-range attractive forces between them which are known as the London dispersion forces. In the quantum mechanical calculation of the interaction energy between two molecules, these forces appear in the second-order perturbation terms. They are called dispersion forces as the perturbation terms are expressed in terms of oscillator strengths as appear in the equations for the dispersion of light.
Classically, the origin of the dispersion forces may be explained as follows. At any instant the electrons in molecule 'a' have a definite configuration so that it has an instantaneous dipole moment. This dipole moment induces a dipole in molecule 'b'. The interaction between the instantaneous and induced dipole moment result in an attractive force between the two molecules. Similarly, there will be other terms due to the higher multipole moments. This classical picture however, do not come in the quantum mechanical treatment of the dispersion forces. The dispersion forces can be expressed in the following form of a convergent series

$$\sum_{\ell=0}^{\infty} \frac{\phi_{\ell}}{\ell!} + \frac{\mathcal{C}}{\ell^6} + \frac{\mathcal{C}'}{\ell^8} + \frac{\mathcal{C}''}{\ell^{10}} + \ldots \ldots$$

where the first term on the right hand side of equation (64) is due to the induced dipole-induced dipole interaction and the subsequent terms are due to induced-dipole-induced quadrupole and induced-quadrupole-induced quadrupole interactions.

In addition to the dispersion forces, there may be resonance forces which are long-range in nature and have no classical analogue. The possibility of resonance forces, between two like molecules arises when a quantum of energy can be emitted readily by 'a' and absorbed by 'b'. In order for the resonance to occur, it is necessary for at least one of the molecules to be in the excited state.
The long-range forces can be determined from the pressure and dielectric virial coefficients, transport properties, crystal properties and molecular beam scattering data. At present considerable attention is being paid to the last method particularly by rainbow scattering phenomenon.

As stated above, it is difficult to make ab initio quantum mechanical calculation of intermolecular forces and frequently potential models involving a number of parameters are used which can be determined from different types of experimental data. It may be mentioned that recently some progress has been made in determining directly intermolecular potential from differential scattering cross-section data without assuming any particular form of the potential model. As this method is yet to develop fully, the use of potential models is still a very important method for determining intermolecular forces.

A number of potential models have been proposed to represent the potential function between two molecules. These models can be classified into two groups. (1) Spherically symmetric potential (2) Angle dependent potentials. We summarize below the various models used by us.

(1) **Angle-independent Potentials**

(i) **Lennard-Jones (12:6) potential**

\[ \phi(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right] \]

\( r \) = separation of the molecules, \( \varepsilon \) is the maximum energy of attraction and \( \sigma \) is the value of \( r \) for which \( \phi(r) \) is zero.
This model gives a fairly realistic representation of both attractive and repulsive forces between spherically symmetric non-polar molecule. The collision integrals in tabular form have been summarized by Hirschfelder et al.\(^1\).

(ii) Core-Potential

The core model of Kihara allows a convex core of any shape to be assigned to a molecule while the potential energy of interaction is assumed to depend only on the shortest distance between core surface and to be of the Lennard-Jones forms.

For simplicity, the potential function only for spherical core is given by

\[
\phi(r) = 4\epsilon \left[ \frac{(\sigma - 2a)}{r - 2a} \right]^{12} - \frac{(\sigma - 2a)^6}{(r - 2a)^3}, \quad r \geq 2a
\]

\[
= \infty, \quad r < 2a
\]

where 'a' is the core radius, \(\sigma\) is the value of \(r\) for which \(\phi(r) = 0\) and \(\epsilon\) is the maximum energy of attraction. For zero core size the model reduces to the Lennard-Jones (12:6) potential.

The transport properties collision integrals for this model have been evaluated by Barker et al.\(^2\).

(iii) Modified Buckingham or exp-6 Potential

\[
\phi(r) = \frac{\epsilon}{1 - \frac{6}{\alpha}} \exp(\alpha [1 - \frac{r}{r_m}]) - \left(\frac{r_m}{r}\right)^6, \quad r \geq r_{\text{max}}
\]

\[
= \infty, \quad r \leq r_{\text{max}}
\]

\(r_m\) is that value of \(r\) for which \((r)\) has a spurious maximum.
The ratio \( \frac{r_{\text{max}}}{r} \) is given by the smallest root of

\[
\left( \frac{r_{\text{max}}}{r_m} \right)^7 \exp \left( \alpha \left[ 1 - \frac{r_{\text{max}}}{r_m} \right] \right) = 1
\]

The constant \( \alpha \) represents the steepness of the exponential repulsion and \( \xi \) refers to the depth of the potential at the minima. The advantage of this model over the Lennard-Jones (12:6) model is that there is a third parameter \( \alpha \) which can be changed arbitrarily to fit the experimental data. The collision integrals needed for the calculation of transport properties were calculated by Meson and Rice.88

2. Angle Dependent Potential

(i) Stockmayer Potential

\[
\Phi (\tau, \theta_a, \theta_b, \phi_a - \phi_b) = 4 \varepsilon \left[ (\frac{\sigma}{\tau})^12 - (\frac{\sigma}{\tau})^6 \right] - \frac{M_a M_b}{\tau^3} \varrho (\theta_a, \theta_b, \phi_b - \phi_a)
\]

where \( \varrho (\theta_a, \theta_b, \phi_a - \phi_b) = 2 C_{ab} \cos \theta_a \cos \theta_b - \sin \theta_a \sin \theta_b \cos (\phi_a - \phi_b) \)

\( M_a \) and \( M_b \) are the dipole moment of the two interacting molecules, \( \theta_a \) and \( \theta_b \) are the angles of the inclination of the axes of the two dipoles to the line joining the centres of the two molecules and \( (\phi_a - \phi_b) \) is the azimuthal angle between them. Monchick and Mason89 have tabulated the collision integral for this potential taking all possible orientations into consideration i.e. by assuming a central force field.
(ii) For interaction between quadrupolar molecules the potential can be written as,

$$\varphi(\gamma, \theta_1, \theta_2, \phi) = 4\epsilon_{12} \left[ \left( \frac{Q_{12}}{r} \right)^2 - \left( \frac{Q_{12}}{r} \right)^6 \right] + \frac{Q_1 Q_2}{r^8} F(\theta_1, \theta_2, \phi)$$

where $Q_1$ and $Q_2$ are the quadrupole moments of the molecules and $F(\theta_1, \theta_2, \phi)$ is an orientation dependent term given by

$$F(\theta_1, \theta_2, \phi) = \frac{3}{4} \left[ -5 \cos^2 \theta_1 - 5 \cos^2 \theta_2 - 15 \cos \theta_1 \cos \theta_2 \cos^2 \theta_2 + 2 \left( 4 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \phi \right)^2 \right]$$

$\theta_1, \theta_2$ are the angles of inclination of the molecular axes to the line joining the centres and $\phi$ is the azimuthal angle. The collision integrals for this model were calculated by Smith, Munn and Mason.°
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