INVESTIGATIONS ON SOME DIFFUSION PROBLEMS IN RAREFIED GASES

Thesis by

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In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

California Institute of Technology

Pasadena, California

1969

(Submitted December 16, 1968)

ACKNOWLEDGMENTS

I wish to express my deep gratitude to Professor G. R. Gavalas who has helpfully guided me throughout the course of this investigation. I am also indebted to Professor F. H. Shair for his frequent assistance in various ways.

The financial support from the California Institute of Technology in the form of Tuition Scholarships, Graduate Research and Teaching Assistantships, and a Woodrow Wilson Summer Fellowship is deeply appreciated.

Finally, I wish to thank my parents for their sacrifice and continuous encouragement throughout the course of my education.

ABSTRACT

This is a theoretical study of diffusion problems in transitional rarefied gases with surface dissociation and recombination reactions. The method of composite solution, which is a simplified version of the exact composite expansion theory with similarity to the mean free path method, has proved to be very successful.

Both the methods of Lester Lees and of composite solution have been used to solve the problem of simultaneous heat and mass transfer of a partially dissociated diatomic gas of transitional rarefaction from a hot fine wire to a surrounding cylinder. We have employed a sticking probability to describe the dissociation reaction of the diatomic gas at the wire but have used continuum type boundary conditions at the outer cylinder. We have also assumed a small total temperature variation and a small mole fraction of the dissociated atoms. The results obtained by both methods are identical and agree very well with the existing formulas in many limiting cases.

Owing to its simplicity, the method of composite solution was applied to the problem of a subsonic viscous flow past a sphere for small Mach number but arbitrary Knudsen number. This problem was considered both as a prerequisite for the investigation of mass transfer from a sphere to a stream of gas mixtures and as a means to acquire familiarity with the matching procedures. The result for the drag force agrees with the known formulas in both the free molecular flow limit and the continuum limit. The agreement with experimental data in the transitional flow regimes is less satisfactory.

The method of composite solution was then applied to the problem of mass transfer from a sphere to a partially dissociated diatomic gas. Surface recombination reaction was assumed to take place at the sphere while the flow conditions were the same as those in the previous problem. Small mole fraction of the dissociated atoms was also assumed, with the implication of a uniform temperature field. The concentration and flux of the dissociated atoms were found in terms of the sticking probability of the recombination reaction.

The problem of simultaneous diffusion and reaction of dissociated atoms in the interior of a sphere is also very interesting and practically important. We have studied the special case of a very fast reaction where the concentration of atoms at the surface of the sphere is given. A new method of solving this unsteady state diffusion problem with moving boundary was proposed and has proved to be more advantageous than the existing ones.

Finally, the sticking probabilities employed in the previous problems were obtained for various mechanisms of dissociation and recombination reactions. These sticking probabilities turn out to be constant over a wide range of Knudsen number and vanish in the continuum limit.

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INTRODUCTION

1.1 General descriptions

A rarefied gas flow is a flow where the mean free path of the gas is comparable to some characteristic length of the flow field. The gas then does not behave entirely as a continuous fluid but rather shows some characteristics of its coarse molecular structure. Although the mechanics of rarefied gases has been a subject of many investigations since the time of Maxwell (24), it is not until recently that a large amount of both experimental and theoretical results has been obtained. Problems that have been studied include those in the field of vacuum engineering aimed at developing pressure and temperature measuring devices, in the field of aerosol mechanics with some applications in the problem of pollution, in high altitude aerodynamics with interest in drag force and heat transfer, and in supersonic flow with sharp velocity gradient in shock waves. Other problems involve the dissociation and ionization of molecular gases, the condensation of low temperature gases in wind tunnels, and some other phenomena caused by the departure of gases from perfect gas behavior due to high speed flow. In some chemical processes such as the reduction of finely ground ore particles and the hydrogenation of coal, rarefaction effect has also to be taken into account.

It has been found convenient and successful to divide the field of rarefied gas flow into several different flow regimes, corresponding to greater or lesser rarefaction. These are characterized by the

Knudsen number Kn which is defined as the ratio of the molecular mean free path to some significant dimension of the flow field. The latter, for example, may be the dimension of a solid body, the boundary layer thickness, the diameter of a temperature probe in a wind tunnel, or the thickness of the shock transition zone. Flow with large Kn is called free molecular flow, for under such conditions intermolecular collisions can be neglected. On the other hand, flow with small but not negligible Kn is called slip flow. In slip flow, the departure from continuum behavior is slight and manifests itself primarily in the phenomena of velocity slip and temperature jump at the boundaries. Flow with intermediate Kn is called transition flow and its behavior lies between the above two. Finally flow with negligible Kn will be referred to as continuum flow. A complete discussion on the ranges of the various flow regimes has been given by Schaaf (26) (27).

Present knowledge about the transition regime is very limited since most investigations in the rarefied gas dynamics have been confined in the free molecular flow regime, the slip flow regime, and that portion of the transition regime immediately adjacent to the free molecular flow regime. Theoretical as well as experimental work in the transition flow regime is needed urgently because of the importance of information about this regime. Besides, problems with chemical reactions have been seldom studied although the phenomenon of molecular dissociation is known to be a major characteristic of rarefied gas flow, and there is a growing evidence that rarefaction effect has to be considered in many chemical reaction systems with low pressure and/or with fine particles. Those problems require a thorough understanding on the kinetics of chemical reactions and often involve very tedious calculations because of the existence of a second molecular species.

It is the purpose of the present research to study some theoretical problems involving the effects of surface chemical reactions on rarefied gases in the transition flow regime. The results will be found useful in studying certain chemical processes involving fine particles, the interaction of dissociated oxygen with high altitude vehicles, and the effect of surface dissociation on the heat transfer to a temperature probe.

1.2 The Boltzmann equation

The study of rarefied gas dynamics in the transition regime is based on the Boltzmann equation whose derivation can be found in many textbooks such as Chapman and Cowling (8). A rigorous mathematical derivation of the Boltzmann equation from Liouville's equation of classical mechanics is given in the famous article of Grad (11), which also contains a thorough discussion on its range of validity. The Boltzmann equation is

$$\frac{\partial f}{\partial t} + \underline{\xi} \cdot \frac{\partial f}{\partial \underline{r}} + \underline{F} \cdot \frac{\partial f}{\partial \underline{\xi}} = \frac{\delta f}{\delta t} , \qquad (1\text{-}1)$$

where $f = f(\underline{\xi}, \underline{r}, t)$ is the distribution function for the gas molecules such that

$$dn = f(\underline{\xi}, \underline{r}, t)\, d^3\xi \qquad (1\text{-}2)$$

is the number of molecules at $\underline{r}$ with velocities in a small volume of $d^3\xi$ centered at $\underline{\xi}$, $\underline{\xi}$ is the random velocity, $\underline{r}$ is the position vector, $\underline{F}$ is the external force, t is the time, and $\frac{\delta f}{\delta t}$ represents the change of the distribution function due to molecular collisions. Equation (1-1) is valid under the assumptions that only binary collisions are important and that the collision time is only a small part of the life time of the molecules.

1.2.1 The equation of change of molecular properties

All molecular properties can be expressed as mean values of some functions of the random velocity $\underline{\xi}$. For example, the average velocity $\underline{u}$ is the mean value of $\underline{\xi}$, the pressure tensor p_{ij} is that of $m\xi_i\xi_j$, the temperature T is the mean value of $m|\xi|^2/3k$ where k is the Boltzmann constant, and the heat flux $\underline{q}$ is that of $\frac{1}{2}m\underline{\xi}|\xi|^2$. Multiplying equation (1-1) by a function ψ of the random velocity and integrating over all the velocity space, we obtain the generalized equation of change of molecular properties,

$$\frac{\partial n\overline{\psi}}{\partial t} + \frac{\partial}{\partial \underline{r}} \cdot n\overline{\psi\underline{\xi}} - n\left(\overline{\frac{\partial\psi}{\partial t}} + \overline{\underline{\xi} \cdot \frac{\partial\psi}{\partial \underline{r}}} + \underline{F} \cdot \overline{\frac{\partial\psi}{\partial\underline{\xi}}}\right) = n\Delta\overline{\psi}_{\text{coll.}}, \qquad (1\text{-}3)$$

where $\overline{\psi} = \frac{1}{n}\int \psi f\, d^3\xi$ is the average value of ψ and $\Delta\psi_{\text{coll.}}$ is the change of ψ due to molecular collisions.

There are several representations of the term $n\Delta\psi_{\text{coll.}}$. The one given by Hirschfelder, Curtiss and Bird (14) is

$$n\Delta\overline{\psi}_{\text{coll.}} = \int\int\int\int (\psi' - \psi) U f_1 f b\, db\, d\eta\, d^3\xi_1\, d^3\xi\ , \qquad (1\text{-}4)$$

where f is the distribution function for the molecule under consideration which has properties ψ' and ψ after and before the collision, f_1 is the distribution function for the molecule that collides with the first molecule, b is an impact parameter, η is the azimuthal angle, and $U = |\underline{\xi}_1 - \underline{\xi}|$ is the relative velocity of the two molecules. The function ψ' depends on $\underline{\xi}_1$, $\underline{\xi}$, b, and the intermolecular force that governs the collision. A graphic illustration can be found in Figure 3 on page 42. Notice that equation (1-3) is also called the moment equation of the Boltzmann equation.

For certain functions of the random velocity, $\Delta\overline{\psi}_{coll.}$ is known to be zero by virtue of the conservation laws. These are $\psi^{(1)} = m$, $\underline{\psi}^{(2)} = m\underline{\xi}$, and $\psi^{(3)} = m|\xi|^2$; and are called summational invariants for encounters.

In a mixture, equation (1-3) can be applied to each component with $\Delta\overline{\psi}_{coll.}$ replaced by a sum of $\Delta_1\overline{\psi}_{coll.}$, $\Delta_2\overline{\psi}_{coll.}$, etc. which are the change of the function ψ due to collisions with species 1, 2, etc. respectively. That is,

$$n\Delta\overline{\psi}_{coll.} = n\Delta_1\overline{\psi}_{coll.} + n\Delta_2\overline{\psi}_{coll.} + \dots \quad . \qquad (1-5)$$

1.2.2 Solution of the Boltzmann equation for a uniform gas

In a steady flow of a uniform gas the distribution function has a simple form which can be obtained either by Boltzmann's H-theorem (8) or by statistical thermodynamics (10). This function, called the Maxwellian distribution function after its first derivation by Maxwell

(24) in 1866, is

$$f = n\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m(\underline{\xi} - \underline{u})^2}{2kT}\right] , \qquad (1\text{-}6)$$

where $\underline{u}$ is the mean velocity of the gas stream, m is the molecular mass, n is the number density, k is the Boltzmann constant, and T is the temperature.

1.3 Methods of solving the Boltzmann equation for non-uniform gases

Although Maxwell's original paper has been published more than a century, no method has been developed that can solve exactly the Boltzmann equation under general non-uniform conditions. However, solutions have been obtained for many important special cases. Among these is the pioneering work of Enskog who used an infinite series for the distribution function and assumed that the first term is Maxwellian. Enskog and Chapman (8) have succeeded in calculating the transport properties of gases in terms of the intermolecular forces. Since then not much progress has been made until recently when Grad (12) proposed the idea of solving the moment equation (1-3) instead of the Boltzmann equation itself. In this way the distribution function can be approximated by a function including parameters to be determined from moment equations. Grad used a distribution function which is a Maxwellian multiplied by a sum of Hermite polynomials and obtained good results in some linearized problems. Another improvement was made by separating the distribution function into two parts, each being valid only in a certain velocity range. Gross, Jackson and Ziering (13), as well as Krook (15), used this method by setting each part equal to a Maxwellian function multiplied by some polynomial. Wang Chang and Uhlenbeck (31) used a Maxwellian function multiplied by a function which is the sum of some Sonine-Legendre polynomials. Ziering (32) applied this method to solve a diffusion problem, the first of its kind.

1.3.1 The method of Lees

All the methods mentioned above have not utilized the geometric effect for problems with curved boundaries. Those problems call for a larger freedom in the choice of the form of distribution functions. Lees (19) has proposed the "line of sight" principle for constructing the distribution function in a region outside a solid body. At each point an infinite number of lines can be drawn tangent to the body of influence. The opposite extention of these lines forms a cone called the cone of influence (Region I in Figure 1). The distribution function will have the form f_1 if the velocity of the molecule lies inside the cone while it assumes the form f_2 if the velocity lies outside the cone (Region II in Figure 1), where

$$f_1 = n_1(\underline{r},t)\left(\frac{m}{2\pi k T_1(\underline{r},t)}\right)^{3/2} \exp\left[-\frac{m[\underline{\xi} - \underline{u}_1(\underline{r},t)]^2}{2kT_1(\underline{r},t)}\right] , \qquad (1\text{-}7)$$

$$f_2 = n_2(\underline{r},t)\left(\frac{m}{2\pi k T_2(\underline{r},t)}\right)^{3/2} \exp\left[-\frac{m[\underline{\xi} - \underline{u}_2(\underline{r},t)]^2}{2kT_2(\underline{r},t)}\right] . \qquad (1\text{-}8)$$

Here n_1, n_2, T_1, T_2, $\underline{u}_1$, $\underline{u}_2$ are ten initially undetermined func-

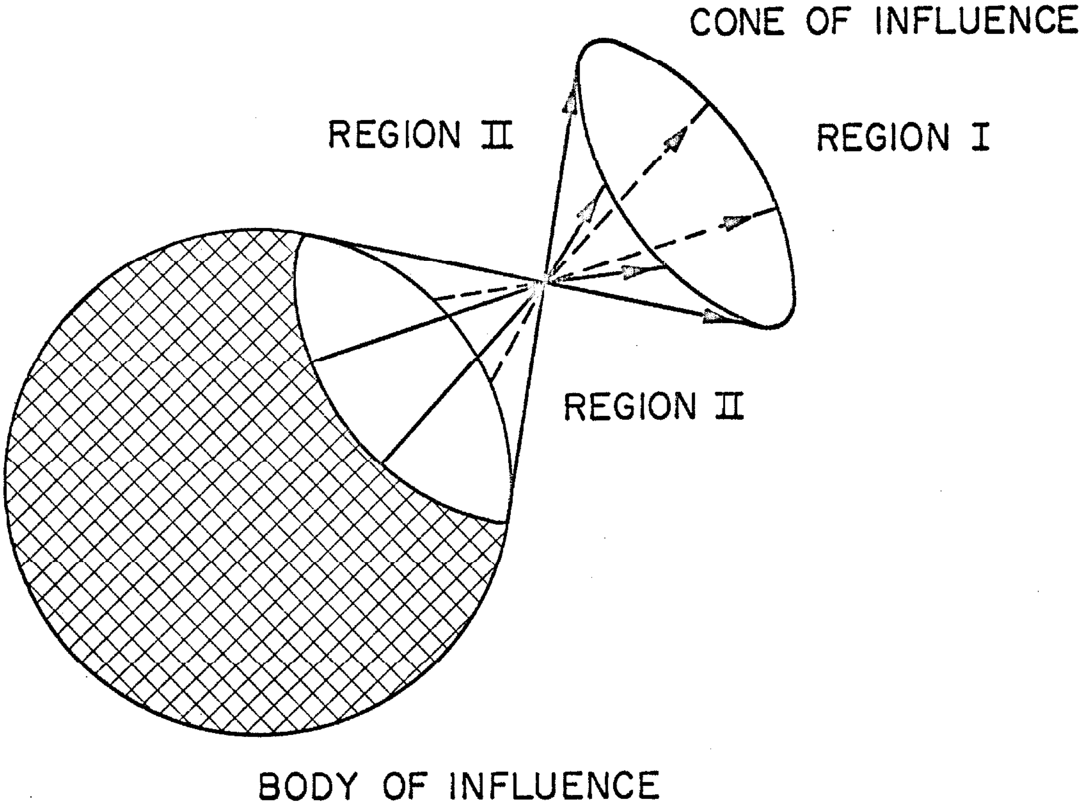

Fig. I CONE OF INFLUENCE

tions of $\underline{r}$ and t. A proper number of moment equations is required in order to solve for the undetermined functions.

Lees and his coworkers have applied the above method to the following problems:

Plane couette flow (20),
Rayleigh's problem (21),
Flow generated by a suddenly heated flat plate (22),
Conductive heat transfer from a thin wire to a concentric surrounding cylinder (22) (23).

The good agreement of Lees' results with experimental data provides the motivation for further applications of the method.

1.3.2 Limitations of the existing methods

All the existing methods are, in addition to their approximate nature, subject to many limitations. Strictly speaking, they apply to monatomic gases only. For polyatomic gases the exchange of translational energy with rotational energy and vibrational energy will require a more general and more complicated form of the Boltzmann equation. However, in most cases the exchange between translational energy and rotational energy is assumed to be very fast. The vibrational energy for most diatomic molecules is very small except at high temperatures. For example, at 1000 $^{\circ}$K 0.251% of the hydrogen molecules is in the first excited state and has a vibrational energy corresponding to 0.0142 kT. Therefore the vibrational energy can be neglected.

The type of intermolecular force appears in the collision term and has direct influence on the results. Methods using half or full range polynomial expansions can handle any type of intermolecular forces arising from a spherically symmetric potential. In Lees' method the collision integrals can be evaluated explicitly only for Maxwellian molecules, i.e. molecules with an intermolecular force obeying the inverse fifth law. A more general force law would greatly complicate the numerical work.

In addition, the interaction between gas molecules and the solid surface, entering into the boundary conditions, depends on the crystalline form of the surface and the adsorbed gas films. Experimental data are usually interpreted in terms of various kinds of accommodation coefficients. In the case of chemical reactions, it is convenient to describe the surface reactions in terms of a "reaction rate constant" or a "sticking probability." Both of them, however, may depend on the gas density, the temperature, and the history of the surface.

Chapter 2

HEAT AND MASS TRANSFER FROM A HOT FINE WIRE TO A SURROUNDING CYLINDER--METHOD OF LEES

2.1 Description of the problem

A hot fine wire is placed at the center of a cylinder filled with a partially dissociated diatomic gas whose mean free path has the same order of magnitude as the radius of the wire but is much smaller than the radius of the cylinder. The temperature of the wire and the temperature of the cylinder are kept constant with the former being higher than the latter. We assume that both the wire and the cylinder are inert to the gas but that the molecular gas particles will dissociate into atoms on the surface of the hot fine wire while the atoms recombine into molecules at the outer cylinder. At steady state there is a net flow of heat (energy) and of the dissociated atoms toward the outer cylinder. As an example we may consider hydrogen at a pressure of 10 mm Hg as the medium with 0.05 mm Nichol wire at 1500 ^{o}F and 2 cm glass cylinder at 1200 ^{o}F.

The main characteristic of this problem is that the gas is in transitional flow regime near the wire while it behaves like a continuum near the surrounding cylinder. The method employed by Lees (22) solving a pure heat transfer problem will be used in the present chapter. We shall neglect the end effect to consider this problem as two dimensional. Furthermore, the mole fraction of the dissociated atoms is assumed to be much smaller than unity.

2.2 The two-sided distribution functions

At each point in the space between the wire and the cylinder two planes can be drawn tangent to the wire. These two planes form two regions Ω_1 and Ω_2 such that all the molecules and the atoms with velocities located in the region Ω_1 behave like being emitted directly from the wire while those with velocities located in Ω_2 are not influenced by the wire at all. We now assign different distribution functions in different regions as follows:

$$f_1 = \begin{cases} f_{11} = n_{11}\left(\dfrac{m_1}{2\pi kT_1}\right)^{3/2} \exp\left[-\dfrac{m_1}{2kT_1}(\xi_p^2+\xi_z^2)\right], \ \phi \in \Omega_1 & \text{(2-1)} \\ f_{12} = n_{12}\left(\dfrac{m_1}{2\pi kT_2}\right)^{3/2} \exp\left[-\dfrac{m_1}{2kT_2}(\xi_p^2+\xi_z^2)\right], \ \phi \in \Omega_2 & \text{(2-2)} \end{cases}$$

$$f_2 = \begin{cases} f_{21} = n_{21}\left(\dfrac{m_2}{2\pi kT_1}\right)^{3/2} \exp\left[-\dfrac{m_2}{2kT_1}(\xi_p^2+\xi_z^2)\right], \ \phi \in \Omega_1 & \text{(2-3)} \\ f_{22} = n_{22}\left(\dfrac{m_2}{2\pi kT_2}\right)^{3/2} \exp\left[-\dfrac{m_2}{2kT_2}(\xi_p^2+\xi_z^2)\right], \ \phi \in \Omega_2 & \text{(2-4)} \end{cases}$$

where f_1 and f_2 are the distribution functions for the atoms and the molecules, n_{11}, n_{12}, n_{21}, n_{22}, T_1, and T_2 are six variables to be determined later. The random velocity $\underline{\xi}$ is written in cylindrical coordinates with $\phi = \arctan \xi_r/\xi_\theta$ and $\xi_p^2 = \xi_r^2 + \xi_\theta^2$. m_1 is the atomic weight and m_2 is the molecular weight. Mathematically Ω_1 and Ω_2 are defined by

$$\Omega_1 = \{\phi \mid \alpha \le \phi \le \pi - \alpha\} \qquad \text{(2-5)}$$

$$\Omega_2 = \{\phi \mid \pi - \alpha \leq \phi \leq 2\pi, \text{ or } 0 \leq \phi \leq \alpha\} \tag{2-6}$$

with

$$\alpha = \arccos \frac{R_i}{r} , \tag{2-7}$$

where r is the distance of the point from the center of the wire and R_i is the radius of the wire. Figure 2 is a schematic diagram showing all the definitions and some of the boundary conditions.

The number densities n_1, n_2, and the mean radial velocities u_{1r}, u_{2r} for the atoms and the molecules, the local temperature T and the heat flux q_r in the radial direction can be expressed in terms of the six variables,

$$n_1 = \frac{\pi - 2\alpha}{2\pi} n_{11} + \frac{\pi + 2\alpha}{2\pi} n_{12} , \tag{2-8}$$

$$n_2 = \frac{\pi - 2\alpha}{2\pi} n_{21} + \frac{\pi + 2\alpha}{2\pi} n_{22} , \tag{2-9}$$

$$u_{1r} = \left(\frac{2\pi k}{m_1}\right)^{\frac{1}{2}} \cos\alpha \, \frac{n_{11}T_1^{\frac{1}{2}} - n_{12}T_2^{\frac{1}{2}}}{n_{11}(\pi - 2\alpha) + n_{12}(\pi + 2\alpha)} , \tag{2-10}$$

$$u_{2r} = \left(\frac{2\pi k}{m_2}\right)^{\frac{1}{2}} \cos\alpha \, \frac{n_{21}T_1^{\frac{1}{2}} - n_{22}T_2^{\frac{1}{2}}}{n_{21}(\pi - 2\alpha) + n_{22}(\pi + 2\alpha)} , \tag{2-11}$$

$$T = \frac{(\pi - 2\alpha)(n_{11} + n_{21})T_1 + (\pi + 2\alpha)(n_{12} + n_{22})T_2}{(\pi - 2\alpha)(n_{11} + n_{21}) + (\pi + 2\alpha)(n_{12} + n_{22})} , \tag{2-12}$$

$$q_r = k\left(\frac{k}{2\pi}\right)^{\frac{1}{2}} \cos\alpha \left[T_1^{3/2}\left(\frac{2n_{11}}{\sqrt{m_1}} + \frac{3n_{21}}{\sqrt{m_2}}\right) - T_2^{3/2}\left(\frac{2n_{12}}{\sqrt{m_1}} + \frac{3n_{22}}{\sqrt{m_2}}\right)\right] + n_1 u_{1r} \overline{E}_1^{el} , \tag{2-13}$$

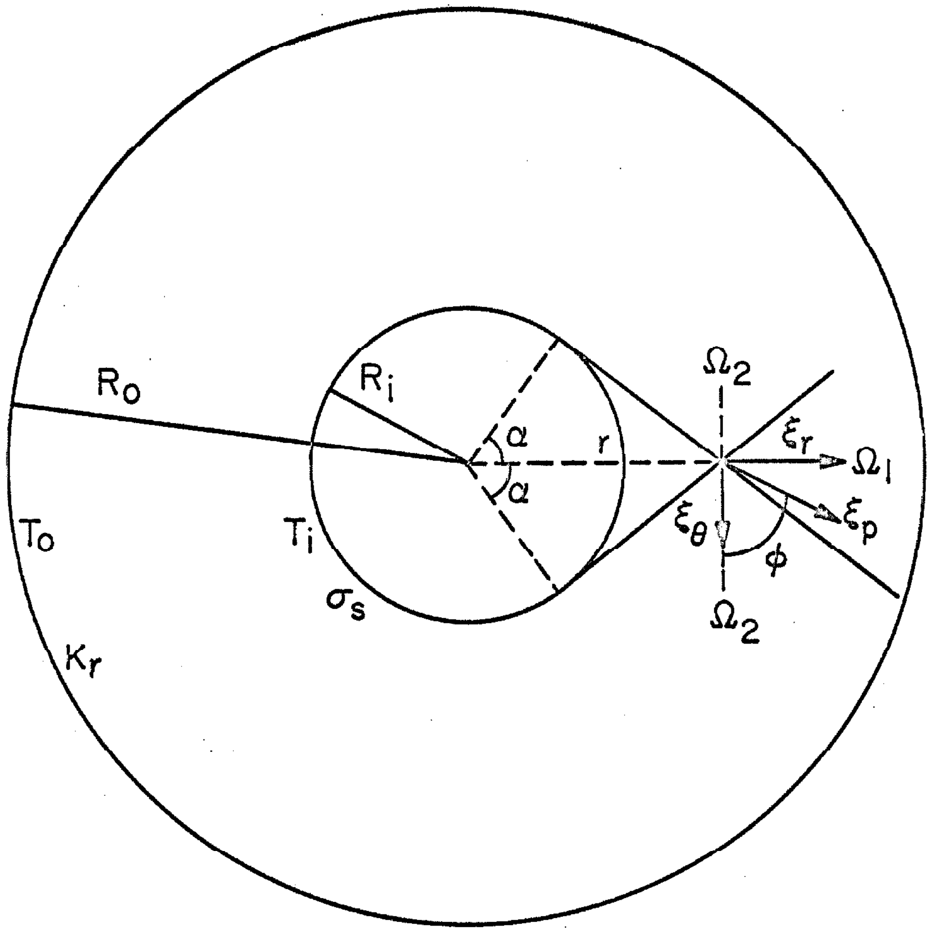

Fig. 2 DEFINITIONS OF Ω_1 AND Ω_2

where $\overline{E}_1^{el}$ is one half of the bond dissociation energy.

The first five equations can be obtained easily by direct integration while the last equation needs some detailed discussion which is given in Appendix 2A.

2.3 The moment equations and the boundary conditions

In order to obtain all the physical quantities of interest, we have to find the six variables defined in equations (2-1) to (2-4) by solving six moment equations. In fact more than six moment equations can be formed and our choice is based on taking the six which have more physical significance than the others. A more rigorous way is to linearize all the equations and pick up the six which neither contradict each other nor give trivial information. The six moment equations which meet these requirements are obtained by successively letting ψ in equation (1-3) be the mass of the atoms, the mass of the molecules, the total momentum in the radial direction, the momentum of the atoms in the radial direction, the total energy, and a linear combination of the heat flux for the atoms and for the molecules, both in the radial direction.

2.3.1 Continuity equation for the atoms

We consider the mass of an atom, which does not change under ordinary collision, as the function ψ. The collision term in equation (1-3) is clearly zero while the left-hand side, after integration, becomes

$$r n_1 u_{1r} = C' \quad , \tag{2-14}$$

where C' is an integration constant.

Substituting equations (2-8) and (2-10) into (2-14), we obtain

$$\left(\frac{2\pi k}{m_1}\right)^{\frac{1}{2}} \frac{r \cos \alpha}{2\pi} \left(n_{11} T_1^{\frac{1}{2}} - n_{12} T_2^{\frac{1}{2}}\right) = C' \quad . \tag{2-15}$$

2.3.2 Continuity equation for the molecules

If we let ψ be the mass of a molecule, we get an expression similar to that in equation (2-14) with different integration constant. However, using the fact that the mean velocity is zero at any point, we obtain

$$r n_2 u_{2r} = -\frac{C'}{2} \quad , \tag{2-16}$$

which, by substituting equations (2-9) and (2-11), becomes

$$\left(\frac{2\pi k}{m_2}\right)^{\frac{1}{2}} \frac{r \cos \alpha}{2\pi} \left(n_{21} T_1^{\frac{1}{2}} - n_{22} T_2^{\frac{1}{2}}\right) = -\frac{C'}{2} \quad . \tag{2-17}$$

2.3.3 Conservation equation for the total momentum in the radial direction

We take ψ to be $m_1\underline{\xi}$ for the atoms and $m_2\underline{\xi}$ for the molecules to obtain the following equation in the radial direction,

$$r \frac{dp_{rr}}{dr} + p_{rr} - p_{\theta\theta} = 0 \tag{2-18}$$

where the collision term is zero and p_{ij} is defined by

$$p_{ij} = \int m_1 \xi_i \xi_j f_1 \, d^3\xi + \int m_2 \xi_i \xi_j f_2 \, d^3\xi \quad . \tag{2-19}$$

Carrying out the integration in equation (2-19) and substituting into equation (2-18), there is obtained

$$(\sin 2\alpha - 2\alpha) \frac{d}{dr}(n_{11}T_1 - n_{12}T_2 + n_{21}T_1 - n_{22}T_2)$$

$$+ \pi \frac{d}{dr}(n_{11}T_1 + n_{12}T_2 + n_{21}T_1 + n_{22}T_2) = 0 \quad . \tag{2-20}$$

2.3.4 Conservation equation for the total energy

Since the total energy is conserved during the process of collision, the heat flux in the radial direction must satisfy the relation

$$rq_r = B' \quad , \tag{2-21}$$

where B' is an integration constant. Using equation (2-13), we have

$$k\left(\frac{k}{2\pi}\right)^{\frac{1}{2}} r \cos\alpha \left[T_1^{3/2}\left(\frac{2n_{11}}{\sqrt{m_1}} + \frac{3n_{21}}{\sqrt{m_2}}\right) - T_2^{3/2}\left(\frac{2n_{12}}{\sqrt{m_1}} + \frac{3n_{22}}{\sqrt{m_2}}\right)\right]$$

$$= B' - C'\overline{E}_1^{el} \quad . \tag{2-22}$$

2.3.5 Momentum equation for the atoms in the radial direction

The collision term in this equation no longer vanishes because of the interchange of momentum between the atoms and the molecules. Following the same step as in section 2.3.3, we have

$$(\pi - 2\alpha + \sin 2\alpha) r \frac{d}{dr}(n_{11}T_1) + (\pi + 2\alpha - \sin 2\alpha) r \frac{d}{dr}(n_{12}T_2)$$

$$= - \frac{\pi C'}{k} 2\pi A_1 (8\overline{m} d_{12})^{\frac{1}{2}} (n_1 + 2n_2) \ , \qquad (2\text{-}23)$$

where in the last term, $\overline{m}$ is the reduced mass $m_1 m_2/(m_1+m_2)$, A_1 is a constant in the collision integral, and d_{12} is the constant of intermolecular force potential. In evaluating the collision integral as given in Appendix 2B, the intermolecular potential is assumed to be Maxwellian.

2.3.6 Equation of heat flux in the radial direction

In general we can write two equations of heat flux, one for each species. However, as we need only one more equation, we choose a linear combination of them which gives rise to simpler expressions. Letting ψ be $m_1 \underline{\xi} |\xi|^2$, the radial component of the moment equation becomes

$$\frac{de_{1rr}}{dr} + \frac{e_{1rr} - e_{1\theta\theta}}{r} = n_1 \Delta\overline{\psi}_{1\,\text{coll.}} \ , \qquad (2\text{-}24)$$

where

$$e_{1ij} = \int m_1 f_1 \xi_i \xi_j |\xi|^2 \, d^3\xi \ . \qquad (2\text{-}25)$$

The evaluation of the collision term is given in Appendix 2C. A similar equation for the molecules is

$$\frac{de_{2rr}}{dr} + \frac{e_{2rr} - e_{2\theta\theta}}{r} = n_2 \Delta\overline{\psi}_{2\,\text{coll.}} \ , \qquad (2\text{-}26)$$

where

$$e_{2ij} = \int m_2 f_2 \xi_i \xi_j |\xi|^2 \, d^3\xi \quad . \tag{2-27}$$

Combining equations (2-24) and (2-26) together, we obtain

$$\begin{aligned}
&(\pi - 2\alpha + \sin 2\alpha)\frac{d}{dr}[(n_{11} - n_{21})T_1^2] + (\pi + 2\alpha - \sin 2\alpha)\frac{d}{dr}[(n_{12} - n_{22})T_2^2] \\
&= (4m_1 d_{11})^{\frac{1}{2}} \frac{4}{5} \cos\alpha \left(\frac{2\pi}{km_1}\right)^{\frac{1}{2}} A_2 \Bigg\{ -(n_{11}T_1^{\frac{3}{2}} - n_{12}T_2^{\frac{3}{2}})[n_{11}(\pi - 2\alpha) + n_{12}(\pi + 2\alpha)] \\
&\quad - \frac{C'}{2R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha + \sin 2\alpha)n_{11}T_1 + (\pi + 2\alpha - \sin 2\alpha)n_{12}T_2] \\
&\quad + \frac{3C'}{R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha)n_{11}T_1 + (\pi + 2\alpha)n_{12}T_2] \Bigg\} \\
&\quad + (8\overline{m}d_{12})^{\frac{1}{2}} \frac{4}{15} \cos\alpha \left(\frac{2\pi}{km_1}\right)^{\frac{1}{2}} A_1 \Bigg\{ -5(n_{11}T_1^{\frac{3}{2}} - n_{12}T_2^{\frac{3}{2}})[n_{21}(\pi - 2\alpha) + n_{22}(\pi + 2\alpha)] \\
&\quad + \frac{C'}{2R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha + \sin 2\alpha)n_{11}T_1 + (\pi + 2\alpha - \sin 2\alpha)n_{12}T_2] \\
&\quad - \frac{3C'}{2R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha)n_{21}T_1 + (\pi + 2\alpha)n_{22}T_2] \\
&\quad + \frac{3C'}{4R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha)n_{11}T_1 + (\pi + 2\alpha)n_{12}T_2] \\
&\quad - \frac{2C'}{R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha + \sin 2\alpha)n_{21}T_1 + (\pi + 2\alpha - \sin 2\alpha)n_{22}T_2] \\
&\quad + \frac{7}{\sqrt{2}}(n_{21}T_1^{\frac{3}{2}} - n_{22}T_2^{\frac{3}{2}})[n_{11}(\pi - 2\alpha) + n_{12}(\pi + 2\alpha)] \Bigg\} \\
&\quad - (4m_2 d_{22})^{\frac{1}{2}} \frac{4}{5} \cos\alpha \left(\frac{2\pi}{km_2}\right)^{\frac{1}{2}} A_2 \Bigg\{ -(n_{21}T_1^{\frac{3}{2}} - n_{22}T_2^{\frac{3}{2}})[n_{21}(\pi - 2\alpha) + n_{22}(\pi + 2\alpha)] \\
&\quad + \frac{\sqrt{2}C'}{4R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha + \sin 2\alpha)n_{21}T_1 + (\pi + 2\alpha - \sin 2\alpha)n_{22}T_2] \\
&\quad - \frac{3\sqrt{2}C'}{2R_i}\left(\frac{\pi m_1}{2k}\right)^{\frac{1}{2}}[(\pi - 2\alpha)n_{21}T_1 + (\pi + 2\alpha)n_{22}T_2] \Bigg\} \quad ,
\end{aligned} \tag{2-28}$$

where we have used the fact that $m_2 = 2m_1$ to simplify the equation.

d_{11} and d_{22} are force constants for the atoms and the molecules respectively, and A_2 is another constant arising from the collision integral.

2.3.7 Boundary conditions

We have used, first of all, the condition that the mean velocity is zero in evaluating the continuity equations. The conditions for the temperature field are

$$T_1 = T_i \qquad \text{at} \quad r = R_i \tag{2-29}$$

$$T_2 = T_0 \qquad \text{at} \quad r = R_0 \tag{2-30}$$

where T_i is the temperature of the wire, T_0 is the temperature of the cylinder, and R_0 is the radius of the cylinder.

For chemical reactions, the condition at the outer cylinder can be written in a form appropriate to the continuum conditions. The recombination rate is equal to the flux of the atoms toward the cylinder. We have

$$n_1 u_{1r} = k_r n_1^2 \qquad \text{at} \quad r = R_0 \tag{2-31}$$

where k_r is the rate constant for the second order recombination reaction. Using equation (2-14), we obtain

$$n_1 = \left(\frac{C'}{k_r R_0} \right)^{\frac{1}{2}} \qquad \text{at} \quad r = R_0 \; . \tag{2-32}$$

On the other hand, the condition at the wire cannot be obtained in this way so that we have to resort to the sticking probability concept for the dissociation reaction. The sticking probability σ_s is defined as

$$\sigma_s = \frac{j_{2i} - j_{20}}{j_{2i}} \qquad \text{at} \quad r = R_i \ , \tag{2-33}$$

where j_{2i} and j_{20} are the incident and the reflected fluxes for the molecules. We assume σ_s to be constant without going to details which will be discussed in Chapter 7. Carrying out the calculations for the fluxes, we have

$$\sigma_s = 1 - \frac{n_{21}}{n_{22}} \left(\frac{T_1}{T_2} \right)^{\frac{1}{2}} \qquad \text{at} \quad r = R_i \ . \tag{2-34}$$

The last condition is a statement that the density at some given point is known. This is equivalent to the condition that the total number of molecules and atoms is given since the two conditions are linearly related. We choose the number density of the molecules to be

$$n_2 = n_i \qquad\qquad \text{at} \quad r = R_i \ . \tag{2-35}$$

2.4 Simplification of the moment equations

We are going to make the moment equations dimensionless by letting

$$\bar{n}_{11} = \frac{n_{11}}{n_i} \ , \tag{2-36}$$

$$\bar{n}_{12} = \frac{n_{12}}{n_i} \ , \tag{2-37}$$

$$\overline{n}_{21} = \frac{n_{21}}{n_i} \quad , \qquad (2\text{-}38)$$

$$\overline{n}_{22} = \frac{n_{22}}{n_i} \quad , \qquad (2\text{-}39)$$

$$\overline{T}_1 = \frac{T_1}{T_i} \quad , \qquad (2\text{-}40)$$

$$\overline{T}_2 = \frac{T_2}{T_i} \quad , \qquad (2\text{-}41)$$

$$\epsilon = 1 - \frac{T_0}{T_i} \quad , \qquad (2\text{-}42)$$

$$\overline{r} = \frac{r}{R_i} \quad , \qquad (2\text{-}43)$$

$$\overline{R} = \frac{R_0}{R_i} \quad , \qquad (2\text{-}44)$$

$$C = \frac{C'}{n_i R_i} \left(\frac{2\pi m_i}{kT_i} \right)^{\frac{1}{2}} \quad , \qquad (2\text{-}45)$$

$$B = (B' - C'\overline{E}_1^{el}) \,/\, \left(k\,T_i\, n_i R_i \left(\frac{kT_i}{2\pi m_i} \right)^{\frac{1}{2}} \right) \quad . \qquad (2\text{-}46)$$

We also define the following characteristic quantities:

$$v = \left(\frac{2kT_i}{m_1} \right)^{\frac{1}{2}} \quad , \qquad (2\text{-}47)$$

$$\mu_1 = \frac{kT_i}{3A_2\pi} \left(\frac{m_1}{2d_{11}} \right)^{\frac{1}{2}} \quad , \qquad (2\text{-}48)$$

$$\mu_2 = \frac{kT_i}{3A_2\pi} \left(\frac{m_2}{2d_{22}} \right)^{\frac{1}{2}} \quad , \qquad (2\text{-}49)$$

$$D_{12} = \frac{kT_i}{8A_1 n_i} \left(\frac{2}{\pi \bar{m} d_{12}}\right)^{\frac{1}{2}} , \tag{2-50}$$

$$\lambda_1 = \frac{\mu_1 \sqrt{\pi}}{n_i m_1 v} , \tag{2-51}$$

$$\lambda_2 = \frac{\mu_2 \sqrt{\pi}}{n_i m_2 v} , \tag{2-52}$$

$$\lambda_{12} = \frac{D_{12}}{v} . \tag{2-53}$$

Using these expressions, we may write the six equations as

$$\bar{n}_{11}\bar{T}_1 - \bar{n}_{12}\bar{T}_2 = C , \tag{2-54}$$

$$\bar{n}_{21}\bar{T}_1 - \bar{n}_{22}\bar{T}_2 = -\frac{\sqrt{2}}{2} C , \tag{2-55}$$

$$\begin{aligned}(\sin 2\alpha - 2\alpha) \frac{d}{d\bar{r}} (\bar{n}_{11}\bar{T}_1 - \bar{n}_{12}\bar{T}_2 + \bar{n}_{21}\bar{T}_1 - \bar{n}_{22}\bar{T}_2) \\ + \pi \frac{d}{d\bar{r}} (\bar{n}_{11}\bar{T}_1 + \bar{n}_{12}\bar{T}_2 + \bar{n}_{21}\bar{T}_1 + \bar{n}_{22}\bar{T}_2) = 0 ,\end{aligned} \tag{2-56}$$

$$\left(2\bar{n}_{11} + \frac{3}{\sqrt{2}}\bar{n}_{21}\right)\bar{T}_1^{\frac{3}{2}} - \left(2\bar{n}_{12} + \frac{3}{\sqrt{2}}\bar{n}_{22}\right)\bar{T}_2^{\frac{3}{2}} = B , \tag{2-57}$$

$$\begin{aligned}(\sin 2\alpha - 2\alpha) \frac{d}{d\bar{r}} (\bar{n}_{11}\bar{T}_1 - \bar{n}_{12}\bar{T}_2) + \pi \frac{d}{d\bar{r}} (\bar{n}_{11}\bar{T}_1 + \bar{n}_{12}\bar{T}_2) \\ = -\frac{1}{2}\pi C \frac{R_i}{\lambda_{12}} \frac{1}{r} \left[\frac{\pi - 2\alpha}{2\pi} (n_{11} + 2n_{21}) + \frac{\pi + 2\alpha}{2\pi} (n_{12} + 2n_{22}) \right] ,\end{aligned} \tag{2-58}$$

$$
\begin{aligned}
&(\pi-2\alpha+\sin 2\alpha)\frac{d}{d\bar{r}}[(\bar{n}_{11}-\bar{n}_{21})\bar{T}_1^2] + (\pi+2\alpha-\sin 2\alpha)\frac{d}{d\bar{r}}[(\bar{n}_{12}-\bar{n}_{22})\bar{T}_2^2] \\
&= -\frac{4\sqrt{2}}{15}\frac{R_i}{\lambda_1}\frac{1}{r}\Big\{(\bar{n}_{11}\bar{T}_1^{\frac{3}{2}}-\bar{n}_{12}\bar{T}_2^{\frac{3}{2}})[(\pi-2\alpha)\bar{n}_{11}+(\pi+2\alpha)\bar{n}_{12}] \\
&\qquad +\frac{1}{4}C[(\pi-2\alpha+\sin 2\alpha)\bar{n}_{11}\bar{T}_1+(\pi+2\alpha-\sin 2\alpha)\bar{n}_{12}\bar{T}_2] \\
&\qquad -\frac{3}{2}C[(\pi-2\alpha)\bar{n}_{11}\bar{T}_1+(\pi+2\alpha)\bar{n}_{12}\bar{T}_2]\Big\} \\
&\quad -\frac{2}{15}\frac{R_i}{\lambda_{12}}\frac{1}{r}\Big\{5(\bar{n}_{11}\bar{T}_1^{\frac{3}{2}}-\bar{n}_{12}\bar{T}_2^{\frac{3}{2}})[\bar{n}_{21}(\pi-2\alpha)+\bar{n}_{22}(\pi+2\alpha)] \\
&\qquad -\frac{1}{4}C[(\pi-2\alpha+\sin 2\alpha)\bar{n}_{11}\bar{T}_1+(\pi+2\alpha-\sin 2\alpha)\bar{n}_{12}\bar{T}_2] \\
&\qquad +\frac{3}{4}C(\pi-2\alpha)\bar{n}_{21}\bar{T}_1+(\pi+2\alpha)\bar{n}_{22}\bar{T}_2] \\
&\qquad -\frac{3}{8}C[(\pi-2\alpha)\bar{n}_{11}\bar{T}_1+(\pi+2\alpha)\bar{n}_{12}\bar{T}_2] \\
&\qquad +\frac{1}{2}C[(\pi-2\alpha+2\sin\alpha)\bar{n}_{21}\bar{T}_1+(\pi+2\alpha-\sin 2\alpha)\bar{n}_{22}\bar{T}_2] \\
&\qquad -\frac{7}{\sqrt{2}}(\bar{n}_{21}\bar{T}_1^{\frac{3}{2}}-\bar{n}_{22}\bar{T}_2^{\frac{3}{2}})[(\pi-2\alpha)\bar{n}_{11}+(\pi+2\alpha)\bar{n}_{12}]\Big\} \\
&\quad -\frac{4\sqrt{2}}{15}\frac{R_i}{\lambda_2}\frac{1}{r}\Big\{-\frac{1}{\sqrt{2}}(\bar{n}_{21}\bar{T}_1^{\frac{3}{2}}-\bar{n}_{22}\bar{T}_2^{\frac{3}{2}})[\bar{n}_{21}(\pi-2\alpha)+(\pi+2\alpha)\bar{n}_{22}] \\
&\qquad +\frac{1}{8}C[(\pi-2\alpha+\sin 2\alpha)\bar{n}_{21}\bar{T}_1+(\pi+2\alpha-\sin 2\alpha)\bar{n}_{22}\bar{T}_2] \\
&\qquad -\frac{3}{4}C[(\pi-2\alpha)\bar{n}_{21}\bar{T}_1+(\pi+2\alpha)\bar{n}_{22}\bar{T}_2]\Big\}\ .
\end{aligned}
\tag{2-59}
$$

Notice that the relative importance of the collision terms depends on the ratio R_i/λ_2 whose inverse is a measure of the degree of rarefaction. In the present case all λ_1, λ_{12}, and λ_2 have the same order of magnitude.

The boundary conditions become, after simplification,

$$\overline{T}_1 = 1 \;, \qquad \text{at } \overline{r} = 1 \;, \tag{2-60}$$

$$\overline{T}_2 = 1 - \epsilon \;, \qquad \text{at } \overline{r} = \overline{R} \;, \tag{2-61}$$

$$\overline{n}_1 = A\sqrt{C} \;, \qquad \text{at } \overline{r} = \overline{R} \;, \tag{2-62}$$

$$\sigma_s = 1 - \frac{\overline{n}_{21}(\overline{T}_1)^{\frac{1}{2}}}{\overline{n}_{22}(\overline{T}_2)^{\frac{1}{2}}} \;, \qquad \text{at } \overline{r} = 1 \;, \tag{2-63}$$

$$\overline{n}_2 = 1 \;, \qquad \text{at } \overline{r} = 1 \;, \tag{2-64}$$

where $\overline{n}_1$ and $\overline{n}_2$ are dimensionless number densities normalized with respect to n_i and A is defined as

$$A = \left[\left(\frac{kT_i}{2\pi m_1} \right)^{\frac{1}{2}} / \; (k_r n_i \overline{R}) \right]^{\frac{1}{2}} \tag{2-65}$$

Also we define α_0 as

$$\alpha_0 = \text{arc cos } \frac{1}{\overline{R}} \;, \tag{2-66}$$

which will appear later in the results.

2.5 Solution for constant temperature

Equations (2-54) to (2-59) cannot be solved analytically without some simplification. Let us take the temperature field to be constant. Concentration gradients can still exist if the surface of the wire has catalytic effect on the dissociation reaction. The variables are now reduced to four and only four equations are needed. The two equations to be discarded are equations (2-59) and (2-57). The former is irrelevant since there is no heat flow while the latter is less exact than the remaining equations because the internal energy is calculated approximately. In addition, we keep equation (2-58) so that the binary diffusivity may appear in the results. Therefore we have

$$\bar{n}_{11} - \bar{n}_{12} = C \quad , \tag{2-67}$$

$$\bar{n}_{21} - \bar{n}_{22} = -\frac{\sqrt{2}}{2} C \quad , \tag{2-68}$$

$$\bar{n}_{11} + \bar{n}_{12} + \bar{n}_{21} + \bar{n}_{22} = E \quad , \tag{2-69}$$

$$\frac{d}{d\bar{r}}(\bar{n}_{11}+\bar{n}_{12}) = -\frac{1}{2} C \frac{R_i}{\lambda_{12}\bar{r}} \left[E - \frac{1}{2}(\bar{n}_{11}+\bar{n}_{12}) + \frac{\alpha}{\pi}(\sqrt{2}-1)C \right] , \tag{2-70}$$

where E is an integration constant.

Solving these equations we have

$$\bar{n}_{11} = \frac{1}{2}\left\{ C + \frac{\sqrt{2}-1}{\pi} 2C\alpha + 2E + \bar{r}^{\frac{C}{4\delta_{12}}}[F - f(\alpha)] \right\} , \tag{2-71}$$

$$\bar{n}_{12} = \frac{1}{2}\left\{ -C + \frac{\sqrt{2}-1}{\pi} 2C\alpha + 2E + \bar{r}^{\frac{C}{4\delta_{12}}}[F - f(\alpha)] \right\} , \tag{2-72}$$

$$\bar{n}_{21} = \frac{1}{2}\left\{ -\frac{\sqrt{2}}{2} C - \frac{\sqrt{2}-1}{\pi} 2C\alpha - E - \bar{r}^{\frac{C}{4\delta_{12}}}[F - f(\alpha)] \right\} , \tag{2-73}$$

$$\bar{n}_{22} = \frac{1}{2}\left\{ \frac{\sqrt{2}}{2} C - \frac{\sqrt{2}-1}{\pi} 2C\alpha - E - \bar{r}^{\frac{C}{4\delta_{12}}}[F - f(\alpha)] \right\} , \tag{2-74}$$

where F is another integration constant and δ_{12} and $f(\alpha)$ are defined as

$$\delta_{12} = \frac{\lambda_{12}}{R_i} = \frac{D_{12}}{R_i v} \tag{2-75}$$

$$f(\alpha) = \frac{2(\sqrt{2}-1)C}{\pi} \int_0^{\alpha} (\cos\alpha')^{\frac{C}{4\delta_{12}}} \, d\alpha' \; . \tag{2-76}$$

The results depend primarily on the dimensionless quantity δ_{12} which is the ratio of the mean free path to the radius of the wire or the ratio of the difussive velocity to the random velocity. Therefore δ_{12} is a quantity proportional to the Knudsen number and will be used to characterize the degree of rarefaction.

2.5.1 Free molecular flow regime

In this case δ_{12} becomes infinity so that we have

$$f(\alpha) = \frac{2(\sqrt{2}-1)C\alpha}{\pi} \; , \tag{2-77}$$

and all the $\bar{n}_{ij}$'s are constant. This result is what we have expected. Applying the boundary conditions there is obtained

$$\bar{n}_1 = \frac{\alpha_0 - \alpha}{\pi} \; \frac{2\sqrt{2}\,\sigma_s}{2-\sigma_s} + A\left(\frac{2\sqrt{2}\,\sigma_s}{2-\sigma_s}\right)^{\frac{1}{2}} \; , \tag{2-78}$$

$$\bar{n}_2 = 1 + \frac{\alpha}{\pi} \frac{2\sigma_s}{2-\sigma_s} \; , \tag{2-79}$$

as the concentration distributions. It is interesting to note that there are atoms near the inner surface no matter how fast the recombination reaction at the surrounding cylinder is. This is not true in the case of two parallel plates where $\bar{n}_1$ vanishes everywhere when A vanishes because both α_0 and α are zero. This shows the importance of the radius of curvature in a problem with general geometric shape.

2.5.2 Continuum flow regime

This is the case where δ_{12} approaches zero. The results in Chapter 7 show that σ_s vanishes in this regime and consequently C vanishes. Equations (2-67) to (2-70) now becomes

$$\bar{n}_{11} = \bar{n}_{12} \quad , \tag{2-80}$$

$$\bar{n}_{21} = \bar{n}_{22} \quad , \tag{2-81}$$

$$\bar{n}_{11} + \bar{n}_{12} + \bar{n}_{21} + \bar{n}_{22} = E \quad , \tag{2-82}$$

$$\frac{d}{d\bar{r}}(\bar{n}_{11} + \bar{n}_{12}) = -\frac{1}{2}\frac{CE}{\delta_{12}\bar{r}} \quad , \tag{2-83}$$

where we have used the assumption that $\bar{n}_1$ is small compared with unity. Solving the above four equations with boundary conditions given by equations (2-62) and (2-64), we obtain

$$\bar{n}_1 = \frac{\frac{1}{2}\sqrt{2}\cdot S_{12}\log\frac{\bar{R}}{\bar{r}}}{1-\frac{1}{2}\sqrt{2}\cdot S_{12}\log\bar{R}} \quad , \tag{2-84}$$

$$\bar{n}_2 = \frac{1-\frac{1}{2}\sqrt{2}\cdot S_{12}\log\frac{\bar{R}}{\bar{r}}}{1-\frac{1}{2}\sqrt{2}\cdot S_{12}\log\bar{R}} \quad , \tag{2-85}$$

where

$$S_{12} = \lim_{\delta_{12}\to 0} \frac{\sigma_s}{\delta_{12}} \quad , \tag{2-86}$$

depends on the mechanism of the dissociation reaction. Equations (2-84) and (2-85) are identical to the steady state solutions of the ordinary diffusion equation.

2.5.3 Transitional flow regime

We shall use the assumption that n_1 is much smaller than n_2 to treat the case of transitional flow. The equations to be solved are

$$\bar{n}_{11} - \bar{n}_{12} = C \quad , \tag{2-87}$$

$$\bar{n}_{21} - \bar{n}_{22} = -\tfrac{1}{2}\sqrt{2}\, C \quad , \tag{2-88}$$

$$\bar{n}_{11} + \bar{n}_{12} + \bar{n}_{21} + \bar{n}_{22} = E \quad , \tag{2-89}$$

$$\frac{d}{d\bar{r}}(\bar{n}_{11} + \bar{n}_{12}) = -\frac{1}{2}\,\frac{CE}{\delta_{12}\bar{r}} \quad . \tag{2-90}$$

The solution is

$$\bar{n}_1 = \left[\frac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)} \log \bar{R} + \frac{\alpha_0}{\pi}\,\frac{2\sqrt{2}\,\sigma_s}{2-\sigma_s} + A\left(\frac{2\sqrt{2}\,\sigma_s}{2-\sigma_s}\right)^{\frac{1}{2}} \right] \frac{1 - \dfrac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)}\log \bar{r}}{1 - \dfrac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)}\log \bar{R}}$$

$$- \frac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)} \log \bar{r} - \frac{2\sigma_s \alpha}{\pi(2-\sigma_s)} \quad , \tag{2-91}$$

$$\bar{n}_2 = 1 + \left[\frac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)} \log \bar{R} + \frac{\alpha_0}{\pi} \frac{2\sqrt{2}\,\sigma_s}{2-\sigma_s} + A\left(\frac{2\sqrt{2}\,\sigma_s}{2-\sigma_s}\right)^{\frac{1}{2}} \right] \frac{\dfrac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)} \log \bar{r}}{1 - \dfrac{\sqrt{2}\,\sigma_s}{\delta_{12}(2-\sigma_s)} \log \bar{R}}$$

$$+ \frac{\sqrt{2}\,\sigma_s}{\delta_{12}(1-\sigma_s)} \log \bar{r} + \frac{2\sigma_s \alpha}{\pi(2-\sigma_s)} \quad . \tag{2-92}$$

Equations (2-91) and (2-92) agree with both equations (2-78) and (2-79) by taking the free molecular flow limit, and with equations (2-84) and (2-85) by taking the continuum flow limit.

2.6 General solution by the method of linearization

To linearize the six moment equations given by equations (2-54) to (2-59), the temperature variation is assumed to be small. In general the sticking probability σ_s is also small except in the free molecular flow regime. The assumption that $\bar{n}_1 \ll 1$ and $|\bar{n}_2 - 1| \ll 1$ affords considerable simplification. At a large distance from the wire, $\bar{n}_{12}$ and $\bar{n}_{22}$ are the main contributions to $\bar{n}_1$ and $\bar{n}_2$ respectively. This implies that $\bar{n}_{12} \ll 1$ and $|\bar{n}_{22} - 1| \ll 1$. On the other hand, $\bar{n}_{11}$ and $\bar{n}_{12}$ contribute equally at the wire to $\bar{n}_1$ so that $\bar{n}_{11} \ll 1$. Similarly $\bar{n}_{21}$ and $\bar{n}_{22}$ contribute equally to $\bar{n}_2$ at the wire so that $|\bar{n}_{21} - 1| \ll 1$. We let

$$\bar{n}_{11} = y_1 \quad , \tag{2-93}$$

$$\bar{n}_{12} = y_2 \quad , \tag{2-94}$$

$$\bar{n}_{21} = 1 + z_1 \quad , \tag{2-95}$$

$$\bar{n}_{22} = 1 + z_2 \quad , \tag{2-96}$$

$$\bar{T}_1 = 1 + x_1 \quad , \tag{2-97}$$

$$\bar{T}_2 = 1 + x_2 \quad . \tag{2-98}$$

Substituting these relations into equations (2-54) to (2-59) and neglecting all second and higher order terms we obtain

$$y_1 - y_2 = C \quad , \tag{2-99}$$

$$z_1 - z_2 = B \quad , \tag{2-100}$$

$$x_1 - x_2 = -\sqrt{2}\, C - 2B \quad , \tag{2-101}$$

$$\frac{d}{d\bar{r}} (y_1 + y_2 + z_1 + z_2 + x_1 + x_2) = 0 \quad , \tag{2-102}$$

$$\frac{d}{d\bar{r}} (y_1 + y_2) = - \frac{CR_i}{\lambda_{12}\bar{r}} \quad , \tag{2-103}$$

$$\frac{d}{d\bar{r}} (y_1 + y_2 - z_1 - z_2) = - \frac{7CR_i}{3\lambda_{12}\bar{r}} + \frac{7\sqrt{2}\, CR_i}{1 \quad \lambda_2\bar{r}} + \frac{16\, BR_i}{15\, \lambda_2\bar{r}} \; , \tag{2-104}$$

with the linearized boundary conditions,

$$x_1 = 0 \qquad \text{at} \quad \bar{r} = 1 \quad , \tag{2-105}$$

$$x_2 = -\epsilon \qquad \text{at} \quad \bar{r} = \bar{R} \quad , \tag{2-106}$$

$$(x_1 - x_2) + 2(z_1 - z_2) = -\sigma_s \qquad \text{at} \quad \bar{r} = 1 \quad , \tag{2-107}$$

$$\frac{1}{2}(y_1 + y_2) + \frac{\alpha_0}{\pi}(y_2 - y_1) = A\sqrt{C} \qquad \text{at} \quad \bar{r} = \bar{R} \quad , \tag{2-108}$$

$$z_1 + z_2 = 0 \qquad \text{at} \quad \bar{r} = 1 \quad . \tag{2-109}$$

The solution of these equations is

$$x_1 - x_2 = \delta\epsilon - \sigma_s(1 - \delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\,\lambda_{12}}\right) \quad , \tag{2-110}$$

$$y_1 - y_2 = \sqrt{2}\,\sigma_s \quad , \tag{2-111}$$

$$z_1 - z_2 = -\frac{1}{2}\delta\epsilon - \sigma_s + \sigma_s(1 - 8)\left(\frac{1}{8} + \frac{5\sqrt{2}\,\lambda_2}{16\,\lambda_{12}}\right) \quad , \tag{2-112}$$

$$\begin{aligned} x_1 + x_2 = {} & -\delta\epsilon + \sigma_s(1 - \delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\,\lambda_{12}}\right) \\ & - (1 - \delta)\left(2\epsilon + \frac{1}{2}\sigma_s + \sigma_s \frac{5\sqrt{2}\,\lambda_2}{4\,\lambda_{12}}\right)\frac{\log \bar{r}}{\log \overline{R}} \quad , \end{aligned} \tag{2-113}$$

$$\begin{aligned} y_1 + y_2 = {} & \sigma_s \frac{15\sqrt{2}(1-\delta)\lambda_2}{4\delta\lambda_{12}}\left(1 - \frac{\log \bar{r}}{\log \overline{R}}\right) + 2\sqrt{2}\,\sigma_s \frac{\alpha_0}{\pi} \\ & + 2A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} \quad , \end{aligned} \tag{2-114}$$

$$\begin{aligned} z_1 + z_2 = {} & \sigma_s \frac{15\sqrt{2}(1-\delta)\lambda_2}{4\delta\lambda_{12}}\,\frac{\log \bar{r}}{\log \overline{R}} \\ & + (1 - \delta)\left(2\epsilon + \frac{1}{2}\sigma_s + \sigma_s \frac{5\sqrt{2}\,\lambda_2}{4\lambda_{12}}\right)\frac{\log \bar{r}}{\log \overline{R}} \quad , \end{aligned} \tag{2-115}$$

where

$$\delta = \frac{1}{1 + \frac{4\,R_i}{15\,\lambda_2}\log \overline{R}} \quad . \tag{2-116}$$

The quantity δ is defined to simplify the results but also serves as a measure of the degree of rarefaction. $\delta \rightarrow 0$ represents continuum flow while $\delta \rightarrow 1$ represents free molecular flow.

All the physical quantities can be obtained by substituting these results back into equations (2-8) to (2-13) as

$$\frac{T_i - T}{T_i} = \frac{1}{2}\delta - \frac{1}{2}\sigma_s(1-\delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\,\lambda_{12}}\right) + \frac{1}{2}(1-\delta)\left(2\epsilon + \frac{1}{2}\sigma_s + \frac{5\sqrt{2}\,\lambda_2}{4\,\lambda_{12}}\sigma_s\right)\frac{\log \bar{r}}{\log \bar{R}} + \frac{\alpha}{\pi}\delta\epsilon - \frac{\alpha}{\pi}\sigma_s(1-\delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\,\lambda_{12}}\right), \qquad (2\text{-}117)$$

$$\frac{n_1}{n_i} = \sigma_s \frac{15\sqrt{2}\,(1-\delta)\lambda_2}{8\,\delta\,\lambda_{12}}\left(1 - \frac{\log \bar{r}}{\log \bar{R}}\right) + \frac{\sqrt{2}\,\sigma_s}{\pi}(\alpha_0 - \alpha) + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}}, \qquad (2\text{-}118)$$

$$\frac{n_2}{n_i} = 1 + \sigma_s \frac{15\sqrt{2}\,(1-\delta)\lambda_2}{8\,\delta\,\lambda_{12}} - \frac{\log \bar{r}}{\log \bar{R}} + (1-\delta)\left(\epsilon + \frac{1}{4}\sigma_s + \frac{5\sqrt{2}\,\lambda_2}{8\,\lambda_{12}}\sigma_s\right)\frac{\log \bar{r}}{\log \bar{R}} + \frac{\alpha}{\pi}\left[\frac{1}{2}\delta\epsilon + \sigma_s - \sigma_s(1-\delta)\left(\frac{1}{8} + \frac{5\sqrt{2}\,\lambda_2}{16\,\lambda_{12}}\right)\right], \qquad (2\text{-}119)$$

$$Q_r = \pi R_i n_i k T_i\left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}}\left[3\,\delta\epsilon + \sigma_s - 3\sigma_s(1-\delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\,\lambda_{12}}\right)\right], \qquad (2\text{-}120)$$

$$J_{1r} = 2\pi n_i R_i \sigma_s m_1\left(\frac{kT_i}{\pi m_1}\right)^{\frac{1}{2}}, \qquad (2\text{-}121)$$

$$J_{2r} = -\sqrt{2}\,\pi m_i R_i \sigma_s m_2 \left(\frac{kT_i}{\pi m_2}\right)^{\frac{1}{2}} \quad , \tag{2-122}$$

where Q_r is the total heat transfer rate per unit wire length, and J_{1r}, J_{2r} are the mass transfer rates per unit wire length for the atoms and the molecules.

The results do not depend on λ_1, showing the negligible effect of the atom-atom collisions since the concentration of the atoms is low. However λ_{12} appears in equal importance with λ_2 although collisions between the atoms and the molecules are far less frequent than those between the molecules themselves. This is due to the fact that collision between different species has an effect on the momentum equation while collision among the same species has effect only on the heat flow equation.

2.6.1 Limiting case of no dissociation reaction

If we set σ_s equal to zero to represent the situation of no dissociation reaction, we obtain

$$\frac{T_i - T}{T_i - T_0} = \frac{1}{2}\delta\left(1 + \frac{2\alpha}{\pi}\right) + (1 - \delta)\frac{\log \overline{r}}{\log \overline{R}} \quad , \tag{2-123}$$

$$Q_r = 3\pi m_i R_i k \left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}} \delta(T_i - T_0) \quad , \tag{2-124}$$

where we have approximated α_0 by $\pi/2$ since $\overline{R} >> 1$.

Equation (2-123) agrees exactly with that of Lees (22). The first part of the right-hand side represents a "local" collision-free temperature distribution weighted by the rarefaction parameter δ

while the second part represents the temperature field caused by collision. If we take the continuum limit of equation (2-124) we obtain

$$Q_{r\infty} = \frac{45\pi\mu_2 k(T_i - T_0)}{4\sqrt{2}\, m_2 \log \bar{R}} \qquad (2\text{-}125)$$

Comparing this with the solution obtained from the heat equation, we conclude that

$$\kappa_2 = \frac{45\, k\mu_2}{8\sqrt{2}\, m_2} = \frac{45\, \mu_2 C_v}{8\sqrt{2}\, m_2} (\gamma - 1) \quad , \qquad (2\text{-}126)$$

where κ_2 is the thermal conductivity of the molecules. This formula agrees exactly with the one given by Chapman and Cowling (8). Also we have

$$\frac{Q_r}{Q_{r\infty}} = \frac{1}{1 + \dfrac{15\,\lambda_2}{4 R_i \log \bar{R}}} \quad , \qquad (2\text{-}127)$$

which is identical to the expression obtained by Lees (22).

2.6.2 Fourier limit

This is the case of continuum flow with $\delta \rightarrow 0$. However, as we have discussed in section 2.5, the sticking probability σ_s becomes zero in this limit. Let us assume that

$$\lim_{\delta \to 0} \frac{\sigma_s}{\delta} = S \quad , \qquad (2\text{-}128)$$

where S is finite. Taking this limit on equations (2-117) to (2-122), we obtain the following results:

$$\frac{T_i - T}{T_i - T_0} = \frac{\log \bar{r}}{\log \bar{R}} , \tag{2-129}$$

$$\frac{n_1}{n_i} = \frac{15\sqrt{2}}{8} S \frac{\lambda_2}{\lambda_{12}} \left(1 - \frac{\log \bar{r}}{\log \bar{R}}\right) , \tag{2-130}$$

$$\frac{n_2}{n_i} = 1 + \frac{15\sqrt{2}}{8} S \frac{\lambda_2}{\lambda_{12}} \frac{\log \bar{r}}{\log \bar{R}} + \frac{\log \bar{r}}{\log \bar{R}} \epsilon , \tag{2-131}$$

$$Q_r = \frac{15\pi k T_i \mu_2}{4\sqrt{2}\, m_2 \log \bar{R}} \left(3\epsilon + \frac{1}{4} S - \frac{15\sqrt{2}}{8} S \frac{\lambda_2}{\lambda_{12}}\right) \tag{2-132}$$

$$J_{1r} = \frac{15\pi\mu_2}{4\sqrt{2} \log \bar{R}} S , \tag{2-133}$$

$$J_{2r} = - \frac{15\pi\mu_2}{4\sqrt{2} \log \bar{R}} S . \tag{2-134}$$

These agree with the solution of the appropriate continuum type equations. In equation (2-131) the second term is due to diffusion while the third term represents the variation of concentration with temperature. In equation (2-132) the first term is the conductive heat transfer while the other two represent the contribution to energy transfer by diffusion.

2.6.3 Knudsen limit

This corresponds to the free molecular flow regime where the effect of collisions is negligible. Taking $\delta = 1$, we obtain

$$\frac{T_i - T}{T_i - T_0} = \frac{1}{2}\left(1 + \frac{2\alpha}{\pi}\right) , \tag{2-135}$$

$$\frac{n_1}{n_i} = \frac{\sqrt{2}\,\sigma_s}{\pi}(\alpha_0 - \alpha) + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} \quad , \tag{2-136}$$

$$\frac{n_2}{n_i} = 1 + \frac{\alpha}{\pi}\left(\frac{1}{2}\epsilon + \sigma_s\right) \quad , \tag{2-137}$$

$$Q_r = J_{1r} = J_{2r} = 0 \quad . \tag{2-138}$$

Here the temperature field is independent of σ_s and it has a jump at the wire with a value of half the total temperature variation. The jump is almost zero at the cylinder. It is very interesting to notice that the value of n_1 at the wire depends on α_0. In contrast, in the two parallel plates geometry there is a temperature jump of $\frac{1}{2}$ on both plates and the values of n_1 and n_2 are both constant.

2.6.4 Limiting case of uniform temperature

We wish here to set in equations (2-117) to (2-122) $T_i = T_0$ to see whether the results agree with those of section 2.5 or not. We have $\epsilon = 0$ so that

$$\frac{T_i - T}{T_i} = \sigma_s(1-\delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\lambda_{12}}\right)\left(\frac{\log \bar{r}}{\log \bar{R}} - \frac{1}{2} - \frac{\alpha}{\pi}\right) \quad , \tag{2-139}$$

$$\frac{n_1}{n_i} = \sigma_s \frac{15\sqrt{2}\,\lambda_2}{8\delta\lambda_{12}}(1-\delta)\left(1 - \frac{\log \bar{r}}{\log \bar{R}}\right) + \sqrt{2}\,\sigma_s \frac{\alpha_0 - \alpha}{\pi} + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} , \tag{2-140}$$

$$\begin{aligned}\frac{n_2}{n_i} = 1 &+ \sigma_s \frac{15\sqrt{2}\,\lambda_2}{8\delta\lambda_{12}}(1-\delta)\frac{\log \bar{r}}{\log \bar{R}} \\ &+ (1-\delta)\sigma_s\left(\frac{1}{4} + \frac{15\sqrt{2}\,\lambda_2}{8\lambda_{12}}\right)\left(\frac{\log \bar{r}}{\log \bar{R}} - \frac{\alpha}{2\pi}\right) + \frac{\alpha}{\pi}\sigma_s \quad ,\end{aligned} \tag{2-141}$$

$$Q_r = \pi n_i R_i k T_i \left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}} \left[\sigma_s - 3\sigma_s(1-\delta)\left(\frac{1}{4} + \frac{5\sqrt{2}\,\lambda_2}{8\lambda_{12}}\right)\right] , \qquad (2\text{-}142)$$

$$J_1 = 2\pi n_i R_i m_1 \sigma_s \left(\frac{kT_i}{\pi m_1}\right)^{\frac{1}{2}} , \qquad (2\text{-}143)$$

$$J_{2r} = -\sqrt{2}\,\pi n_i R_i m_2 \sigma_s \left(\frac{kT_i}{\pi m_2}\right)^{\frac{1}{2}} . \qquad (2\text{-}144)$$

Apparently the results do not agree with those of section 2.5 since the temperature field is not uniform even with $T_i = T_0$. This phenomenon is caused by the collisions between the molecules and the atoms. We have assumed a fast exchange between the rotational energy and translational energy of the molecules. Hence the translational energy is not conserved during a collision process and, therefore, the temperature field will change since it is defined as two thirds of the translational energy. The nonvanishing heat flow in equation (2-142) is due to the difference of the energy carried by the molecules and the atoms.

The concentration fields given in equations (2-140) and (2-141) agree very well with those obtained in section 2.5 provided that σ_s is small.

Appendix 2A

CALCULATION OF THE HEAT FLUX

The heat flux q_r consists of two parts, the translational energy flux and the internal energy flux. The first can be calculated by direct integration to be

$$q_r^{tr} = k\left(\frac{2k}{\pi}\right)^{\frac{1}{2}} \cos\alpha \left[T_1^{\frac{3}{2}}\left(\frac{n_{11}}{\sqrt{m_1}} + \frac{n_{21}}{\sqrt{m_2}}\right) - T_2^{\frac{3}{2}}\left(\frac{n_{12}}{\sqrt{m_1}} + \frac{n_{22}}{\sqrt{m_2}}\right)\right] , \quad (2A-1)$$

by using the distribution functions given in equations (2-1) to (2-4). As for the second part, the internal energy carried by the molecules contains the rotational energy, the vibrational energy, and the electronic energy, while that carried by the atoms has only electronic energy. We assume that the exchange between translational energy and rotational energy is instantaneous while the vibrational energy can be neglected except at high temperatures. Choosing the electronic energy of the atoms to be one half of the bond dissociation energy $\overline{E}_1^{el}$, we can set the electronic energy of the molecules equal to zero. Let us write

$$q_r^{int} = n_1 u_{1r} \overline{E}_1^{el} + q_{2r}^{rot} \quad , \qquad (2A-2)$$

where q_r^{int} is the internal energy flux and q_{2r}^{rot} is the rotational energy flux carried by the molecules. Using Euckens approximation and assuming that the distribution of rotational energy is independent of velocity, we have

$$q_{2r}^{rot} = \sum_{j}^{\substack{\text{rotational}\\ \text{state}}} \int \xi_r f_{2j} E_{2j}\, d^3\xi \quad , \tag{2A-3}$$

where

$$f_{2j} = \begin{cases} f_{21j}, & \text{for } \phi \in \Omega_1 \quad , & \text{(2A-4)} \\ f_{22j}, & \text{for } \phi \in \Omega_2 \quad , & \text{(2A-5)} \end{cases}$$

with

$$f_{21j} = f_{21} \frac{\exp\{-[E_{2j}(T_1)]/(kT_1)\}}{\sum_j \exp\{-[E_{2j}(T_1)]/(kT_1)\}} \quad , \tag{2A-6}$$

$$f_{22j} = f_{22} \frac{\exp\{-[E_{2j}(T_2)]/(kT_2)\}}{\sum_j \exp\{-[E_{2j}(T_2)]/(kT_2)\}} \quad . \tag{2A-7}$$

We have, here, introduced two distribution functions for each rotational state. Direct integration gives

$$q_{2r}^{rot} = \cos\alpha \left(\frac{k}{2\pi m_2}\right)^{\frac{1}{2}} \left[n_{21} \overline{E}_2^{rot}(T_1) T_1^{\frac{1}{2}} - n_{22} \overline{E}_2^{rot}(T_2) T_2^{\frac{1}{2}} \right] \quad , \tag{2A-8}$$

where $\overline{E}_2^{rot}(T)$ is the average equilibrium rotational energy per molecule. For symmetrical diatomic molecules, a good approximation from a quantum mechanical treatment is

$$\overline{E}_2^{rot}(T) = kT \quad . \tag{2A-9}$$

Thus we have

$$q_r = k\left(\frac{k}{2\pi}\right)^{\frac{1}{2}} \cos\alpha \left[T_1^{\frac{3}{2}} \left(\frac{2n_{11}}{\sqrt{m_1}} + \frac{3n_{21}}{\sqrt{m_2}} \right) - T_2^{\frac{3}{2}} \left(\frac{2n_{12}}{\sqrt{m_1}} + \frac{3n_{22}}{\sqrt{m_2}} \right) \right] + n_1 u_{1r} \overline{E}_1^{el} \quad . \tag{2A-10}$$

Appendix 2B

COLLISION TERM IN THE MOMENTUM EQUATION FOR THE ATOMS

The average momentum of the atoms changes because of collisions with the molecules. Detailed mechanism of collision must be studied in order to understand the total variation. Let $\underline{\xi}_1$, $\underline{\xi}_1'$, m_1, and $\underline{\xi}_2$, $\underline{\xi}_2'$, m_2 be the velocity before collision, the velocity after collision, and the mass of an atom and a molecule respectively. Referring to Figure 3 where $\underline{U} = \underline{\xi}_2 - \underline{\xi}_1$ is the relative velocity, we have the following relations:

$$\underline{\xi}_1' = \underline{\xi}_1 + \frac{2m_2}{m_1 + m_2} (\underline{e}_\alpha \cdot \underline{U}) \underline{e}_\alpha \quad , \tag{2B-1}$$

$$\underline{\xi}_2' = \underline{\xi}_2 - \frac{2m_1}{m_1 + m_2} (\underline{e}_\alpha \cdot \underline{U}) \underline{e}_\alpha \quad . \tag{2B-2}$$

where $\underline{e}_\alpha$ is a unit vector pointing to the closest point of approach. This vector can be expressed by an orthogonal set of unit vectors. We choose one of them to be $\underline{U}/U$ and the remaining two arbitrarily in the plane perpendicular to $\underline{U}$. Hence

$$\underline{e}_\alpha = \frac{\underline{U}}{U} \cos\theta + \underline{e}_1 \sin\theta \cos\eta - \underline{e}_2 \sin\theta \sin\eta \quad . \tag{2B-3}$$

The relation between θ and χ is

$$\cos^2\theta = (1 - \cos\chi)/2 \quad . \tag{2B-4}$$

The collision term in the momentum equation after putting $\psi_1 = m_1 \underline{\xi}_1$

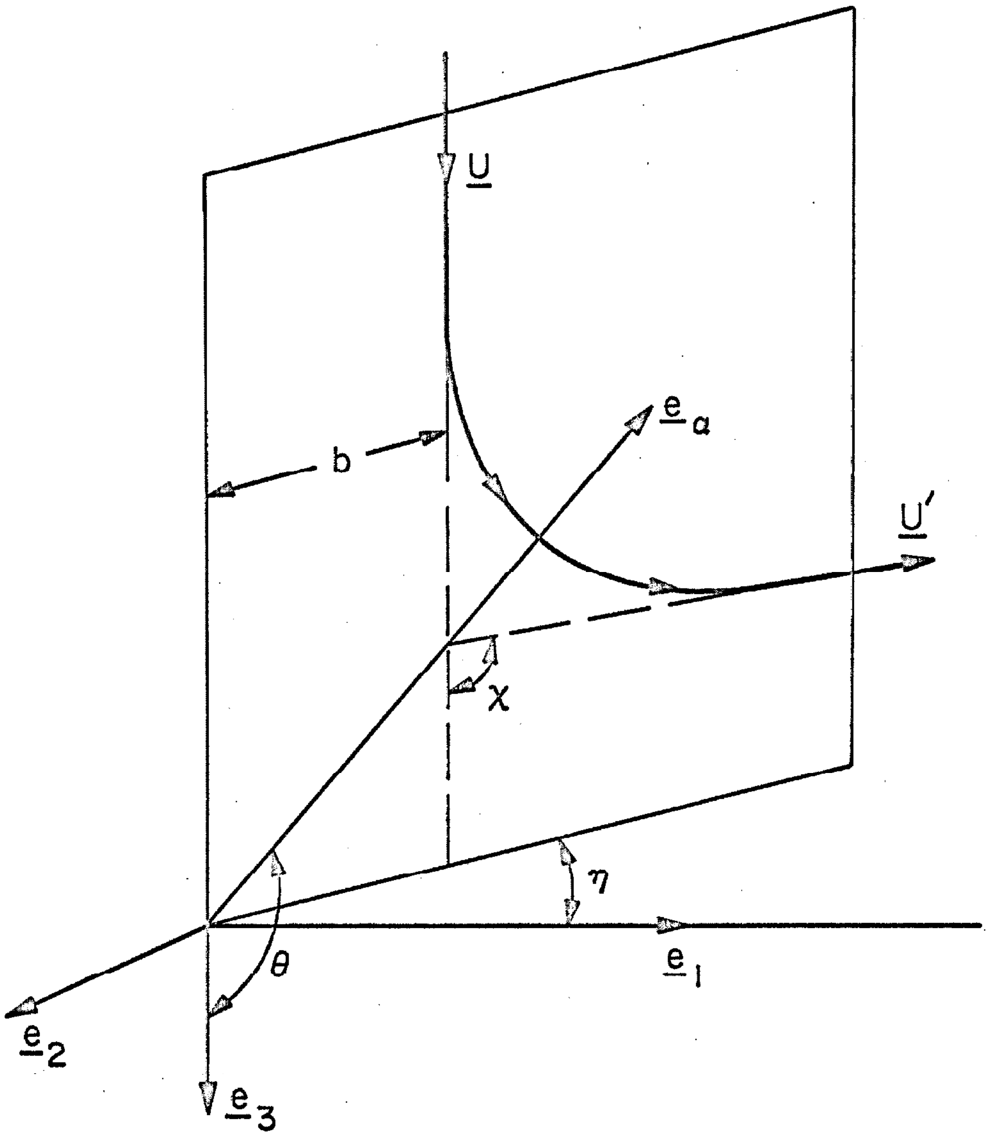

Fig. 3 DEFLECTION OF MOLECULE IN RELATIVE COORDINATES

becomes

$$n_1\overline{\Delta\psi}_{1\,\mathrm{coll}} = \int\int\int\int m_1(\underline{\xi}_1' - \underline{\xi}_1)Uf_1(\underline{\xi}_1)f_2(\underline{\xi}_2)b\,db\,d\eta\,d^3\xi_1\,d^3\xi_2 \; . \tag{2B-5}$$

Let

$$J = \int_0^{2\pi}\int_0^{\infty}(\psi_1' - \psi_1)\,b\,db\,d\eta \quad , \tag{2B-6}$$

and

$$Q^{(i)} = \int_0^{2\pi}\int_0^{\infty}(1 - \cos^i\chi)b\,db\,d\eta \quad . \tag{2B-7}$$

We have the following relation for $\psi_1 = m_1\underline{\xi}_1$:

$$J = \overline{m}\,\underline{U}\,Q^{(1)} \quad . \tag{2B-8}$$

Hirschfelder (14) has given the relation of $Q^{(i)}$ with the intermolecular force arising from a potential

$$\Phi(r) = \frac{d_{12}}{r^n} \quad . \tag{2B-9}$$

For Maxwellian molecules with $n = 4$, we have

$$Q^{(i)} = 2\pi\left(\frac{8d_{12}}{\overline{m}\,U^2}\right)^{\frac{1}{2}} A_i \quad , \tag{2B-10}$$

where $\overline{m}$ is the reduced mass and A_i's are constants listed in Table I (14). From these we have

$$n_1\overline{\Delta\psi}_{1\,\mathrm{coll}} = \int\int 2\pi(8\overline{m}d_{12})^{\frac{1}{2}}A_1(\underline{\xi}_2 - \underline{\xi}_1)f_1(\underline{\xi}_1)f_2(\underline{\xi}_2)\,d^3\xi_1\,d^3\xi_2 \; . \tag{2B-11}$$

We then substitute the expressions for f_1 and f_2 into equation (2B-11), take the radial component, and integrate to get the final form of the collision term,

$$n_1\overline{\Delta\psi}_{1\,\mathrm{coll}} = -2\pi(8\overline{m}d_{12})^{\frac{1}{2}}\,\frac{A_1 C}{r}\,(n_2+\tfrac{1}{2}n_1)\ . \qquad \text{(2B-12)}$$

Table I. Values of A_i for different values of n

n	4	6	8	10	12	14	∞
A_1	0.298	0.306	0.321	0.333	0.346	0.356	0.500
A_2	0.308	0.283	0.279	0.278	0.279	0.280	0.333

Appendix 2C

COLLISION TERM IN THE HEAT FLUX EQUATION

The equation of the heat flux employed in this chapter is a linear combination of the two individual heat flux equations for the atoms and the molecules. The collision term for the atoms consist of two parts, the change due to collisions with molecules and the change due to collisions with atoms. We are going to work out the first part and obtain the second by interchanging the subscripts. With $\psi_1 = m_1 |\xi_1|^2 \underline{\xi}_1$, equations (2B-1) and (2B-2) give

$$\psi_1' - \psi_1 = 4\overline{m}(\underline{e}_\alpha \cdot \underline{U})(\underline{e}_\alpha \cdot \underline{\xi}_1)\underline{\xi}_1 + 2\overline{m}\omega(\underline{e}_\alpha \cdot \underline{U})^2 \underline{\xi}_1 + 2\overline{m}(\underline{e}_\alpha \cdot \underline{U})\underline{e}_\alpha |\xi_1|^2$$

$$+ 4\overline{m}\omega(\underline{e}_\alpha \cdot \underline{U})^2 (\underline{e}_\alpha \cdot \underline{\xi}_1)\underline{e}_\alpha + 2\overline{m}\omega^2 (\underline{e}_\alpha \cdot \underline{U})^3 \underline{e}_\alpha \quad , \qquad (2C\text{-}1)$$

where

$$\omega = \frac{2m_2}{m_1 + m_2} \quad . \qquad (2C\text{-}2)$$

Substituting equations (2C-1), (2B-3), (2B-4), and (2B-7) into equations (2B-6), we obtain an expression for J which is too long to be given here. Since J is a function of $\underline{\xi}_1$ and $\underline{\xi}_2$, and

$$n_1 \overline{\Delta_2 \psi_1}_{\text{coll}} = \int\int J U f_1(\underline{\xi}_1) f_2(\underline{\xi}_2)\, d^3\xi_1\, d^3\xi_2 \quad , \qquad (2C\text{-}3)$$

the collision term is obtained by integrating the right-hand side of equation (2C-3). In fact we have

$$\iint |\xi_1|^2 \xi_{1r} f_1 f_2 \, d^3\xi_1 \, d^3\xi_2$$

$$= \frac{k\cos\alpha}{\pi m_1}\left(\frac{2k}{\pi m_1}\right)^{\frac{1}{2}} (n_{11}T_1^{\frac{3}{2}} - n_{12}T_2^{\frac{3}{2}})[n_{21}(\pi-2\alpha)+n_{22}(\pi+2\alpha)] \quad , \qquad (2C-4)$$

$$\iint (\underline{\xi}_1 \cdot \underline{\xi}_2)\xi_{1r} f_1 f_2 \, d^3\xi_1 \, d^3\xi_2$$

$$= \frac{k\cos\alpha}{4\pi m_1}\left(\frac{2k}{\pi m_2}\right)^{\frac{1}{2}} (n_{21}T_1^{\frac{1}{2}} - n_{22}T_2^{\frac{1}{2}})[(\pi-2\alpha+\sin 2\alpha)n_{11}T_1$$

$$+ (\pi+2\alpha-\sin 2\alpha)n_{12}T_2] \quad , \qquad (2C-5)$$

$$\iint |\xi_2|^2 \xi_{1r} f_1 f_2 \, d^3\xi_1 \, d^3\xi_2$$

$$= \frac{3k\cos\alpha}{4\pi m_2}\left(\frac{2k}{\pi m_1}\right)^{\frac{1}{2}} (n_{11}T_1^{\frac{1}{2}} - n_{12}T_2^{\frac{1}{2}})[(\pi-2\alpha)n_{21}T_1+(\pi+2\alpha)n_{22}T_2] \; ; \qquad (2C-6)$$

and three similar expressions by interchanging the subscripts 1 and 2. These are used to obtain the first part of the collision term as

$$n_1\overline{\Delta_2\psi_1}_{\text{coll}} = -(8\overline{m}d_{12})^{\frac{1}{2}} \frac{2k\cos\alpha}{9}$$

$$\times\Bigg\{(7A_1+4A_2)\frac{1}{m_1}\left(\frac{2k}{\pi m_1}\right)^{\frac{1}{2}} (n_{11}T_1^{\frac{1}{2}}-n_{12}T_2^{\frac{1}{2}})[n_{21}(\pi-2\alpha)+n_{22}(\pi+2\alpha)]$$

$$+ (2A_1-10A_2)\frac{C'}{4m_1R_i}[(\pi-2\alpha+\sin 2\alpha)n_{11}T_1+(\pi+2\alpha-\sin 2\alpha)n_{12}T_2]$$

$$+ (4A_1-14A_2)\frac{3C'}{2m_2R_i}[(\pi-2\alpha)n_{21}T_1+(\pi+2\alpha)n_{22}T_2]$$

$$+ (A_1+10A_2)\frac{3C'}{4m_1R_i}[(\pi-2\alpha)n_{11}T_1+(\pi+2\alpha)n_{12}T_2]$$

$$+ (8A_1+2A_2)\frac{C'}{2m_2R_i}[(\pi-2\alpha+\sin 2\alpha)n_{21}T_1+(\pi+2\alpha-\sin 2\alpha)n_{22}T_2]$$

$$+(-16A_1+8A_2)\frac{1}{m_2}\left(\frac{2k}{\pi m_2}\right)^{\frac{1}{2}}(n_{21}T_1^{\frac{3}{2}}-n_{22}T_2^{\frac{3}{2}})[n_{11}(\pi-2\alpha)+n_{12}(\pi+2\alpha)]\Bigg\} \; . \qquad (2C-7)$$

The second part is obtained by changing the expressions of f_2 to those of f_1. We have

$$
\begin{aligned}
&n_1\overline{\Delta_1\psi}_{1\,\mathrm{coll}} \\
&\quad = -(4m_1 d_{11})^{\frac{1}{2}}\,\frac{2k\cos\alpha}{m_1}\,A_2\Big\{(n_{11}T_1^{\frac{3}{2}}-n_{12}T_2^{\frac{3}{2}})[\,n_{11}(\pi-2\alpha)+n_{12}(\pi+2\alpha)]\left(\frac{2k}{\pi m_1}\right)^{\frac{1}{2}} \\
&\qquad + \frac{C'}{2m_1R_i}[\,(\pi-2\alpha+\sin 2\alpha)n_{11}T_1+(\pi+2\alpha-\sin 2\alpha)n_{12}T_2] \\
&\qquad + \frac{3C'}{m_1R_i}[\,(\pi-2\alpha)n_{11}T_1+(\pi+2\alpha)n_{12}T_2]\Big\} \quad .
\end{aligned}
\tag{2C-8}
$$

We can derive the collision term for the molecules in a similar way. The right-hand side of equation (2-28) is obtained by subtracting twice the collision term for the molecules from the collision term for the atoms.

Chapter 3

HEAT AND MASS TRANSFER FROM A HOT FINE WIRE TO A SURROUNDING CYLINDER -- METHOD OF COMPOSITE SOLUTION

3.1 Introduction

The problem of the previous chapter will now be investigated by a different approach based on perturbation methods. Since there are two characteristic lengths R_i and R_0 with different order of magnitude, regular perturbation cannot be applied to this problem. We have, therefore, to resort to singular perturbation methods such as those presented in the books of Van Dyke (29) and Cole (9).

Physically, we notice that the gas behaves like a continuum near the outer cylinder since its mean free path is quite small compared with the radius of the cylinder. Near the inner wire, however, molecules and atoms collide with the surface of the wire far more frequently than among themselves. This suggests that the distribution function in the Boltzmann equation can be expressed by two series; one valid in the region near the cylinder and another valid in the region near the wire. We could then match the two series and obtain a composite solution which is valid in the whole region. Mathematically, however, this method cannot be carried out easily because of the complex expression of the collision term in the Boltzmann equation.

An alternate method is suggested based on the same physical argument with less rigorous mathematical justification. First we obtain the distribution functions for the atoms and the molecules near the wire by assuming free molecular flow there. Near the surrounding cylinder we will not be concerned with the distribution functions but we shall solve the transport equations of continuum type directly. Then we match some macroscopic quantities to determine the unknown constants in the two solutions and obtain the composite solution by appropriately overlapping the two solutions.

We shall refer to the solution near the cylinder as the "outer" solution and that near the wire as the "inner" solution. Since the matching procedure is the most crucial in this method, its details will be given in section 3.4.

3.2 The "outer" solution

In the region near the surrounding cylinder, transport equations of the continuum type are being used. First of all, the equation of motion implies a constant pressure field since there is no bulk flow. Applying the ideal gas law there is obtained for the total number density n

$$n = \frac{p}{kT} \quad . \tag{3-1}$$

The fact of no bulk flow also implies

$$j_{1r} = -2j_{2r} \quad , \tag{3-2}$$

where j_{1r} and j_{2r} are the atomic and molecular fluxes in the radial direction. Two other equations, the equation of continuity of the atoms and the equation of energy, are written as

$$\frac{d}{dr} rj_{1r} = 0 \quad , \tag{3-3}$$

$$\frac{d}{dr} rq_r = 0 \quad , \tag{3-4}$$

where q_r is the radial heat flux. Relations between the fluxes j_{1r} and q_r and the appropriate gradients have been given by Bird et al. (1) as

$$j_{1r} = -nD_{12}\frac{dx_1}{dr} - \frac{1}{T}D^T\frac{dT}{dr} \quad , \tag{3-5}$$

$$q_r = -\kappa_{12}\frac{dT}{dr} + H_1 j_{1r} + H_2 j_{2r} \quad , \tag{3-6}$$

where x_1 is the mole fraction of the atoms, D_{12} is the binary diffusivity, D^T is the thermal diffusivity, κ_{12} is the thermal conductivity of the mixture, and H_1 and H_2 are the enthalpies carried by each atom and by each molecule respectively.

In general the thermal diffusivity is small so that the second term on the right-hand side of equation (3-5) is negligible unless there is a large temperature gradient. We can approximate H_1 by $\frac{5}{2}kT + \overline{E}_1^{el}$ and H_2 by $\frac{7}{2}kT$, with $\overline{E}_1^{el}$ defined as half the bond dissociation energy. Consequently equations (3-3) and (3-4) become

$$\frac{d}{dr} r\left(nD_{12}\frac{dx_1}{dr}\right) = 0 \quad , \tag{3-7}$$

$$\frac{d}{dr} r\left[\kappa_{12}\frac{dT}{dr} + \left(\frac{3}{4}kT + \overline{E}_1^{el}\right)nD_{12}\frac{dx_1}{dr}\right] = 0 \quad , \tag{3-8}$$

which are the differential equations to be solved.

Two of the boundary conditions are given at the cylinder, namely

$$T = T_0 \qquad \text{at} \quad r = R_0 \quad , \tag{3-9}$$

$$j_{1r} = k_r n_1^2 \qquad \text{at} \quad r = R_0 \quad , \tag{3-10}$$

where we have assumed second order kinetics for the surface recombination reaction. In order to solve equations (3-7) and (3-8), two more boundary conditions are required. We let

$$T = T_a \qquad \text{at} \quad r = R_i \quad , \tag{3-11}$$

$$j_{1r} = j_{1a} \qquad \text{at} \quad r = R_i \quad , \tag{3-12}$$

as the two other boundary conditions where the values of T_a and j_{1a} will be determined in the matching process.

The bindary diffusivity D_{12} and the thermal conductivity κ_{12} are functions of temperature and concentrations. However, under the assumption of small temperature variation and small fraction of the atoms, we could approximately treat them as constants corresponding to the conditions of the wire. In addition, κ_{12} can be replaced by κ_2, the thermal conductivity of the molecules.

Solving equations (3-7) and (3-8) with the boundary conditions (3-9) to (3-12), we obtain

$$n_1 = -\frac{j_{1a} R_i}{D_{12}} \log \frac{r}{R_0} + \left(\frac{j_{1a} R_i}{k_r R_0} \right)^{\frac{1}{2}} \quad , \tag{3-13}$$

$$T = T_0 - (T_0 - T_a) \frac{\log (R_0/r)}{\log (R_0/R_i)} \quad , \tag{3-14}$$

$$n_2 = n_i + \left(\frac{T_i - T_0}{T_i} + \frac{T_0 - T_a}{T_i}\,\frac{\log (R_0/r)}{\log (R_0/R_i)}\right) n_i$$

$$- \frac{j_{1a} R_i}{D_{12}} \log (R_i/r) \; , \tag{3-15}$$

$$j_{1r} = j_{1a} \frac{R_i}{r} \; , \tag{3-16}$$

$$q_r = \kappa_2 \frac{T_a - T_0}{\log(R_0/R_i)} \frac{1}{r} + \left(\frac{3}{4} kT + \overline{E}_1^{el}\right) \frac{R_i}{r} j_{1a} \; , \tag{3-17}$$

where n_i is the number density of the molecules at the wire and T_i is the temperature of the wire.

3.3 The "inner" solution

Free molecular flow is assumed in the region near the wire where the collisions between the gas particles are far less important than the collisions between the gas and the wire. We assume that the incident fluxes coming from infinity are in Maxwellian distribution with temperature T_∞ and number densities $n_{1\infty}$ and $n_{2\infty}$. Thus the incident fluxes j_{1i}, j_{2i} of the atoms and the molecules are given by

$$j_{1i} = n_{1\infty} \left(\frac{kT_\infty}{2\pi m_1}\right)^{\frac{1}{2}} \; , \tag{3-18}$$

$$j_{2i} = n_{2\infty} \left(\frac{kT_\infty}{2\pi m_2}\right)^{\frac{1}{2}} \; . \tag{3-19}$$

The outgoing fluxes j_{1o}, j_{2o} coming from the surface of the wire are assumed in Maxwellian distribution with temperature T_i and number densities n_{1i} and n_{2i},

$$j_{1o} = n_{1i} \left(\frac{kT_i}{2\pi m_1}\right)^{\frac{1}{2}} \; , \tag{3-20}$$

$$j_{2o} = n_{2i}\left(\frac{kT_i}{2\pi m_2}\right)^{\frac{1}{2}} \quad , \tag{3-21}$$

The temperature and concentration fields can be calculated as

$$T = T_i\left(\frac{1}{2} - \frac{\alpha}{\pi}\right) + T_\infty\left(\frac{1}{2} + \frac{\alpha}{\pi}\right) \quad , \tag{3-22}$$

$$n_1 = n_{1i}\left(\frac{1}{2} - \frac{\alpha}{\pi}\right) + n_{1\infty}\left(\frac{1}{2} + \frac{\alpha}{\pi}\right) \quad , \tag{3-23}$$

$$n_2 = n_{2i}\left(\frac{1}{2} - \frac{\alpha}{\pi}\right) + n_{2\infty}\left(\frac{1}{2} + \frac{\alpha}{\pi}\right) \quad , \tag{3-24}$$

where we have used the assumption $\frac{n_1}{n_2} << 1$ in obtaining the temperature field. The angle α is defined as

$$\alpha = \text{arc cos } \frac{R_i}{r} \quad . \tag{3-25}$$

On the surface of the wire, the condition of no accumulation implies

$$j_{1i} + 2j_{2i} = j_{1o} + 2j_{2o} \quad . \tag{3-26}$$

Another condition is formulated by defining a sticking probability σ_s for the dissociation,

$$\sigma_s = \frac{j_{2i} - j_{2o}}{j_{2i}} \quad , \tag{3-27}$$

which is taken as a constant. Detailed study of the sticking probability will be given in Chapter 7.

From the above two relations, we obtain formulas for the heat flux q_r, the flux of the atoms j_{1r}, and the flux of the molecules j_{2r}, all in the radial direction and evaluated at $r = R_i$,

$$q_r = 2j_{1i}k(T_i - T_\infty) + 3j_{2i}(T_i - T_\infty) + \sigma_s j_{2i}kT_i \quad , \tag{3-28}$$

$$j_{1r} = 2\sigma_s j_{2i} \quad , \tag{3-29}$$

$$j_{2r} = -\sigma_s j_{2i} \quad , \tag{3-30}$$

where we have assumed that the energy carried by an atom is $2kT$ and that by a molecule $3kT$. Further simplification is achieved by replacing $n_{2\infty}$ by n_i and T_∞ by T_i in the expression for f_{2i} so that

$$j_{1r} = 2\sigma_s n_i \left(\frac{kT_i}{2\pi m_2}\right)^{\frac{1}{2}} \quad , \tag{3-31}$$

$$j_{2r} = -\sigma_s n_i \left(\frac{kT_i}{2\pi m_2}\right)^{\frac{1}{2}} \quad . \tag{3-32}$$

3.4 Matching

Two different kinds of quantities are to be matched. The temperature T and the number densities n_1 and n_2 are intensive quantities while the heat flux q_r and the molar fluxes j_{1r} and j_{2r} are extensive quantities. When matching an intensive quantity, we match the "inner" solution at $r = \infty$ with the "outer" solution at $r = R_i$. This is a general matching principle suggested by Prandtl (29). The extensive quantities in both solutions will be matched at the same position, $r = R_i$. This is necessary since matching extensive quantities at different positions makes no sense. Specifically, the matching equations are

$$\lim_{r\to R_i} (T)_{outer} = \lim_{r\to\infty} (T)_{inner} \quad , \tag{3-33}$$

$$\lim_{r\to R_i} (n_1)_{outer} = \lim_{r\to\infty} (n_i)_{inner} \quad , \tag{3-34}$$

$$\lim_{r\to R_i} (n_2)_{outer} = \lim_{r\to\infty} (n_2)_{inner} \quad , \tag{3-35}$$

$$(j_{1r})_{outer} = (j_{1r})_{inner} \qquad \text{at } r = R_i \quad , \tag{3-36}$$

$$(q_r)_{outer} = (q_r)_{inner} \qquad \text{at } r = R_i \quad . \tag{3-37}$$

The above conditions are combined with the expressions obtained in the previous two sections to give

$$T_a = T_\infty \quad , \tag{3-38}$$

$$\frac{j_{1a}R_i}{D_i} \log \frac{R_0}{R_i} + \left(\frac{j_{1a}R_i}{k_r R_0}\right)^{\frac{1}{2}} n_i = n_{1\infty} \quad , \tag{3-39}$$

$$n_i + \frac{T_i - T_a}{T_i} n_i = n_{2\infty} \quad , \tag{3-40}$$

$$j_{ia} = 2\sigma_s n_i \left(\frac{kT}{2\pi m_2}\right)^{\frac{1}{2}} , \tag{3-41}$$

$$\frac{\kappa_2(T_a - T_0)}{R_i \log(R_0/R_i)} + \frac{3}{4} j_{1a} k T_a = 2j_{1i} k(T_i - T_\infty) + 3j_{2i}(T_i - T_\infty) + \sigma_s j_{2i} k T_i \quad . \tag{3-42}$$

We now define

$$\lambda_2 = \frac{4\kappa_2}{45 n_i k\left(\frac{kT_i}{2\pi m_2}\right)^{\frac{1}{2}}} \quad , \tag{3-43}$$

$$\lambda_{12} = \frac{D_{12}}{2\left(\frac{kT_i}{2\pi m}\right)^{\frac{1}{2}}} \quad , \tag{3-44}$$

$$A = \left[\frac{R_i}{k_r n_i R_0}\left(\frac{kT_i}{\pi m_2}\right)^{\frac{1}{2}}\right]^{\frac{1}{2}} \quad , \tag{3-45}$$

$$\delta = \frac{1}{1 + \frac{4}{15}\frac{R_i}{\lambda_2}\log\frac{R_0}{R_i}} \quad , \tag{3-46}$$

$$\epsilon = 1 - \frac{T_0}{T_i} \quad , \tag{3-47}$$

and substitute these together with equations (3-18) and (3-19) into equations (3-38) to (3-42) to obtain

$$T_a = \delta T_0 + (1 - \delta)T_i(1 - \tfrac{1}{6}\sigma_s) \; , \tag{3-48}$$

$$n_{1\infty} = \sigma_s \frac{15\sqrt{2}}{8} n_i \frac{\lambda_2(1-\delta)}{\lambda_{12}\delta} + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} n_i \quad , \tag{3-49}$$

$$n_{2\infty} = n_i + n_i[\delta\epsilon + \tfrac{1}{6}\sigma_s(1-\delta)] \quad . \tag{3-50}$$

3.5 Results

Substituting the expressions for T_a and j_{1a} into equations (3-13), (3-14), and (3-15), we obtain for the "outer" solution

$$\frac{T_i - T}{T_i} = \epsilon - (1-\delta)(\epsilon - \tfrac{1}{6}\sigma_s)\frac{\log(R_0/r)}{\log(R_0/R_i)} \quad , \tag{3-51}$$

$$n_1 = \sigma_s \frac{15\sqrt{2}}{8} n_i \frac{\lambda_2(1-\delta)}{\lambda_{12}\delta} \frac{\log(R_0/r)}{\log(R_0/R_i)} + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} n_i , \qquad (3\text{-}52)$$

$$\begin{aligned} n_2 = n_i &+ \left[\epsilon - (1-\delta)(\epsilon - \tfrac{1}{6}\sigma_s)\frac{\log(R_0/r)}{\log(R_0/R_i)}\right] n_i \\ &- \frac{5\sqrt{2}}{8} n_i \sigma_s \frac{\lambda_2}{\lambda_{12}} \frac{1-\delta}{\delta} \frac{\log(R_i/r)}{\log(R_0/R_i)} \quad . \end{aligned} \qquad (3\text{-}53)$$

Equations (3-22), (3-23), and (3-24) yield the "inner" solution,

$$\frac{T_i - T}{T_i} = (\tfrac{1}{2} + \tfrac{\alpha}{\pi})[\delta\epsilon + \frac{\sigma_s}{6}(1-\delta)] \quad , \qquad (3\text{-}54)$$

$$n_1 = \sigma_s \frac{15\sqrt{2}}{8} \frac{\lambda_2}{\lambda_{12}} \frac{1-\delta}{\delta} n_i + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} n_i + \sqrt{2}\,\sigma_s(\tfrac{1}{2} - \tfrac{\alpha}{\pi}) n_i , \qquad (3\text{-}55)$$

$$n_2 = n_i + \frac{\alpha}{\pi}[\delta\epsilon + \frac{\sigma_s}{6}(1-\delta)] n_i \quad . \qquad (3\text{-}56)$$

The composite solution is obtained by the following method. For any variable v, we write

$$v = (v)_{outer} + (v)_{inner} - \lim_{r \to \infty} (v)_{inner} , \qquad (3\text{-}57)$$

in order to satisfy the boundary conditions at both ends. When this is applied to the present case there is obtained

$$\frac{T_i - T}{T_i} = \frac{1}{2}\delta\epsilon + \frac{\sigma_s}{12}(1-\delta) + (1-\delta)(\epsilon - \frac{\sigma_s}{6})\frac{\log \bar{r}}{\log \bar{R}} + \frac{\alpha}{\pi}[\delta\epsilon + \frac{\sigma_s}{6}(1-\delta)] , \qquad (3\text{-}58)$$

$$\frac{n_1}{n_i} = \sigma_s \frac{15\sqrt{2}}{8} \frac{\lambda_2}{\lambda_{12}} \frac{1-\delta}{\delta}(1 - \frac{\log \bar{r}}{\log \bar{R}}) + \sqrt{2}\,\sigma_s(\tfrac{1}{2} - \tfrac{\alpha}{\pi}) + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} , \qquad (3\text{-}59)$$

$$\frac{n_2}{n_1} = 1 + \sigma_s \frac{15\sqrt{2}}{8} \frac{\lambda_2}{\lambda_{12}} \frac{1-\delta}{\delta} \frac{\log \overline{r}}{\log \overline{R}} + (1-\delta)(\epsilon - \frac{\sigma_s}{6}) \frac{\log \overline{r}}{\log \overline{R}}$$

$$+ \frac{\alpha}{\pi} [\delta\epsilon + \frac{\sigma_s}{6}(1-\delta)] \quad , \tag{3-60}$$

where $\overline{r}$ and $\overline{R}$ are defined by

$$\overline{r} = \frac{r}{R_i} \quad , \tag{3-61}$$

$$\overline{R} = \frac{R_0}{R_i} \quad . \tag{3-62}$$

The total heat flow rate Q_r and the mass flow rates J_{1r} and J_{2r} for the atoms and the molecules are

$$Q_r = \pi n_i R_i k T_i \left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}} [3\delta\epsilon + \frac{\sigma_s}{2}(1-\delta) + \sigma_s] \quad , \tag{3-63}$$

$$J_{1r} = 2\pi n_i R_i m_1 \sigma_s \left(\frac{kT_i}{\pi m_1}\right)^{\frac{1}{2}} \quad , \tag{3-64}$$

$$J_{2r} = -\sqrt{2}\ \pi n_i R_i m_2 \sigma_s \left(\frac{kT_i}{\pi m_2}\right)^{\frac{1}{2}} \quad . \tag{3-65}$$

3.5.1 Limiting case of no dissociation

We put $\sigma_s = 0$ to describe the case of no dissociation. Equations (3-58) and (3-63) then give

$$\frac{T_i - T}{T_i - T_0} = \frac{\delta}{2}(1 + \frac{2\alpha}{\pi}) + (1-\delta) \frac{\log \overline{r}}{\log \overline{R}} \quad , \tag{3-66}$$

$$Q_r = 3\pi n_i R_i k (T_i - T_0) \delta \left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}} \quad , \tag{3-67}$$

which are identical to equations (2-123) and (2-124) in Chapter 2.

2.5.2 Fourier limit

In this limit we have $\delta = 0$ and let

$$\lim_{\delta \to 0} \frac{\sigma_s}{\delta} = S \; . \tag{3-68}$$

Taking this limit on equations (3-58) to (3-60), and (3-63) to (3-65), there is obtained

$$\frac{T_i - T}{T_i - T_0} = \frac{\log \bar{r}}{\log \bar{R}} \; , \tag{3-69}$$

$$\frac{n_1}{n_i} = S \, \frac{15\sqrt{2}}{8} \, \frac{\lambda_2}{\lambda_{12}} \left(1 - \frac{\log \bar{r}}{\log \bar{R}}\right) \; , \tag{3-70}$$

$$\frac{n_2}{n_i} = 1 + S \frac{15\sqrt{2}}{8} \, \frac{\lambda_2}{\lambda_{12}} \, \frac{\log \bar{r}}{\log \bar{R}} + \epsilon \frac{\log \bar{r}}{\log \bar{R}} \; , \tag{3-71}$$

$$Q_r = \frac{15 \pi \mu_2 k}{4\sqrt{2}\, m_2 \log \bar{R}} \left(3\epsilon + \frac{3}{2} S\right) T_i \; , \tag{3-72}$$

$$J_{1r} = \frac{15 \pi \mu_2 S}{4\sqrt{2} \log \bar{R}} \; , \tag{3-73}$$

$$J_{2r} = - \frac{15 \pi \mu_2 S}{4\sqrt{2} \log \bar{R}} \; , \tag{3-74}$$

where μ_2 is defined as the viscosity of the molecules by

$$\mu_2 = n_i m_2 \left(\frac{2kT_i}{\pi m_1}\right)^{\frac{1}{2}} \lambda_2 \; . \tag{3-75}$$

Equations (3-69), (3-70), (3-71), (3-73) and (3-74) agree exactly with equations (2-129), (2-130), (2-131), (2-133) and (2-134) respectively. However there is a difference in the heat transfer rate Q_r between equation (3-72) and equation (2-132). This will be discussed in the next section.

3.5.3 Knudsen limit

In this limiting case we set $\delta = 1$ in equations (3-58), (3-59) and (3-60) to obtain

$$\frac{T_i - T}{T_i - T_0} = \frac{1}{2} + \frac{\alpha}{\pi} \quad , \tag{3-76}$$

$$\frac{n_1}{n_i} = \sqrt{2}\,\sigma_s\left(\frac{1}{2} - \frac{\alpha}{\pi}\right) + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} \quad , \tag{3-77}$$

$$\frac{n_2}{n_i} = 1 + \frac{\alpha\epsilon}{\pi} \quad . \tag{3-78}$$

The first two are the same as equations (2-135) and (2-136), while the third one differs from equation (2-137). It seems that equation (3-78) is preferable, for when combined with the temperature field, it satisfies the ideal gas law while equation (2-137) does not.

3.5.4 Limiting case of uniform temperature

When the temperature of the cylinder is equal to that of the wire, $\epsilon = 0$, so that we have

$$\frac{T_i - T}{T_i} = \sigma_s (1-\delta)\left(\frac{1}{12} + \frac{\alpha}{6\pi} - \frac{1}{6}\,\frac{\log \overline{r}}{\log \overline{R}}\right) \quad , \tag{3-79}$$

$$\frac{n_1}{n_i} = \sigma_s \frac{15\sqrt{2}}{8}\,\frac{\lambda_2}{\lambda_{12}}\,\frac{1-\delta}{\delta}\left(1 - \frac{\log \overline{r}}{\log \overline{R}}\right) + \sqrt{2}\,\sigma_s\left(\frac{1}{2} - \frac{\alpha}{\pi}\right) + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} \quad , \tag{3-80}$$

$$\frac{n_2}{n_i} = 1 + \sigma_s \frac{15\sqrt{2}}{8}\,\frac{\lambda_2}{\lambda_{12}}\,\frac{1-\delta}{\delta}\,\frac{\log \overline{r}}{\log \overline{R}} + \frac{\sigma_s}{6}(1-\delta)\left(\frac{\alpha}{\pi} - \frac{\log \overline{r}}{\log \overline{R}}\right) \quad , \tag{3-81}$$

$$Q_r = \pi n_i R_i k T_i \sigma_s \left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}} \left(\frac{3}{2} - \frac{\delta}{2}\right) \quad , \tag{3-82}$$

$$J_{1r} = 2\pi n_i R_i m_1 \sigma_s \left(\frac{kT_i}{\pi m_1}\right)^{\frac{1}{2}} \quad ,$$

$$J_{2r} = -\sqrt{2}\,\pi n_i R_i m_2 \sigma_s \left(\frac{kT_1}{\pi m_2}\right)^{\frac{1}{2}} \quad . \tag{3-84}$$

Here the temperature field is not uniform even if there is no temperature difference between the wire and the cylinder. This has been explained in section 2.6. Notice, however, that the temperature field is uniform throughout the whole region in both the continuum flow limit and the free molecular flow limit.

3.6 Comparisons and discussions

In Chapters 2 and 3 we have used two entirely different methods to solve the problem of heat and mass transfer from a hot fine wire to a surrounding cylinder. The results obtained by these two methods agree with each other quite well. Although experimental data are not available for comparison, the formulas obtained agree with the existing ones in many limiting cases.

The main difficulty in Lees' method is the calculation of the collision terms. In the conservation equation for the total energy, the assumption that the vibrational energy of the diatomic molecule is negligible at ordinary temperatures and that the rotational energy exchanges instantaneously with the translational energy has been made. In the equation of the radial heat flux, only the translational energy flux has been considered, because there is no way to account for the interchange between the translational energy flux and the internal energy flux. This does not affect the heat transfer problem for a monatomic gas investigated by Lees (22). In a mixture where diatomic molecules are present, the error involved in this equation has an effect in the final results. However, a modification can be made as given in the next subsection.

3.6.1 Modification to the solution of Chapter 2

We shall follow the procedure Lees (22) employed to obtain the heat transfer rate of a diatomic gas from a hot fine wire from that of a monatomic gas. Since the formulas for diatomic and monatomic gases differ only in coefficients, Lees took the continuum limit of the formula for a monatomic gas and compared it with existing formula to evaluate the coefficients for a diatomic gas. Similarly, we can calculate the heat transfer rate at the wire in the continuum flow regime to be

$$Q_r = -2\pi R_i \kappa_2 \frac{dT}{dr}\bigg|_{r=R_i} + \frac{5kT_i}{2m_1} J_{1r} + \frac{7kT_i}{2m_2} J_{2r}$$

$$= \frac{15\,\pi\mu_2 kT_i}{4\sqrt{2}\, m_2 \log \overline{R}} \left(3\epsilon + \frac{3}{2} S\right) \quad . \tag{3-85}$$

Equation (3-85) agrees exactly with equation (3-72) of this chapter, while equation (2-132) of the previous chapter shows inconsistency. Consequently we replace the term $\frac{1}{4} + \frac{5\sqrt{2}}{8} \frac{\lambda_2}{\lambda_{12}}$ in the results of Chapter 2 by $-\frac{1}{6}$ in order to make equation (2-132) the same as equation (3-85). The results after correction are

$$\frac{T_i - T}{T_i} = \frac{1}{2}\delta\epsilon + \frac{\sigma_s}{12}(1-\delta) + (1-\delta)\left(\epsilon - \frac{\sigma_s}{6}\right)\frac{\log \overline{r}}{\log \overline{R}} + \frac{\alpha}{\pi}\delta\epsilon + \frac{\sigma_s}{6}\frac{\alpha}{\pi}(1-\delta) \quad , \tag{3-86}$$

$$\frac{n_1}{n_i} = \sigma_s \frac{15\sqrt{2}}{8} \frac{\lambda_2}{\lambda_{12}} \frac{1-\delta}{\delta}\left(1 - \frac{\log \overline{r}}{\log \overline{R}}\right) + \sqrt{2}\,\sigma_s\left(\frac{1}{2} - \frac{\alpha}{\pi}\right) + A\left(\sqrt{2}\,\sigma_s\right)^{\frac{1}{2}} \quad , \tag{3-87}$$

$$\frac{n_2}{n_i} = 1 + \sigma_s \frac{15\sqrt{2}}{8} \frac{\lambda_2}{\lambda_{12}} \frac{1-\delta}{\delta} \frac{\log \overline{r}}{\log \overline{R}} + (1-\delta)\left(\epsilon - \frac{\sigma_s}{6}\right)\frac{\log \overline{r}}{\log \overline{R}} + \frac{\alpha}{\pi}\left[\delta\epsilon + \frac{\sigma_s}{6}(1-\delta)\right] \quad , \tag{3-88}$$

$$Q_r = \pi n_i R_i k T_i \left(\frac{2kT_i}{\pi m_2}\right)^{\frac{1}{2}} \left[3\delta\epsilon + \sigma_s + \frac{1}{2}\sigma_s(1-\delta)\right] \quad , \tag{3-89}$$

$$J_{1r} = 2\pi n_i R_i m_1 \left(\frac{kT_i}{\pi m_1}\right)^{\frac{1}{2}} \quad , \tag{3-90}$$

$$J_{2r} = -\sqrt{2}\,\pi m_i R_i m_2 \left(\frac{kT_i}{\pi m_2}\right)^{\frac{1}{2}} , \tag{3-91}$$

where in equation (3-88) we have replaced $\frac{1}{2}\delta\epsilon + \sigma_s + \frac{\sigma_s}{12}(1 - \delta)$ by $\delta\epsilon + \frac{\sigma_s}{6}(1 - \delta)$ in order to satisfy the ideal gas law. It is interesting to see that these modified results are exactly the same as what we have obtained in this chapter.

3.6.2 Numerical results

Having modified the solutions of Chapter 2 to agree with those of the present chapter, we wish to present some numerical results. Figure 4 is a plot of Q_r/Q_∞ versus the Knudsen number with different values of the sticking probability σ_s, where Q_∞ is the radial heat flow in the continuum limit. To make the plot valid near the continuum flow regime we have used the empirical formula $\frac{S}{Kn+1}\,\delta\epsilon$ for σ_s. In Figure 5 the reduced temperature field is plotted as a function of the radial position with different values of Knudsen number where the sticking probability σ_s is assumed to have the form $\frac{Kn}{Kn+0.1}\,\epsilon$. Finally the group $\delta n_i/\epsilon n_i$ is plotted in Figure 6 versus the radial position with different values of δ.

3.6.3 Conclusions

The method of composite solution seems to work very well in this problem. The equations for both the "outer" solution and the "inner" solution are simple. It needs only a few calculations, and yet its results are identical to those obtained by Lees' method including

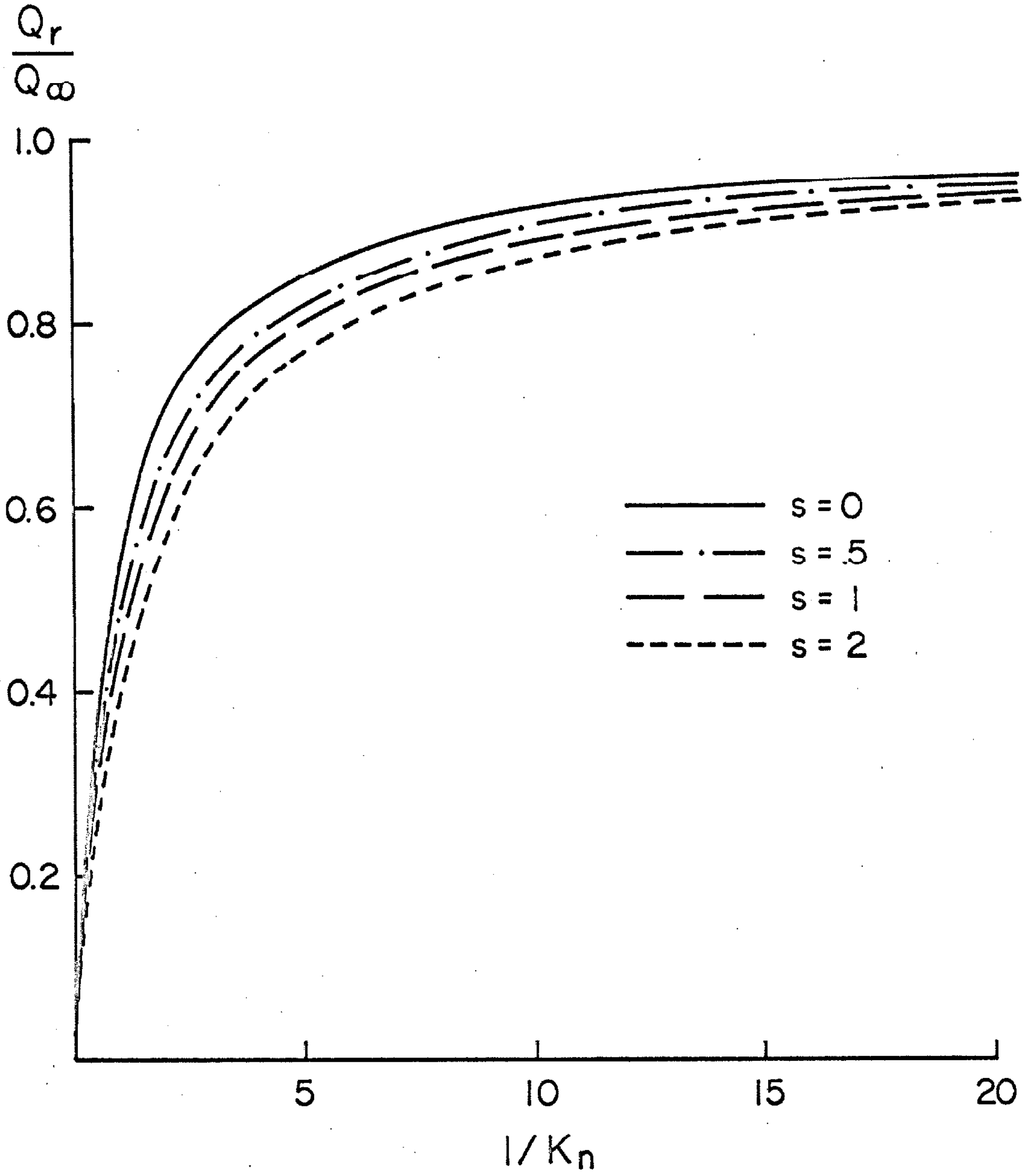

Fig. 4 HEAT TRANSFER FROM A HOT FINE WIRE TO A SURROUNDING CYLINDER

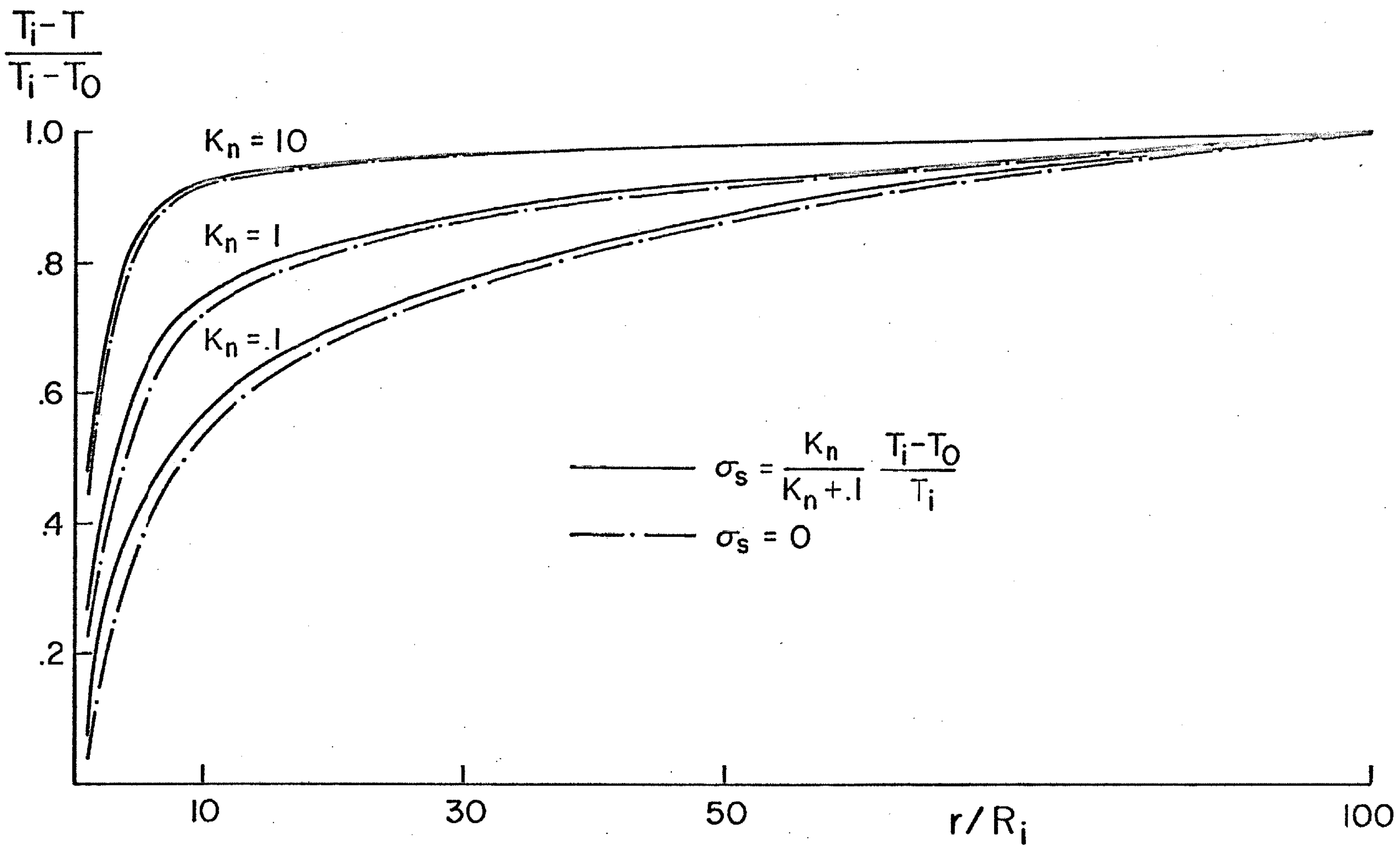

Fig. 5 TEMPERATURE DISTRIBUTION BETWEEN A HOT FINE WIRE AND A SURROUNDING CYLINDER

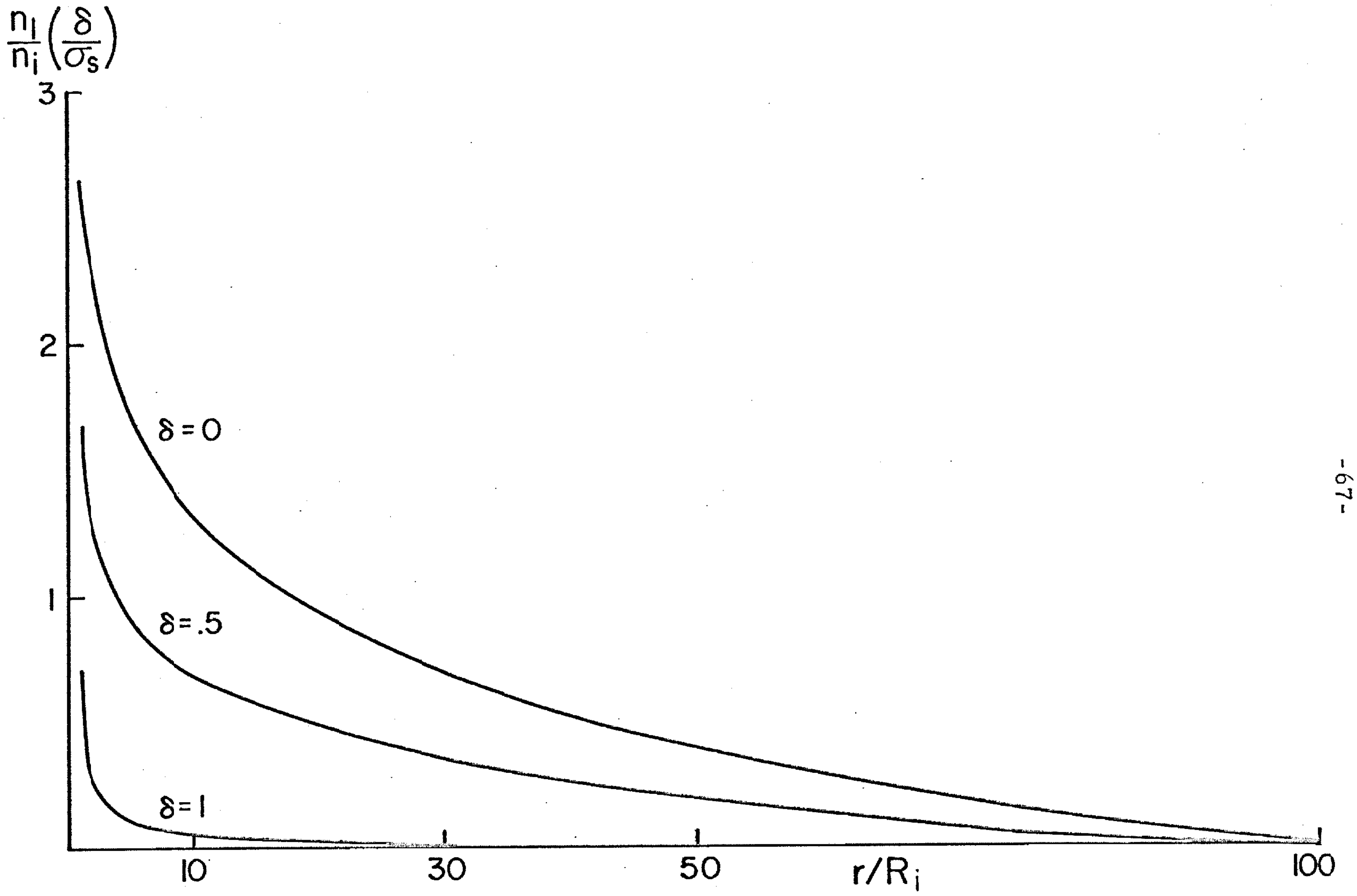

Fig. 6 DISTRIBUTION OF THE DISSOCIATED ATOMS BETWEEN A HOT FINE WIRE AND A SURROUNDING CYLINDER

the corrections of section 3.6.1. We shall, hereafter, use this method to solve some more complex problems as described in the following chapters.

Since matching is the most crucial procedure in this method, we have to be very careful about the property of the quantity being matched. As we have stated in section 3.4, matching extensive quantities at different position makes no sense at all. Finally we like to point out that there is no exact rule for matching because it is an art and depends on each individual's taste.

3.6.4 More about the sticking probability

We would like to say a few words about the case when the sticking probability σ_s is not a constant. This happens in the regime between the transitional flow and the continuum flow. As will be discussed in Chapter 7, the sticking probability σ_s, if it is not a constant, is a function of the incoming flux j_{2i} only. In the previous solution we have approximated j_{2i} by $n_i\left(kT_i/2\pi m_2\right)^{\frac{1}{2}}$. Therefore σ_s is known and the results are not affected at all.

Chapter 4

FLOW OF A RAREFIED GAS PAST A SPHERE

4.1 Introduction

We consider the flow of a rarefied gas past a sphere because of the prominent effect of rarefaction on the drag force and the role the sphere plays as an important geometry. This problem has been studied extensively by various theoretical approaches as well as experiments. However, most previous methods are dealing with small ranges of Knudsen number and therefore have limited applicability. Recently Cercignani (7) gave an expression for the drag force coefficient over the whole range of Knudsen number, which agrees very well with Millikan's data (25). In this chapter the method of composite solution is applied also for the whole range of Knudsen number to serve as a means to acquire familiarity with the matching procedures. Although the result seems to be somewhat inferior (see Figure 7), this method has the advantage of requiring very simple calculations and can be applied to more complex problems such as the one in Chapter 5. We shall only consider isothermal flow with low Mach and Reynolds numbers. Problems with other geometry and other flow conditions can be handled similarly.

This problem has two characteristic lengths, the radius of the sphere and the mean free path of the gas. We observe that no matter how large the mean free path is, there is a region far from the sphere that the gas can be viewed as a continuum. On the other hand no matter how small the mean free path is, there is a region so close to the sphere that interaction between the gas and the sphere is more important than the collisions among the gas particles themselves. Having these in mind, we shall solve equations of continuum type for the region far from the sphere to obtain the "outer" solution and shall use free molecular flow theory to obtain the "inner" solution near the sphere. The composite solution is then obtained by matching which will be given in section 4.4.

We shall use U_0, p_0, and ρ as the velocity, the pressure, and the density of the upstream gas; T the temperature of the system; m the molecular mass of the gas; and a the radius of the sphere. We assume the kinematic viscosity ν to be constant. We shall use polar coordinates as well as Cartesian coordinates with the X axis parallel to the upstream velocity.

4.2 The "outer" solution

Since the gas in the "outer" region can be taken as continuum, we use the equation of motion and the equation of continuity to describe the flow field. In fact, we take Oseen's equation as the equation of motion, and apply the equation of continuity for an incompressible fluid. A complete discussion on the validity of Oseen's equation is given by Lamb (18). Furthermore, a modern treatment based on perturbation theory can be found in the book of Van Dyke (29). We have

$$U_0 \frac{\partial \underline{u}}{\partial x} = -\frac{1}{\rho}\nabla p + \nu\nabla^2 \underline{u} \quad , \tag{4-1}$$

$$\nabla \cdot \underline{u} = 0 \quad , \tag{4-2}$$

with the boundary conditions

$$\underline{u} = U_0 \underline{e}_x \qquad \text{at} \quad r = \infty \quad , \tag{4-3}$$

$$p = p_0 \qquad \text{at} \quad r = \infty \ , \tag{4-4}$$

where $\underline{e}_x$ is the unit vector along the X-axis, and $\underline{u}$, p, ρ, ν all have their conventional meanings. The two boundary conditions given here are not sufficient to solve the problem. A third one is necessary to make the solution unique. This will appear when we match the "outer" solution with the "inner" solution in section 4.4. Defining dimensionless variables,

$$\overline{r} = \frac{r}{a} \quad , \tag{4-5}$$

$$\overline{p} = \frac{p - p_0}{\rho U_0^2} \quad , \tag{4-6}$$

$$\overline{\underline{u}} = \frac{\underline{u}}{U_0} - \underline{e}_x \quad . \tag{4-7}$$

We can write the equation of motion and the equation of continuity as

$$\frac{\partial}{\partial \overline{x}} \overline{\underline{u}} = - \overline{\nabla}\, \overline{p} + \frac{1}{R_e} \overline{\nabla}^2 \overline{\underline{u}} \quad , \tag{4-8}$$

$$\overline{\nabla} \cdot \overline{\underline{u}} = 0 \quad , \tag{4-9}$$

with the boundary conditions,

$$\overline{\underline{u}} = 0 \qquad \text{at} \quad \overline{r} = \infty \quad , \tag{4-10}$$

$$\overline{p} = 0 \qquad \text{at} \quad \overline{r} = \infty \quad , \tag{4-11}$$

where

$$R_e = \frac{U_0 a}{\nu} \quad . \tag{4-12}$$

Equations (4-8), (4-9), (4-10), and (4-11) can be solved to give the results (see Appendix 4A),

$$\underline{\overline{u}} = -\overline{\nabla}\Phi + \frac{1}{2g_1}\overline{\nabla}X - X\underline{e}_x \quad , \tag{4-13}$$

$$\overline{p} = \frac{\partial \Phi}{\partial \overline{x}} \quad , \tag{4-14}$$

where

$$\Phi = \sum_{\ell=0}^{\infty} \overline{A}_\ell P_\ell(\cos\theta)\,\overline{r}^{-(\ell+1)} \quad , \tag{4-15}$$

$$X = \sum_{\ell=0}^{\infty} \overline{B}_\ell P_\ell(\cos\theta) h_\ell^{(1)}(ig_1\overline{r}) \exp(g_1\overline{x}) \quad , \tag{4-16}$$

where P_ℓ is the Legendre polynomial, $h_\ell^{(1)}$ is the spherical Hankel function of the first kind, and g_1 is defined as

$$g_1 = \frac{R_e}{2} \quad . \tag{4-17}$$

The coefficients $\overline{A}_\ell$ and $\overline{B}_\ell$ are unknown constants and will be determined later when we match the "inner" and "outer" solutions.

According to Lamb (18), we need to keep only two terms in the series of equation (4-15) and only one term in the series of equations (4-16). In fact, we can show that the drag force coefficient will not be improved by taking more terms. Thus we have

$$\frac{\underline{u}}{U_0} = \left\{1 + \frac{\overline{B}_0}{2g_1\overline{r}} \exp\left[-g_1\overline{r}(1 - \cos\theta\right]\right\} (\underline{e}_r\cos\theta - \underline{e}_\theta\sin\theta)$$

$$+ \left\{\frac{\overline{A}_0}{\overline{r}^2} + \frac{2\overline{A}_1\cos\theta}{\overline{r}^3} + \frac{\overline{B}_0}{2g_1}\left(\frac{1}{\overline{r}} + \frac{1}{g_1\overline{r}^2}\right) \exp\left[-g_1\overline{r}(1 - \cos\theta)\right]\right\} \underline{e}_r$$

$$+ \frac{\overline{A}_1\sin\theta}{\overline{r}^3}\,\underline{e}_\theta \qquad (4\text{-}18)$$

$$p = p_0 - \rho U_0^2\left[\frac{\overline{A}_0\cos\theta}{\overline{r}^2} + \frac{\overline{A}_1(3\cos^2\theta - 1)}{\overline{r}^3}\right], \qquad (4\text{-}19)$$

where $\underline{e}_r$, $\underline{e}_\theta$ are unit vectors in the r,θ direction.

4.3 The "inner" solution

We look for an "inner" solution based on the assumption that the distribution function for the molecules coming toward the surface of the sphere is Maxwellian. That is,

$$f_i = \frac{\rho}{m}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left\{-\frac{m}{2kT}\left[(\xi_r - W_r)^2 + (\xi_\theta - W_\theta)^2 + \xi_\phi^2\right]\right\}, \qquad (4\text{-}20)$$

where ρ is the density, m the molecular mass, T the temperature, $\underline{W}$ the mean velocity, and $\underline{\xi}$ the random velocity. The third component of the mean velocity vanishes since the problem is independent of the azimuthal angle.

The stress tensor, which contributes to the aerodynamic force on the sphere, is calculated in Appendix 4B. In the present case the only significant components are p_{rr} and $p_{r\theta}$ given by

$$p_{rr} = \frac{\rho kT}{m}\left\{\frac{2-\sigma'}{\sqrt{\pi}}\left[-S_r \exp(-S_r^2) + \sqrt{\pi}\left(\frac{1}{2} + S_r^2\right)(1 - \operatorname{erf}(S_r))\right] + \frac{\sigma'}{2}\left[\exp(-S_r^2) - \sqrt{\pi}S_r(1 - \operatorname{erf}(S_r))\right]\right\} , \tag{4-21}$$

$$p_{r\theta} = -\sigma\frac{\rho kT}{m\sqrt{\pi}} S_\theta\left[\exp(-S_r^2) - \sqrt{\pi}S_r(1 - \operatorname{erf}(S_r))\right] , \tag{4-22}$$

where S_r and S_θ are molecular speed ratios defined as

$$S_r = \frac{W_r}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}} , \tag{4-23}$$

$$S_\theta = \frac{W_\theta}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}} , \tag{4-24}$$

erf (S_r) is the error function of S_r, and σ, σ' are the accommodation coefficients for the shear stress and the normal stress. Schaaf (26) has given a complete discussion on the various kinds of accommodation coefficients. By using the assumption of low Mach number flow there is obtained

$$p_{rr} = \frac{\rho kT}{m}\left[1 - \frac{4}{\sqrt{\pi}}S_r + \sigma'\left(\frac{2}{\sqrt{\pi}} - \frac{\sqrt{\pi}}{2}\right)S_r\right] , \tag{4-25}$$

$$p_{r\theta} = -\sigma\frac{\rho kT}{\sqrt{\pi m}} S_\theta . \tag{4-26}$$

4.4 Matching

This is the crucial point of the present method since it provides the boundary conditions needed for both the "outer" and the "inner" solutions. The principles given in Chapter 3 will be employed here for the velocity field and the stress tensor. We match the velocity of the "outer" solution at $r = a$ with the velocity of the "inner" solution at infinity. That is

$$\lim_{r\to a} (\underline{u})_{\text{outer}} = \lim_{r\to\infty} (\underline{u})_{\text{inner}} \quad . \tag{4-27}$$

This leads to the result,

$$\begin{aligned}\underline{W} = {} & U_0 \left\{ 1 + \frac{\overline{B}_0}{2g_1} \exp[-g_1(1 - \cos\theta)] \right\} (\underline{e}_r \cos\theta - \underline{e}_\theta \sin\theta) \\ & + U_0 \left\{ \overline{A}_0 + 2\overline{A}_1 \cos\theta + \frac{\overline{B}_0}{2g_1}\left(1 + \frac{1}{g_1}\right) \exp[-g_1(1 - \cos\theta)] \right\} \underline{e}_r \\ & + \overline{A}_1 U_0 \sin\theta\, \underline{e}_\theta \quad . \end{aligned} \tag{4-28}$$

On the other hand, we shall match the stress tensor of the two solutions at the same position, namely at $r = a$,

$$(\underline{\underline{p}})_{\text{outer}} = (\underline{\underline{p}})_{\text{inner}} \qquad \text{at} \quad r = a \quad . \tag{4-29}$$

Schaaf (26) has identified the component p_{rr} with the thermodynamic pressure p in the free molecular flow case. In the continuum flow regime, the relation between $p_{r\theta}$ and the velocity gradient is given by Bird (1)

$$p_{r\theta} = -\mu\left[r\frac{\partial}{\partial r}\left(\frac{u_\theta}{r}\right) + \frac{1}{r}\,\frac{\partial u_r}{\partial\theta} \right] \tag{4-30}$$

where μ is the viscosity of the gas. Evaluating p and $p_{r\theta}$ at the sphere, we obtain

$$p = p_0 - \rho U_0^2[\overline{A}_0 \cos\theta + \overline{A}_1(3\cos^2\theta - 1)] \quad , \tag{4-31}$$

$$p_{r\theta} = \frac{U_0\mu}{a}\left\{6\overline{A}_1 + \overline{B}_0 \cos\theta \exp[-g_1(1-\cos\theta)]\right\}\sin\theta \quad . \tag{4-32}$$

By equating (4-25) with (4-31) and (4-26) with (4-32) we obtain

$$\overline{A}_0\cos\theta + \overline{A}_1(3\cos^2\theta - 1)$$
$$= \frac{a\ell}{2R_e\lambda}[\cos\theta + \overline{A}_0 + 2\overline{A}_1\cos\theta + \frac{\overline{B}_0}{2g_1^2}(1 + 2g_1\cos\theta)] \quad , \tag{4-33}$$

$$6\overline{A}_1 + \overline{B}_0\cos\theta(1 - g_1 + g_1\cos\theta)$$
$$= -\frac{\sigma a}{2\lambda}[-1 + \overline{A}_1 - \frac{\overline{B}_0}{2g_1}(1 - g_1 + g_1\cos\theta)] \quad , \tag{4-34}$$

where we have used the ideal gas law,

$$p_0 = \frac{\rho kT}{m} \quad , \tag{4-35}$$

and have defined λ and ℓ as

$$\lambda = \frac{\nu}{\left(\frac{2kT}{\pi m}\right)^{\frac{1}{2}}} \quad , \tag{4-36}$$

$$\ell = 4 - \sigma'(2 - \frac{\pi}{2}) \quad . \tag{4-37}$$

Since the functions 1, $\cos\theta$, $3\cos^2\theta - 1$, ... form an orthogonal set for θ from 0 to π, their individual coefficients must be equal on both sides. Therefore

$$\overline{A}_0 + \frac{\overline{B}_0}{2g_1^2} = 0 \quad , \tag{4-38}$$

$$\overline{A}_0 = \frac{a\ell}{2R_e\lambda}(1 + 2\overline{A}_1 + \frac{\overline{B}_0}{g_1}) \quad , \tag{4-39}$$

$$6\overline{A}_1 = -\frac{\sigma a}{2\ell}\left[-1 + \overline{A}_1 - \frac{\overline{B}_0}{2g_1}(1 - g_1)\right] \quad , \tag{4-40}$$

and other relations that are not needed.

Solving equations (4-38), (4-39), (4-40), we obtain

$$\overline{A}_0 = \frac{6\,Kn + \frac{3}{2}\sigma}{\frac{12\,Kn^2}{\ell} + (\frac{\sigma}{\ell} + 6)Kn + \sigma - \frac{\sigma}{2}g_1} \frac{\nu}{U_0 a} \quad , \tag{4-41}$$

$$\overline{A}_1 = \frac{\frac{\sigma}{\ell}Kn + \frac{\sigma}{4} + \frac{\sigma}{4}g_1}{\frac{12\,Kn^2}{\ell} + (\frac{\sigma}{\ell} + 6)Kn + \sigma - \frac{\sigma}{2}g_1} \quad , \tag{4-42}$$

$$\overline{B}_0 = -g_1 \frac{6\,Kn + \frac{3}{2}\sigma}{\frac{12\,Kn^2}{\ell} + (\frac{\sigma}{\ell} + 6)Kn + \sigma - \frac{\sigma}{2}g_1} \quad , \tag{4-43}$$

where Kn is defined as

$$Kn = \frac{\lambda}{a} \quad . \tag{4-44}$$

4.5 Results and comparisons

The drag force on the sphere can be calculated by taking the X-component of the equation

$$\underline{f} = p_{rr}\underline{e}_r - p_{r\theta}\underline{e}_\theta \quad , \tag{4-45}$$

and integrating it over the whole surface of the sphere:

$$F_D = 2\pi U_0 \mu a \frac{4(\ell + 2\sigma)Kn + (3 + Re)\sigma\ell}{12\,Kn^2 + (\sigma + 6\ell)Kn + \sigma\ell(1 - \frac{Re}{4})} \quad . \tag{4-46}$$

The continuum flow limit of this equation,

$$(F_D)_{\text{cont.}} = 6\pi\mu U_0 a\left(1 + \frac{7}{12}\text{Re}\right) \quad , \tag{4-47}$$

agrees with Stokes' formula for low Reynolds number flow. On the other hand, the free molecular flow limit is

$$(F_D)_{\text{f.m.}} = S_0 \rho a^2 \frac{kT}{m} \frac{4\sqrt{\pi}}{3} (\ell + 2\sigma) \quad , \tag{4-48}$$

where

$$S_0 = \frac{U_0}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}} \quad . \tag{4-49}$$

For the case of diffuse reflection, where $\ell = 2 + \frac{\pi}{2}$ and $\sigma = 1$, we have

$$(F_D)_{\text{f.m.}} = \frac{16}{3}\sqrt{\pi}\left(1 + \frac{\pi}{8}\right)\frac{kT}{m} S_0 \rho a^2 \quad , \tag{4-50}$$

which agrees exactly with the corresponding expression given by Willis (30).

Defining a drag force coefficient C_D as

$$C_D = \frac{F_D}{\frac{1}{2}\rho U_0^2 a^2} \quad , \tag{4-51}$$

we obtain

$$\frac{C_D}{(C_D)_{\text{f.m.}}} = \frac{3\,\text{Kn}\left[4(\ell + 2\sigma)\text{Kn} + \sigma\ell(3 + \text{Re})\right]}{\left[12\,\text{Kn}^2 + (\sigma + 6\ell)\text{Kn} + \sigma\ell\left(1 - \frac{1}{4}\text{Re}\right)\right](\ell + 2\sigma)} \quad , \tag{4-52}$$

where $(C_D)_{\text{f.m.}}$ is the drag force coefficient in the free molecular flow limit. Values of $C_D/(C_D)_{\text{f.m.}}$ are listed in Table II and plotted in Figure 7.

Table II. Drag force coefficient on a sphere versus the Knudsen number Kn

Kn	The present results (Eq. (4-52))	Millikan's formula (Eq. (4-53))	Sherman's formula (Eq. (4-54))
100.0	0.986	0.996	0.994
50.0	0.973	0.992	0.988
20.0	0.936	0.981	0.971
10.0	0.881	0.962	0.943
5.0	0.791	0.925	0.892
2.0	0.617	0.824	0.767
1.0	0.468	0.685	0.622
0.5	0.331	0.499	0.452
0.2	0.191	0.264	0.248
0.1	0.117	0.147	0.141
0.05	0.067	0.078	0.076
0.01	0.016	0.016	0.016

In his famous oil drop experiment Millikan (25) obtained from the data of the drag force on a sphere the empirical formula,

$$\frac{C_D}{(C_D)_{f.m.}} = \frac{1.648}{1.234 + \frac{1}{Kn} + 0.414 \exp(-0.876/Kn)} \quad . \tag{4-53}$$

Sherman (28) also proposed an interpolation formula,

$$\frac{C_D}{(C_D)_{f.m.}} = \frac{1}{1 + \frac{0.685\sqrt{\pi}}{2\,Kn}} \quad . \tag{4-54}$$

Both formulas are tabulated in Table II and plotted in Figure 7 for comparison.

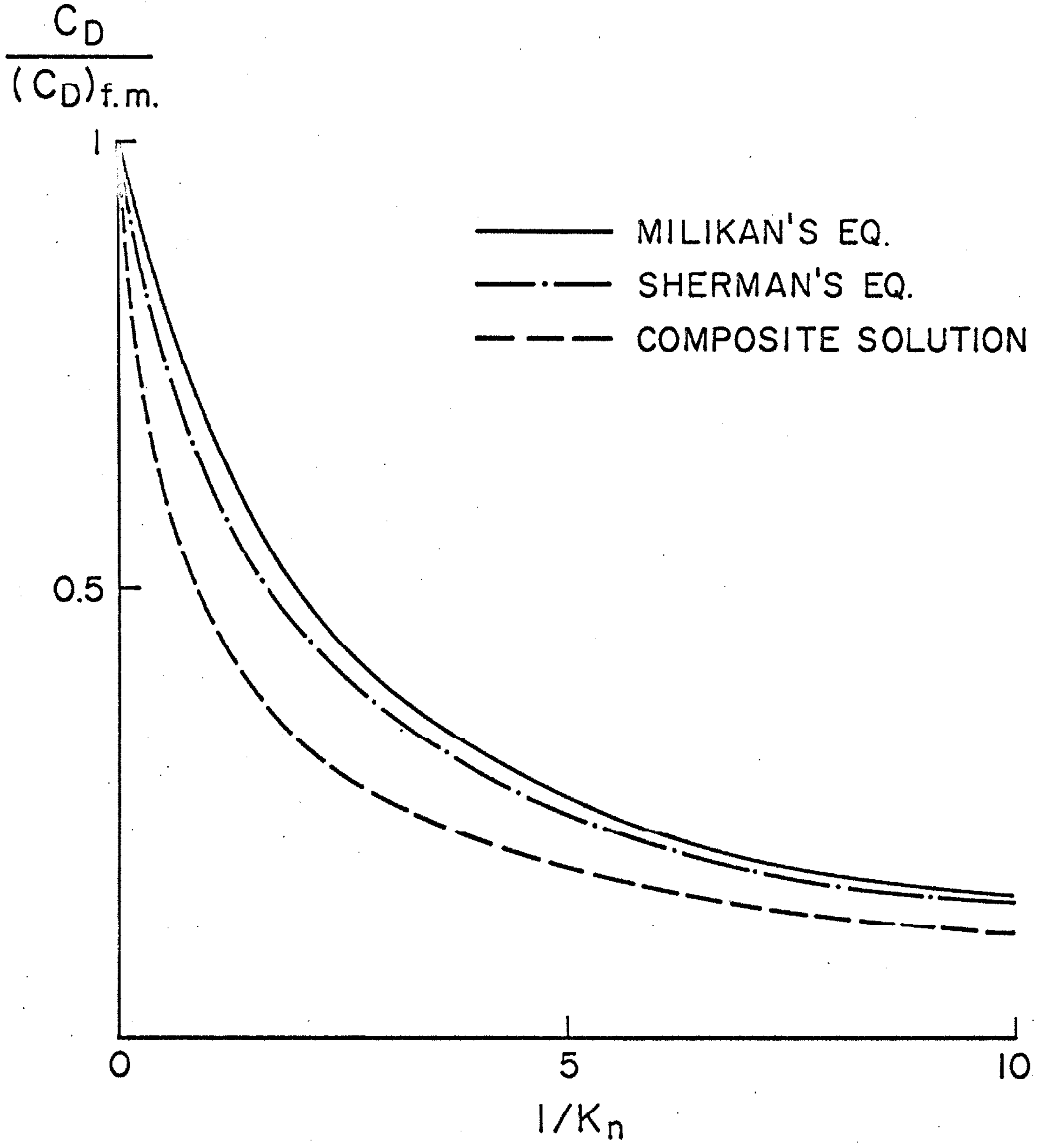

Fig. 7 DRAG FORCE COEFFICIENT OF A SPHERE

Appendix 4A

SOLUTION OF THE DIMENSIONLESS OSEEN'S EQUATION

We shall solve

$$\frac{\partial \underline{\bar{u}}}{\partial \bar{x}} = - \bar{\nabla} \bar{p} + \frac{1}{R_e} \bar{\nabla}^2 \underline{\bar{u}} \ , \tag{4A-1}$$

$$\bar{\nabla} \cdot \underline{\bar{u}} = 0 \ , \tag{4A-2}$$

with the boundary conditions

$$\underline{\bar{u}} = 0 \qquad \text{at} \quad \bar{r} = \infty \ , \tag{4A-3}$$

$$\bar{p} = 0 \qquad \text{at} \quad \bar{r} = \infty \ , \tag{4A-4}$$

following the method of Lamb (18).

In the first place we have

$$\bar{\nabla}^2 \bar{p} = 0 \ , \tag{4A-5}$$

therefore, a particular solution is obtained if we write

$$\underline{\bar{u}} = - \bar{\nabla} \Phi \ , \tag{4A-6}$$

$$\bar{p} = \frac{\partial \Phi}{\partial \bar{x}} \ , \tag{4A-7}$$

where Φ satisfies

$$\bar{\nabla}^2 \Phi = 0 \ . \tag{4A-8}$$

We complete our solution by writing

$$\underline{\bar{u}} = - \bar{\nabla} \Phi + \underline{\bar{u}}' \ , \tag{4A-9}$$

where $\underline{\bar{u}}'$, the rotational velocity field, satisfies

$$\frac{\partial \underline{\bar{u}}'}{\partial \bar{x}} = \frac{1}{2g_1} \bar{\nabla}^2 \underline{\bar{u}}' \quad , \tag{4A-10}$$

$$\bar{\nabla} \cdot \underline{\bar{u}}' = 0 \quad . \tag{4A-11}$$

Here we have written, for simplicity,

$$g_1 = \frac{R_e}{2} \quad . \tag{4A-12}$$

Taking the curl of equations (4A-10) and (4A-11), there is obtained

$$\bar{\nabla}^2 \underline{\bar{\omega}} = 2g_1 \frac{\partial \underline{\bar{\omega}}}{\partial \bar{x}} \quad , \tag{4A-13}$$

$$\bar{\nabla} \cdot \underline{\bar{\omega}} = 0 \quad , \tag{4A-14}$$

where $\underline{\bar{\omega}}$ is the vorticity given by

$$\underline{\bar{\omega}} = \bar{\nabla} \wedge \underline{\bar{u}}' \quad . \tag{4A-15}$$

From the symmetry of the problem, the X-component of $\underline{\bar{\omega}}$ must vanish so that if we put

$$\bar{\omega}_x = 0 \quad , \tag{4A-16}$$

$$\bar{\omega}_y = - \frac{\partial X}{\partial \bar{z}} \quad , \tag{4A-17}$$

$$\bar{\omega}_z = \frac{\partial X}{\partial \bar{y}} \quad , \tag{4A-18}$$

equation (4A-14) is obviously satisfied and equation (4A-13) gives

$$\frac{\partial}{\partial \bar{y}}\left[\left(\bar{\nabla}^2 - 2g_1 \frac{\partial}{\partial \bar{x}}\right)X\right] = 0 \quad , \tag{4A-19}$$

$$\frac{\partial}{\partial \bar{z}}\left[\left(\bar{\nabla}^2 - 2g_1 \frac{\partial}{\partial \bar{x}}\right)X\right] = 0 \quad , \tag{4A-20}$$

which, upon integration, lead to

$$\left(\bar{\nabla}^2 - 2g_1 \frac{\partial}{\partial \bar{x}}\right) X = 0 \quad . \tag{4A-21}$$

The right-hand side of equation (4A-21) is in general a function of $\bar{x}$. Since, however, this function has no effect on the final results it has been set equal to zero.

Using the vector identity,

$$\bar{\nabla}^2 \underline{\bar{u}}' = -\,\overline{\text{curl}}\ \overline{\text{curl}}\ \underline{\bar{u}}' + \overline{\text{grad}}\,(\bar{\nabla}\cdot\underline{\bar{u}}') \quad , \tag{4A-22}$$

we obtain from equation (4A-10)

$$\frac{\partial \underline{\bar{u}}'}{\partial \bar{x}} = -\frac{1}{2g_1}\,\overline{\text{curl}}\ \underline{\bar{\omega}} \quad . \tag{4A-23}$$

Therefore we have

$$\underline{\bar{u}}' = \frac{1}{2g_1} \nabla X - X\underline{e}_x \quad . \tag{4A-24}$$

To find Φ and X, equations (4A-8) and (4A-21) are solved, under the restriction that equations (4A-3) and (4A-4) must be satisfied, to give

$$\Phi = \sum_{\ell=0}^{\infty} \bar{A}_\ell P_\ell(\cos\,\theta)\,\bar{r}^{-(\ell+1)} \quad , \tag{4A-25}$$

$$X = \sum_{\ell=0}^{\infty} \overline{B}_{\ell} P_{\ell}(\cos\theta) h_{\ell}^{(1)}(ig_1\overline{r}) \exp(g_1\overline{x}) \quad , \tag{4A-26}$$

where P_{ℓ} is the Legendre polynomial and $h_{\ell}^{(1)}$ is the spherical Hankel function of the first kind. Finally we have

$$\underline{\overline{u}} = - \overline{\nabla}\Phi + \frac{1}{2g_1} \overline{\nabla} X - X\underline{e}_x \quad , \tag{4A-27}$$

$$\overline{p} = \frac{\partial\Phi}{\partial\overline{x}} \quad . \tag{4A-28}$$

Appendix 4B

STRESS TENSOR IN THE "INNER" SOLUTION

Two components of the stress tensor, p_{rr} and $p_{r\theta}$, will be calculated on the surface of the sphere. Since each of them consists of a part due to the incident molecules and a part due to the reemitted molecules, we write

$$p_{rr} = (p_{rr})_i + (p_{rr})_r \quad , \tag{4B-1}$$

$$p_{r\theta} = (p_{r\theta})_i - (p_{r\theta})_r \quad , \tag{4B-2}$$

where the minus sign in front of $(p_{r\theta})_r$ arises because of change of normal direction during reflection. From the definition of stress tensor, we have

$$\begin{aligned}(p_{rr})_i &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{0} m\xi_r^2 f_i \, d^3\xi \\ &= \frac{\rho kT}{m\sqrt{\pi}} \left\{ -S_r \exp(-S_r^2) + \sqrt{\pi}\left(\frac{1}{2} + S_r^2\right)(1 - \mathrm{erf}(S_r)) \right\} ,\end{aligned} \tag{4B-3}$$

$$\begin{aligned}(p_{r\theta})_i &= \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{0} m\xi_r\xi_\theta f_i \, d^3\xi \\ &= \frac{\rho kT}{m\sqrt{\pi}} S_\theta \left\{ \exp(-S_r^2) - \sqrt{\pi}\, S_r(1 - \mathrm{erf}(S_r)) \right\} ,\end{aligned} \tag{4B-4}$$

where S_r and S_θ are the molecular speed ratios defined by

$$S_r = \frac{W_r}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}} \quad , \tag{4B-5}$$

$$S_\theta = \frac{W_\theta}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}} , \tag{4B-6}$$

and erf (S_r) is the error function of S_r. To obtain $(p_{rr})_r$ and $(p_{r\theta})_r$, we define the accommodation coefficients σ and σ' as

$$\sigma = \frac{(p_{r\theta})_i - (p_{r\theta})_r}{(p_{r\theta})_i - (p_{r\theta})_w} , \tag{4B-7}$$

$$\sigma' = \frac{(p_{rr})_i - (p_{rr})_r}{(p_{rr})_i - (p_{rr})_w} , \tag{4B-8}$$

where $(p_{r\theta})_w$ and $(p_{rr})_w$ correspond to molecules reflected with Maxwellian distribution at the surface temperature. The values of σ and σ' vary from 1 to 0 and depend on the nature of the solid gas interaction. The case $\sigma = \sigma' = 1$ is called diffuse reflection as all the reflected molecules are in Maxwellian distribution, while the case $\sigma = \sigma' = 0$, in which no molecules are reflected in Maxwellian distribution, is called specular reflection.

It can be calculated easily that $(p_{r\theta})_w = 0$ and

$$(p_{rr})_w = \frac{1}{2}(2\pi mkT)^{\frac{1}{2}} j_r , \tag{4B-9}$$

where j_r is the reflected flux which in steady state is equal to the incident flux j_i given by

$$j_i = -\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{0} \xi_r f_i \, d^3\xi$$

$$= \frac{\rho}{m}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}\left[\exp(-S_r^2) - \sqrt{\pi}\, S_r(1 - \mathrm{erf}(S_r))\right] . \tag{4B-10}$$

Combining all these together, we obtain equations (4-21) and (4-22).

Chapter 5

FLOW OF A PARTIALLY DISSOCIATED GAS PAST A SPHERE

5.1 Introduction

In this chapter we consider the same flow problem as before, with the flow medium being a partially dissociated diatomic gas. Surface recombination reaction of the dissociated atoms will be considered here. From now on, we shall refer to the dissociated atoms as species 1 and the undissociated molecules as species 2. We assume the mole fraction of species 1 to be small so that the temperature field can be taken as constant.

We shall solve this problem in a way similar to that in Chapter 4. All the assumptions and notations in Chapter 4 still hold in the present case.

5.2 The "outer" solution

Since the variation of concentration is small, all the physical properties are assumed to be constant. The diffusion equation is written as

$$(\underline{u} \cdot \nabla) x_1 = D_{12} \nabla^2 x_1 \quad , \tag{5-1}$$

where x_1 is the mole fraction of species 1. Using the fact that the diffusivity D_{12} has the same order of magnitude as the kinematic viscosity ν for the gas, an approximate equation similar to the Oseen's equation for equation (5-1) can be obtained. In dimensionless form it is

$$\frac{\partial x_1}{\partial \bar{x}} = \frac{1}{\mathrm{Re}\ \mathrm{Sc}} \bar{\nabla}^2 x_1 \quad , \tag{5-2}$$

where

$$\mathrm{Re} = \frac{aU_0}{\nu} \quad , \tag{5-3}$$

$$\mathrm{Sc} = \frac{\nu}{D_{12}} \quad , \tag{5-4}$$

with given boundary condition at infinity,

$$x_1 = X_1 \qquad \text{at} \qquad \bar{r} = \infty \quad . \tag{5-5}$$

In addition, we have the dimensionless Oseen's equation and the equation of continuity,

$$\frac{\partial \underline{\bar{u}}}{\partial \bar{x}} = -\bar{\nabla}\,\bar{p} + \frac{1}{\mathrm{Re}} \bar{\nabla}^2 \underline{\bar{u}} \quad , \tag{5-6}$$

$$\bar{\nabla} \cdot \underline{\bar{u}} = 0 \quad , \tag{5-7}$$

with

$$\underline{\bar{u}} = 0 \qquad \text{at} \qquad \bar{r} = \infty \quad , \tag{5-8}$$

$$\bar{p} = 0 \qquad \text{at} \qquad \bar{r} = \infty \quad , \tag{5-9}$$

where $\underline{\bar{u}}$ and $\bar{p}$ have the same meaning as in Chapter 4. The missing boundary conditions at the sphere will be determined in the process of matching. Notice that the equation for x_1 is independent of the flow field because of the assumed low Reynolds number. This fact will simplify the matching procedure in section 5.4. The flow field has the same solution as before,

$$\underline{\bar{u}} = -\overline{\nabla}\Phi + \frac{1}{2g_1}\overline{\nabla} X - X\underline{e}_x \quad , \tag{5-10}$$

$$\bar{p} = \frac{\partial \Phi}{\partial \bar{x}} \quad , \tag{5-11}$$

where Φ and X are given by

$$\Phi = \sum_{\ell=0}^{\infty} \bar{A}_\ell P_\ell(\cos\theta)\,\bar{r}^{-(\ell+1)} \quad , \tag{5-12}$$

$$X = \sum_{\ell=0}^{\infty} \bar{B}_\ell P_\ell(\cos\theta) h_\ell^{(1)}(ig_1\bar{r}) \exp(g_1\bar{x}) \quad , \tag{5-13}$$

where g_1 has the same meaning as in Chapter 4. Similarly, equations (5-2) and (5-5) yield

$$x_1 = X_1 - \sum_{\ell=0}^{\infty} \bar{C}_\ell P_\ell(\cos\theta) h_\ell^{(1)}(ig_2\bar{r}) \exp(g_2\bar{x}) \quad , \tag{5-14}$$

where

$$g_2 = \frac{\mathrm{Re}\ \mathrm{Sc}}{2} \quad . \tag{5-15}$$

Following Chapter 4 we take one term in the series of equations (5-13) and (5-14) and two terms in that of equation (5-12) to obtain

$$\begin{aligned} \underline{u} = {} & U_0\left\{1 + \frac{\bar{B}_0}{2g_1\bar{r}} \exp[-g_1\bar{r}(1-\cos\theta)]\right\}(\underline{e}_r\cos\theta - \underline{e}_\theta\sin\theta) \\ & + U_0\left\{\frac{\bar{A}_0}{\bar{r}^2} + \frac{2\bar{A}_1\cos\theta}{\bar{r}^3} + \frac{\bar{B}_0}{2g_1}\left(\frac{1}{\bar{r}} + \frac{1}{g_1\bar{r}^2}\right) \exp[-g_1\bar{r}(1-\cos\theta)]\right\}\bar{e}_r \\ & + \frac{\bar{A}_1}{\bar{r}^3} U_0 \sin\theta\, \underline{e}_\theta \quad , \end{aligned} \tag{5-16}$$

$$p = p_0 - \rho U_0^2\left(\overline{A}_0 \frac{\cos\theta}{\overline{r}^3} + \overline{A}_1 \frac{3\cos^2\theta - 1}{\overline{r}^3}\right) \quad , \tag{5-17}$$

$$x_1 = X_1 - \frac{\overline{C}_0}{g_2\overline{r}}\exp[-g_2\overline{r}(1 - \cos\theta)] \quad . \tag{5-18}$$

For future matching, we calculate the shear stress $p_{r\theta}$ and the flux of species 1 j_{1r} on the surface of the sphere to be

$$p_{r\theta} = \frac{U_0\mu}{a}(6\overline{A}_1 \sin\theta + \overline{B}_0 \sin\theta\cos\theta) \quad , \tag{5-19}$$

$$\begin{aligned} j_{1r} &= -\frac{\rho}{\overline{m}_0} D_{12} \left.\frac{\partial x_1}{\partial r}\right|_{r=a} \\ &= -\frac{\overline{C}_0 D_{12}}{a g_2 \overline{m}_0}[1 + O(g_2^2)] \quad , \end{aligned} \tag{5-20}$$

where the second and higher order terms of g_1 and g_2 have been neglected, and $\overline{m}_0$ is the upstream mean molecular mass.

5.3 The "inner" solution

The "inner" solution is very complex because of the surface recombination reaction of species 1. Formulation of the boundary conditions at the sphere depends on the nature of reaction and on the degree of rarefaction. For simplicity we define the sticking probability as the fraction of the incoming flux of species 1 that undergoes recombination. That is

$$\sigma_s' = \frac{j_{1i} - j_{10}}{j_{1i}} \quad , \tag{5-21}$$

where j_{1i} is the incident flux and j_{10} is the outgoing flux for species i. In the transitional flow regime this sticking probability is independent of both the incident and the outgoing fluxes.

Following Chapter 4, the parts of species 1 and 2 coming towards the sphere are assumed to be in Maxwellian distribution with mean velocities $\underline{W}_1$ and $\underline{W}_2$ respectively. It should be mentioned that $\underline{W}_1$ and $\underline{W}_2$, to be determined by the matching procedure, are different because of the diffusion effect in the "outer" solution. Thus we have

$$f_{1i} = \frac{\rho_1}{m_1}\left(\frac{m_1}{2\pi kT}\right)^{\frac{3}{2}} \exp\left\{-\frac{m_1}{2kT}[(\xi_{1r} - W_{1r})^2 + (\xi_{1\theta} - W_{1\theta})^2 + \xi_{1\phi}^2]\right\} , \tag{5-22}$$

$$f_{2i} = \frac{\rho_2}{m_2}\left(\frac{m_2}{2\pi kT}\right)^{\frac{3}{2}} \exp\left\{-\frac{m_2}{2kT}[\xi_{2r} - W_{2r})^2 + (\xi_{2\theta} - W_{2\theta})^2 + \xi_{2\phi}^2]\right\} , \tag{5-23}$$

where the density ρ_i, the molecular mass m_i, the random velocity $\underline{\xi}_i$ are for species i. Because of the symmetry of the problem, the mean velocities $\underline{W}_1$ and $\underline{W}_2$ have no components in the azimuthal direction.

It can be calculated easily that the incident fluxes for species 1 and 2 are

$$j_{1i} = \frac{\rho_1}{m_1}\left(\frac{kT}{2\pi m_1}\right)^{\frac{1}{2}} [\exp(-S_{1r}^2) - \sqrt{\pi}\, S_{1r}(1 - \mathrm{erf}(S_{1r}))] , \tag{5-24}$$

$$j_{2i} = \frac{\rho_2}{m_2}\left(\frac{kT}{2\pi m_2}\right)^{\frac{1}{2}} [\exp(-S_{2r}^2) - \sqrt{\pi}\, S_{2r}(1 - \mathrm{erf}(S_{2r}))] , \tag{5-25}$$

where $\mathrm{erf}(S_{ir})$ is the error function of S_{ir} and

$$S_{1r} = \frac{W_{1r}}{\left(\frac{2kT}{m}\right)^{\frac{1}{2}}} \quad , \tag{5-26}$$

$$S_{2r} = \frac{W_{2r}}{\left(\frac{2kT}{m_2}\right)^{\frac{1}{2}}} \quad . \tag{5-27}$$

Using the definition of the sticking probability and the fact that at steady state there is no accumulation of mass on the surface, we obtain the outgoing fluxes,

$$j_{1o} = (1 - \sigma'_s)\frac{\rho_1}{m_1}\left(\frac{kT}{2\pi m_1}\right)^{\frac{1}{2}}[\exp(-S_{1r}^2) - \sqrt{\pi}\, S_{1r}(1 - \mathrm{erf}(S_{1r}))] \quad , \tag{5-28}$$

$$\begin{aligned} j_{2o} = {} & \frac{\sigma'_s \rho_1}{2m_1}\left(\frac{kT}{2\pi m_1}\right)^{\frac{1}{2}}[\exp(-S_{1r}^2) - \sqrt{\pi}\, S_{1r}(1 - \mathrm{erf}(S_{1r}))] \\ & + \frac{\rho_2}{m_2}\left(\frac{kT}{2\pi m_2}\right)^{\frac{1}{2}}[\exp(-S_{2r}^2) - \sqrt{\pi}\, S_{2r}(1 - \mathrm{erf}(S_{2r}))] \quad . \end{aligned} \tag{5-29}$$

Hence the net outward flux of species 1 is

$$\begin{aligned} j_{1r} &= j_{1o} - j_{1i} \\ &= -\sigma'_s \frac{\rho_1}{m_1}\left(\frac{kT}{2\pi m_1}\right)^{\frac{1}{2}}[\exp(-S_{1r}^2) - \sqrt{\pi}\, S_{1r}(1 - \mathrm{erf}(S_{1r}))] \quad . \end{aligned} \tag{5-30}$$

The normal pressure and the shear stress on the surface of the sphere can be calculated in a way similar to that of Chapter 4, only with more terms involved. In fact, each of the species contributes independently so that

$$p_{rr} = (p_{rr})_1 + (p_{rr})_2 \quad , \tag{5-31}$$

$$p_{r\theta} = (p_{r\theta})_1 + (p_{r\theta})_2 \quad , \tag{5-32}$$

where the subscripts 1 and 2 represent the parts contributed by species 1 and 2. If we define σ_1', σ_2' the accommodation coefficients of the normal stress and σ_1, σ_2 those of the shear stress for species 1 and 2, we get

$$\begin{aligned}(p_{rr})_1 = {} & (2-\sigma_1')\frac{\rho_1 kT}{m_1\sqrt{\pi}}[-S_{1r}\exp(-S_{1r}^2) + \sqrt{\pi}(\tfrac{1}{2}+S_{1r}^2)(1-\operatorname{erf}(S_{1r}))] \\ & + \frac{\sigma_1'}{2}(1-\sigma_s')\frac{\rho_1 kT}{m_1}[\exp(-S_{1r}^2) - \sqrt{\pi}S_{1r}(1-\operatorname{erf}(S_{1r}))] \quad ,\end{aligned} \tag{5-33}$$

$$\begin{aligned}(p_{rr})_2 = {} & (2-\sigma_2')\frac{\rho_2 kT}{m_2\sqrt{\pi}}[-S_{2r}\exp(-S_{2r}^2) + \sqrt{\pi}(\tfrac{1}{2}+S_{2r}^2)(1-\operatorname{erf}(S_{2r}))] \\ & + \sqrt{2}\,\sigma_s'\sigma_2'\frac{\rho_1 kT}{4m_1}[\exp(-S_{1r}^2) - \sqrt{\pi}S_{1r}(1-\operatorname{erf}(S_{1r}))] \\ & + \frac{\sigma_2'}{2}\frac{\rho_2 kT}{m_2}[\exp(-S_{2r}^2) - \sqrt{\pi}S_{2r}(1-\operatorname{erf}(S_{2r}))] \quad ,\end{aligned} \tag{5-34}$$

$$(p_{r\theta})_1 = -\sigma_1\frac{\rho_1 kT}{m_1\sqrt{\pi}}[\exp(-S_{1r}^2) - \sqrt{\pi}\,S_{1r}(1-\operatorname{erf}(S_{1r}))]\,S_{1\theta} \quad , \tag{5-35}$$

$$(p_{r\theta})_2 = -\sigma_2\frac{\rho_2 kT}{m_2\sqrt{\pi}}[\exp(-S_{2r}^2) - \sqrt{\pi}\,S_{2r}(1-\operatorname{erf}(S_{2r}))]\,S_{2\theta} \quad , \tag{5-36}$$

where

$$S_{1\theta} = \frac{W_{1\theta}}{\left(\frac{2kT}{m_1}\right)^{\frac{1}{2}}} \quad , \tag{5-37}$$

$$S_{2\theta} = \frac{W_{2\theta}}{\left(\frac{2kT}{m_2}\right)^{\frac{1}{2}}} \quad . \tag{5-38}$$

Finally using the low Mach number assumption, we obtain

$$p_{rr} = p_0 - [4 - \sigma_1'(2 - \frac{\pi}{2})] \frac{S_{1r}}{\sqrt{\pi}} p_0 Y_1 - [4 - \sigma_2'(2 - \frac{\pi}{2})] \frac{S_{2r}}{\sqrt{\pi}} p_0 (1 - Y_1)$$

$$- \frac{\sigma_s'}{2} (\sigma_1' - \frac{\sqrt{2}}{2} \sigma_2')(1 - \sqrt{\pi}\, S_{1r}) Y_1 p_0 \quad , \tag{5-39}$$

$$p_{r\theta} = - \sigma_1 \frac{S_{1\theta}}{\sqrt{\pi}} p_0 Y_1 - \sigma_2 \frac{S_{2\theta}}{\sqrt{\pi}} p_0 (1 - Y_1) \quad , \tag{5-40}$$

$$j_{1r} = - \sigma_s' \frac{Y_1 p_0}{(2\pi m_1 kT)^{\frac{1}{2}}} (1 - \sqrt{\pi}\, S_{1r}) \quad , \tag{5-41}$$

where we have used the ideal gas law,

$$p_0 = \left(\frac{\rho_1}{m_1} + \frac{\rho_2}{m_2} \right) kT \quad , \tag{5-42}$$

and the definition of the mole fraction for species 1 at infinity

$$Y_1 = \frac{\rho_1 / m_1}{\frac{\rho_1}{m_1} + \frac{\rho_2}{m_2}} \quad . \tag{5-43}$$

5.4 Matching

Matching is extremely difficult in this case because the "inner" solution contains so many terms. In order to simplify the problem and to get a clear view of the results, we have to use the assumption of low mole fraction of species 1 and neglect all second and higher order terms in it. The matching principles employed in Chapters 3 and 4 will be used. They are

$$\lim_{r \to a} (\underline{u}_i)_{\mathrm{outer}} = \lim_{r \to \infty} (\underline{u}_i)_{\mathrm{inner}} \quad , \tag{5-44}$$

$$\lim_{r \to a} (x_1)_{\mathrm{outer}} = \lim_{r \to \infty} (x_1)_{\mathrm{inner}} \quad , \tag{5-45}$$

$$(\underline{\underline{p}})_{\mathrm{outer}} = (\underline{\underline{p}})_{\mathrm{inner}} \qquad \text{at} \quad r = a \quad , \tag{5-46}$$

$$(j_{1r})_{\mathrm{outer}} = (j_{1r})_{\mathrm{inner}} \qquad \text{at} \quad r = a \quad , \tag{5-47}$$

where equation (5-44) holds for $i = 1$ and 2. These lead to the following relations:

$$\begin{aligned} \underline{W}_1 = {} & U_0(\cos\theta\,\underline{e}_r - \sin\theta\,\underline{e}_\theta) + U_0[\overline{A}_0 + 2\overline{A}_1\cos\theta + \frac{\overline{B}_0}{2g_1^2}(1 + 2g_1\cos\theta)]\underline{e}_r \\ & + U_0[\overline{A}_1 - \frac{\overline{B}_0}{2g_1}(1 - g_1 + g_1\cos\theta)]\sin\theta\,\underline{e}_\theta - \frac{m_2}{Y_1\overline{m}_0}D_{12}\nabla x_1\Big|_{r=a} , \end{aligned} \tag{5-48}$$

$$\begin{aligned} \underline{W}_2 = {} & U_0(\cos\theta\,\underline{e}_r - \sin\theta\,\underline{e}_\theta) + U_0[\overline{A}_0 + 2\overline{A}_1\cos\theta + \frac{\overline{B}_0}{2g_1^2}(1 + 2g_1\cos\theta)]\underline{e}_r \\ & + U_0[\overline{A}_1 - \frac{\overline{B}_0}{2g_1}(1 - g_1 + g_1\cos\theta)]\sin\theta\,\underline{e}_\theta + \frac{m_1 D_{12}}{(1-Y_0)\overline{m}_0}\nabla x_1\Big|_{r=a} , \end{aligned} \tag{5-49}$$

$$Y_1 = X_1 - \frac{\overline{C}_0}{g_2}(1 - g_2 + g_2\cos\theta) \quad , \tag{5-50}$$

$$\begin{aligned} & \rho U_0^2[\overline{A}_0\cos\theta - \overline{A}_1(1 - 3\cos^2\theta)] \\ & \qquad = \frac{\ell Y_1 p_0 W_{1r}}{\left(\frac{2\pi kT}{m_1}\right)^{\frac{1}{2}}} + \frac{\ell(1-Y_1)p_0 W_{2r}}{\left(\frac{2\pi kT}{m_2}\right)^{\frac{1}{2}}} + \frac{\sigma_s'\sigma'}{2}(1 - \frac{\sqrt{2}}{2})Y_1 p_0\left(1 - \frac{W_{1r}}{\left(\frac{2kT}{\pi m_1}\right)^{\frac{1}{2}}}\right), \end{aligned} \tag{5-51}$$

$$\frac{U_0\mu}{a}\left[\,6\overline{A}_1+\overline{B}_0\cos\theta(1-g_1+g_1\cos\theta)\right]\sin\theta$$
$$= -\frac{\sigma Y_1 p_0 W_{1\theta}}{\left(\frac{2\pi kT}{m_1}\right)^{\frac{1}{2}}}-\frac{\sigma(1-Y_1)p_0 W_{2\theta}}{\left(\frac{2\pi kT}{m_2}\right)^{\frac{1}{2}}} \quad , \tag{5-52}$$

$$\frac{\overline{C}_0 D_{12}\rho}{a g_2 \overline{m}_0}=\frac{\sigma_s Y_1 p_0}{(2\pi m_1 kT)^{\frac{1}{2}}}\left(1-\frac{W_{1r}}{\left(\frac{2kT}{\pi m_1}\right)^{\frac{1}{2}}}\right) \quad , \tag{5-53}$$

where, for simplicity, we have taken equal accommodation coefficients for the two species:

$$\sigma_1=\sigma_2=\sigma \quad , \tag{5-54}$$

$$\sigma'_1=\sigma'_2=\sigma' \quad , \tag{5-55}$$

and ℓ is defined by

$$\ell = 4-\sigma'(2-\frac{\pi}{2}) \quad . \tag{5-56}$$

Solving equations (5-48) to (5-53), we obtain (see Appendix 5A) expressions for $\overline{A}_0$, $\overline{A}_1$, $\overline{B}_0$, $\overline{C}_0$ as

$$\overline{A}_0=\frac{\nu}{U_0 a}\Delta_2+\frac{\nu}{U_0 a}\,\frac{3+\frac{12\,Kn}{\sigma}(1-\Delta_1)-2\frac{Kn}{\ell}\Delta_2-24\frac{Kn^2}{\sigma\ell}\Delta_2}{\frac{24\,Kn^2}{\sigma\ell}(1-2\Delta_1)+\frac{12\,Kn}{\sigma}(1-\Delta_1)+\frac{2\,Kn}{\ell}(1-\Delta_1)+2-g_1} \quad , \tag{5-57}$$

$$\overline{A}_1=\frac{\frac{1}{2}+2\frac{Kn}{\ell}(1-\Delta_1)+\frac{g_1}{2}+\frac{Kn}{\ell}\Delta_2}{\frac{24\,Kn^2}{\sigma\ell}(1-2\Delta_1)+12\frac{Kn}{\sigma}(1-\Delta_1)+2\frac{Kn}{\ell}(1-\Delta_1)+2-g_1} \quad , \tag{5-58}$$

$$\overline{B}_0 = -g_1 \frac{3 + \frac{12\,Kn}{\sigma}(1 - \Delta_1) - \frac{2\,Kn}{\ell}\Delta_2 - 24\frac{Kn^2}{\sigma\ell}\Delta_2}{\frac{24\,Kn^2}{\sigma\ell}(1-2\Delta_1) + \frac{12\,Kn}{\sigma}(1 - \Delta_1) + \frac{2\,Kn}{\ell}(1 - \Delta_1) + 2 - g_1} , \qquad (5\text{-}59)$$

$$\overline{C}_0 = \frac{\sqrt{2}\,\sigma'_s g_2 X}{\frac{2\,Kn}{\overline{G}} + \sqrt{2}\,\sigma_s} , \qquad (5\text{-}60)$$

where

$$\Delta_1 = \left(1 - \frac{\sqrt{2}}{2}\right)\frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,Kn}{\overline{G}} + \sqrt{2}\,\sigma'_s} , \qquad (5\text{-}61)$$

$$\Delta_2 = \left(1 - \frac{\sqrt{2}}{2}\right)\frac{\ell - \sigma'\pi}{\ell}\;\frac{\sigma'_s X_1}{2\,Kn + \sqrt{2}\,\sigma'_s\overline{G}} , \qquad (5\text{-}62)$$

$$\overline{G} = \frac{g_2}{g_1} , \qquad (5\text{-}63)$$

$$Kn = \frac{\nu}{a\left(\frac{2kT}{\pi m_2}\right)^{\frac{1}{2}}} . \qquad (5\text{-}64)$$

5.5 Results and discussions

We are interested in finding the concentration distribution, the molar flux of species 1 toward the sphere, and the effect of the recombination reaction on the drag force. First of all, the mole fraction x_1 in the "outer" solution can be obtained by substituting the expression for $\overline{C}_0$ into equation (5-18)

$$(x_1)_{outer} = X_1 - \frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,Kn}{\overline{G}} + \sqrt{2}\,\sigma'_s}\;\frac{1}{\overline{r}}\exp\left[-g_2\overline{r}(1 - \cos\theta)\right] . \qquad (5\text{-}65)$$

To get x_1 in the "inner" solution, we have to calculate the number densities for the two species. It can be shown that

$$n_1 = \frac{1}{2}\frac{\rho_1}{m_1}\left(1+\sin\alpha - 2\frac{S_{1r}}{\sqrt{\pi}}\cos^2\alpha\right) + \frac{1}{2}(1-\sigma'_s)\frac{\rho_1}{m_1}(1-\sqrt{\pi}S_{1r})(1-\sin\alpha)\ , \tag{5-66}$$

$$n_2 = \frac{1}{2}\frac{\rho_2}{m_2}\left(1+\sin\alpha - 2\frac{S_{2r}}{\sqrt{\pi}}\cos^2\alpha\right) + \frac{1}{2}\left[\frac{\rho_2}{m_2}(1-\sqrt{\pi}S_{2r}) + \sigma'_s\frac{1}{\sqrt{2}}\frac{\rho_1}{m_1}(1-\sqrt{\pi}S_{1r})\right](1-\sin\alpha)\ , \tag{5-67}$$

where n_1 and n_2 are the number densities for species 1 and 2, and

$$\alpha = \text{arc}\cos\frac{a}{r}\ . \tag{5-68}$$

Therefore

$$(x_1)_{\text{inner}} = \frac{n_1}{n_1+n_2} = Y_1\left[1 - \frac{\sigma'_s}{2}(1-\sin\alpha)\right]\ . \tag{5-69}$$

Substituting the value of Y_1 from Appendix 5A, we obtain

$$(x_1)_{\text{inner}} = \left[1 - \frac{\sigma'_s}{2}(1-\sin\alpha)\right]\frac{\frac{2\,Kn}{\overline{G}} + \sqrt{2}\,\sigma_s g_2(1-\cos\theta)}{\frac{2\,Kn}{\overline{G}} + \sqrt{2}\,\sigma'_s}X_1\ . \tag{5-70}$$

Finally we use equation (3-57) to obtain the composite solution,

$$x_1 = X_1 - \frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,Kn}{\nu}D_{12} + \sqrt{2}\,\sigma'_s}\frac{a}{r}\exp\left[-\frac{U_0 r}{2D_{12}}(1-\cos\theta)\right] - \frac{\sigma_s}{2}(1-\sin\alpha)\frac{2\frac{Kn}{\nu}D_{12} + \sqrt{2}\,\sigma'_s U_0 a(1-\cos\theta)/2D_{12}}{\frac{2\,Kn}{\nu}D_{12} + \sqrt{2}\,\sigma'_s}X_1\ . \tag{5-71}$$

On the surface of the sphere we have

$$x_{1s} = \frac{\left(1 - \frac{\sigma'_s}{2}\right)\left[\frac{2\,\mathrm{Kn}}{\nu} D_{12} + \sqrt{2}\,\sigma'_s U_0 a(1 - \cos\theta)/2D_{12}\right]}{\frac{2\,\mathrm{Kn}}{\nu} D_{12} + \sqrt{2}\,\sigma'_s} X_1 \,. \tag{5-72}$$

From equation (5-20) the molar flux of species 1 is calculated to be

$$j_{1r} = - \frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,\mathrm{Kn}}{\nu} D_{12} + \sqrt{2}\,\sigma'_s} \, \frac{D_{12}\rho}{a\overline{m}_0} \;, \tag{5-73}$$

where the minus sign means that the net flux is actually coming toward the sphere. Finally the drag force on the sphere can be found using the formula in Chapter 4:

$$F_D = 2\pi\mu U_0 a\left[\frac{2}{3}\Delta_2 + \frac{4\,\mathrm{Kn}(1-\Delta_1)(1+2\frac{\sigma}{\ell}) + (3+2g_1)\sigma - 8\,\mathrm{Kn}^2\frac{\Delta_2}{\ell} + \frac{10}{3}\frac{\sigma\,\mathrm{Kn}\,\Delta_2}{\ell}}{\frac{12\,\mathrm{Kn}^2}{\ell}(1-2\Delta_1) + (6+\frac{\sigma}{\ell})\mathrm{Kn}(1-\Delta_1) + \sigma(1-g_1/2)}\right]. \tag{5-74}$$

We will look at some limiting cases and some numerical results.

5.5.1 Continuum flow limit

According to chemical kinetic theory the sticking probability σ'_s vanishes in the continuum flow regime in such a way that

$$\lim_{\mathrm{Kn}\to 0} \frac{\sigma'_s}{\mathrm{Kn}} = S_k \;, \tag{5-75}$$

where S_k *is finite.* Therefore by taking the continuum limit we obtain

$$x_1 = X_1 - \frac{X_1}{1 + \frac{\sqrt{2}\,D_{12}}{S_k \nu}} \frac{a}{r} \exp\left[-\frac{U_0 r}{2D_{12}}(1 - \cos\theta)\right] , \tag{5-76}$$

$$x_{1s} = \frac{\frac{\sqrt{2}\,D_{12}}{S_k \nu} + \frac{U_0 a}{2D_{12}}(1 - \cos\theta)}{1 + \frac{\sqrt{2}\,D_{12}}{S_k \nu}} X_1 \quad , \tag{5-77}$$

$$j_{1r} = - \frac{1}{1 + \frac{\sqrt{2}\,D_{12}}{S_k \nu}} \; \frac{D_{12}\rho}{a\bar{m}_0} X_1 \quad , \tag{5-78}$$

$$F_D = 6\pi \; U_0 a(1 + \frac{7}{12}\,\mathrm{Re}) \quad , \tag{5-79}$$

where in equation (5-79) we have neglected Δ_2 since its value can be shown to be less than $0.035\ X_1$. Notice that if S_k is zero we would get a uniform concentration field and zero flux. On the other hand, if S_k is infinity, we would have

$$x_1 = X_1 \left\{1 - \frac{a}{r} \exp\left[- \frac{U_0 r}{2D_{12}}(1 - \cos\theta)\right]\right\} \quad , \tag{5-80}$$

$$x_{1s} = \frac{U_0 a}{2D_{12}}(1 - \cos\theta)\, X_1 \quad , \tag{5-81}$$

$$j_{1r} = - \frac{D_{12}\rho}{a\bar{m}_0} X_1 \quad . \tag{5-82}$$

The quantity x_{1s} in equation (5-81) is very small because of the assumption of low Reynolds number flow. All these results agree with existing formulas.

5.5.2 Free molecular flow limit

In this limit Kn becomes infinity so that

$$x_1 = X_1[1 - \frac{1}{2}\sigma_s'(1 - \sin\alpha)] \quad , \tag{5-83}$$

$$x_{1s} = X_1(1 - \frac{1}{2}\sigma_s') \quad , \tag{5-84}$$

$$j_{1r} = -\sigma_s' X_1 \frac{\rho}{m_0}\left(\frac{kT}{2\pi m_1}\right)^{\frac{1}{2}} \quad , \tag{5-85}$$

$$F_D = S_0' \frac{4\sqrt{\pi}}{3} \frac{\rho}{m_2} kTa^2(\ell + 2\sigma) \quad , \tag{5-86}$$

where

$$S_0' = \frac{U_0}{\left(\frac{2kT}{m_2}\right)^{\frac{1}{2}}} \quad . \tag{5-87}$$

Equation (5-83) gives a simple idea of how the mole fraction of species 1 varies with the distance from the sphere. Equation (5-84) shows that x_1 has half the value of X_1 even if σ_s' is unity. Equation (5-86) shows that in the present approximation the drag force is not changed by the recombination reaction.

5.5.3 Numerical results

Since the results contain so many parameters, they cannot be plotted in a two-dimensional diagram unless we specify some of the parameters whose effects are not so important. We shall neglect the terms proportional to the Reynolds number and take the Schmidt number Sc to be unity,

$$\frac{D_{12}}{\nu} = 1 \quad . \tag{5-88}$$

We also use an empirical formula for σ_s' (Chapter 7),

$$\sigma_s' = \frac{S_k \mathrm{Kn}}{1 + \beta S_k \mathrm{Kn}} \quad , \tag{5-89}$$

where β is a constant. With these relations equations (5-72), (5-73), (5-84), and (5-85) yield

$$\frac{x_{1s}}{(x_{1s})_{f.m.}} = \frac{1}{1 + \frac{1}{2}\,\frac{\sqrt{2}\,S_k}{1 + \beta S_k \mathrm{Kn}}} \quad , \tag{5-90}$$

$$\frac{j_{1r}}{(j_{1r})_{f.m.}} = \frac{1}{1 + \frac{1}{2}\,\frac{\sqrt{2}\,S_k}{1 + \beta S_k \mathrm{Kn}}} \quad . \tag{5-91}$$

These two equations are plotted in Figure 8 with various numbers of β and S_k. The change of drag force due to the recombination reaction as a function of Knudsen number is

$$\frac{F_D}{(F_D)_0} = \frac{\frac{2}{3}\Delta_2 + \frac{4(\ell + 2)\mathrm{Kn}(1 - \Delta_1) + 3\ell - 8\,\mathrm{Kn}^2\Delta_2 + \frac{10}{3}\mathrm{Kn}\,\Delta_2}{12\,\mathrm{Kn}^2(1 - 2\Delta_1) + (1 + 6\ell)\mathrm{Kn}(1 - \Delta_1) + \ell}}{\frac{4(\ell + 2)\mathrm{Kn} + 3\ell}{12\,\mathrm{Kn}^2 + (1 + 6\ell)\mathrm{Kn} + \ell}} \quad , \tag{5-92}$$

where $(F_D)_0$ is the drag force with no recombination reaction. Values of $[F_D/(F_D)_0] - 1$ are plotted in Figure 9 for the case of diffuse reflection and $X_1 = 0.1$. The drag force correction due to the recombination is so small that we are not sure whether Figure 9 is correct or not.

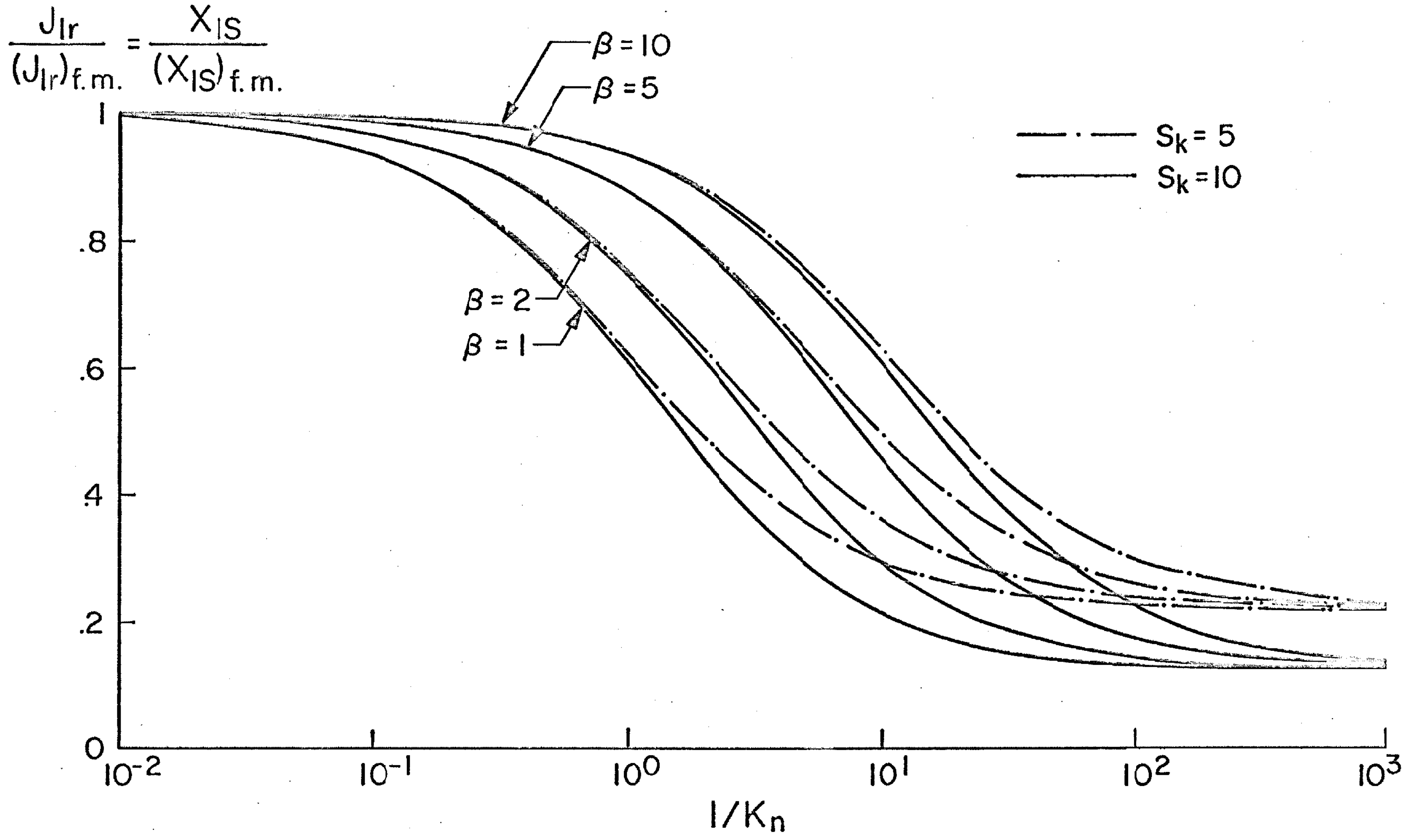

Fig. 8 RADIAL FLUX AND THE CONCENTRATION OF THE ATOMS ON THE SPHERE

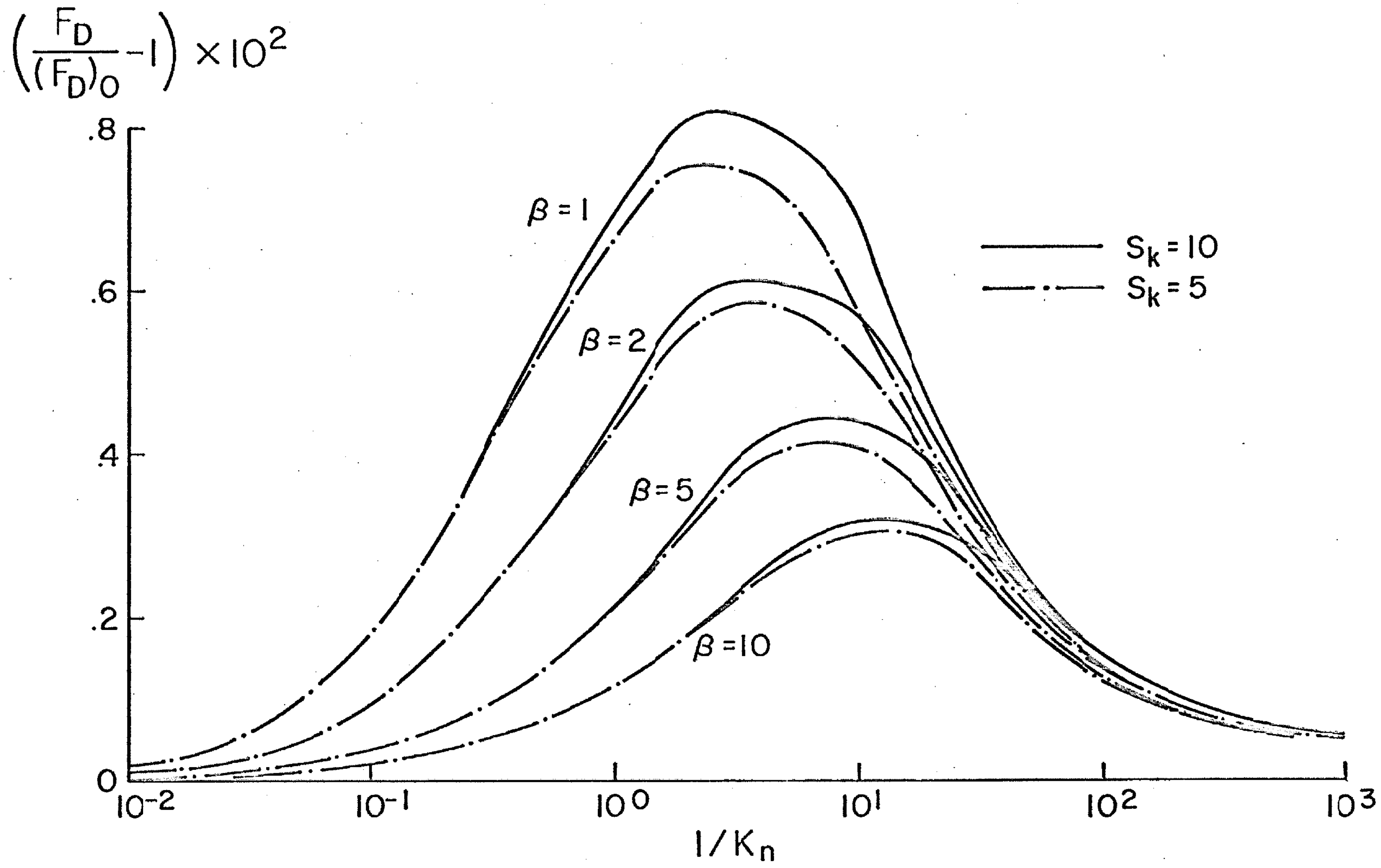

Fig. 9 DRAG FORCE CORRECTIONS DUE TO SURFACE RECOMBINATION REACTION

Appendix 5A

SOLUTION FOR $\overline{A}_0, \overline{A}_1, \overline{B}_0, \overline{C}_0$

We shall solve for $\overline{A}_0, \overline{A}_1, \overline{B}_0, \overline{C}_0$ the following equations:

$$\underline{W}_1 = U_0(\cos\theta\,\underline{e}_r - \sin\theta\,\underline{e}_\theta) + U_0[\overline{A}_0 + 2\overline{A}_1\cos\theta + \frac{\overline{B}_0}{2g_1^2}(1+2g_1\cos\theta)]\,\underline{e}_r$$

$$+ U_0[\overline{A}_1 - \frac{\overline{B}_0}{2g_1}(1-g_1+g_1\cos\theta)]\sin\theta\,\underline{e}_\theta - \frac{m_2}{Y_1\overline{m}_0}D_{12}\nabla x_1\Big|_{r=a}, \qquad (5A\text{-}1)$$

$$\underline{W}_2 = U_0(\cos\theta\,\underline{e}_r - \sin\theta\,\underline{e}_\theta) + U_0[\overline{A}_0 + 2\overline{A}_1\cos\theta + \frac{\overline{B}_0}{2g_1^2}(1+2g_1\cos\theta)]\,\underline{e}_r$$

$$+ U_0[\overline{A}_1 - \frac{\overline{B}_0}{2g_1}(1-g_1+g_1\cos\theta)]\sin\theta\,\underline{e}_\theta + \frac{m_1D_{12}}{(1-Y_1)\overline{m}}\nabla x_1\Big|_{r=a}, \qquad (5A\text{-}2)$$

$$Y_1 = X_1 - \frac{\overline{C}_0}{g_2}(1-g_2+g_2\cos\theta) \quad , \qquad (5A\text{-}3)$$

$$\rho U_0^2[\overline{A}_0\cos\theta - \overline{A}_1(1-3\cos^2\theta)]$$

$$= \frac{\ell Y_1 p_o W_{1r}}{\left(\frac{2\pi kT}{m_1}\right)^{\frac{1}{2}}} + \frac{\ell(1-Y_1)p_o W_{2r}}{\left(\frac{2\pi kT}{m_2}\right)^{\frac{1}{2}}} + \frac{1}{2}\sigma'_s\sigma'\left(1-\frac{\sqrt{2}}{2}\right)\left(1-\frac{W_{1r}}{\left(\frac{2kT}{\pi m_1}\right)^{\frac{1}{2}}}\right)Y_1p_0 \;. \qquad (5A\text{-}4)$$

$$\frac{U_0\mu}{a}[6\overline{A}_1 + \overline{B}_0\cos\theta(1-g_1+g_1\cos\theta)]\sin\theta$$

$$= -\frac{\sigma Y_1 p_0 W_{1\theta}}{\left(\frac{2\pi kT}{m_1}\right)^{\frac{1}{2}}} - \frac{\sigma(1-Y_1)p_o W_{2\theta}}{\left(\frac{2\pi kT}{m_2}\right)^{\frac{1}{2}}} \quad , \qquad (5A\text{-}5)$$

$$\frac{\overline{C}_0 D_{12}\rho}{ag_2\overline{m}_0} = \frac{\sigma'_s Y_1 p_0}{(2\pi m_1 kT)}\left(1 - \frac{W_{1r}}{\left(\frac{2kT}{\pi m_1}\right)^{\frac{1}{2}}}\right) \;. \qquad (5A\text{-}6)$$

First we define

$$\mathrm{Kn} = \frac{\nu}{a\left(\frac{2kT}{\pi m_2}\right)^{\frac{1}{2}}} \quad , \tag{5A-7}$$

$$\overline{G} = \frac{g_2}{g_1} = \frac{\nu}{D_{12}} \quad . \tag{5A-8}$$

Equations (5A-3) and (5A-6) can be solved for $\overline{C}_0$ by neglecting the second term on the right-hand side of equation (5A-6). Thus we obtain

$$\overline{C}_0 = \frac{\sqrt{2}\,\sigma'_s g_2 X_1}{\frac{2\mathrm{Kn}}{\overline{G}} + \sqrt{2}\,\sigma'_s} \quad , \tag{5A-9}$$

$$Y_1 = \frac{2\,\mathrm{Kn}/\overline{G} + \sqrt{2}\,\sigma'_s g_2 (1 - \cos\theta)}{\frac{2\,\mathrm{Kn}}{\overline{G}} + \sqrt{2}\,\sigma'_s} \quad . \tag{5A-10}$$

Substituting these results into equation (5-18), there is obtained

$$\left.\frac{\partial x_1}{\partial r}\right|_{r=a} = \frac{\sqrt{2}\,\sigma'_s X_1}{\left(\frac{2\,\mathrm{Kn}}{\overline{G}} + \sqrt{2}\,\sigma'_s\right) a} \quad , \tag{5A-11}$$

$$\left.\frac{1}{r}\frac{\partial x_1}{\partial \theta}\right|_{r=a} = \frac{\sqrt{2}\,\sigma'_s g_2 X_1 \sin\theta}{\left(\frac{2\,\mathrm{Kn}}{\overline{G}} + \sqrt{2}\,\sigma'_s\right) a} \quad . \tag{5A-12}$$

By using equations (5A-1), (5A-2), (5A-11) and (5A-12), equations (5A-4) and (5A-5) can be simplified to

$$8g_1^2\mathrm{Kn}[\overline{A}_0\cos\theta+\overline{A}_1(1-3\cos^2\theta)] = \left(1-\frac{1}{\sqrt{2}}\right)(\sigma'\pi-\ell)\frac{\sigma'_s X_1}{2\,\mathrm{Kn}+\sqrt{2}\,\sigma'_s\overline{G}}$$

$$+2g_1\ell\left[1+\left(1-\frac{1}{\sqrt{2}}\right)\frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,\mathrm{Kn}}{\overline{G}}+\sqrt{2}\,\sigma'_s}\right]\left[\cos\theta+\overline{A}_0+2\overline{A}_1\cos\theta+\frac{\overline{B}_0}{2g_1^2}(1+2g_1\cos\theta)\right], \quad (5A\text{-}13)$$

$$2\,\mathrm{Kn}[\,6\overline{A}_1+\overline{B}_0\cos\theta(1-g_1+g_1\cos\theta)]$$

$$= -\sigma\left[-1+\overline{A}_1-\frac{\overline{B}_0}{2g_1}(1-g_1+g_1\cos\theta)\right]\left[1+\left(1-\frac{1}{\sqrt{2}}\right)\frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,\mathrm{Kn}}{\overline{G}}+\sqrt{2}\,\sigma'_s}\right]. \quad (5A\text{-}14)$$

Since the functions 1, $\cos\theta$, $3\cos^2\theta-1$, etc. form an orthogonal set for θ from 0 to π, we have from equations (5A-13) and (5A-14) the relations,

$$4g_1\mathrm{Kn}\,\overline{A}_0 = \ell\,(1+\Delta_1)\left(1+2\overline{A}_1+\frac{\overline{B}_0}{g_1}\right), \quad (5A\text{-}15)$$

$$2g_1(1+\Delta_1)\left(\overline{A}_0+\frac{\overline{B}_0}{2g_1^2}\right)-\Delta_2 = 0, \quad (5A\text{-}16)$$

$$12\overline{A}_1\mathrm{Kn} = \sigma\left[1-\overline{A}_1+\frac{\overline{B}_0}{2g_1}(1-g_1)\right](1+\Delta_1), \quad (5A\text{-}17)$$

where

$$\Delta_1 = \left(1-\frac{1}{\sqrt{2}}\right)\frac{\sqrt{2}\,\sigma'_s X_1}{\frac{2\,\mathrm{Kn}}{\overline{G}}+\sqrt{2}\,\sigma'_s}, \quad (5A\text{-}18)$$

$$\Delta_2 = \left(1-\frac{1}{\sqrt{2}}\right)\frac{\ell-\sigma'\pi}{\ell}\;\frac{\sigma'_s X_1}{2\,\mathrm{Kn}+\sqrt{2}\,\sigma'_s\overline{G}}. \quad (5A\text{-}19)$$

Solving equations (5A-15) to (5A-17), we obtain

$$\overline{A}_0 = \frac{1}{2}\frac{1}{g_1}\Delta_2 + \frac{1}{2}\frac{1}{g_1}\frac{3 + \frac{12\,\mathrm{Kn}}{\sigma}(1-\Delta_1) - \frac{2\,\mathrm{Kn}}{\ell}\Delta_2 - \frac{24\,\mathrm{Kn}^2}{\sigma\ell}\Delta_2}{\frac{24\,\mathrm{Kn}^2}{\sigma\ell}(1-2\Delta_1) + \frac{12\,\mathrm{Kn}}{\sigma}(1-\Delta_1) + \frac{2\,\mathrm{Kn}}{\ell}(1-\Delta_1) + 2 - g_1}, \tag{5A-20}$$

$$\overline{B}_0 = -g_1\frac{3 + \frac{12\,\mathrm{Kn}}{\sigma}(1-\Delta_1) - \frac{2\,\mathrm{Kn}}{\ell}\Delta_2 - \frac{24\,\mathrm{Kn}^2}{\sigma\ell}\Delta_2}{\frac{24\,\mathrm{Kn}^2}{\sigma\ell}(1-2\Delta_1) + \frac{12\,\mathrm{Kn}}{\sigma}(1-\Delta_1) + \frac{2\,\mathrm{Kn}}{\ell}(1-\Delta_1) + 2 - g_1}, \tag{5A-21}$$

$$\overline{A}_1 = \frac{\frac{1}{2} + \frac{2\,\mathrm{Kn}}{\ell}(1-\Delta_1) + \frac{1}{2}g_1 + \frac{\mathrm{Kn}}{\ell}\Delta_2}{\frac{24\,\mathrm{Kn}^2}{\sigma\ell}(1-2\Delta_1) + \frac{12\,\mathrm{Kn}}{\sigma}(1-\Delta_1) + \frac{2\,\mathrm{Kn}}{\ell}(1-\Delta_1) + 2 - g_1}. \tag{5A-22}$$

Chapter 6

REACTION OF A PARTIALLY DISSOCIATED GAS WITH A SPHERE

6.1 Introduction

In this chapter we consider the flow of a partially dissociated diatomic gas past a sphere with surface recombination reaction and diffusion and reaction of the dissociated atoms in the interior of the sphere. We assume this latter reaction to be instantaneous due to the high reactivity of the dissociated atoms so that the diffusion process of the atoms inside the sphere controls the total rate. Also the product of the reaction is assumed to be solid. Examples of such reactions are the formation of hydrides and the oxidation of the transition metals.

The general problem is very complex because the diffusion process inside the sphere is in unsteady state which, through boundary relations, causes the flow field in the gas stream also to be in unsteady state. Besides, a complete study of the gas-solid interaction on the interface is too complex to be included in the present work. We shall, therefore, take a simple case where diffusion of the dissolved atoms inside the solid is so slow that the flow field in the gas stream can be considered in steady state, with modified boundary conditions which include the effect of diffusion in the sphere. In section 6.2 we shall study the interfacial phenomena to find the relation between the fluxes in the gas stream and the concentration of the atoms in the solid. In section 6.3 the unsteady state diffusion equation with infinitely fast chemical reaction will be solved. Finally the effect of the solid-gas reaction on the gas stream will be given in section 6.4

6.2 Interfacial relationship between the atomic flux in the gas solid phases

Let the concentration of the dissolved atoms in the solid sphere be c with saturation concentration c^*, and let the fraction of the surface sites occupied by the adsorbed atoms be θ_1. The rate that the adsorbed atoms penetrate into the sphere r_p is proportional to the surface concentration of the adsorbed atoms and the vacancies available for the atoms inside the sphere. That is

$$r_p = k_p \theta_1 (c^* - c) \quad . \tag{6-1}$$

On the other hand, the rate r_0 at which atoms in the solid phase jump to the surface is proportional to the concentration of the atoms in the sphere and the vacant sites on the surface. That is

$$r_0 = k_0 (1 - \theta_1) c \quad . \tag{6-2}$$

The net flow through the surface of the sphere, which can be expressed by Fick's first law of diffusion inside the sphere, is the difference of these two equations. Thus we have

$$-D \frac{\partial c}{\partial r} = k_0 (1 - \theta_1) c + k_p \theta_1 (c - c^*) \quad , \tag{6-3}$$

where $\underline{r}$ is the position vector written in spherical coordinates. The diffusivity D_s is small so that if we neglect the left-hand side of equation (6-3), we have

$$c = \frac{c^*}{1 + \frac{k_0(1-\theta_1)}{k_p \theta_1}} \quad . \tag{6-4}$$

The assumption of small D_s also implies that θ_1 is actually independent of the diffusion process in the sphere since its effect is small. We shall use the empirical formula for θ_1,

$$\theta_1 = \frac{\beta' j_{1i}}{1 + \beta' j_{1i}} \quad , \tag{6-5}$$

based on the results in Chapter 7. Substituting equation (6-5) into equation (6-4), we obtain

$$c = \frac{\beta j_{1i}}{1 + \beta j_{1i}} c^* \quad , \tag{6-6}$$

where

$$\beta = \frac{k_p}{k_0} \beta' \quad , \tag{6-7}$$

as the relation between the concentration of the dissolved atoms in the sphere and the incident atomic flux of the gas stream.

6.3 Diffusion of the dissolved atoms inside the solid sphere with infinitely fast chemical reaction

We assume that the reaction between the dissolved atoms and the solid is instantaneous so that there is a moving reaction boundary with a position at r^*. In the region $r^* < r < a$ the reaction has been completed while in the region $0 < r < r^*$ no reaction has taken place. The moving boundary r^* starts from the surface of the sphere and decreases to zero monotonically. Therefore the diffusion is described by

$$\frac{\partial c}{\partial t} = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial c}{\partial r}\right) \qquad \text{for} \quad r^* < r < a \quad , \tag{6-8}$$

$$c = 0 \qquad \text{for} \quad 0 \leq r \leq r^* \quad , \tag{6-9}$$

with

$$c = 0 \quad \text{at} \quad t = 0 \;, \qquad \text{for all } r \;, \tag{6-10}$$

$$c = c_0 \quad \text{at} \quad r = a \;, \qquad \text{for} \quad t > 0 \;, \tag{6-11}$$

$$c = 0 \quad \text{at} \quad r = r^* \;, \qquad \text{for} \quad t > 0 \;, \tag{6-12}$$

where we have defined

$$c_0 = \frac{\beta j_{1i}}{1 + \beta j_{1i}} c^* \quad . \tag{6-13}$$

In order to carry out the solution, we need one more equation to show the variation of the moving boundary r^* with time. This relation is obtained by considering the mass balance at r^* where the diffusion rate per unit area must be equal to the reaction rate per unit volume swept by the moving boundary in unit time. That is

$$-D_s \frac{\partial c}{\partial r}\bigg|_{r^*} = \bar{\eta} c \frac{dr^*}{dt} \quad , \tag{6-14}$$

with initial condition

$$r^* = a \qquad \text{at} \qquad t = 0 \quad , \tag{6-15}$$

where c_s is the concentration of the pure solid and $\bar{\eta}$ is a stoichiometric constant depending on the type of chemical reaction. Equations (6-8) to (6-12) and (6-14) to (6-15) form a well posed mathematical problem whose exact solution has not been obtained analytically. We shall discuss the approximate method used by Bischoff (2) and shall propose a new approximate method.

6.3.1 The pseudo steady state solution

Bischoff (2) has proposed a method which he called the pseudo steady state solution by considering first the steady state solution of the diffusion equation with fixed r^*, then letting r^* vary with t according to equation (6-14) to obtain

$$r^* = r_0^*\left(1 + \frac{1}{6}\frac{c_0}{\bar{\eta}c_s}\frac{a^2 - r_0^* a}{r_0^{*2}} + \dots\right) , \qquad (6\text{-}16)$$

where r_0^* is the solution of

$$a^3 - 3r_0^{*2}a + 2r_0^{*3} = 6\frac{tD_s}{a^2}\frac{c_0}{\bar{\eta}c_s} . \qquad (6\text{-}17)$$

Equation (6-16) has been commented upon by Bowen (4) who gives a formula for r^* based on a perturbation solution,

$$r^* = a\left[1 - \frac{c_0tD_s}{\bar{\eta}c_sa^2} + \frac{1}{2}\epsilon'\left(\frac{c_0tD_s}{\bar{\eta}c_sa^2}\right)^2\left(1 - \frac{2}{3}\frac{c_0tD_s}{\bar{\eta}c_sa^2}\right) + \dots\right] , \qquad (6\text{-}18)$$

where ϵ' is a perturbation parameter. However, as discussed by Bischoff (3), what Bowen has solved is a reaction controlling problem instead of the diffusion controlling problem under consideration here.

6.3.2 The unsteady solution

We shall use Laplace transform to solve the unsteady state diffusion equation, equation (6-8). Written in dimensionless form, the transformed equation is

$$s\bar{c} = \frac{1}{\bar{r}^2}\frac{d}{d\bar{r}}\left(\bar{r}^2 \frac{d\bar{c}}{d\bar{r}}\right) \quad , \tag{6-19}$$

with boundary conditions

$$\bar{c} = \frac{1}{s} \quad , \qquad \text{at} \qquad r = a \quad , \tag{6-20}$$

$$\bar{c} = 0 \quad , \qquad \text{at} \qquad r = r^* \quad , \tag{6-21}$$

where s is the transform parameter and $\bar{c}$ is the transformed concentration normalized with respect to c_0. Equations (6-19) to (6-21) can be solved by taking r^* as constant. Using inverse transform we obtain

$$\frac{c}{c_0} = \frac{a(r - r^*)}{r(a - r^*)} + \sum_{i=1}^{\infty} \frac{2a(\sin K_i r - \tan K_i a \cos K_i r)}{K_i r(a - r^*)\sec K_i a} \exp(-K_i^2 t D_s) \quad , \tag{6-22}$$

where

$$K_i = \frac{i\pi}{a - r^*} \quad , \qquad i = 1, 2, 3, \ldots \quad . \tag{6-23}$$

The value of $\frac{\partial c}{\partial r}$ is calculated from equation (6-22) and then substituted into equation (6-14) to give

$$\frac{dr^*}{dt} = -\frac{c_0 D_s a}{\bar{\eta} c_s} \frac{1}{r^*(a - r^*)} \left[1 + \sum_{i=1}^{\infty} 2 \exp(-K_i^2 D_s t)\right] \quad , \tag{6-24}$$

with the initial condition,

$$r^* = a \qquad \text{at} \qquad t = 0 \quad . \tag{6-25}$$

The initial value problem (6-24) and (6-25) can be solved numerically but it is interesting to obtain an approximate analytical solution by considering K_i as constant and integrating equation (6-24) to give

$$a^3 - 3r^{*2}a + 2r^{*3} = \frac{6c_0a^3}{\overline{\eta}c_s}\left\{\frac{tD_s}{a^2} + \sum_{i=1}^{\infty}\frac{2}{K_i^2}\left[1 - \exp(-K_i^2tD_s)\right]\right\} , \tag{6-26}$$

6.3.3 Comparisons and discussions

Numerical results for both the unsteady and the pseudo steady state solutions are plotted in Figure 10. The two curves coincide at small t for $c_0/\overline{\eta}c_s = \frac{1}{2}\times 10^{-3}$, but deviate somewhat at large t. Mathematically, if we make a total differentiation of equation (6-12) with respect to time, we would obtain a necessary condition for the moving boundary r^*,

$$\frac{dr^*}{dt} = - \left.\frac{\partial c/\partial t}{\partial c/\partial r}\right|_{r=r^*} \quad . \tag{6-27}$$

It can be calculated that the unsteady solution satisfies this rotation while the pseudo steady state solution does not. This indicates a strong support for the unsteady solution over the pseudo steady state solution. Furthermore, the pseudo steady state solution requires a small $c_0/\overline{\eta}c_s$ to make the series in equation (6-16) converging fast so that it is not valid for liquid-gas interaction where $c_0/\overline{\eta}c_s$ usually

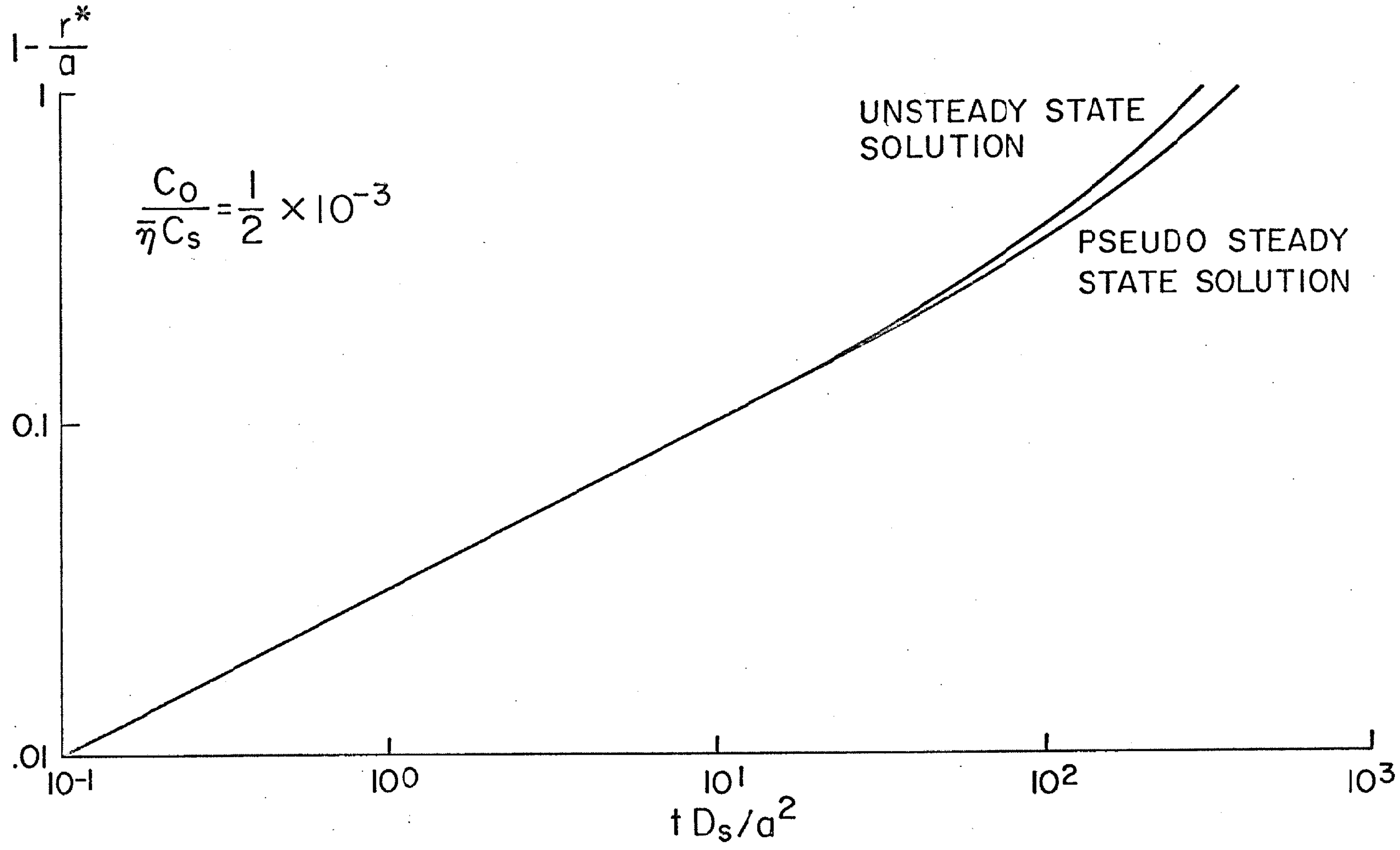

Fig. 10 COMPARISON OF THE UNSTEADY STATE SOLUTION WITH THE PSEUDO STEADY STATE SOLUTION

has a value around unity. The unsteady solution does not require this restriction and, therefore, has a broader range of application.

6.4 The effects of the gas-solid reaction on the gas stream

Although we have stated at the beginning of this chapter that the gas-solid reaction does not change the steady state nature of the gas stream, it does have effects on the gas stream because the total incident mass flux is no longer equal to the reflected one. To obtain a new relation, the flux for the dissolved atoms j_s inside the sphere has to be calculated. From equation (6-22) there is obtained

$$j_s = - D_s c_0 \left\{ \frac{r^*}{a(a - r^*)} + \sum_{i=1}^{\infty} \frac{2}{a - r^*} \exp\left[- \left(\frac{i\pi}{a - r^*} \right)^2 D_s t \right] \right\} \quad , \qquad (6\text{-}28)$$

which is a function of time. Let

$$\Gamma(t) = \frac{r^*}{a - r^*} + \sum_{i=}^{\infty} \frac{2a}{a - r^*} \exp\left[- \left(\frac{i\pi}{a - r^*} \right)^2 D_s t \right] \quad , \qquad (6\text{-}29)$$

be a dimensionless function of time, so that, after substituting equation (6-13), equation (6-28) takes the form

$$j_s = - \frac{D_s \Gamma(t)}{a} \frac{\beta j_{1i}}{1 + \beta j_{1i}} c^* \quad . \qquad (6\text{-}30)$$

Now if the sticking probability σ'_s is defined in the same way as in Chapter 5, we have

$$j_{2o} = j_{2i} + \frac{1}{2} \sigma'_s j_{1i} \quad . \qquad (6\text{-}31)$$

However, instead of equation (5-21), the conservation law on the surface of the sphere becomes

$$j_{1i} + 2j_{2i} + j_s = j_{1o} + 2j_{2o} \quad , \tag{6-32}$$

which implies

$$j_{1o} = j_{1i}\left(1 - \sigma_s' - \frac{\beta}{1+\beta j_{1i}} \frac{D_s\Gamma(t)}{a} c^*\right) \quad . \tag{6-33}$$

With this new boundary condition replacing equation (5-21), the problem in Chapter 5 can be solved once again to give

$$\begin{aligned} x_1 = X_1 &- \frac{\sqrt{2}(\sigma_s' + \sigma_r')X_1}{\frac{2\,\mathrm{Kn}}{\nu} D_{12} + \sqrt{2}(\sigma_s' + \sigma_r')} \frac{a}{r} \exp\left[-\frac{U_0 r}{2D_{12}}(1 - \cos\theta)\right] \\ &- \frac{1}{2}(\sigma_s' + \sigma_r')(1 - \sin\alpha) \frac{\frac{2\mathrm{Kn}}{\nu} D_{12} + \frac{1}{2}\sqrt{2}(\sigma_s' + \sigma_r')U_0 a(1 - \cos\theta)/D_{12}}{\frac{2\,\mathrm{Kn}}{\nu} D_{12} + 2(\sigma_s' + \sigma_r')} X_1 \quad , \end{aligned} \tag{6-34}$$

$$j_{1r} = -\frac{\sqrt{2}(\sigma_s' + \sigma_r')X_1}{\frac{2\,\mathrm{Kn}}{\nu} D_{12} + \sqrt{2}(\sigma_s' + \sigma_r')} \quad \frac{D_{12}\rho}{a\overline{m}} \quad , \tag{6-35}$$

$$F_D = 2\pi\mu U_0 a\left[\frac{2}{3}\Delta_2' + \frac{4\mathrm{Kn}(1-\Delta_1')(1+2\frac{\sigma}{\ell}) + (3+2g_1)\sigma + 8\mathrm{Kn}^2\frac{\Delta_2'}{\ell} - \frac{10\sigma\,\mathrm{Kn}}{3\ell}\Delta_2'}{\frac{12\,\mathrm{Kn}}{\ell}(1 - 2\Delta_1') + (6 + \frac{\sigma}{\ell})\mathrm{Kn}(1 - \Delta_1') + \sigma(1 - \frac{1}{2}g_1)}\right], \tag{6-36}$$

where

$$\sigma_r' = \frac{\beta}{1 + \beta\frac{p_0 X_1}{(2\pi m_1 kT)^{\frac{1}{2}}}} \quad \frac{D_s\Gamma(t)}{a} c^* \quad , \tag{6-37}$$

$$\Delta_1' = (1 - \frac{1}{2}\sqrt{2}) \frac{\sqrt{2}(\sigma_s' + \sigma_r')X_1}{\frac{2\,\mathrm{Kn}}{\overline{G}} + \sqrt{2}(\sigma_s' + \sigma_r')} \quad , \tag{6-38}$$

$$\Delta_2' = \frac{\{(1 - \frac{1}{2}\sqrt{2})\sigma_s' - \frac{\sigma'\pi}{\ell}[(1 - \frac{1}{2}\sqrt{2})\sigma_s' + \sigma_r']\}}{2\,\mathrm{Kn} + \sqrt{2}\,(\sigma_s' + \sigma_r')\,\overline{G}} X_1. \tag{6-39}$$

Notice that σ_r' plays a role similar to σ_s', except that it is a function of time. In general, D_s is small and σ_r' can be neglected.

Chapter 7

THE NATURE OF THE STICKING PROBABILITIES

7.1 Introduction

In this chapter we shall investigate the nature of the sticking probabilities employed in the previous chapters. We consider only the case of dissociation and recombination reactions of a diatomic gas. We are particularly interested in hydrogen because a large amount of work has been associated with it. Both the sticking probability for the dissociation reaction σ_s and the sticking probability for the recombination reaction σ'_s will be discussed. We shall start with the most general case by considering all possible mechanisms and get an overall picture. Then we discuss the mechanisms proposed by Brennan (6) and Laidler (17) separately.

7.2 General case

When a solid surface is placed in contact with a partially dissociated diatomic gas, its surface is covered with adsorbed atoms and adsorbed molecules and is under the constant bombardment by both the atoms and the molecules in the gas stream. Let L be the total number of active sites per unit surface area, θ_1 the fraction of the surface sites occupied by the adsorbed atoms, and θ_2 the fraction occupied by the adsorbed molecules. Also let j_{1i} and j_{2i} be the incident fluxes for atoms and molecules respectively. The most general mechanism which covers all the possible reactions is

$$G_2 + S \underset{k_1}{\overset{\gamma_1}{\rightleftharpoons}} SG_2 \quad ,$$

$$G + S \underset{k_2}{\overset{\gamma_2}{\rightleftharpoons}} SG \quad ,$$

$$SG + G \underset{k_3}{\overset{\gamma_3}{\rightleftharpoons}} SG_2 \quad ,$$

$$SG_2 + S \underset{k_5}{\overset{k_4}{\rightleftharpoons}} 2\,SG \quad ,$$

where S is a surface site, G is a gas atom, and G_2 is a gas molecule. The γ's and the k's are functions of temperature only, and will be taken as constants in the present analysis.

In order to find θ_1 and θ_2, and then the sticking probabilities σ_s and σ_s', we make a steady state assumption on the adsorbed atoms and molecules to obtain

$$\begin{aligned}\gamma_1 j_{2i}(1-\theta_1-\theta_2)L - k_1\theta_2 L + \gamma_3 j_{1i}\theta_1 L - k_3\theta_2 L \\ + k_5\theta_1^2 L^2 - k_4(1-\theta_1-\theta_2)\theta_2 L^2 = 0 \quad ,\end{aligned} \tag{7-1}$$

$$\begin{aligned}\gamma_2 j_{1i}(1-\theta_1-\theta_2)L - k_2\theta_1 L - \gamma_3 j_{1i}\theta_1 L + k_3\theta_3 L \\ - 2k_5\theta_1^2 L^2 + 2k_4(1-\theta_1-\theta_2)\theta_2 L^2 = 0 \quad ,\end{aligned} \tag{7-2}$$

which yield the following expressions for θ_1 and θ_2,

$$\theta_1 = \frac{-(k_4\phi_5 L+\phi_1\phi_3)+[(k_4\phi_5 L+\phi_1\phi_3)^2+(k_5\phi_1^2-\phi_4\phi_7 k_4)(\phi_1\phi_2 L+k_4\phi_6 L^2)]^{\frac{1}{2}}}{(k_5\phi_1^2-k_4\phi_4\phi_7)L} \, , \tag{7-3}$$

if $k_5\phi_1^2 \neq k_4\phi_4\phi_7$,

$$\theta_1 = \frac{\phi_1\phi_2 + k_4\phi_6 L}{2(k_4\phi_5 L + \phi_1\phi_3)} \tag{7-4}$$

if $k_5\phi_1^2 = k_4\phi_4\phi_7$, and

$$\theta_2 = \frac{(2\gamma_1 j_{2i} + \gamma_2 j_{1i}) - \phi_7\theta_1}{\phi_1} \quad , \tag{7-5}$$

where

$$\phi_1 = 2k_1 + k_3 + 2\gamma_1 j_{2i} + \gamma_2 j_{1i} \ , \tag{7-6}$$

$$\phi_2 = k_3\gamma_1 j_{2i} + (k_1 + k_3)\gamma_2 j_{1i} \ , \tag{7-7}$$

$$\phi_3 = \frac{1}{2}[\,(k_1+k_3)k_2 + (k_2+k_3)\gamma_1 j_{2i} + (k_1+k_3)\gamma_2 j_{1i} + \gamma_1\gamma_3 j_{1i} j_{2i} + \gamma_2\gamma_3 j_{1i}^2\,] \quad , \tag{7-8}$$

$$\phi_4 = 2k_1 + k_3 - k_2 + \gamma_3 j_{1i} \ , \tag{7-9}$$

$$\phi_5 = \frac{1}{2}(2k_1+k_3)(k_2 - \gamma_3 j_{1i} + 2\gamma_1 j_{2i} + \gamma_2 j_{1i}) + \frac{1}{2}(2k_1 + k_3 - k_2 + \gamma_3 j_{1i})(2\gamma_1 j_{2i} + \gamma_2 j_{1i}) \quad , \tag{7-10}$$

$$\phi_6 = (2k_1+k_3)(2\gamma_1 j_{2i} + \gamma_2 j_{1i}) \quad , \tag{7-11}$$

$$\phi_7 = k_2 - \gamma_3 j_{1i} + 2\gamma_1 j_{2i} + \gamma_2 j_{1i} \ . \tag{7-12}$$

The sticking probability σ_s is the ratio of the molecular dissociation rate to the incident molecular flux. That is,

$$\sigma_s = \frac{\gamma_1 j_{2i}(1-\theta_1-\theta_2)L - K_1\theta_2 L}{j_{2i}} \, , \qquad (7\text{-}13)$$

ile the sticking probability σ'_s is the ratio of the atomic recombina- on rate to the incident atomic flux. That is

$$\sigma'_s = \frac{\gamma_2 j_{1i}(1-\theta_1-\theta_2)L + \gamma_3 j_{1i}\theta_1 L - k_2\theta_1 L - k_3\theta_2 L}{j_{1i}} \, . \qquad (7\text{-}14)$$

In general both σ_s and σ'_s are functions of temperature through their relationship with the reaction rate constants k's and γ's, and are functions of pressure through their relationship with the incident fluxes. In all the cases we have considered, the temperature on the surface is uniform so that the variation of sticking probability with temperature need not be considered. Equations (7-13) and (7-14), giving the the most general expressions for σ_s and σ'_s, are very tedious because the expressions for θ_1 and θ_2 are very complex. In order to get a better picture, we are going to take some limiting cases in the next two subsections.

7.2.1 Free molecular flow limit

In this case both j_{1i} and j_{2i} are very small so that equations (7-3) and (7-4) yield the same result,

$$\theta_1 = \frac{\gamma_2 j_{1i}}{k_2} + \frac{(k_3 + 2k_4 L)\gamma_1 j_{2i}}{k_2(k_1 + k_3 + k_4 L)} \, , \qquad (7\text{-}15)$$

while equation (7-5) becomes

$$\theta_2 = \frac{\gamma_1 j_{2i}}{k_1 + k_3 + k_4 L} \quad . \tag{7-16}$$

Therefore from equations (7-13) and (7-14) we have

$$\sigma_s = \frac{\gamma_1 (k_3 + k_4 L) L}{k_1 + k_3 + k_4 L} \quad , \tag{7-17}$$

$$\sigma'_s = O(j_{1i}) \rightarrow 0 \quad , \tag{7-18}$$

where in equation (7-18) we have put γ_1 equal to zero to insure no dissociation reaction. Notice that σ_s is a constant while σ'_s is proportional to the incident flux j_{1i}, because the dissociation reaction is of first order while the recombination reaction is of second order in the free molecular flow regime.

7.2.2 Continuum flow limit

In the continuum flow regime we shall discuss the dissociation and recombination reactions separately. For a pure dissociation reaction we assume $\gamma_3 = 0$ and obtain

$$\theta_1 = \frac{k_3 \gamma_1 j_{2i} + (k_1 + k_3) \gamma_2 j_{1i}}{(k_2 + k_3) \gamma_1 j_{2i} + (k_1 + k_3) \gamma_2 j_{1i}} \, , \tag{7-19}$$

after letting both j_{1i} and j_{2i} approach infinity.

From equation (7-5) and (7-13) we obtain

$$\sigma_s = \frac{k_2 k_3 \gamma_1 L}{(k_2 + k_3) \gamma_1 j_{2i} + (k_1 + k_3) \gamma_2 j_{1i}} \quad . \tag{7-20}$$

In the case of a pure recombination, we set $k_3 = k_4 = 0$ to obtain

$$\theta_1 = \frac{k_1 \gamma_2 j_{1i}}{(\gamma_1 j_{2i} + \gamma_2 j_{1i}) \gamma_3 j_{1i}} \quad , \tag{7-21}$$

$$\sigma'_s = \frac{2\gamma_2 k_1 L}{\gamma_1 j_{2i} + \gamma_2 j_{1i}} \quad . \tag{7-22}$$

These results confirm the fact that both σ_s and σ'_s become zero when either of the incident fluxes becomes infinity.

7.3 Mechanism by Brennan

7.3.1 Dissociation reaction

Brennan (5) (6) has investigated the problem of atomization of diatomic molecules on metal surfaces in a thorough and systematic way and has concluded that the mechanism involves a fast equilibrium relation maintained between the adsorbed atoms and the molecules in the gas stream, and a rate determining reaction in which an adsorbed atom breaks away. However, the former relation is no longer true when we reach the free molecular flow regime. Modification can be made by applying the steady state assumption on the adsorbed atoms to the following reaction mechanism:

$$G_2 + 2S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,SG$$

$$SG \xrightarrow{k_2} S + G$$

Thus we have

$$2k_1 j_{2i}(1 - \theta_1)^2 L^2 - 2k_{-1}\theta_1^2 L^2 - k_2 \theta_1 L = 0 \quad , \tag{7-23}$$

which gives

$$\theta_1 = \frac{k_1 j_{2i} L + \frac{1}{4} k_2 - [\, k_1 j_{2i} L(\frac{1}{2} k_2 + k_{-1} L) + k_2^2/16]^{\frac{1}{2}}}{k_1 j_{2i} L - k_{-1} L} \quad , \quad (7\text{-}24)$$

if $k_1 j_{2i} \neq k_{-1}$, and

$$\theta_1 = \frac{k_1 j_{2i} L}{2 k_1 j_{2i} L + \frac{1}{2} k_2} \quad (7\text{-}25)$$

if $k_1 j_{2i} = k_{-1}$. The sticking probability σ_s therefore is

$$\sigma_s = \frac{\frac{1}{2} k_2 \theta_1 L}{j_{2i}}$$

$$= \frac{\frac{1}{2} k_2 [\, k_1 j_{2i} L + \frac{1}{4} k_2 - (k_1 j_{2i} L(\frac{1}{2} k_2 + k_{-1} L) + k_2^2/16)^{\frac{1}{2}}]}{j_{2i}(k_1 j_{2i} - k_{-1})} \quad , \quad (7\text{-}26)$$

if $k_1 j_{2i} \neq k_{-1}$, and

$$\sigma_s = \frac{\frac{1}{2} k_1 k_2 L^2}{2 k_1 j_{2i} L + \frac{1}{2} k_2} \quad , \quad (7\text{-}27)$$

if $k_1 j_{2i} = k_{-1}$. In the free molecular flow limit we have

$$\sigma_s = k_1 L^2 \quad , \quad (7\text{-}28)$$

from either equation (7-26) or (7-27). From the transition regime up to the continuum regime, Brennan has claimed that k_2 is negligible so that

$$\sigma_s = \frac{\frac{1}{2}k_2(k_1 j_{2i})^{\frac{1}{2}}L}{j_{2i}\left((k_1 j_{2i})^{\frac{1}{2}} + (k_{-1})^{\frac{1}{2}}\right)} \quad . \tag{7-29}$$

Notice that if $k_1 j_{2i} << k_{-1}$, we have

$$\sigma_s = \frac{1}{2}k_2 L \frac{(k_1)^{\frac{1}{2}}}{(k_{-1}j_{2i})^{\frac{1}{2}}} \quad , \tag{7-30}$$

while if $k_1 j_{2i} >> k_{-1}$, we have

$$\sigma_s = \frac{\frac{1}{2}k_2 L}{j_{2i}} \quad . \tag{7-31}$$

All these agree with experimental results given by Brennan (5) and confirm our assumptions in the previous chapters.

7.3.2 Recombination reaction

The recombination reaction has the mechanism,

$$G + S \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} SG \quad ,$$

$$2\,SG \xrightarrow{k_{-1}} 2S + G_2 \quad .$$

Using the steady state approximation for the adsorbed atoms, we obtain

$$k_{-2}j_{1i}(1-\theta_1)L - k_2\theta_1 L - 2k_{-1}\theta_1^2 L^2 = 0 \quad , \tag{7-32}$$

which gives

$$\theta_1 = \frac{-(k_2+k_{-2}j_{1i}) + [(k_2+k_{-2}j_{1i})^2 + 8k_{-1}k_{-2}j_{1i}L]^{\frac{1}{2}}}{4k_{-1}L} \quad . \tag{7-33}$$

Therefore the sticking probability for the recombination reaction is

$$\sigma'_s = \frac{2k_{-1}\theta_1^2L^2}{j_{1i}}$$

$$= k_{-2}(1-\theta_1)L - \frac{k_2\theta_1L}{j_{1i}} \quad . \tag{7-34}$$

In the free molecular flow limit where the surface is only sparsely covered, we have

$$\theta_1 = \frac{k_{-2}}{k_2} j_{1i} \quad , \tag{7-35}$$

so that

$$\sigma'_s = O(j_{1i}) \rightarrow 0 \quad . \tag{7-36}$$

On the other hand, by taking the continuum limit there is obtained

$$\theta_1 = 1 \quad , \tag{7-37}$$

$$\sigma'_s = \frac{2k_{-1}L^2}{j_{1i}} \quad . \tag{7-38}$$

7.4 Mechanism by Laidler

7.4.1 Dissociation reaction

Laidler (16) (17) disagrees with Brennan and proposes another mechanism for the dissociation reaction,

$$2S + G_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2\,SG \quad ,$$

$$G_2 + S \underset{k_3}{\rightarrow} SG + G \quad .$$

Following the same procedure as that in section 7.3.1, we apply the steady state approximation to the adsorbed atoms to obtain

$$2k_1 j_{2i}(1-\theta_1)^2 L^2 - 2k_{-1}\theta_1^2 L^2 + k_3 j_{2i}(1-\theta_1)L = 0 \quad , \tag{7-39}$$

and this implies that for $k_1 j_{2i} \neq k_{-1}$

$$\theta_1 = 1 - \frac{-(k_{-1}L + \frac{1}{4}k_3 j_{2i}) + [(k_{-1}L + \frac{1}{4}k_3 j_{2i})^2 + k_{-1}(k_1 j_{2i} - k_{-1})L^2]^{\frac{1}{2}}}{(k_1 j_{2i} - k_{-1})L} \, , \tag{7-40}$$

and for $k_1 j_{2i} = k_{-1}$

$$\theta_1 = 1 - \frac{k_{-1}}{2k_{-1}L + \frac{1}{2}k_3 j_{2i}} \quad . \tag{7-41}$$

Therefore we have for $k_1 j_{2i} \neq k_{-1}$

$$\sigma_s = \frac{k_3 j_{2i}(1-\theta_1)L}{2j_{2i}}$$

$$= \frac{k_3 L}{2} \frac{[(k_{-1}L + \frac{1}{4}k_3 j_{2i})^2 + k_{-1}(k_1 j_{2i} - k_{-1})L^2]^{\frac{1}{2}} - (k_{-1}L + \frac{1}{4}k_3 j_{2i})}{(k_1 j_{2i} - k_{-1})L} \, , \tag{7-42}$$

and for $k_1 j_{2i} = k_{-1}$

$$\sigma_s = \frac{\frac{1}{2}k_3k_{-1}L}{2k_{-1}L + \frac{1}{2}k_3j_{2i}} \quad . \tag{7-43}$$

Taking the free molecular flow limit, we have

$$\sigma_s = \frac{1}{2}k_3L \quad , \tag{7-44}$$

while taking continuum limit, we obtain

$$\sigma_s = \frac{k_{-1}L^2}{j_{2i}} \quad . \tag{7-45}$$

7.4.2 Recombination reaction

The recombination reaction has the mechanism,

$$S + G \underset{k_2}{\overset{k_{-2}}{\rightleftharpoons}} SG \quad ,$$

$$G + SG \underset{k_{-3}}{\rightarrow} S + G_2 \quad .$$

By using the steady state approximation for the adsorbed atoms, we obtain

$$k_{-2}j_{1i}(1 - \theta_1)L - k_2\theta_1L - k_{-3}j_{1i}\theta_1L = 0 \quad , \tag{7-46}$$

which implies

$$\theta_1 = \frac{k_{-2}j_{1i}}{k_{-2}j_{1i} + k_2 + k_{-3}j_{1i}} \quad , \tag{7-47}$$

and the sticking probability σ'_s is

$$\sigma'_s = \frac{k_{-3}k_{-2}j_{1i}L}{k_{-2}j_{1i} + k_2 + k_{-3}j_{1i}} \quad . \tag{7-48}$$

Laidler claims that, except at high temperatures, most metal surfaces are fully covered by atoms even at very low pressure. This implies that k_2 and k_{-3} are so small that

$$\sigma'_s = k_{-3}L \quad , \tag{7-49}$$

which is a constant. However, the value of σ'_s does not vanish when we take the continuum limit. This can be explained by the fact that we have neglected the adsorbed molecules which actually occupy all the surface area in the continuum flow regime.

7.5 Conclusions

We have discussed the most general mechanism where all the possible reactions are taken into account, as well as the two mechanisms proposed by Brennan and Laidler. From the present analysis and the arguments given by Brennan and Laidler we may draw the following conclusions:

1. The sticking probability for the dissociation reaction σ_s is a constant over a wide range of Knudsen numbers from the free molecular flow regime to the transition regime, while above the transition regime it becomes inversely proportional to the square root of the incident flux.

2. The sticking probability for the recombination reaction σ_s' is a constant in the transition regime and is proportional to the incident flux when the pressure becomes extremely low.

3. In the continuum regime, both σ_s and σ_s' are inversely proportional to the incident fluxes for molecules and atoms respectively. This implies that both σ_s and σ_s' are zero in the continuum regime.

These conclusions confirm our assumptions in the previous chapters that the sticking probabilities σ_s and σ_s' are constants in the transition regime and become inversely proportional to the incident fluxes in the continuum regime.

NOTATIONS

A	Constant defined by Eqs. (2-65) and (3-45).
$\overline{A}_0, \overline{A}_1$	Constant coefficients.
A_1, A_2	Constants in collision integrals.
a	Radius of sphere.
B, B'	Integration constants.
$\overline{B}_0$	Constant coefficient.
b	Impact parameter, Figure 3.
C, C'	Integration constants.
$\overline{C}_0$	Constant coefficient.
C_D	Drag force coefficient.
c	Concentration of gas in solid sphere.
c^*	Saturation concentration of gas in solid sphere.
c_0	Defined by equation (6-13).
c_s	Concentration of pure solid in sphere.
$\overline{c}$	Laplace transform of c.
D_{12}	Binary diffusivity, equation (2-50).
D_s	Diffusivity of gas in solid.
D^T	Thermal diffusivity.
d_{ij}	Intermolecular force constants.
E	Integration constant.
$\overline{E}_1^{el}$	Average electronic energy per atom.
$\overline{E}_2^{rot}$	Average rotational energy per molecule.
E_{2j}	Rotational energy states for a molecule.

$\underline{e}_i, \underline{e}_x, \underline{e}_r,$ $\underline{e}_\theta, \underline{e}_\alpha$	Unit vectors.
$\underline{\underline{e}}_i$	Energy flux tensor, equations (2-25) and (2-27).
erf (x)	Error function of x.
F	Integration constant.
$\underline{F}$	External force vector.
F_D	Drag force.
$f, f_i, f_{ij},$ f_{ijk}	Molecular distribution functions.
$f(\alpha)$	Function defined by equation (2-76).
$\underline{f}$	Surface force vector.
G	Symbol of a gas atom.
$\overline{G}$	Defined by equation (5-63).
g_1, g_2	Defined by equations (4-17) and (5-15).
H_i	Molecular enthalpies.
$h_\ell^{(1)}$	Spherical Hankel function of the first kind.
J	Defined by equation (2B-6).
J_{ir}	Mass transfer per unit wire length for species i.
j_i, j_{1i}, j_{2i}	Incident fluxes.
j_r, j_{10}, j_{20}	Reflected fluxes.
j_1, j_2	Total fluxes.
j_{1r}, j_{2r}	Fluxes in the radial direction.
j_s	Flux in solid sphere.
Kn	Knudsen number, equations (4-44) and (5-64).
K_i	Defined by equation (6-23).

k	Boltzmann constant.
k_r	Recombination rate constant, equation (2-31).
k_p, k_0	Constants, equations (6-1) and (6-2).
k_i	Reaction rate constants in Chapter 7.
L	Concentration of surface sites.
ℓ	Defined by equations (4-37) and (5-56).
m, m_1, m_2	Molecular (atomic) masses.
$\overline{m}$	Reduced mass.
$\overline{m}_0$	Average molecular mass.
n, n_i, n_{ij}	Number densities.
$\overline{n}_i, \overline{n}_{ij}$	Dimensionless number densities.
P_ℓ	Legendre polynomials.
p, p_0	Thermodynamic pressures.
$\underline{\underline{p}}, \underline{\underline{p}}_i$	Pressure tensors.
Q_r	Total heat transfer per unit wire length.
$Q^{(i)}$	Defined by equation (2B-7).
$\underline{q}$	Heat (energy) flux vector.
$\underline{q}^{\text{trans.}}$	Translational energy flux vector.
$\underline{q}^{\text{int.}}$	Internal energy flux vector.
$\underline{q}_2^{\text{rot}}$	Rotational energy flux for a diatomic molecule.
R_i	Radius of wire.
R_0	Radius of cylinder.
$\overline{R}$	Dimensionless radius of cylinder.
Re	Reynolds number.
$\underline{r}$	Position vector.
$\overline{\underline{r}}$	Dimensionless position vector.

r	Radial distance.
$\bar{r}$	Dimensionless radial distance.
r_p	Rate atoms penetrate into sphere.
r_0	Rate atoms jump out to surface of sphere.
r^*	Moving boundary.
$\bar{r}^*$	Dimensionless moving boundary.
r_0^*	Solution of equation (6-17).
S	Defined by equations (2-128) and (3-68).
$S_r, S_\theta, S_0,$ $S'_0, S_{ir}, S_{i\theta}$	Molecular speed ratios.
S_{12}	Defined by equation (2-90).
S_k	Defined by equation (5-75).
Sc	Schmidt number.
s	Laplace transform parameter.
T, T_j	Temperatures.
$\bar{T}, \bar{T}_j$	Dimensionless temperatures.
t	Time.
$\underline{U}$	Relative velocity in collision integral.
U_0	Upstream velocity.
$\underline{u}, \underline{u}_i$	Local velocities.
v	Molecular speed, equation (2-47).
$\underline{W}, \underline{W}_i$	Mean velocities.
X	Dimensionless function in equation (4-16).
X_1	Mole fraction of species 1 at infinity.
x_1	Mole fraction of species 1.

x_{1s}	Mole fraction of species 1 at sphere.
Y_1	Mole fraction of species 1 in matching process.

Greek Letters

α	Angle defined by equations (2-7) and (3-25).
α_0	Angle defined by equation (2-66).
β, β'	Empirical constants.
$\Gamma(t)$	Defined by equation (6-29).
γ_i	Reaction rate constants in Chapter 7.
Δ_i, Δ_i'	Dimensionless constants.
δ	Defined by equations (2-116) and (3-46).
δ_{12}	Defined by equation (2-75).
ϵ	Defined by equations (2-42) and (3-47).
ϵ'	Perturbation parameter.
η	Azimuthal angle.
$\bar{\eta}$	Stoichiometric constant.
θ	Polar angle.
θ_i	Fraction of surface sites occupied by species i.
κ_2, κ_{12}	Thermal conductivities.
λ	Mean free path.
$\lambda_1, \lambda_2, \lambda_{12}$	Mean free paths defined by equations (2-51) to (2-53).
μ	Viscosity.
μ_1, μ_2	Viscosities defined by equations (2-48) and (2-49).
ν	Kinematic viscosity.
$\underline{\xi}, \underline{\xi}_i, \underline{\xi}_i'$	Molecular random velocities.
ρ, ρ_i	Mass densities.

σ_s, σ'_s	Sticking probabilities.
σ'_r	Defined by equation (6-37)
$\sigma, \sigma', \sigma_i, \sigma'_i$	Accommodation coefficients.
Φ	Dimensionless function in equation (4-15).
$\Phi(r)$	Potential function of intermolecular force.
ϕ	Angle in Figure 2.
ϕ_i	Defined by equations (7-6) to (7-12).
χ	Angle in Figure 3.
ψ	Function of random velocity.
$\overline{\psi}$	Mean value of ψ.
$\Delta\psi$	Change of ψ due to collisions.
Ω_i	Regions defined by equations (2-5) and (2-6).
ω	Defined by equation (2C-2).
$\overline{\underline{\omega}}$	Dimensionless vorticity.

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PROPOSITION I

SIZE DISTRIBUTION OF PARTICLES CRYSTALLIZED FROM A STATIONARY SUPERSATURATED SOLUTION

A mathematical method is developed to calculate the rate of formation of crystals of spherical shape in a stationary slightly supersaturated solution. As time goes on crystals are growing and new nuclei are being formed until finally all the supersaturated solute is precipitated. Then the particle size distribution can be found from the time each crystal is formed and the growth rate of the crystal.

In a slightly supersaturated solution nuclei will be formed by small agitation. The rate of formation of new nuclei is proportional to the degree of supersaturation by the relation (3),

$$\frac{dN}{dt} = k_1 V(c - c^*)^4 \quad , \tag{I-1}$$

where N is the total number of nuclei in the solution, t is the time, c is the concentration of the solution, c^* is the saturation concentration at the same temperature and pressure, V is the available volume for nucleation, and k_1 is a proportional constant to be determined by experiment.

The particle growth rate is a very complicated function of the time through which the particle has grown, the concentration of the solution, and the other particles presented. For the present case, the solution is slightly supersaturated and the equation of Rhead (4) as well as Coriell and Parker (1) can be used with a small modification. They give the equation of the radius of a growing sphere with constant concentration in the solution,

$$R = 2\lambda(D_s t)^{\frac{1}{2}} \quad , \tag{I-2}$$

where

$$\lambda = \left(\frac{c - c^*}{2(C - c^*)}\right)^{\frac{1}{2}} \quad , \tag{I-3}$$

under the assumption $\lambda^2 << 1$, where R is the radius of the particle, D_s is the surface diffusion coefficient, and C is the concentration inside the precipitate. For a solution with variable concentration, we differentiate R^2 with respect to t to get

$$\frac{dR^2}{dt} = 4\lambda^2 D_s \quad . \tag{I-4}$$

Therefore, there is obtained

$$R = \left[\int_0^t \frac{2(c - c^*)D_s}{C - c^*} dt' + r_c^2\right]^{\frac{1}{2}} , \tag{I-5}$$

where r_c is the critical nucleation radius.

Because small particles have higher chemical potential than larger ones, new nuclei formed near a particle with larger size tend to be dissolved away. This is called "Ostwald ripening." Consequently there exists a minimum distance d from a particle so that any new nucleus formed at a distance less than d will be dissolved away. For each particle there will be a corresponding volume $\frac{4}{3}\pi(R + d + r_c)^3$ in which no nucleus can be formed. The total volume for nucleation must be equal to the initial volume subtracted by the volume in which nucleation is inhibited.

$$V = V_0 - \int_0^t \frac{4}{3}\pi(R + d + r_c)^3 \frac{dN}{d\tau}\, d\tau \quad . \tag{I-6}$$

The formula for d is given (2) by

$$d = \frac{k_3}{\lambda^2}\left(\frac{R}{r_c} - 1\right) \quad , \tag{I-7}$$

where

$$k_3 = \frac{k_2 \gamma \Omega}{4\pi k T} \quad , \tag{I-8}$$

where kT is the thermal energy, γ is the surface energy of the particle, Ω is the atomic volume, and k_2 is a geometrical factor of the order of unity. Substituting equation (I-6) into (I-1), we obtain

$$\frac{dN}{dt} = k_1 (c - c^*)^4 \left\{ V_0 - \int_0^t \frac{4}{3}\pi [\, R(t,\tau) + d(t,\tau) + r_c]^3 \frac{dN}{d\tau} d\tau \right\} , \tag{I-9}$$

where

$$R(t,\tau) = \left(\int_0^{t-\tau} \frac{2[\, c\,(t' + \tau) - c^*] D_s}{C - c^*} dt' + r_c^2 \right)^{\frac{1}{2}} \quad , \tag{I-10}$$

$$d(t,\tau) = \frac{k_3}{\lambda^2}\left[\frac{R(t,\tau)}{r_c} - 1 \right] \quad . \tag{I-11}$$

The concentration c of the solution can be related to the precipitated mass by the equation

$$c = c_0 - \frac{1}{mV_0}\int_0^t \frac{4}{3}\pi\rho R^3(t,\tau) \frac{dN}{d\tau}\, d\tau \quad , \tag{I-12}$$

where c_0 is the initial concentration, m is the molecular mass and ρ is the density of the solute. Simultaneous solution for c and dN/dt as functions of time can be obtained from equations (I-9) and (I-12) by applying numerical methods. At a final time t_1 when $c = c^*$, both dN/dt and dR/dt become zero so that no further precipitation occurs. In fact, t_1 satisfies

$$\int_0^{t_1} \frac{4}{3}\pi R^3(t,\tau)\rho \frac{dN}{d\tau}\, d\tau = (c_0 - c^*)mV_0 \quad . \tag{I-13}$$

The final distribution of particle sizes can be found by the equation,

$$\frac{dN}{dR} = \frac{dN}{dt}\left|\frac{dt}{dR}\right| \quad , \tag{I-14}$$

where dN/dt is given by equations (I-9) and (I-12), and

$$\frac{dR}{dt} = -\frac{D_s[\,c(t) - c^*]}{R(C - c^*)} \quad . \tag{I-15}$$

Here we take the absolute value of dt/dR because the earlier the particle is formed, the larger it grows, so that dt/dR is negative. After solving equations (I-9) and (I-12), equation (I-14) can be solved immediately.

The final particle size distribution, i.e. equation (I-14), should coincide with experimental results. From equation (I-9) it is noticed that more nuclei are formed at an early stage, while equation (I-15) shows that particles with larger radii grow more slowly. Therefore, most particles fall into the region near the mean radius and the distribution function is like a normal distribution.

It is also interesting to find the radius of the largest particle, which is

$$R_M = \left\{ \int_0^{t_1} \frac{2[c(t') - c^*] D_s}{C - c^*} \, dt' + r_c^2 \right\}^{\frac{1}{2}} . \qquad \text{(I-16)}$$

This can be compared with the largest particle found in experiments.

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PROPOSITION II

A METHOD OF SOLVING THE BOUNDARY VALUE PROBLEMS FOR THE DISTRIBUTED CHEMICAL REACTION SYSTEMS

Of the distributed chemical reaction systems, those with a single reaction in a planar region present the simplest problem for analysis due to the fact that they can be described by a single state variable. In particular, chemical reactions with second order kinetics appear more frequently than any other reaction. We shall discuss the following reaction system:

$$2A_1 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A_2$$

with uniform temperature in a region bounded by two parallel planes, by introducing a new iterative method as a modification to the existing Picard's method. Numerical examples turn out to support this new method very strongly. The same theory holds for cases with variable temperature field as long as all the physical properties can be taken as constant. A complete general description may be found in the book by Gavalas (2).

The conservation equations are

$$D_1 \frac{d^2 c_1}{dx^2} = k_1 c_1^2 - 2k_2 c_2 \quad , \qquad \text{(II-1)}$$

$$D_2 \frac{d^2 c_2}{dx^2} = -\frac{1}{2} k_1 c_1^2 + k_2 c_2 \quad , \qquad \text{(II-2)}$$

where c_1 and c_2 are the concentrations for A_1 and A_2, D_1 and D_2 the diffusivities for A_1 and A_2, k_1 and k_2 the reaction rate constants. We shall consider the following boundary conditions:

$$\frac{dc_i}{dx} = 0 \qquad \text{at} \quad x = 0 \quad , \tag{II-3}$$

$$c_i = c_{i0} \qquad \text{at} \quad x = L \quad , \tag{II-4}$$

for $i = 1,2$.

Adding equation (II-1) with twice of equation (II-2) and using boundary conditions (II-3) and (II-4) we obtain

$$c_2 = c_{20} + \frac{D_1}{2D_2}(c_{10} - c_1) \quad , \tag{II-5}$$

which combined with equation (II-1) yields

$$D_1 \frac{d^2c_1}{dx^2} = k_1 \left\{ c_1^2 - 2K[\, c_{20} + \frac{D_1}{2D_1}(c_{10} - c_1)] \right\} \quad . \tag{II-6}$$

where

$$K = \frac{k_2}{k_1} \quad . \tag{II-7}$$

Now if we let

$$A = -\frac{D_1 K}{2D_2} + \frac{1}{2}\left[\left(\frac{D_1 K}{D_2}\right)^2 + 4K\left(2c_{20} + c_{10}\frac{D_1}{D_2}\right)\right]^{\frac{1}{2}} , \tag{II-8}$$

$$u = \frac{c_1 - A}{c_{10} - A} \quad , \tag{II-9}$$

$$\xi = \frac{x}{L} \quad , \tag{II-10}$$

$$k = \left[\frac{k_1 L^2}{D_1} \left(2A + K \frac{D_1}{D_2} \right) \right]^{-\frac{1}{2}} , \tag{II-11}$$

$$\lambda = (c_{10} - A) \frac{k_1 L^2}{D_1} , \tag{II-12}$$

we obtain from equation (II-6)

$$\frac{d^2u}{d\xi^2} = k^2 u + \lambda u^2 , \tag{II-13}$$

with

$$u = 1 \qquad \text{at} \qquad \xi = 1 , \tag{II-14}$$

$$\frac{du}{d\xi} = 0 \qquad \text{at} \qquad \xi = 0 . \tag{II-15}$$

Although equations (II-13), (II-14) and (II-15) can be solved analytically in terms of elliptical integrals, we shall proceed to develop a method of iteration which can be applied to multireaction systems. The existing Picard's method uses the left-hand side of equation (II-13) as main operator and iterate on the right-hand side. We shall, however, obtain the sequence, $u_0, u_1, u_2, \ldots$ by solving

$$\frac{d^2u_i}{d\xi^2} - k^2 u_i = M k^2 u_{i-1}^2 , \tag{II-16}$$

with

$$u_i = 1 \qquad \text{at} \qquad \xi = 1 , \tag{II-17}$$

$$\frac{du_i}{d\xi} = 0 \qquad \text{at} \qquad \xi = 0 , \tag{II-18}$$

for $i = 0, 1, 2, \ldots$, where we set

$$u_{-1} = 0 \tag{II-19}$$

and

$$M = \frac{\lambda}{k^2} \; . \tag{II-20}$$

It can be easily shown that

$$u_0 = \frac{\cosh k\xi}{\cosh k} \; . \tag{II-21}$$

To obtain u_i in terms of u_{i-1}, the Green's function is constructed using standard methods, Friedman (1), as

$$G(\xi, x) = \begin{cases} -\dfrac{\cosh kx \sinh k(1-\xi)}{k \cosh k} & 0 \leq x < \xi \\ -\dfrac{\cosh k\xi \sinh k(1-x)}{k \cosh k} & \xi < x \leq 1 \end{cases} \; . \tag{II-22}$$

From this we have

$$u_i(\xi) = -\frac{kM \sinh k(1-\xi)}{\cosh k} \int_0^{\xi} \cosh kx \, u_{i-1}^2(x) \, dx - \frac{kM \cosh k\xi}{\cosh k} \int_{\xi}^{1} \sinh k(1-x) \, u_{i-1}^2(x) \, dx + \frac{\cosh k\xi}{\cosh k} \; , \tag{II-23}$$

for $i = 1, 2, 3, \ldots$.

To prove the convergence of the sequence u_i, we have to show first the boundedness of u_i. Clearly $|u_0| \leq 1$ and if we assume $|u_{i-1}| \leq 1$, we want to show $|u_i| \leq 1$ under constraint, if any. From equation (II-23) we have

$$|u_i(\xi)| \leq \frac{k|M|\sinh k(1-\xi)}{\cosh k}\int_0^{\xi} \cosh kx\, dx$$

$$+ \frac{k|M|\cosh k\xi}{\cosh k}\int_{\xi}^{1} \sinh k(1-x)\, dx + \frac{\cosh k\xi}{\cosh k}$$

$$= |M| + (1-|M|)\frac{\cosh k\xi}{\cosh k} \quad . \tag{II-24}$$

If we restrict $|M| \leq 1$, we get $|u_i| \leq 1$ for all i.

Now we let

$$\nu_i = u_i - u_{i-1} \quad , \tag{II-25}$$

for $i = 1,2,3,\ldots,$ and have from equation (II-23)

$$\nu_i \leq \frac{1}{2}(2|M|)^i \quad , \tag{II-26}$$

by mathematical induction. Therefore, for $|M| < \frac{1}{2}$, the sequence ν_i converges to zero and from theories of convergence the sequence u_i converges to a value u. It can be shown that once the sequence u_i converges, the limit is the solution of equations (II-13) to (II-15).

From the definitions of M, λ, and k, we know that M is bounded by

$$-\frac{1}{2} < M < \infty \quad . \tag{II-27}$$

The above investigation has taken care of the range $-\frac{1}{2} < M < \frac{1}{2}$. For $M \geq \frac{1}{2}$, we write equation (II-13) in the form

$$\frac{d^2u}{d\xi^2} = \bar{k}^2 u + \frac{M}{1+M}\bar{k}^2 u(u-1) \quad , \tag{II-28}$$

where

$$\bar{k}^2 = k^2(1 + M) \quad , \tag{II-29}$$

with the same given boundary conditions. Obviously $\bar{k}$ is real since M is always larger than $-\frac{1}{2}$. We now form a sequence $\bar{u}_1$ by solving

$$\frac{d^2\bar{u}_i}{d\xi^2} - \bar{k}^2\bar{u}_i = \frac{M}{1+M}\bar{k}^2\bar{u}_{i-1}(\bar{u}_{i-1} - 1) \quad , \tag{II-30}$$

with

$$\bar{u}_i = 1 \qquad \text{at} \qquad \xi = 1 \quad , \tag{II-31}$$

$$\frac{d\bar{u}_i}{d\xi} = 0 \qquad \text{at} \qquad \xi = 0 \quad , \tag{II-32}$$

for $i = 1,2,3,\ldots$, where we have set

$$\bar{u}_{-1} = 0 \quad . \tag{II-33}$$

There is obtained

$$\bar{u}_0 = \frac{\cosh \bar{k}\xi}{\cosh \bar{k}} \quad . \tag{II-34}$$

The Green's function for equations (II-30) to (II-32) has the same form as that of equation (II-22), only with $\bar{k}$ replacing k. Hence we have

$$\bar{u}_i(\xi) = -\frac{M}{1+M}\,\frac{\bar{k}\sinh \bar{k}(1-\xi)}{\cosh \bar{k}}\int_0^{\xi} \cosh \bar{k}x\,\bar{u}_{i-1}(x)[\bar{u}_{i-1}(x) - 1]\;dx$$

$$- \frac{M}{1+M}\,\frac{\bar{k}\cosh \bar{k}\xi}{\cosh \bar{k}}\int_{\xi}^{1} \sinh \bar{k}(1-x)\,\bar{u}_{i-1}(x)[\bar{u}_{i-1}(x) - 1]\;dx$$

$$+ \frac{\cosh \bar{k}\xi}{\cosh \bar{k}} \quad . \tag{II-35}$$

We shall show by mathematical induction that the following relation holds for all i:

$$0 < \overline{u}_i \leq 1 \quad . \qquad \text{(II-36)}$$

From equation (II-34) it is obvious that equation (II-36) is satisfied by $\overline{u}_0$. Now if we assume that $\overline{u}_{i-1}$ satisfies equation (II-36), the value of $\overline{u}_{i-1}(\overline{u}_{i-1} - 1)$ lies between $-\frac{1}{4}$ and 0. Therefore for $M > 0$ we have

$$\begin{aligned} \overline{u}_i(\xi) \leq {} & \frac{1}{4}\,\frac{M}{1+M}\,\frac{\overline{k}\sinh \overline{k}(1-\xi)}{\cosh \overline{k}} \int_0^{\xi} \cosh \overline{k}x \, dx \\ & + \frac{1}{4}\,\frac{M}{1+M}\,\frac{\overline{k}\cosh \overline{k}\xi}{\cosh \overline{k}} \int_{\xi}^{1} \sinh \overline{k}(1-x)\, dx + \frac{\cosh \overline{k}\xi}{\cosh \overline{k}} \\ = {} & \frac{1}{4}\,\frac{M}{1+M} + \frac{1+\frac{3}{4}M}{1+M}\,\frac{\cosh \overline{k}\xi}{\cosh \overline{k}} \leq 1 \quad , \qquad \text{(II-37)} \end{aligned}$$

and

$$\overline{u}_i(\xi) \geq \frac{\cosh \overline{k}\xi}{\cosh \overline{k}} > 0 \quad . \qquad \text{(II-38)}$$

Therefore equation (II-36) holds for all i.

Next we have to show the convergence of $\overline{u}_i$. Let

$$\overline{\nu}_i = \overline{u}_i - \overline{u}_{i-1} \quad , \qquad \text{(II-39)}$$

for $i = 1, 2, 3, \ldots$. It can be shown by mathematical induction that

$$|\overline{\nu}_i| \leq \frac{1}{4}\left(\frac{M}{1+M}\right)^{i}\left(1 - \frac{1}{\cosh \overline{k}}\right)^{i} \quad . \qquad \text{(II-40)}$$

Therefore ν_i converges to zero and $\overline{u}_i$ converges to a limit which is the desired solution.

The numerical example shown below confirms the convergence theory just proved and also shows how fast the sequence converges. We take, for simplicity, k to be unity and use the first method of iteration to calculate the values of $du_i/d\xi$ at $\xi = 1$ for different values of M. Table I shows that the sequence u_i converges for M up to 2 although the theory holds only for $|M| < \frac{1}{2}$. The limiting values in all cases agree with those obtained from the exact solution whose details will not be given here. For large values of M, the second method of iteration is used to give values of $d\bar{u}_i/d\xi$ at $\xi = 1$ shown in Table II where the rapidness of convergence can be easily noticed.

Table I. First method of iteration (k = 1)

At $\xi = 1$	M = 0.1	M = 0.5	M = 2	M = 10
$du_0/d\xi$	0.76159	0.76159	0.76159	0.76159
$du_1/d\xi$	0.80814	0.99499	1.69569	5.43242
$du_2/d\xi$	0.80642	0.96419	1.27548	4.92537
$du_3/d\xi$	0.80701	0.96876	1.48747	135.742
Exact solution $du/d\xi$	0.80678	0.96884	1.41825	2.74212

Table II. Second method of iteration (k = 1)

At $\xi = 1$	M = 2	M = 10
$d\bar{u}_0/d\xi$	1.62689	3.30789
$d\bar{u}_1/d\xi$	1.41344	2.75211
$d\bar{u}_2/d\xi$	1.41753	2.65922
Exact solution $du/d\xi$	1.41825	2.74212

We have, thus, demonstrated a new method of iteration which gives a fast converging sequence for this special single reaction system. For multi-reaction systems, iterative methods prove to be effective for different individual cases. Therefore, more work is suggested along this line in the future in order to achieve a general method.

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PROPOSITION III

LIGHT INTENSITY INSIDE AN INFINITELY LONG CYLINDER

In the research paper "PHOTOCHEMICAL REACTION ENGINEERING" of Cassano, Silveston, and Smith (1), the light intensity inside an infinitely long cylinder is obtained by applying Lambert's law for monochromatic radiation to the cylindric coordinates. Their result shows a singularity at the center of the cylinder with an infinite light intensity. Physically it is not the case because the center of the cylinder is neither a sink nor a source. This leads to the investigation of the problem and the proposition of a new mathematical model.

Lambert's law is

$$\nabla \cdot \underline{I} = -\mu |I| \quad , \tag{III-1}$$

where $\underline{I}$ is the intensity of light and μ is the attenuation coefficient which represents the absorbability. Lambert's law states that the amount of light going into a point is equal to the amount of light absorbed there. In case the medium does not absorb light, i.e. $\mu = 0$, we have $\nabla \cdot \underline{I} = 0$ which is identical to the continuity equation for incompressible fluid.

The authors of the above paper have applied Lambert's law to the cylinder by writing

$$\frac{1}{r} \frac{\partial}{\partial r} rI = \pm \mu I \quad , \tag{III-2}$$

with boundary condition,

$$I = I_w \qquad \text{at} \qquad r = R \quad , \tag{III-3}$$

where R is the radius of the cylinder. The solution of this first order ordinary differential equation is (1)

$$I = I_w \frac{R}{r} \left\{ \exp\left[-\mu(R-r)\right] + \exp\left[-\mu(R+r)\right] \right\} \quad . \tag{III-4}$$

Equation (III-4) not only has a singularity at $r = 0$ but also gives a value which does not satisfy the boundary condition at $r = R$. Therefore the validity of this mathematical model is doubtful.

In actual physical cases, we can hardly obtain infinite light intensity at a point. The idealized condition where the intensity at the center of a cylinder is infinite is that there is an infinite number of sources at the surface of the cylinder, each of them having the same monochromatic coherent light which is focused at the center of the cylinder. In the present case the light is neither coherent nor focused at the center.

The reason why equation (III-4) is wrong is that we cannot apply equation (III-1) to get equation (III-2). Although the problem is axially symmetric, the light beams are not all directed to the center of the cylinder. If we consider a light beam which starts from the surface and goes toward the center of the cylinder, it will penetrate the center and keep going until it hits the opposite wall. After that, part of the light will reflect back, part of it will diffuse back and the remaining part will be absorbed. Consequently, not all the light beams are radially directed and equation (III-2) is not valid.

The exact solution for the light intensity inside an infinitely long cylinder depends on the nature of the surface and the medium. For simplification, we shall consider the surface to be purely diffusive, i.e. the white wall, and the medium to absorb light without scattering, e.g. gases at low pressure and low temperature. We can then apply Lambert's law in the following way.

Considering a point P in Figure 1, we try to find its intensity due to a beam coming from a point Q on the wall. Let the coordinates of P and Q be $(r \cos \theta, r \sin \theta)$ and $(R \cos \phi, R \sin \phi)$, the line joining the two points has a slope $\tan \alpha$ given by

$$\tan \alpha = \frac{R \sin \phi - r \sin \theta}{R \cos \phi - r \cos \theta} . \tag{III-5}$$

Let $\underline{I}^Q$ be the intensity along the beam coming from the point Q. Its components are

$$I_x^Q = - I^Q \cos \alpha \quad , \tag{III-6}$$

$$I_y^Q = - I^Q \sin \alpha \quad , \tag{III-7}$$

where

$$I^Q = |\underline{I}^Q| \quad . \tag{III-8}$$

Along this light beam, Lambert's law becomes

$$\frac{\partial I_x^Q}{\partial x} + \frac{\partial I_y^Q}{\partial y} = - \mu I^Q \quad . \tag{III-9}$$

Substituting equations (III-6) to (III-8) into equation (III-9), we obtain

$$\cos \alpha \frac{\partial I^Q}{\partial x} + \sin \alpha \frac{\partial I^Q}{\partial y} = \mu I^Q \quad . \tag{III-10}$$

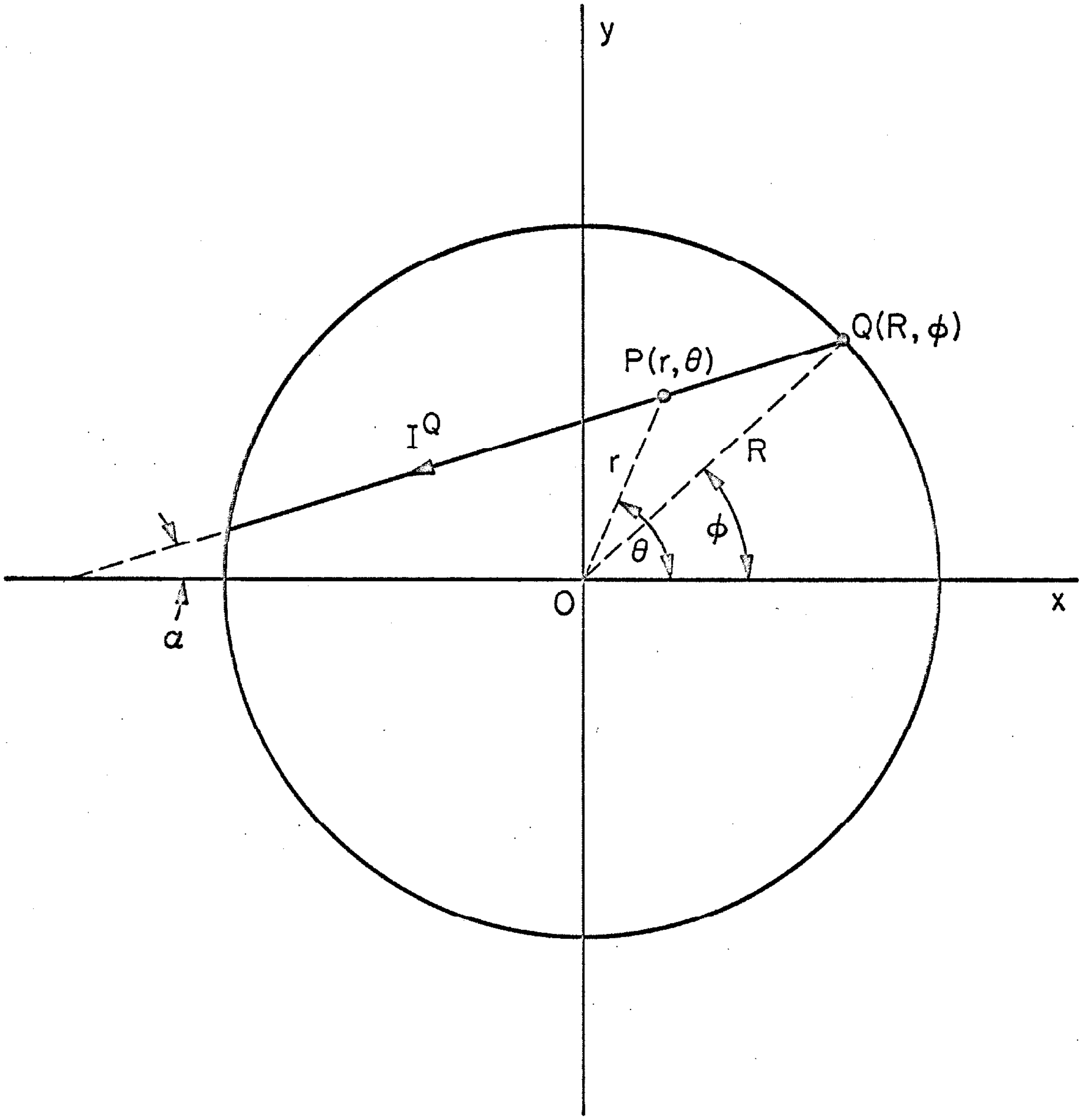

Fig. I RELATION BETWEEN THE POINTS P AND Q.

If the intensity at Q is I_w, the value of I^Q at Q is $I_w/2\pi$ because the source is equally distributed in all directions. Therefore the boundary condition for equation (III-10) is

$$I^Q = \frac{I_w}{2\pi} \quad \text{at} \quad x = R\cos\phi\,,\; y = R\sin\phi\,. \tag{III-11}$$

The solution of equations (III-10) and (III-11) is

$$I^Q = \frac{I_w}{2\pi}\exp\left[-R\mu\cos(\phi-\alpha) + \mu x\cos\alpha + \mu y\sin\alpha\right] \quad . \tag{III-12}$$

The intensity at P influenced by Q is, therefore, obtained by substituting the values of x and y at P into equation (III-12) to be

$$I^Q(P) = \frac{I_w}{2\pi}\exp\left[-R\mu\cos(\phi-\alpha) + r\mu\cos(\theta-\alpha)\right] \quad . \tag{III-13}$$

The total intensity at point P can be obtained by integrating equation (III-13) either with respect to ϕ or with respect to α. The former measures the sum over all the sources while the latter measures the sum over all the directions of the beams. Both of them give the same results. We shall eliminate the angle ϕ to get

$$I^Q(P) = \frac{I_w}{2\pi}\exp\left\{-\mu[R^2 - r^2\sin^2(\alpha-\theta)]^{\frac{1}{2}} + \mu r\cos(\alpha-\theta)\right\} \quad . \tag{III-14}$$

The total intensity at the point P is

$$I(P) = \frac{I_w}{2\pi}\int_0^{2\pi}\exp\left\{-\mu[R^2 - r^2\sin^2(\alpha-\theta)]^{\frac{1}{2}} + \mu r\cos(\alpha-\theta)\right\} d\alpha\,. \tag{III-15}$$

Letting $\psi = \alpha - \theta$, we have

$$I(P) = \frac{I_w}{2\pi}\int_{-\theta}^{2\pi-\theta} \exp[-\mu(R^2 - r^2\sin^2\psi)^{\frac{1}{2}} + \mu r\cos\psi]\, d\psi \quad . \tag{III-16}$$

For most gases, μ is very small so that equation (III-16) becomes

$$I(P) = \frac{I_w}{2\pi}\int_{-\theta}^{2\pi-\theta} [1 - \mu(R^2 - r^2\sin^2\psi)^{\frac{1}{2}} + \mu r\cos\psi]\, d\psi \quad . \tag{III-17}$$

Carrying out the integration we obtain

$$I(P) = \frac{I_w}{2\pi}[2\pi - 4\mu R E(\tfrac{1}{2}\pi, \tfrac{r}{R})] \quad , \tag{III-18}$$

where $E(\frac{1}{2}\pi, \frac{r}{R})$ is the elliptical integral of the second kind which has the asymptotic expansion,

$$E(\tfrac{1}{2}\pi, \tfrac{r}{R}) = \tfrac{1}{2}\pi\left\{1 - \frac{1}{2^2}\left(\frac{r}{R}\right)^2 - \frac{1^2 3}{2^2 4^2}\left(\frac{r}{R}\right)^4 - \frac{1^2 3^2 5}{2^2 4^2 6^2}\left(\frac{r}{R}\right)^6 - \cdots\right\} . \tag{III-19}$$

Therefore, the final result is

$$I(P) = I_w\left\{1 - \mu R\left[1 - \frac{1}{2^2}\left(\frac{r}{R}\right)^2 - \frac{1^2 3}{2^2 4^2}\left(\frac{r}{R}\right)^4 - \frac{1^2 3^2 5}{2^2 4^2 6^2}\left(\frac{r}{R}\right)^6 - \cdots\right]\right\} . \tag{III-20}$$

This new formula has the following advantages over the old one:

1). The solution is independent of θ, which is the true physical case, although we have started with an equation involving θ.

2). Equation (III-20) gives $I(P) = I_w$ at $r = R$, which satisfies the boundary condition.

3). There is no singularity at the center of the cylinder.

4). $I(P)$ increases with r, which means the closer to the wall the higher the intensity.

5). If $\mu = 0$, we have $I(P) = I_w$ everywhere. This is true because in a vacuum cylinder with purely diffusive wall of same intensity, the intensity in the cylinder is everywhere uniform.

It is further suggested that this same problem can be studied by considering the light beams to be in a more realistic three dimensional space.

Reference

1. Cassano, A. E., Silveston, P. L., and Smith, J. M. Research Paper, Dept. of Chem. Eng., Univ. of Calif., Davis.