The influence of the various transport properties of the nitriding atmosphere on the formation of reaction-bonded Si_3N_4

Part 1 *Molecular diffusivity and viscosity*

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The diffusivities and viscosities of binary gas mixtures, containing different properties of nitrogen gas to second-component gases, were computed, and the manner in which these different transport properties affect the formation of reaction-bonded Si_3N_4 are discussed. The computed data have shown that the diffusivities of N_2–H_2 and N_2–He systems are, respectively, 2.65 and 3.3 times as large as those of the N_2–Ar system, in the range 1200 to 1700 K, almost independent of composition. The viscosity of the nitriding atmosphere decreases with the amount of added hydrogen, but increases with helium or argon. We discuss the influence these results have on the diffusion and flow of nitrogen through the porous silicon compact. It is suggested that hydrogen enables nitrogen gas to be distributed uniformly throughout the silicon compact during nitridation, thus making the reaction rates uniform throughout the compact, hence developing a uniform microstructure. In addition, it is explained why the flowing nitriding condition has the deleterious effects on structure and strength of RBSN, and how the addition of hydrogen eliminates such effects.

1. Introduction

While the effects of the various atmospheric conditions on the formation of reaction-bonded Si_3N_4 (RBSN) have been discussed by many investigators [1–7], no work appears to consider the alteration of the various transport properties of the nitriding atmosphere by addition of second-component gases and also the influence of such alterations of the transport properties on the formation of RBSN.

Recently, many workers [2–5] have reported that even small additions of hydrogen have been shown to improve the microstructure compared with material prepared under nitrogen alone. In particular, Lindley and co-workers [3, 4, 8] reported that although under "flowing" nitriding conditions much larger critical defects are formed and the resulting strength is some 30% lower than that of material produced under "static"

conditions, a small addition of hydrogen to the nitrogen gas eliminates the reducing effect of the gas flow on structure and strength. Therefore, many studies have been undertaken [1, 4, 7, 9] to determine the exact role of the hydrogen in the nitridation process.

There seems to be general agreement that the main function of hydrogen is most probably to accelerate the rate of removal of the protective native silica film on the silicon surfaces by the reaction [4, 9]:

$$SiO_2(s) + H_2(g) \rightarrow H_2O(g) + SiO(g)$$
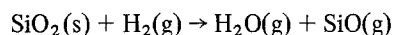
$$\Delta G^{\theta}_{1643\,K} = 226\,kJ\,mol^{-1}$$

The additional question remains [9], however, of whether there is a continuing subsequent function, such as the assistance of a nitridation reac-

tion involving silicon monoxide vapour:

$$3SiO(g) + 2N_2(g) \rightarrow Si_3N_4(c) + 3/2O_2(g)$$
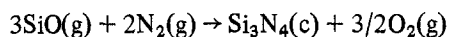
However, ΔG^θ for this reaction is large and positive ($545\,kJ\,mol^{-1}$ at $1700\,K$) and as a minimum requirement an efficient sink for oxygen at low partial pressure ($\sim 10^{-16}$ atm) is required if the reaction is to be an effective source of silicon nitride. On the other hand, subsequent to the reaction initiation stage which is the stage of removal of the reaction-inhibiting silica film from the silicon, the continuing presence of hydrogen in the nitriding atmosphere is also beneficial to a formation of the microstructure in RBSN compared with that in nitrogen alone. This implies that hydrogen is involved in the normal nitridation process, and that its function is not solely that of aiding removal of the silica film.

Dalgleish et al. [10] have shown that, in spite of perfect removal of a silica film from the surface of single crystal slices of semiconductor-grade silicon before nitridation, the morphology of the nitride grown on single-crystal slices reacted in highly purified N_2/H_2 gas mixtures was a finer, more uniform microstructure which was quite different from the morphology formed under nitrogen alone. It seems, therefore, to be evident that, regardless of the existence of the native silica, hydrogen has a function in aiding the formation of more uniform microstructure.

Recently, Mangels [11] has reported that, in addition, a high quality RBSN material can be produced by using a "nitrogen demand nitriding cycle" with the addition of hydrogen and helium which have high thermal conductivities, and which, when present in large concentrations, can increase the thermal conductivities of the nitriding atmosphere, allowing the heat generated by the nitriding exotherm to be dissipated from the compact into the nitriding atmosphere, and the large variable helium atmosphere resulted in superior strength and a more desirable microstructure. On the other hand, when these gases were present in small concentrations, the increase of the thermal conductivities was nearly negligible. However, Mangels also reported that even small additions (7%) of helium have shown a high nitriding rate. Therefore, taking the inert property of helium into consideration, it is evident that besides the effect on thermal conductivity, another function of helium exists in the nitriding process.

For that reason, the attention of the present study will be focussed particularly on the influence of the second-component gases on diffusivity and viscosity among the various transport properties of the nitriding atmosphere. The transport properties of gas mixtures can be predicted with sufficient accuracy from the kinetic theory of gases developed by Enskog—Chapman [12–14]. Generally, the molecular transfer of mass, momentum, and energy are interrelated transport processes of diffusion under a concentration gradient, viscous flow in a velocity gradient, and heat conduction in a thermal gradient. In this study, the diffusivity and viscosity of binary gas mixtures containing different proportions of nitrogen to second-component gases (hydrogen, helium and argon) were computed, and consideration has been given to the influence such transport properties have on the diffusion and flow of nitrogen through the pores of silicon compacts and hence the distribution of nitrogen throughout the compact during the nitriding process. Explanations of why the microstructures with a nonuniform morphology are formed under "flowing" nitriding conditions and such deleterious effects can be eliminated by addition of hydrogen, are developed in connection with the description of Atkinson et al. [15] of how temperature and nitrogen pressure influence the formation of the microstructure of RBSN in the early stages of nitridation.

2. Computation of the diffusivity and viscosity for binary gas mixtures

The derivation of the transport properties from the rigorous kinetic theory of gases, known as the Chapman—Enskog theory, is described in depth by Chapman and Cowling [12] and Hirschfelder et al. [13]. This derivation is based on the evaluation of the intermolecular energy of attraction, ϵ, the collision diameter, δ, and the collision integral, $\Omega^{(1,s)}$, involving explicitly the dynamics of a molecular encounter and hence the intermolecular force law.

For the present purpose, among the various transport properties of gases, mass diffusivity and viscosity, for binary gas mixtures containing different proportions of nitrogen to second-component gases (hydrogen, helium and argon), were calculated by using the basic equations outlined in Appendix I.
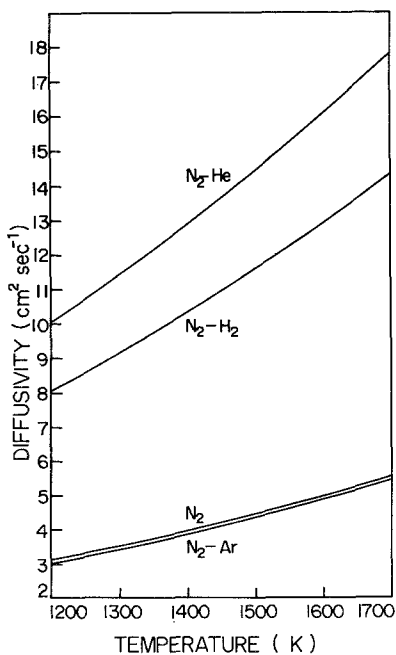
Figure 1 Diffusivity as a function of temperature for the various nitriding atmosphere at 1 atm.
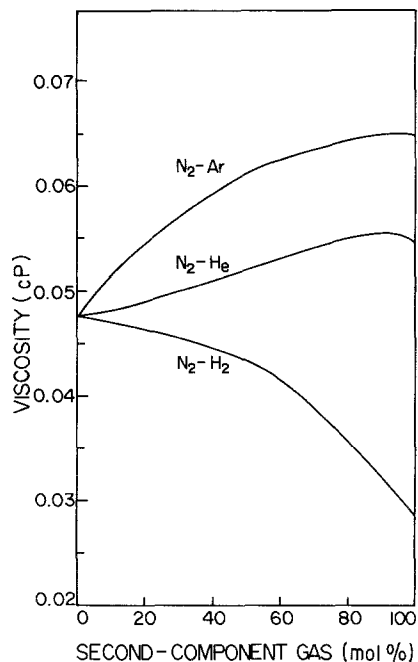

Figure 2 Variation of viscosity of nitriding atmosphere with additions of the various second-component gases at 1500 K.

3. Results
3.1. Diffusivity

Fig. 1 gives the diffusivities of pure nitrogen and several binary gas mixtures as a function of temperature, calculated using Equations A1 and A2 in Appendix I. These equations indicate that for binary gas mixtures at low pressures, e.g. below 10 atm, the diffusion coefficient is inversely proportional to the pressure, increases with increasing temperature, and is almost independent of composition for the given gas pairs. Fig. 1 also shows that the diffusivities of N_2–H_2 and N_2–He systems are, respectively, 2.65 and 3.3 times as large as those of the N_2–Ar system, in the range 1200 to 1700 K.

In gases, since any tendency for A molecules to go in one direction and for B molecules to go in the opposite direction is immediately counteracted by a pressure gradient build up, there is no problem of the Kirkendall shift phenomena as in solids; thus in gases, $D_{AB} = D_{BA}$ where D_{AB} (D_{BA}) refers the interdiffusivity of the A(B) molecule in the A–B binary gas mixture. In addition, it should be noted that the presence of hydrogen and helium molecules affects the diffusivity of nitrogen molecules by intermolecular force and collision.

3.2. Viscosity

The data on viscosities of pure gases and binary gas mixtures as a function of composition at 1500 K, calculated using Equations A3 and A4, are given in Fig. 2. The addition of helium or argon to nitrogen increases the viscosity of the nitriding atmosphere, whereas the addition of hydrogen decreases it, as shown in Fig. 2. Generally, the magnitude of viscosity does not soley depend on the molecular weight of the gas and the viscosities of all gases increase with temperature [13].

4. Discussion

In order to relate these results to the mechanisms of formation of silicon nitride, it is necessary to review some experimental results reported by several investigators.

The fabrication method of silicon nitride by reaction-bonding can provide several advantages if it can be fabricated in a reliable and reproducible manner to high strengths with a low strength variability. However, many workers have found that this is difficult to achieve because frequently lower than normal and occasionally abnormally low strengths are recorded [16, 17]. Abnormally low strengths have been tentatively

ascribed to contamination of the nitriding gas, but recent evidence given by Elias *et al.* [16] has indicated that whilst contamination of the nitriding atmosphere with oxygen and water vapour [18] has little influence on strength, gas flow during nitriding has a significant effect. For example, when nitrogen is allowed to flow through the reaction furnace even at very slow rates, the structure of the product becomes nonuniform, and much larger critical defects are formed, and the resulting strength is lower than the strength of material produced under "static" conditions at all equivalent degrees of conversion. Lindley *et al.* [3, 4] have demonstrated that the use of flowing N_2/H_2 gas mixtures eliminates this adverse effect of gas flow on strength when nitrogen alone is used. Mangels [2] has also reported that the addition of hydrogen to the nitrogen gas resulted in material with a finer, more uniform microstructure and greater strength compared with material prepared under nitrogen alone. Many studies have been undertaken [2–5, 7, 11] to determine the exact role of hydrogen in the nitridation process but the explanations are unsatisfactory in several respects as summarized in Section 1.

In the present work, the diffusion and flow fluxes for nitrogen gas through the porous silicon compacts are discussed in order to explain the effect of hydrogen on the mass fluxes of nitrogen molecules. The mass fluxes of nitrogen through the silicon compact are considered in two parts. The first is the permeation of nitrogen molecules into the porous compact to meet the silicon particles and the second is the mass fluxes of nitrogen inside the compact due to the concentration and pressure gradients between the several parts within the compact during the nitriding reaction. In both cases, several mechanisms of transport, including molecular diffusion, Knudsen diffusion, viscous and slip flow, as well as surface migration may contribute to the flux of nitrogen gas through the porous silicon compacts. On the other hand, the pore structure of silicon compacts is not well understood, so that the relationship between the structure and fluxes is not easily delineated. As a consequence, in the present study, the simple model which is based on a reasonably well-developed theory for diffusion and flow in capillaries [19], which are outlined in Appendix II, is applied to the consideration of the mass fluxes of nitrogen through the pores of the compact.

4.1. Diffusion

When the pressure outside the silicon compact is the same with the pressure inside the compact ($P_o = P_i$) and the concentration gradients present, the mass flux is diffusive in nature and may involve Knudsen diffusion, and ordinary molecular diffusion. If the radius of the capillary and the nitrogen gas pressure is such that the mean free path is large compared to the diameter of the pores, the rate of transport of the molecules is governed only by collisions with the capillary wall. Since the rate of transport is governed by collisions with the capillary wall, the nitrogen gas diffuses independent of the presence of other species, and regardless of the existence of a total pressure gradient. This type of transport is usually referred to as Knudsen diffusion [14]. Qualitatively, Knudsen diffusion appears to dominate for values of r/λ less than 0.1. When it is borne in mind that the mean free path of nitrogen at atmospheric pressure and $1400^\circ C$ is $0.6\,\mu m$ [20], it seems reasonable to suspect that Knudsen diffusion dominates for r less than $0.06\,\mu m$.

When reaction-bonding is initiated with compacts comprising particles of mean diameter approximately $20\,\mu m$, the pore-size distribution, measured by mercury porosimetry of commercial silicon nitride indicated that 80% by volume of the pores had diameters in the range 0.1 to $1\,\mu m$ [20]. It is clear from measurements of this type that a very considerable reduction in pore size occurs during the reaction. However, since the ratio r/λ is greater than about 10, it is evident that ordinary molecular diffusion predominates during the nitridation of the silicon compact and the flux of nitrogen may be simply described by Equation A5 in Appendix II. This mass flux due to the concentration gradient is proportional to the molecular diffusion coefficient D_{AB} which is, of course, independent of the size of the capillary and also composition of binary gas mixtures. This suggests that the higher the value of D_{AB}, the rates at which systems with a concentration gradient approach the steady state are the faster. As illustrated in Fig. 1, the diffusivities of nitrogen in N_2-H_2 and N_2-He mixtures are, respectively, 2.65 and 3.3 times as large as those of nitrogen in the N_2-Ar mixture, in the range 1200 to 1700 K. Therefore, when the nonuniform distribution of the nitrogen concentration present throughout the silicon compact during the nitriding reaction, the N_2-He and

N_2-H_2 systems can eliminate such a nonuniform distribution more rapidly than other systems. Since with higher degrees of uniformity of nitrogen distribution the possibility of the formation of a nonuniform microstructure increases, these results partially explain Mangel's reports [11] that the variable helium atmosphere resulted with more uniform microstructure and superior strength.

4.2. Viscous flow

Since the initial reaction between the silicon compact and nitrogen is a very rapid one, it seems to be necessary to consider the possible importance of forced flow into the compact under a pressure gradient $(P_o > P_i)$. So the total molar flux is given by Equation A7 which is the sum of the contributions from diffusion and forced flow, where the forced flow is given by Equation A6. Generally, the forced flow consists of two types of flow: viscous and slip flow. The slip flow is important only at $r/\lambda \simeq 1$. For the present cases of practical interest, the slip flow term in omitted.

According to the Equation A6, the viscous flow is inversely proportional to viscosity, η_{AB}. This suggests that, the lower the value of η_{AB}, the faster the rates at which systems with a pressure gradient approach the steady state. Therefore, when pressure gradients are present the rate at which systems can approach the steady state increases with the amount of hydrogen because the addition of hydrogen decreases the viscosity of the nitriding atmosphere, as shown in Fig. 2, whereas in the cases of additions of argon or helium, the situation is the reverse.

Accordingly, when both pressure and concentration gradients are simultaneously present throughout the silicon compact, the system with the higher D_{AB} and lower η_{AB} can approach the steady state more rapidly, hence, the permeation of nitrogen gas through the porous compact to meet the silicon particles is also most rapid compared with other systems, and this permeability is an important factor in the uniform nitriding throughout large diameter compacts because the reaction rate at the centre of a large compact is generally slower than the rate at the surface.

In the same way, when both pressure and concentration gradients due to the complex nitriding reaction are present between the several parts inside a silicon compact, the system with

the higher D_{AB} and lower η_{AB} can approach the uniform nitrogen distribution state more rapidly than other systems. Accordingly, addition of hydrogen or helium to the nitrogen gas make the reaction rates more uniform throughout the compacts, hence forming a more uniform microstructure, as shown by Dalgleish et al. [11] and many other other workers [2–5].

In addition, it should be noted that in accurate use of Equations A2 and A3 due account should be taken of the composition independence of the molecular diffusion coefficient, and the composition dependence of the viscosity. For example, when hydrogen is present in a small concentration, the diffusivity of nitrogen is increased no less than about 2.65 times, independent of composition, as shown in Fig. 1 and Equation A2, whereas the decrease in the viscosity of the nitriding atmosphere is no more than a negligible degree, as shown in Fig. 2. However, when the initial reaction proceeds at a much too rapid rate, the resulting pressure gradient between the outside and inside of the compact leads to a continuing viscous flow of nitrogen gas together with a second-component gas into the compact, and then the continuing consumption of only nitrogen gas promotes the build-up of a second-component gas inside the silicon compact, and this pile-up advances until the resulting concentration gradient is balanced by the diffusion which tends to equalize composition. It is expected that with a faster initial reaction, pile-up of a second-component gas prevails over the opposed diffusion. Since the resulting concentration of the second-component gas inside the silicon compact may be greatly increased above the composition, even a small addition of hydrogen can decrease the viscosity of the nitriding atmosphere inside the silicon compact greater than the extent expected. Therefore, the influence of additions of second-component gases will be more effective than expected from initial composition. However, Fig. 2 shows that even large additions of these gases have a negligible influence on viscosity, so it is not considered to have a significant effect on the viscous flow.

On the other hand, the reason why, under 'flowing' nitriding conditions, a nonuniform microstructure is formed and such deleterious effects are eliminated by the additions of hydrogen, can be deduced from the fact that the concentration gradients can be more easily eliminated

by the addition of hydrogen. That is, this suggests that the gas "flow" through the reaction furnace during the nitriding process disturbs a uniform distribution of nitrogen, resulting in a concentration gradients between the several parts within the silicon compact, as well as inside the reaction furnace, and such a nonuniform distribution of nitrogen can be eliminated to some extent when hydrogen is present.

Atkinson et al. [15] showed that in the initial region of reaction the reaction rate increases with nitrogen pressure at constant temperature, and the higher the nitridation temperature at constant nitrogen pressure the more rapid the nitridation reaction rate obtained. Their results showed that at different nitridation temperatures and nitrogen pressures different microstructures are formed. Accordingly, when the nitridation is performed under "flowing" conditions, reac-- tions at different rates due to the nonuniformity of the nitrogen distribution are expected to take place between the various parts within the silicon compacts in the first few minutes of reaction, and this nonuniform distribution of nitrogen will be masked, to some extent, by the presence of added hydrogen. On the other hand, the different rates of reactions cause the nonuniform temperature distributions throughout the silicon compacts, due to the highly exothermic nature of the reaction, and the resultant nonuniform temperature distributions again make the reaction rates within the compact more nonuniform. Again, these more nonuniformed reaction rates influence the temperature distributions inside the compact. Therefore, the compacts nitrided under "flowing" conditions will have very nonuniform microstructures compared to samples nitrided under "static" conditions. However, since hydrogen acts to aid the nitrogen gases to achieve a more uniform distribution and to increase the thermal conductivity of the nitriding atmosphere, the resultant increase in the uniformity in nitrogen concentration and temperature distribution within the silicon compact makes the reaction rates more uniform throughout the compact nitrided under "flowing" or "static" hydrogen-added conditions, hence resulting in a development of RBSN with a more uniform microstructure.

5. Conclusion
Particular emphasis has been placed on the need to consider the unknown functions of hydrogen and helium in the silicon nitridation process. Attention has been focused on the influence that the alterations of the various transport properties of the nitriding atmosphere on addition of second-component gases, have on the microstructure formation of RBSN. The diffusivities and viscosities by binary gas mixtures containing different proportions of nitrogen to second-component gases were, therefore, calculated using the basic equations derived from the rigorous kinetic theory of gases developed by Enskog–Chapman.

On the other hand, there appear to be important differences between the nitrogen alone system and the binary gas system, in providing ready access for the nitrogen to the inner interstices of the silicon compact, that is, when the initial nitridation proceeds at a rapid rate, the continuing consumption of nitrogen causes the pressure gradient between the outside and inside of the compact, and the resulting pressure difference results in the continuing viscous flows of the nitriding atmosphere through the pores into the silicon compact. Thus, in the nitrogen-alone system, only nitrogen gas permeates into the compact by viscous flow as nitridation advances, whereas, in the binary gas systems, the added second-component gases as well as nitrogen gas, permeate into the compact but only the consumption of nitrogen gas promotes a pule up of second-component gases inside the compact, and this pile up increases until the resulting opposed concentration gradient is balanced by the diffusion which tends to equalize composition. Accordingly, in the binary gas mixture system, both diffusion and flow contribution to the total flux in providing the nitrogen to the inner interstices of the compact, hence the effects that the added second-component gas have on the diffusivity and viscosity of nitriding atmosphere are very important and must be considered.

The diffusivities of the N_2–H_2 and N_2–He systems are, respectively, 2.65 and 3.3 times as large as those of the N_2–Ar system, in the range 1200 to 1700 K, almost independent of composition. Since the rates at which the systems with a concentration gradient can approach the steady state are faster with higher diffusivity, this suggests that by the presence of hydrogen and/or helium the nitriding atmosphere can

eliminate more rapidly the nonuniform distribution in the nitrogen concentration during the complex nitriding reaction, hence maintaining the more uniform nitrogen distribution within the silicon compact and thus making the reaction rates more uniform throughout the compact, resulting in the formation of a more uniform microstructure.

On the other hand, when nitridation is carried out under nitrogen alone in "flowing" conditions, the "flow" of nitrogen around the silicon compact may affect the uniform viscous flow from surface to inner interstices through every pore of the compact, making the amounts and velocities of viscous flow through every pore generally nonuniform, and hence the resultant nonuniform nitrogen distribution within the compact will develop a microstructure with a nonuniform morphology. However, as mentioned above, the presence of second-component gases in the nitriding atmosphere reduce the nitrogen supply by the viscous flow due to the pile-up of second-component gases; instead, the mass flux by diffusion becomes important in supplying the nitrogen to the inner interstices of the compact. Moreover, since the presence of hydrogen increases the diffusivity, the deleterious effects from the "flow" of nitrogen can be eliminated by the addition of hydrogen.

Therefore, it appears evident that, regardless of the existence of the silica film, hydrogen has the function of making the reaction rates more uniform throughout the compact, and hence the presence of hydrogen in the nitriding atmosphere results in the development of RBSN with a more uniform microstructure.

Appendix I: Computation of transport properties for gas mixtures

The transport properties of dilute glass, i.e. low-density gases at ordinary pressure, derived from the Chapman–Enskog theory [12] are given by the following equations: self-diffusivity (cm^2 sec^{-1}),

$$D = 1.8583 \times 10^{-3} \, (T^{3/2}/P\delta^2 \, \Omega^{(1,1)*}) \, (2/M)^{1/2}$$
$$\text{(A1)}$$

binary interdiffusivity,

$$D_{AB} = 1.8583 \times 10^{-3} \, (T^{3/2}/P\delta_{AB}^2 \Omega^{(1,1)*}$$
$$(1/M_A + 1/M_B)^{1/2} \qquad \text{(A2)}$$

where P is the pressure, M_A and M_B are molecular weights for unlike molecules of species A and B, δ and $\Omega^{(1,1)*}$ are, respectively, the collision diameter the integral tabulated by Hirschfelder et al. [13] and Bird et al. [14].

viscosity of a pure gas | dyn sec $cm^{-2} \equiv$ g cm^{-1} sec^{-1} (P)|,

$$\eta = 2.6693 \times 10^{-5} \, (MT)^{1/2}/\delta^2 \Omega^{(2,2)*} \quad \text{(A3)}$$

viscosity of multicomponent gas mixtures

$$\eta_{mix} = \sum_{i=1}^{n} \left(\chi_i \eta_i \Big/ \sum_{j=1}^{n} \chi_j \Phi_{ij} \right) \qquad \text{(A4)}$$

in which

$$\Phi_{ij} = 8^{-1/2} (1 + M_i/M_j)^{-1/2} |1 + (\eta_i/\eta_j)^{1/2}$$
$$(M_j/M_i)^{1/4} |^2$$

and where n is the number of chemical species in the mixture; χ_i and χ_j are the mole fractions of species i and j; η_i and η_j are the viscosities of species i and j at the system temperature and pressure; and M_i and M_j are the corresponding molecular weights; Φ_{ij} is dimensionless, and, when $i = j$, $\Phi_{ij} = 1$.

Appendix II: Diffusion and flow in capillaries

Consider a single cylindrical capillary of radius, r, and length, l, through which steady-state transport of components A and B of a binary gas mixture occurs [14, 19]. The gas mixture at the ends of the capillary are maintained at constant pressures, P_o and P_l, when the ratio r/λ is greater than about 10 and the system pressure is uniform ($P_o = P_l$), ordinary molecular diffusion predominates, and the flux of A due to the concentration gradient may be described by

$$J_A^D = -cD_{AB} \, d\chi_A/dz \qquad \text{(A5)}$$

where c is the gas concentration, z the diffusion distance, and D_{AB} the molecular diffusion coefficient. In the presence of a pressure gradient ($P_o \neq P_l$) both diffusion and flow contribute to the net flux through the capillary. When the viscous flow under a pressure gradient is represented by

$$F = -(B_0 P/\eta_{AB} RT) dP/dz \qquad \text{(A6)}$$

the total molar flux is given by the sum of contributions from diffusion and viscous flow:

$$J_t = J^D + F \qquad \text{(A7)}$$

where B_0 is the permeability, P the total pressure and η_{AB} the viscosity of the gas mixture.

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