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HEAT CONDUCTIVITY OF POLYATOMIC AND POLAR GASES AND GAS MIXTURES*

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ABSTRACT

A theory is presented which can be used for the practical calculation of the heat conductivity of polyatomic and polar gases and gas mixtures. For pure gases, the results are based on the Wang Chang-Uhlenbeck equations and involve no approximations, provided that a suitable definition of an internal diffusion coefficient is employed. This is compared with the known results for a gas of rough spheres, and found to hold to all orders of approximation. Approximations enter for real gases only in obtaining numerical estimates of internal diffusion coefficients and relaxation times. The result is essentially the same as that of Mason and Monchick. For mixtures, the results are based on the formal kinetic theory recently obtained by Monchick, Yun, and Mason. A brief digression on sound absorption and dispersion in mixtures is made in order to identify the cross relaxation times in the formulas. Two assumptions are required for mixtures to obtain usable formulas: neglect of "complex collisions," and no correlation between internal energy states and relative velocities (or equal differential cross sections for all scattering channels). With these assumptions plus suitable definitions of internal diffusion coefficients and relaxation times, a usable formula for the heat conductivity is obtained. This formula is further simplified to include only first-order correction terms, and rearranged so that the heat conductivities of the pure components are automatically given correctly. Comparison with experimental results for a number of different types of mixtures showed that the calculated results were rather insensitive to inelastic collision corrections, provided they were forced to go through the correct end points. It was concluded that for most purposes a theory neglecting inelastic effects in the mixture would be adequate, but that inelastic effects must be included in calculations for the pure components.

I. Introduction

By starting with the formal kinetic theory of transport in polyatomic gases developed by Wang Chang and Uhlenbeck[1] and by Taxman[2], it has recently become possible to put the theory and calculation of heat conductivity of polyatomic molecules on a basis comparable to that for monatomic gases. This was achieved for pure gases by introducing an approximate form including first-order correction terms in the relaxation times describing inelastic collisions, with rather good agreement with experiment.[3] The consistency of these first-order results for a gas of rough spheres has also been investigated.[4] Nothing could be said at the time, however, about mixtures of polyatomic gases because of a lack of a formal kinetic theory of transport in such mixtures. Such a formal theory has since been developed,[5] along the lines of the Wang Chang-Uhlenbeck approach for pure gases, with the ultimate aim of using it as a starting point for a first-order theory of heat conduction in polyatomic gas mixtures.

One of the purposes of the present paper is to develop a practical theory which can be used to calculate the heat conductivity of polyatomic gas mixtures. A second is to establish with more precision just where approximations enter into the derivation of usable formulas from the equations of the formal kinetic theory, which are unusable as they stand because of our present inability to follow the dynamics of inelastic collisions for realistic molecular models. It turns out that the necessary approximations can be put into a much less severe form than originally presented; at any rate the approximations can be introduced into the derivations at a later stage and in a physically more transparent way.

We first consider pure gases and show that the final formulas for the coefficient of heat conductivity follow from the Wang Chang-Uhlenbeck equations with no approximations, provided only that a suitable definition of a diffusion coefficient of internal energy is employed.

This result is checked against the known results for rough spheres, and found to hold exactly to all orders of approximation. We then consider mixtures and find that an analogous result does not hold; even with reasonable definitions of cross relaxation times and internal diffusion coefficients, complicated collision terms are left over. Two additional assumptions, which are physically reasonable, are sufficient to remove these latter terms. A brief digression on sound absorption and dispersion is also necessary in order to identify the cross relaxation times which occur in the mixture formulas.

The mixture formula is then expanded and truncated so as to include only first-order correction terms in the relaxation times, and rearranged so that experimental quantities appear in the formula as far as possible. This procedure also assures that the mixture formula automatically goes through the experimental end points; i.e., it reduces to the experimental thermal conductivities of the pure components as the mole fraction of that component goes to unity. In this form the formula is equivalent to the Hirschfelder-Eucken formula for the heat conductivity of polyatomic gas mixtures plus a large number of first-order correction terms. (It is equivalent, not equal, because allowance has been made for resonant effects in the internal diffusion coefficients).

Comparisons with experimental measurements are made for a variety of different types of mixtures, including monatomic with nonpolar polyatomic gases, nonpolar polyatomic gas mixtures, mixtures of nonpolar and polar polyatomic gases, and mixtures of isotopically substituted polar gases. When polar gases are involved it is necessary to take special account of glancing collisions in which a quantum of rotational energy is exchanged between two molecules. This exchange affects the diffusion coefficient for internal energy, especially when the exchange is resonant so that its cross-section is large. A number of detailed conclusions may be drawn from these comparisons, and are summarized at the end of the paper. Four main ones may be mentioned here. (1) The heat conductivity coefficient of polyatomic gas mixtures can usually be calculated from the Hirschfelder-Eucken formula within a few percent if experimental values are known for the component viscosities and heat conductivities and for the diffusion coefficients. (2) The correction terms for inelastic collisions do not affect the shape of the λ_{mix} vs composition curve very much, but only move it up or down, unless very short molecular relaxation times occur, such as in the case of polar gases. Thus if the λ_{mix} curve is forced through the end points corresponding to the pure components, it is usually found to differ only slightly from the Hirschfelder-Eucken curve. (3) The use of correct internal diffusion coefficients is at least as important as the inclusion of corrections for inelastic collisions. In the last section, a crude argument is employed to evaluate the effect of neglecting the angular dependence of the inelastic channel scattering. (4) The easiest *a priori* procedure of reasonable accuracy for the calculation of λ_{mix} is to use the fully corrected formulas to calculate the conductivities of the pure components, and then to use these in the Hirschfelder-Eucken formula to calculate λ_{mix}. To do better requires more knowledge of inelastic collisions than is available for most gases.

II. PURE GASES

The purpose of this section is to show that in the development of a theory involving only experimental quantities, approximations may be introduced at a later stage and in a less severe form than was previously shown.[3] We shall not write down all the formulas of the formal kinetic theory, which are sometimes very long and cumbersome (and are available elsewhere), but will give only enough intermediate results to allow the argument to be followed.

A. Formally Exact Theory

To keep the size of the formulas within reasonable bounds, we define the value of a function F averaged over all the dynamic variables of collisions between molecules of components q and q' as follows:

$$\langle F\rangle_{qq'} \equiv \left(\frac{kT}{2\pi\mu_{qq'}}\right)^{\frac{1}{2}}\left(\frac{1}{Q_q Q_{q'}}\right) \sum_{ijkl} \int_0^\infty d\gamma \int_0^{2\pi} d\Phi \int_0^\pi d\chi \times$$

$$\times \left[F\gamma^3 \exp\left(-\gamma^2 - \epsilon_{qi} - \epsilon_{q'j}\right) I_{ij}^{kl} \sin\chi\right],$$

where the indices i, j, k, l refer to the internal states, i and j to the internal states before collision of q and q', respectively, and k and l to the internal states after collision. Q_q and $Q_{q'}$ are internal partition functions,

$$Q_q \equiv \sum_i \exp\left(-\epsilon_{qi}\right),$$

where ϵ_{qi} is the energy of the i'th internal state of q, divided by kT. The angles χ and Φ are the polar and azimuthal angles, respectively, describing the deflection of a relative trajectory by a collision, and I_{ij}^{kl} is the differential scattering cross section for scattering from states i, j into states k, l with deflection angles χ, Φ, and with relative velocity changed from g to g' by the collision. The reduced mass $\mu_{qq'}$ and reduced relative velocity γ are

$$\mu_{qq'} = m_q m_{q'}/(m_q + m_{q'}),$$

$$\gamma = (\mu_{qq'}/2kT)^{\frac{1}{2}} g_{qq'} \quad .$$

These definitions hold for mixtures as well as for pure gases.

We now define a collision integral for the diffusion of internal energy in a pure gas as

$$(c_{int}/k)\, \Omega_{int}^{(1,1)} \equiv \langle(\epsilon_i - \bar{\epsilon})\, [(\epsilon_i - \epsilon_j)\, \gamma^2 - (\epsilon_k - \epsilon_l)\, \gamma\gamma' \cos \chi]\rangle_{qq} \;, \tag{1}$$

where c_{int} is the internal heat capacity per molecule, $\Omega_{int}^{(1,1)}$ is the collision integral, $\bar{\epsilon}$ is the average internal energy divided by kT, and the other terms are as defined previously. For elastic collisions this definition reduces to the collision integral for self-diffusion,

$$\Omega_{qq}^{(1,1)} = \langle\gamma^2 - \gamma\gamma' \cos \chi\rangle_{qq} \;. \tag{2}$$

In terms of this collision integral, the diffusion coefficient for internal energy is defined as

$$\mathcal{D}_{int} \equiv \frac{3kT}{8nm\, \Omega_{int}^{(1,1)}} \;, \tag{3}$$

which for elastic collisions is equal to the ordinary self-diffusion coefficient, $\mathcal{D}_{11}$.

The foregoing expressions hold quite generally for any number of modes of internal motion, but of course are very difficult to evaluate except in certain special simple cases. If the internal modes are uncoupled so that a separate heat capacity and diffusion coefficient can be defined for each internal mode, the overall internal heat capacity and diffusion coefficient can be written as

$$c_{int} \equiv \sum_k c_{k,int}, \tag{4a}$$

$$c_{int}/\mathcal{D}_{int} \equiv \sum_k (c_{k,int}/\mathcal{D}_{k,int}), \tag{4b}$$

where the summation extends over all the internal modes, $k = 1, 2, \cdots$. The problem of finding numerical values for $\mathcal{D}_{int}$ is postponed to the last step in the calculation.

The relaxation time, τ, for internal energy in a pure gas is defined as[1,2]

$$n\tau = \frac{(c_{int}/k)}{2\langle \Delta\epsilon^2 \rangle}, \tag{5}$$

where n is the number density of molecules and

$$\Delta\epsilon = \epsilon_k + \epsilon_l - \epsilon_i - \epsilon_j . \tag{6}$$

The expression for τ holds for any number of modes of internal motion, but is very difficult to evaluate for any but the most over-simplified models of molecular collisions. Values of τ can, however, be determined experimentally from sound absorption and shock tube measurements. If the internal modes are mechanically independent so that a separate relaxation time can be defined for each mode, then an overall relaxation time can be written as

$$c_{int}/\tau \equiv \sum_k (c_{k,int}/\tau_k) . \tag{7}$$

With the aid of the foregoing definitions, all the complicated integrals appearing in the Wang Chang-Uhlenbeck formulas for the heat conductivity can be expressed in terms of internal diffusion coefficients, relaxation times, and various experimental quantities. The general expressions for the translational and internal contributions to the heat conductivity are[1-3]

$$\lambda_{tr}\left(1 - \frac{Y^2}{XZ}\right) = \frac{75}{8}\frac{k^2T}{m} X^{-1} + \frac{15}{4}\frac{kT\, c_{int}}{m}\left(\frac{Y}{XZ}\right) , \tag{8}$$

$$\lambda_{int}\left(1 - \frac{Y^2}{XZ}\right) = \frac{3}{2}\frac{c^2_{int}\, T}{m} Z^{-1} + \frac{15}{4}\frac{kT\, c_{int}}{m}\left(\frac{Y}{XZ}\right) , \tag{9}$$

where X, Y, and Z are complicated integrals which can be written in terms of defined quantities as follows:

$$X = \frac{5}{2}\frac{kT}{\eta} + \frac{25}{12}\frac{c_{int}}{nk\tau} , \tag{10a}$$

$$Y = \frac{5}{4}\frac{c_{int}}{nk\tau} , \tag{10b}$$

$$Z = \frac{3}{2}\frac{T\, c_{int}}{nm\mathcal{D}_{int}} + \frac{3}{4}\frac{c_{int}}{nk\tau} , \tag{10c}$$

where η is the viscosity. It should be emphasized that in writing these expressions no approximations have been made other than those inherent in the Wang Chang-Uhlenbeck formulation. Substitution of (10a)-(10c) will now yield expressions for λ_{int} and λ_{tr} and for the total conductivity $\lambda = \lambda_{tr} + \lambda_{int}$. Since the correction terms for inelastic collisions always occur in the combination τ/η, it is convenient to define a collision number ζ as

$$\zeta = \frac{4}{\pi}\frac{p\tau}{\eta} , \tag{11}$$

where p = nkT is the pressure. ζ may be thought of as the number of collisions required for the equilibration of molecular internal and translational energy, or more crudely, as the number of collisions required to interchange a quantum of internal with translational energy. The expressions for the heat conductivity can then be written as

$$\frac{\lambda_{tr}\ m}{\eta} = \frac{5}{2}\, c_{Vtr} - \frac{5}{2}\left[\left(\frac{2c_{int}}{\pi\zeta}\right)\left(\frac{5}{2} - \frac{\rho\mathcal{D}_{int}}{\eta}\right)\right]\left[1 + \left(\frac{2}{\pi\zeta}\right)\left(\frac{5}{3}\,\frac{c_{int}}{k} + \frac{\rho\mathcal{D}_{int}}{\eta}\right)\right]^{-1}, \tag{12}$$

$$\frac{\lambda_{int}\ m}{\eta} = \left(\frac{\rho\mathcal{D}_{int}}{\eta}\right) c_{int} + \left(\frac{\rho\mathcal{D}_{int}}{\eta}\right)\left[\left(\frac{2c_{int}}{\pi\zeta}\right)\left(\frac{5}{2} - \frac{\rho\mathcal{D}_{int}}{\eta}\right)\right] \times$$

$$\times \left[1 + \left(\frac{2}{\pi\zeta}\right)\left(\frac{5}{3}\,\frac{c_{int}}{k} + \frac{\rho\mathcal{D}_{int}}{\eta}\right)\right]^{-1}, \tag{13}$$

where $c_{Vtr} = \frac{3}{2}k$ is the constant-volume translational heat capacity per molecule, and $\rho = nm$ is the gas density. These two terms can be combined to give the total conductivity,

$$\frac{\lambda m}{\eta} = \frac{5}{2}\, c_{Vtr} + \left(\frac{\rho\mathcal{D}_{int}}{\eta}\right) c_{int} - \left[\left(\frac{2c_{int}}{\pi\zeta}\right)\left(\frac{5}{2} - \frac{\rho\mathcal{D}_{int}}{\eta}\right)^{2}\right] \times$$

$$\times \left[1 + \left(\frac{2}{\pi\zeta}\right)\left(\frac{5}{3}\,\frac{c_{int}}{k} + \frac{\rho\mathcal{D}_{int}}{\eta}\right)\right]^{-1}. \tag{14}$$

The first two terms of Eq. (14) together are just the old modified Eucken expression, and the last term involving the two square brackets is a correction term that vanishes in the absence of inelastic collisions. It should be remembered, however, that inelastic effects also enter into the estimation of $\mathcal{D}_{int}$. If there are many internal modes that are uncoupled, $\mathcal{D}_{int}$ and ζ may be replaced by Eq's (4b) and (7).

We emphasize again that no approximations have been made. Furthermore, since everything on the right hand sides of Eqs. (12)-(14) can be determined experimentally except for $\mathcal{D}_{int}$, the only way in which approximations <u>must</u> enter is through the determination of $\mathcal{D}_{int}$. There does not seem to be any independent experimental method known for determining $\mathcal{D}_{int}$ directly. If the internal energy is attached rather tightly to the molecules, so that a close collision is required to make it shift into translational energy or from one molecule to another, it is probably reasonable to approximate $\mathcal{D}_{int}$ by the self-diffusion coefficient, $\mathcal{D}_{11}$, which is independently measurable by tracer techniques. Empirically, this seems to work fairly well in a large number of cases.[3] However, if there is some special mechanism whereby internal energy can easily transfer from one molecule to another, $\mathcal{D}_{11}$ is a poor approximation to $\mathcal{D}_{int}$, and some sort of correction is needed. An example is the exchange of rotational energy induced by the dipole field of two polar molecules. This may occur even at large impact parameters. When exchange is energetically resonant, the effect may be calculated fairly easily and leads to a large correction of the form

$$\mathcal{D}_{int} = \mathcal{D}_{11}/(1 + \delta_{11}) \quad , \tag{15}$$

formulas for estimating δ_{11} being given in reference 3. Another example is the surfaces of rough spheres causing large energy exchanges when two molecules come in contact. Rough spheres are discussed further in the next section. These corrections for $\mathcal{D}_{int}$ are very hard to calculate except in special cases such as the two just mentioned, and no other way of determining $\mathcal{D}_{int}$ is known at present, except to back-calculate it from measurements of λ. Indeed, with the present point of view, a measurement of λ is tantamount to a determination of $\mathcal{D}_{int}$.

Equations (12) and (13) show directly that the effect of inelastic collisions is to decrease the flow of translational energy and to increase the flow of internal energy. This phenomenon is corroborated by other available experiments that yield an independent measure of the translational heat conductivity alone.[6-8]

B. Rough Spheres

It is of interest to see whether the foregoing point of view is consistent with the known results for a gas of rough spheres. Since λ_{tr} and λ_{int} are known separately for this model, two sources exist for the determination of $\mathcal{D}_{int}$ and these should check. The deviations of the rough sphere results from the smooth sphere results are given in terms of the dimensionless parameter $K = 4I/m\sigma^2$, where I is the moment of inertia of a sphere of mass m and diameter σ. The value of K ranges from 0 to 2/3. The expressions for λ_{tr}, λ_{int}, and η are given by Chapman and Cowling,[9] from which we obtain the expressions

$$\frac{\lambda_{tr}\, m}{\eta} = \frac{15k}{2} \frac{(6 + 13K)\ (1 + 2K)\ (1 + K)}{(12 + 75K + 101K^2 + 102K^3)} , \tag{16}$$

$$\frac{\lambda_{int} m}{\eta} = \frac{6k}{5} \frac{(6 + 13K)\ (3 + 19K)}{(12 + 75K + 101K^2 + 102K^3)} , \tag{17}$$

$$\frac{\eta}{p\tau} = \frac{4}{\pi\zeta} = \frac{10K}{6 + 13K} . \tag{18}$$

Comparing Eqs. (16) and (17) with the general expressions for λ_{tr} and λ_{int} given by Eqs. (12) and (13), we can solve for $\rho\mathcal{D}_{int}/\eta$ on substituting for ζ and for $c_{int} = 3k/2$, to obtain (from <u>both</u> sets of equations)

$$\frac{\rho\mathcal{D}_{int}}{\eta} = \frac{6 + 13K}{5(1 + K + 2K^2)} , \tag{19}$$

from which we find

$$\mathcal{D}_{int} = \frac{3}{8\rho\sigma^2} \left(\frac{mkT}{\pi}\right)^{\frac{1}{2}} \frac{(1 + K)^2}{(1 + K + 2K^2)} . \tag{20}$$

It is interesting to compare $\mathcal{D}_{int}$ with the known[9] result for $\mathcal{D}_{11}$:

$$\frac{\mathcal{D}_{int}}{\mathcal{D}_{11}} = \frac{(1 + 2K)\ (1 + K)}{1 + K + 2K^2} \ . \qquad (21)$$

This ratio is unity for $K = 0$ and rises monotonically to a value of $35/23 = 1.52$ for the maximum value of $K = 2/3$. That is, for rough spheres we have the apparently peculiar phenomenon of the internal energy diffusing faster than the molecules themselves. An explanation of this phenomenon has been given[4] in terms of energy exchange on collision and the enhanced backward scattering for rough spheres as compared to smooth spheres. That is, a substantial fraction of collisions occurring with a large transfer of linear momentum also involve a large transfer of internal energy.

Another interesting property of rough spheres follows from Eq. (18): the smallest value of ζ possible is only $44/5\pi = 2.80$ collisions. Although one usually thinks of rough spheres readily exchanging internal energy, this value of ζ is actually larger than that for many real molecules having long-range force fields.

Since λ_{tr} and λ_{int} yield the same value of $\mathcal{D}_{int}$, we see that the general results of the preceding section are consistent with the known special results for rough spheres.

III. MIXTURES

In this section we carry over to mixtures the point of view given for pure gases given in the previous section, as far as this is possible. Additional assumptions are necessary for mixtures in order to obtain a theory fully in terms of relaxation times and diffusion coefficients of various sorts. We begin with a digression on sound absorption in gas mixtures in order to identify the cross-relaxation times and to get some idea of what sorts of assumptions might be physically reasonable. In the process, we shall rederive the usual phenomenological expression[10] for the relaxation time of one component of a mixture.

A. Relaxation in Polyatomic Gas Mixtures

This treatment is a straightforward extension of the method used by Monchick[11] in a recent discussion of the case of a pure gas with many internal degrees of freedom, and we therefore limit ourselves to a brief outline of the method. We again assume[11] that the internal energy of the q-th molecular species can be written as the sum of the energies of the various internal modes,

$$E_{qI} = E_{qI_1} + E_{qI_2} + \cdot \cdot \cdot \tag{22}$$

The singlet distribution function f_q is expanded about the local equilibrium distribution function $f_q^{(0)}$:

$$f_q\,(\underset{\sim}{v}_q,\, E_q) = f_q^{(0)}\,(1 + \Phi_q + \cdot \cdot \cdot), \tag{23}$$

$$f_q^{(0)} \equiv (n_q/Q_q)\,[m_q/(2\pi kT)]^{3/2} \exp\,[-(W_q^{\,2} + E_q)], \tag{24}$$

where n_q, m_q and Q_q are the number density, the molecular mass and the internal partition function of the q-th species, $\mathbf{v}_q$ is the velocity, and

$$\mathbf{W}_q = [m_q/(2kT)]^{\frac{1}{2}} (\mathbf{v}_q - \mathbf{v}_0), \tag{25}$$

in which $\mathbf{v}_0$ is the local mass average velocity. The temperature T which appears in Eqs. (23)-(25) is really a local temperature $T(\mathbf{r})$, chosen so that the local energy density at point $\mathbf{r}$ is equal to the total energy density of an equilibrium gas having the same temperature T. After linearization, the Wang Chang-Uhlenbeck extension of the Boltzmann equation takes the following form:

$$\frac{\partial f_q^{(0)}}{\partial t} + \mathbf{v}_q \cdot \frac{\partial f_q^{(0)}}{\partial \mathbf{r}} + f_q^{(0)} \left(\frac{\partial \Phi_q}{\partial t} + \mathbf{v}_q \cdot \frac{\partial \Phi_q}{\partial \mathbf{r}} \right) = - n_q \sum_{q'} n_{q'} I_{qq'} (\Phi_q + \Phi_{q'}), \tag{26}$$

where the linear operator $I_{qq'}$ operating on an arbitrary function F is defined as

$$n_q n_{q'} I_{qq'} (F_{qq'}) \equiv \sum_{JKL} \int d\mathbf{v}_{q'} \int d\phi \int \sin \chi \, d\chi$$

$$\times \, g_{qq'} I_{IJ}^{KL} f_q^{(0)} f_{q'}^{(0)} (F_{qq'} - F'_{qq'}), \tag{27}$$

where

$$F_{qq'} \equiv F (\mathbf{W}_q, E_{qI}, \mathbf{W}_{q'}, E_{q'J}),$$

$$F'_{qq'} \equiv F (\mathbf{W}'_q, E_{qK}, \mathbf{W}'_{q'}, E_{q'L}),$$

the primes in F and $\mathbf{W}$ referring to values after collision.

We are now using the indices I, J, K, L to refer to sets of quantum numbers. We understand I to mean the set $(I_1, I_2, \cdots)$ where I_k may be a single quantum number or a set of quantum numbers specifying the state of an independent or rather semi-independent subset of degrees of freedom. Thus I and J refer to a set of quantum numbers describing the internal state before collision, and K and L refer to the internal state after collision. From here on, however, we will limit ourselves to no more than two internal modes, i.e., independent sets of degrees of freedom, just as in the previous study[11] on pure polyatomic gases. This is reasonable because in most acoustic studies only two internal modes can be distinguished - rotation and vibration. In any event, the extension to more internal modes will be obvious.

The perturbation function Φ_q is now expanded in a set of orthogonal functions,

$$\Phi_q = \sum_{s=0}^{\infty} a^{\alpha\beta\gamma}_{q,s,(\mu)_s} \Psi^{\alpha\beta\gamma}_{q,s} \mathcal{W}_{q,s,(\mu)_s} . \tag{28}$$

This rather complicated notation has been explained previously in connection with the results for pure gases. It is sufficient for the present purposes just to identify the following coefficients:

$$a^{100}_{q0} = - (3/2)^{\frac{1}{2}} (T_{q,tr} - T)/T, \tag{29a}$$

$$a^{010}_{q0} = - (c_{q,1}/k)^{\frac{1}{2}} (T_{q,1} - T)/T, \tag{29b}$$

$$a^{001}_{q0} = - (c_{q,2}/k)^{\frac{1}{2}} (T_{q,2} - T)/T, \tag{29c}$$

where $T_{q,tr}$ is the translational temperature of the q-th species, $T_{q,i}$ is the temperature of the i-th internal mode of the q-th species defined by

$$T_{q,i} - T = \frac{1}{c_{q,i}} \sum_J \int E_{q,J_i} \frac{f_q^{(0)}}{n_q} \Phi_q \, d\underset{\sim}{v}_q ,$$

and 3k/2 and $c_{q,i}$ are the corresponding constant-volume translational and internal heat capacities per molecule. $c_{q,i}$ is evaluated at T.

We now use the above expansion in conjunction with the linearized Boltzmann equation to obtain a transport equation for the average energy of the i-th mode of the q-th species, $\overline{E}_{q,i}$, defined as

$$\overline{E}_{q,i} \equiv n_q^{-1} \sum_J \int E_{q,J_i} \, f_q^{(0)} \, (1 + \Phi_q) \, d\mathbf{v}_q , \tag{30}$$

where the summation extends over all the quantum numbers J_1, J_2, etc. The corresponding quantity evaluated with an equilibrium distribution function for an arbitrary temperature T_a is

$$E_{q,i}^{(0)} \, (T_a) \equiv n_q^{-1} \sum_J \int E_{q,J_i} \, f_q^{(0)} \, d\mathbf{v}_q . \tag{31}$$

When the transport equation for $\overline{E}_{q,i}$ is evaluated, it is found that terms from Eq. (28) with s = 0 are the only ones contributing. The simplest approximation describing the distribution of energy in the various modes is obtained by neglecting the heat flux and all terms except those with $\alpha\beta\gamma$ = 100, 010, and 001. The resulting transport equation for the first internal mode of species q is

$$\begin{aligned} \left(\frac{\partial}{\partial t} + \mathbf{v}_0 \cdot \frac{\partial}{\partial \mathbf{r}}\right) \overline{E}_{q,1} \approx - 4nkT \sum_{q'} x_{q'} \Bigg[\left(\frac{2}{3}\right)^{\frac{1}{2}} \left(\frac{m_q \, a_{q'0}^{100} + m_{q'} \, a_{q0}^{100}}{m_q + m_{q'}} \right) \langle \Delta\epsilon_{1q} \, \Delta\epsilon_{qq'} \rangle_{qq'} \\ + (k/c_{q',1})^{\frac{1}{2}} \, a_{q'0}^{010} \, \langle \Delta\epsilon_{1q} \, \Delta\epsilon_{1q'} \rangle_{qq'} + (k/c_{q,1})^{\frac{1}{2}} \, a_{q0}^{010} \, \langle \Delta\epsilon_{1q}^2 \rangle_{qq'} \\ + (k/c_{q',2})^{\frac{1}{2}} \, a_{q'0}^{001} \, \langle \Delta\epsilon_{1q} \, \Delta\epsilon_{2q'} \rangle_{qq'} + (k/c_{q,2})^{\frac{1}{2}} \, a_{q0}^{001} \, \langle \Delta\epsilon_{1q} \, \Delta\epsilon_{2q} \rangle_{qq'} \Bigg] , \end{aligned} \tag{32}$$

with a similar equation for the second internal mode. The pointed bracket notation has already been defined in Section IIA and the other terms are

$$\Delta\epsilon_{1q} = \epsilon_{1q}' - \epsilon_{1q} ,$$

$$\Delta\epsilon_{qq'} = (\epsilon'_q - \epsilon_q) + (\epsilon'_{q'} - \epsilon_{q'}), \tag{33}$$

the primes on the ϵ referring to values after collision. The factor

$$\frac{m_q a^{100}_{q'0} + m_{q'} a^{100}_{q0}}{m_q + m_{q'}}$$

can be readily interpreted as the deviation of the translation temperature of the average relative motion of species q and q' from T, according to Eq. (29a). It will be assumed to be negligibly different from the translational energy of the whole mixture. Further simplification of Eq. (32) requires additional assumptions.

An attractive approximation is to assume that all complex collisions are very rare. Complex collisions are those involving more than a single quantum jump.[12] This is the usual approximation made in the phenomenological theories of relaxation in gases.[12] Thus we neglect collisions in which the internal states of both colliding molecules change, or in which both internal modes of one of the molecules change in one collision. This assumption will later prevent some of our mixture formulas from passing smoothly over into those for single gases in the limit of a mixture of a gas with itself, since complex collisions in a given mode must be retained if allowance is to be made for resonant exchange collisions. At any rate, if we make this assumption, then Eq. (32) can be reduced to the form of the usual phenomenological equations,

$$\left(\frac{\partial}{\partial t} + \mathbf{v}_0 \cdot \frac{\partial}{\partial r}\right) \bar{E}_{q,i} \approx - \frac{1}{\tau_{q,i}} [\bar{E}_{q,i} - E_{q,i}^{(0)}(T_{tr})], \tag{34}$$

where the relaxation time $\tau_{q,i}$ for the relaxation of the i-th internal mode of the q'th chemical species is given by

$$\frac{1}{\tau_{q,i}} = \sum_{q'} \frac{x_{q'}}{\tau_{qq',i}} \, . \tag{35}$$

Equations (34) and (35) are the same as the phenomenological equations, but we are now able to identify the cross-relaxation times $\tau_{qq',i}$ in terms of inelastic collision integrals, as follows:

$$\frac{1}{\tau_{qq',i}} = \frac{4nk}{c_{q,i}} \langle \Delta\epsilon^2_{iq} \rangle_{qq'} \, . \tag{36}$$

Notice that this expression is not invariant under an interchange of subscripts: $\tau_{qq',i}$ means the relaxation time for the i-th mode of the q-th species on colliding with species q', but $\tau_{q'q,i}$ means the relaxation time for the i-th mode of species q' on colliding with species q. These two times can be widely different - for instance, in the case where q is a complicated polyatomic molecule and q' is a noble gas atom. For q = q', it is seen that Eq. (36) agrees with Eq. (5) only if complex collisions are neglected, in which case $\langle \Delta\epsilon^2_{i,qq} \rangle_{qq} = 2\langle \Delta\epsilon^2_{i,q} \rangle_{qq}$.

It will prove convenient in the following to include the possibility of resonant collisions in a single mode between molecules of the same species. Since these are complex collisions in which $\Delta\epsilon_{i,qq} = 0$, it is seen that these processes contribute nothing to Eq. (32) and so may be safely included in the theory without changing the form of Eqs. (34)-(36). It must be remembered, however, that in the pointed brackets in Eq. (36) all resonant exchange processes must be excluded.

As in the case of a pure gas, it is convenient to define collision numbers $\zeta_{qq',i}$ as follows:

$$\zeta_{qq',i} = (4/\pi) \, (p \, \tau_{qq',i}/\eta_{qq'}), \tag{37}$$

where $\eta_{qq'}$ is a fictitious viscosity (unless q = q', when it is the true viscosity of species q). It is defined formally in terms of a collision integral,

$$\eta_{qq'} = \frac{5}{8}\frac{kT}{\Omega_{qq'}^{(2,2)}} , \tag{38}$$

where

$$\Omega_{qq'}^{(2,2)} = \langle \gamma^2 (\gamma^2 - \gamma'^2 \cos^2\chi) - \frac{1}{6} \Delta\epsilon_{qq'}^2 \rangle_{qq'} . \tag{39}$$

In practice $\eta_{qq'}$ would be determined from an experimental binary diffusion coefficient, $\mathcal{D}_{qq'}$, and a dimensionless ratio of collision integrals, $A^*_{qq'}$, which is not too sensitive to the law of intermolecular force or inelastic collisions[4] [see Eq. (47)]:

$$n\mu_{qq'} \mathcal{D}_{qq'} = \frac{3}{5} A^*_{qq'} \eta_{qq'} . \tag{40}$$

For rotational energy transfer in simple molecules, $\zeta_{qq',i}$ is usually less than 10 collisions and increases slowly with increasing temperature; for vibrational energy transfer $\zeta_{qq',i}$ is usually of the order of 10^3 collisions or more, and decreases rapidly with increasing temperature. Exceptions are rotational transfer in hydrogen, which is difficult, and vibrational transfer in some complicated flexible molecules, which may be easy.

A few words of explanation are in order as to why relaxation in mixtures has been discussed again here, when it had been discussed previously.[4] It turns out that the method used previously is strictly valid only at zero frequency, and so cannot describe sound propagation properly, although it is still satisfactory for the description of the effects of inelastic collisions on transport coefficients. The mathematical details have been given elsewhere.[11]

B. Reduction of the Formally Exact Theory

In reference 4 it was shown that the steady-state thermal conductivity of a multicomponent mixture is given by

$$\lambda_\infty = \lambda_{\infty tr} + \lambda_{\infty int} , \tag{41}$$

$$\lambda_{\infty tr} = 4 \left|\begin{array}{c|c|c} L^{10,10}_{qq'} & L^{10,01}_{qq'} & x_q \\ \hline L^{01,10}_{qq'} & L^{01,10}_{qq'} & x_q \\ \hline x_{q'} & 0 & 0 \end{array}\right| \times \left|\begin{array}{c|c} L^{10,10}_{qq'} & L^{10,01}_{qq'} \\ \hline L^{01,10}_{qq'} & L^{01,01}_{qq'} \end{array}\right|^{-1} , \tag{42}$$

$$\lambda_{\infty int} = 4 \left|\begin{array}{c|c|c} L^{10,10}_{qq'} & L^{10,01}_{qq'} & x_q \\ \hline L^{01,10}_{qq'} & L^{01,01}_{qq'} & x_q \\ \hline 0 & x_{q'} & 0 \end{array}\right| \times \left|\begin{array}{c|c} L^{10,10}_{qq'} & L^{10,01}_{qq'} \\ \hline L^{01,10}_{qq'} & L^{01,01}_{qq'} \end{array}\right|^{-1} . \tag{43}$$

The formal expressions for the elements $L^{rs,r's'}_{qq'}$ have been given previously in terms of collision integrals. We now wish to express them in terms of various relaxation times and internal diffusion coefficients, as well as in terms of various properties of the pure components and other experimental quantities. We have shown in the preceding section how some of the inelastic collision integrals can be eliminated in terms of relaxation times. The following four types of collision integrals can be reduced in analogy with the elastic collision case:

$$\Omega^{(1,1)}_{qq'} \equiv \langle \gamma^2 - \gamma\gamma' \cos \chi \rangle_{qq'} \tag{44a}$$

$$\Omega^{(2,2)}_{qq'} \equiv \langle \gamma^2 \, (\gamma^2 - \gamma'^2 \cos^2 \chi) - \frac{1}{6} \Delta\epsilon^2_{qq'} \rangle_{qq'} , \tag{44b}$$

$$\Omega^{(1,2)}_{qq'} \equiv \langle \gamma^2 \, (\gamma^2 - \gamma\gamma' \cos \chi) \rangle_{qq'} , \tag{44c}$$

$$\Omega^{(1,3)}_{qq'} \equiv \langle \gamma^3 \, (\gamma^3 - \gamma'^3 \cos \chi \rangle_{qq'} . \tag{44d}$$

The first of these can be eliminated in favor of the experimental binary diffusion coefficient $\mathcal{D}_{qq'}$,

$$\mathcal{D}_{qq'} = \frac{3kT}{16n\,\mu_{qq'}\,\Omega_{qq'}^{(1,1)}} \,. \tag{45}$$

The second integral can be eliminated for the case q' = q in favor of the experimental viscosity η_q of the pure gas q,

$$\eta_q = \frac{5}{8}\frac{kT}{\Omega_{qq}^{(2,2)}} \,. \tag{46}$$

To eliminate the other integrals in Eq. (44) we define the dimensionless ratios,

$$A^*_{qq'} \equiv \frac{1}{2}\,\Omega_{qq'}^{(2,2)}\Big/\Omega_{qq'}^{(1,1)} \,, \tag{47}$$

$$B^*_{qq'} \equiv \frac{1}{3}\left[5\Omega_{qq'}^{(1,2)} - \Omega_{qq'}^{(1,3)}\right]\Big/\Omega_{qq'}^{(1,1)} \,. \tag{48}$$

The value of $A^*_{qq'}$ can be approximated by its value for elastic collisions, since it has been shown that the first-order correction to $A^*_{qq'}$ for inelastic collisions is probably quite small.[3,5] This approximation is substantiated by the success in calculating binary diffusion coefficients from measurements of the viscosities of binary mixtures.[13]

The value of $B^*_{qq'}$ is a little harder to determine than that of $A^*_{qq'}$, even for elastic collisions, since it is more sensitive to the force law model than is $A^*_{qq'}$. As a first approximation the elastic collision value of $B^*_{qq'}$ will be used, and is unlikely to be in error by as much as 10%, but it is possible to have a better approximation than this. The value of $B^*_{qq'}$ can be related to the temperature derivative of

$\Omega_{qq'}^{(1,1)}$ and hence to the temperature dependence of $\mathcal{D}_{qq'}$, which is an experimentally accessible quantity. The relation is obtained by successive differentiations of Eq. (44a), and is

$$
\begin{aligned}
B^*_{qq'} = {} & \frac{5}{4} - \frac{2}{3}\,\frac{T}{\Omega_{qq'}^{(1,1)}}\,\frac{d\Omega_{qq'}^{(1,1)}}{dT} - \frac{1}{3}\,\frac{T^2}{\Omega_{qq'}^{(1,1)}}\,\frac{d^2\Omega_{qq'}^{(1,1)}}{dT^2} \\
& + \frac{1}{3}\left[\Omega_{qq'}^{(1,1)}\right]^{-1} \langle(\epsilon_{qi} - \bar{\epsilon}_q + \epsilon_{q'j} - \bar{\epsilon}_q)^2\,(\gamma^2 - \gamma\gamma'\cos\chi)\rangle_{qq'} \\
& - \frac{1}{3}\,(c_{qint} + c_{q'int})/k \\
& - \frac{1}{3}\left[\Omega_{qq'}^{(1,1)}\right]^{-1} \Big[5\langle(\epsilon_{qi} - \bar{\epsilon}_q + \epsilon_{q'j} - \bar{\epsilon}_{q'})\,(\gamma^2 - \gamma\gamma'\cos\chi)\rangle_{qq'} \\
& - \langle(\epsilon_{qi} - \bar{\epsilon}_q + \epsilon_{q'j} - \bar{\epsilon}_{q'})\,(\gamma^4 - \gamma^3\gamma'\cos\chi)\rangle_{qq'} \\
& - \langle(\epsilon_{qi} - \bar{\epsilon}_q + \epsilon_{q'j} - \bar{\epsilon}_{q'})\,(\gamma^4 - \gamma\gamma'^3\cos\chi)\rangle_{qq'}\Big]. \qquad (49)
\end{aligned}
$$

Approximation is necessary to evaluate all but the first few terms of this expression, as will be discussed in more detail shortly.

Another group of inelastic collision integrals can be eliminated formally in terms of diffusion coefficients for internal energy, just as in the case of pure gases. We define collision integrals for internal energy diffusion as

$$(c_{qint}/k)\,\Omega_{qint,q}^{(1,1)} \equiv \langle(\epsilon_{qi} - \bar{\epsilon}_q)\,[(\epsilon_{qi} - \epsilon_{qj})\,\gamma^2 - (\epsilon_{qk} - \epsilon_{ql})\,\gamma\gamma'\cos\chi]\rangle_{qq}\ , \qquad (50a)$$

$$(c_{qint}/k)\,\Omega_{qint,q'}^{(1,1)} \equiv \langle(\epsilon_{qi} - \bar{\epsilon}_q)\,[(\epsilon_{qi} - \bar{\epsilon}_q)\,\gamma^2 - (\epsilon_{qk} - \bar{\epsilon}_q)\,\gamma\gamma'\cos\chi]\rangle_{qq'}\ , \qquad (50b)$$

and binary diffusion coefficients for internal energy as

$$\mathcal{D}_{qint,q'} \equiv \frac{3kT}{16n\,\mu_{qq'}\,\Omega^{(1,1)}_{qint,q'}} \; . \qquad (51)$$

Note that these expressions are not symmetric with respect to interchange of q and q'; that is, $\mathcal{D}_{qint,q'} \neq \mathcal{D}_{q'int,q}$. Physically this means that internal energy of q molecules does not necessarily diffuse through q' molecules at the same rate as internal energy of q' molecules diffuses through q molecules. That this is reasonable is seen by considering the limiting case where q is monatomic and has no internal energy and q' is polyatomic and has a large amount of internal energy. However, if we approximate the internal diffusion coefficients by their elastic collision values, then they are symmetric in the indices q and q', since $\mathcal{D}_{qq'} = \mathcal{D}_{q'q}$. The definitions (50)-(51) have been chosen so that in the limit of elastic collisions $\mathcal{D}_{q'int,q}$ becomes equal to the experimental binary diffusion coefficient $\mathcal{D}_{qq'}$. Also note that $\mathcal{D}_{int,q}$ is <u>not</u> the limit of $\mathcal{D}_{qint,q'}$ as $q' \rightarrow q$. In most of what follows, this has no important consequences, except when we wish to make an allowance for resonant exchange between molecules of different species.

So far we have made no approximations, only definitions of new quantities. At this point in the discussion of a pure gas, no inelastic terms remained except the relaxation time, which in principle was measurable. In the mixture case, a number of extra terms still remain which can be removed only by further approximations. One such approximation has already been made in obtaining expressions for the cross-relaxation times, and can be made again. With the neglect of complex collisions, the following additional relations hold:

$$\langle \Delta\epsilon^2_{qq} \rangle_{qq} = \sum_i \langle \Delta\epsilon^2_{iqq} \rangle_{qq} = \frac{2T}{\pi\eta_q} \sum_i \frac{c_{q,i}}{\zeta_{qq,i}} \; , \qquad (52)$$

$$\langle \Delta\epsilon_q \; \Delta\epsilon_{qq'} \rangle_{qq'} = \langle \Delta\epsilon_q^2 \rangle_{qq'} = \sum_i \langle \Delta\epsilon_{iq}^2 \rangle_{qq'} = \frac{T}{\pi \eta_{qq'}} \sum_i \frac{c_{q,i}}{\zeta_{qq',i}} \quad . \tag{53}$$

Resonant collisions may be safely ignored in Eqs. (52) and (53) since they do not contribute anyway. The quantity $\eta_{qq'}$ in Eq. (53) is obtained from experimental binary diffusion coefficients according to Eq. (40). The sums in Eqs. (52) and (53) can be reduced by noting that (1) the vibrational collision numbers are usually much greater than the rotational ones; (2) at ordinary temperatures $c_{rot} >> c_{vib}$; and (3) the rotational relaxation of most molecules can be described within experimental error by a single collision number. Thus we obtain

$$\langle \Delta\epsilon_{qq}^2 \rangle_{qq} \approx \frac{2T \; c_{q,rot}}{\pi \eta_q \; \zeta_{qq}} \quad , \tag{54}$$

$$\langle \Delta\epsilon_q \; \Delta\epsilon_{qq'} \rangle_{qq'} \approx \frac{T \; c_{q,rot}}{\pi \eta_{qq'} \; \zeta_{qq'}} \quad , \tag{55}$$

where the $\zeta_{qq'}$ are understood to be rotational collision numbers, without further identifying subscripts.

The preceding definitions and the neglect of all complex collisions except exact resonant collisions permit us to express the determinant elements $L_{qq'}^{10,10}$ in terms of experimental or calculable quantities:

$$L_{qq'}^{10,10} = \mathcal{L}_{qq'}^{10,10} + \Delta\mathcal{L}_{qq'}^{10,10} \quad , \tag{56}$$

$$\mathcal{L}_{qq}^{10,10} = - \frac{16}{15} \frac{x_q^2 \; m_q}{\eta_q \; k} - \frac{16}{15} \sum_{q'' \neq q} \frac{x_q \; x_{q''} \; T}{p \mathcal{D}_{qq''} \; (m_q + m_{q''})^2} \times$$

$$\times \left[\frac{15}{2} m_q^2 + \left(\frac{25}{4} - 3B^*_{qq''} \right) m_{q''}^2 + 4 m_q m_{q''} \; A^*_{qq''} \right] , \tag{57a}$$

$$\Delta\mathcal{L}_{qq}^{10,10} = -\frac{32}{9\pi}\frac{x_q^2\, m_q\, c_{q,rot}}{k^2\, \eta_q\, \zeta_{qq}} - \frac{64}{15\pi}\sum_{q''\neq q}\frac{x_q\, x_{q''}\, T\, A^*_{qq''}\, m_q\, m_{q''}}{p\mathcal{D}_{qq''}\,(m_q + m_{q''})^2} \times$$

$$\times\left(\frac{c_{q,rot}}{k\,\zeta_{qq''}} + \frac{c_{q'',rot}}{k\,\zeta_{q''q}}\right), \tag{57b}$$

$$\mathcal{L}_{qq'}^{10,10}\ (q'\neq q) = \frac{16}{25}\frac{x_q\, x_{q'}\, T}{p\mathcal{D}_{qq'}}\frac{m_q m_{q'}}{(m_q + m_{q'})^2}\left(\frac{55}{4} - 3B^*_{qq'} - 4A^*_{qq'}\right), \tag{58a}$$

$$\Delta\mathcal{L}_{qq'}^{10,10}\ (q'\neq q) = -\frac{64}{15\pi}\frac{x_q\, x_{q'}\, T\, A^*_{qq'}\, m_q\, m_{q'}}{p\mathcal{D}_{qq'}\,(m_q + m_{q'})^2}\left(\frac{c_{q,rot}}{k\,\zeta_{qq'}} + \frac{c_{q',rot}}{k\,\zeta_{q'q}}\right). \tag{58b}$$

The elements $\mathcal{L}_{qq'}^{10,10}$ contain no explicit inelastic terms, and have the same formal appearance as the corresponding elastic formula. Inelastic terms are contained implicitly, however, in η_q, $\mathcal{D}_{qq'}$, $A^*_{qq'}$, and $B^*_{qq'}$. All the explicit inelastic terms are in $\Delta\mathcal{L}_{qq'}^{10,10}$.

The diagonal elements $L_{qq}^{01,01}$ can also be expressed in terms of defined quantities:

$$L_{qq}^{01,01} = \mathcal{L}_{qq}^{01,01} + \Delta\mathcal{L}_{qq}^{01,01}, \tag{59}$$

$$\mathcal{L}_{qq}^{01,01} = -\frac{4kT}{p\mathcal{D}_{qint,q}\, c_{q,int}}\left(x_q^2 + \sum_{q''\neq q} x_q\, x_{q''}\frac{\mathcal{D}_{qint,q}}{\mathcal{D}_{qint,q''}}\right), \tag{60a}$$

$$\Delta\mathcal{L}_{qq}^{01,01} = -\frac{8k}{\pi(c_{q,int})^2}\left(\frac{x_q^2\, m_q\, c_{q,rot}}{k\eta_q\, \zeta_{qq}} + \frac{6}{5}\sum_{q''\neq q} x_q x_{q''}\frac{m_q}{m_{q''}}\frac{TA^*_{qq''}}{p\mathcal{D}_{qq''}}\frac{c_{q,rot}}{\zeta_{qq''}}\right). \tag{60b}$$

The reduction so far still leaves the off-diagonal $L_{qq'}^{01,01}$ and all the elements $L_{qq'}^{01,10}$ and $L_{qq'}^{10,01}$. To reduce these we must introduce further approximations, whose ultimate justifications must come from experiment. We notice that $L_{qq'}^{01,01}$ has a term of the form

$$\langle (\epsilon_{qi} - \bar{\epsilon}_q) \left[(\epsilon_{q'j} - \bar{\epsilon}_{q'}) \gamma^2 - (\epsilon_{q'l} - \bar{\epsilon}_{q'}) \gamma\gamma' \cos \chi \right] \rangle_{qq'} \quad , \tag{61}$$

and that the other elements all have terms of the form

$$\langle (\epsilon_{qi} - \bar{\epsilon}_q) \gamma^r (\gamma^s - \gamma'^s \cos \chi) \rangle_{qq'} \quad , \tag{62}$$

where r and s are integers. If these terms are all set equal to zero, the desired reduction will be complete. This approximation can be made to seem plausible on physical grounds. If there is no correlation between initial internal energy states and either the initial or final relative velocities, then such terms go to zero because of the $(\epsilon_{qi} - \bar{\epsilon}_q)$ factors when the summation over internal states is carried out. In somewhat different language, such terms will vanish if the angular scattering distribution is the same for all scattering channels. Such an assumption cannot of course be strictly correct, but should be a good first approximation. We note that for pure gases a similar assumption leads to $\mathcal{D}_{qint,q} \rightarrow \mathcal{D}_{qq}$ and was fairly successful in the description of pure gas thermal conductivities.[3] Furthermore, we will see in the next section that these terms contribute to the final answer only to the extent of second-order corrections. The neglect of terms of (61) and (62), therefore, should not introduce much error.

The neglect, then, of complex collisions and of (61) and (62) enables us to reduce the remaining determinant elements:

$$L_{qq'}^{01,01} \; (q' \neq q) = 0, \tag{63}$$

$$L_{qq}^{10,01} = L_{qq}^{01,10} = \Delta\mathscr{L}_{qq}^{10,01} = \frac{16}{15\pi\, c_{q,int}} \left[\frac{5x_q^{2}\, m_q\, c_{q,rot}}{k\, \eta_q\, \zeta_{qq}} + \right.$$

$$\left. + 2 \sum_{q''\neq q} \frac{x_q\, x_{q''}\, T\, A^*_{qq''}\, m_q\, c_{q,rot}}{p\, \mathscr{D}_{qq''}\, (m_q + m_{q''})\, \zeta_{qq''}} \right] . \tag{64}$$

$$L_{qq'}^{10,01}\ (q'\neq q) = L_{q'q}^{01,10} = \Delta\mathscr{L}_{qq'}^{10,01} = \frac{32}{15\pi\, c_{q'int}} \times$$

$$\times \frac{x_q\, x_{q'}\, T\, A^*_{qq'}\, m_{q'}\, c_{q',rot}}{p\, \mathscr{D}_{qq'}\, (m_q + m_{q'})\, \zeta_{q'q}} . \tag{65}$$

A reduction of $B^*_{qq'}$ as given by Eq. (49) also results, and $B^*_{qq'}$ can now be written entirely in terms of experimentally accessible binary diffusion coefficients:

$$B^*_{qq'} \approx \frac{1}{12} \left[2\left(\frac{\partial \ln \mathscr{D}_{qq'}}{\partial \ln T} \right)_p - 1 \right] \left[9 - 2\left(\frac{\partial \ln \mathscr{D}_{qq'}}{\partial \ln T} \right)_p \right] + \frac{1}{3} \frac{\partial^2 \ln \mathscr{D}_{qq'}}{\partial (\ln T)^2} . \tag{66}$$

Although this has the same appearance as the corresponding expression for elastic collisions,[14] inelastic collisions are concealed in the $\mathscr{D}_{qq'}$. There is one difference in the effect of the neglect of (62) on $B^*_{qq'}$, and on $L_{qq'}^{10,01}$, however: errors introduced by such neglect propagate into the final answer to first order through $B^*_{qq'}$, but only to second order through $L_{qq'}^{10,01}$.

It is now possible to collapse the expressions for λ_∞ given in Eqs. (42)-(43) into more compact expressions containing essentially only measurable quantities or defined diffusion coefficients for internal energy. Mainly because of the diagonalization of $L_{qq'}^{01,01}$ stated in Eq. (63), we can define the following quantities:

$$L_{qq'} \equiv L_{qq'}^{10,10} - \sum_{q''} \frac{L_{qq''}^{10,01} \, L_{q''q'}^{01,10}}{L_{q''q''}^{01,01}} \,, \tag{67a}$$

$$= \mathcal{L}_{qq'}^{10,10} + \Delta\mathcal{L}_{qq'}^{10,10} - \sum_{q''} \left[\frac{\left(\Delta\mathcal{L}_{qq''}^{10,01}\right) \left(\Delta\mathcal{L}_{q''q'}^{01,10}\right)}{\mathcal{L}_{q''q''}^{01,01} + \Delta\mathcal{L}_{q''q''}^{01,01}} \right] \,, \tag{67b}$$

$$y_q \equiv - \sum_{q''} x_{q''} \frac{L_{q''q}^{01,10}}{L_{q''q''}^{01,01}} = - \sum_{q''} \left[\frac{x_{q''} \left(\Delta\mathcal{L}_{q''q}^{01,10}\right)}{\mathcal{L}_{q''q''}^{01,10} + \Delta\mathcal{L}_{q''q''}^{01,01}} \right] \,, \tag{68}$$

and write the thermal conductivities in the form

$$\lambda_{\infty tr} = 4 \left| \begin{array}{c|c} L_{qq'} & x_q + y_q \\ \hline x_{q'} & 0 \end{array} \right| \quad \times \quad |L_{qq'}|^{-1} \,, \tag{69}$$

$$\lambda_{\infty int} = 4 \left| \begin{array}{c|c} L_{qq'} & y_q \\ \hline x_{q'} + y_{q'} & 0 \end{array} \right| \quad \times \quad |L_{qq'}|^{-1} - 4 \sum_{q} \frac{x_q^{2}}{L_{qq}^{01,01}} \,. \tag{70}$$

These formulas are of course approximations in that certain definitions of relaxation times and diffusion coefficients have been used, and certain other kinds of terms have been set equal to zero; the degree of approximation depends on how closely real physical systems are mimicked by such mathematical decrees. It is well to list the fundamental approximations made so far, some only implicitly. They are: (1) use of the Wang Chang-Uhlenbeck formulation of kinetic theory; (2) only Chapman-Enskog first approximations are used for λ, η, and $\mathcal{D}_{qq'}$; (3) neglect of all complex collisions except resonant collisions between like molecules; (4) assumption of uncorrelated internal and translational motions. In addition, formal definitions have been made for the cross-relaxation collision numbers, the diffusion coefficients for internal energy, and the dimensionless ratios $A^*_{qq'}$ and $B^*_{qq'}$.

We should note that the neglect of complex collisions and of the correlation of internal and translational motions deprives us to some extent of the check obtained by passing to the limit of a mixture of a gas with itself. This limit does not agree with the known result for the thermal conductivity of a single gas unless complex collisions are also neglected in the single gas. But this means neglect of resonant (or nearly resonant) exchange collisions.[3] The reason exchange collisions are partly lost in the limit of a mixture of a gas with itself is the neglect of the terms (61) in $L^{01,01}_{qq'}$ $(q'\neq q)$. Although the formulas are wrong in this limit, they are probably satisfactory in most cases since the exchange collisions for like molecules are still properly included in $\mathcal{D}_{q\ \mathrm{int},q}$.

Besides the fundamental approximations, there are additional approximations which sometimes must be made in order to carry out a numerical calculation. Some of these are caused simply by a scarcity of relevant experimental data. The additional approximations may be: (1) approximation of internal energy diffusion coefficients $\mathcal{D}_{q,\mathrm{int},q'}$ and $\mathcal{D}_{q'\mathrm{int},q}$ by the ordinary diffusion coefficient $\mathcal{D}_{qq'}$; (2) approximation of $A^*_{qq'}$ by a calculated elastic collision value; (3) estimation of $\zeta_{qq'}$ and $\zeta_{q'q}$ from values of ζ_{qq} and $\zeta_{q'q'}$; (4) approximation of $B^*_{qq'}$ by a calculated elastic collision value if insufficient diffusion data exist for use of Eq. (66).

C. First-Order Theory

In view of the fact that additional approximations almost always must be made before numerical results can be calculated, the formally exact theory will really be correct only to first-order correction terms, and there is little point in carrying higher-order correction terms in the formulas. In other words, in practice it is justifiable to use formulas which have been linearized with respect to ζ^{-1}. Such a scheme worked well for single gases,[3] and therefore seems worth trying for mixtures. When Eqs. (69) and (70) are linearized, the resulting formulas turn out to be rather complicated because the correction terms are, so to speak, strung out on a line:

$$\lambda_{\infty tr} \approx 4 \sum_q x_q \sum_\alpha \Lambda_{q\alpha} \left[x_\alpha + \sum_\beta \left(\Delta\mathcal{L}_{\alpha\beta}^{10,10} \right) \left(\sum_\gamma \Lambda_{\beta\gamma} x_\gamma \right) - \sum_\beta \left(x_\beta / \mathcal{L}_{\beta\beta}^{01,01} \right) \left(\Delta\mathcal{L}_{\alpha\beta}^{10,01} \right) \right], \tag{71}$$

$$\lambda_{\infty int} \approx - 4 \sum_q \left(x_q / \mathcal{L}_{qq}^{01,01} \right) \left[x_q + \sum_\alpha \left(\Delta\mathcal{L}_{q\alpha}^{10,01} \right) \left(\sum_\beta \Lambda_{\alpha\beta} x_\beta \right) - \left(x_q / \mathcal{L}_{qq}^{01,01} \right) \left(\Delta\mathcal{L}_{qq}^{01,01} \right) \right], \tag{72}$$

where

$$\Lambda_{\alpha\beta} = \left| \begin{array}{c|c} \mathcal{L}_{qq'}^{10,10} & \delta_{q\alpha} \\ \hline \delta_{\beta q'} & 0 \end{array} \right| \times \left| \mathcal{L}_{qq'}^{10,10} \right|^{-1} . \tag{73}$$

Using the expressions for $\mathcal{L}_{qq'}^{rs,r's'}$ and $\Delta\mathcal{L}_{qq'}^{rs,r's'}$ given previously, we see that we have written the thermal conductivities as functions of the experimental viscosities, heat capacities, ordinary and internal energy diffusion coefficients, and relaxation times.

The linearized equations are still not in the best form for comparison with experiment, however. It is the usual practice in such comparisons to force the experimental curves through the experimental end points, which Eqs. (71)-(73) will not do unless exactly the right values are used for $c_{q,int}$, $\mathcal{D}_{qint,q}$ and ζ_{qq}. We therefore take the limits $x_q \to 1$ in Eqs. (71)-(73) to identify the terms that make up the heat conductivities of the pure components. When these terms are regrouped, Eqs. (71) and (72) can be written as

$$\lambda_\infty = \lambda_{HE} + \Delta\lambda \tag{74}$$

where λ_{HE} is the Hirschfelder-Eucken result,

$$\lambda_{HE} = \lambda(\mathrm{mon}) + \sum_q [\lambda_q - \lambda_q(\mathrm{mon})] \left[1 + \sum_{q' \neq q} \frac{x_{q'}}{x_q} \frac{\mathcal{D}_{q\mathrm{int},q}}{\mathcal{D}_{q\mathrm{int},q'}}\right]^{-1} , \tag{75}$$

$$\lambda(\mathrm{mon}) = 4 \left|\begin{array}{c|c} \mathcal{L}_{qq'}^{10,10} & x_q \\ \hline x_{q'} & 0 \end{array}\right| \times \left|\mathcal{L}_{qq'}^{10,10}\right|^{-1} , \tag{76}$$

$$\lambda_q(\mathrm{mon}) = \frac{15}{4} k \, (\eta_q/m_q) , \tag{77}$$

where λ_q is the first-order approximation for the heat conductivity of pure component q and $\Delta\lambda$ is the correction term. The connection $\Delta\lambda$ vanishes as $x_q \to 1$ whatever may be the assigned values of the inelastic collision numbers, and is given by the following rather long formula:

$$\begin{aligned} \Delta\lambda = 4 \sum_q \Bigg\{ & x_q \sum_\alpha \Lambda_{q\alpha} \sum_\beta \left(\Delta\mathcal{L}_{\alpha\beta}^{10,10}\right) \left(\sum_\gamma \Lambda_{\beta\gamma} \, x_\gamma\right) - 2\left(x_q/\mathcal{L}_{qq}^{01,01}\right) \sum_\alpha \left(\Delta\mathcal{L}_{q\alpha}^{10,01}\right)\left(\sum_\beta \Lambda_{\alpha\beta} x_\beta\right) \\ & - \left(x_q{}^2/\mathcal{L}_{qq}^{01,01}\right) \left[\left(\ell_{qq}^{01,01}/\ell_{qq}^{10,10}\right) \left(\Delta\ell_{qq}^{10,10}/\ell_{qq}^{10,10}\right) + 2\left(\ell_{qq}^{10,01}/\ell_{qq}^{10,10}\right) \right. \\ & \left. + \left(\Delta\ell_{qq}^{01,01}/\ell_{qq}^{01,01}\right) - \left(\Delta\mathcal{L}_{qq}^{01,01}/\mathcal{L}_{qq}^{01,01}\right)\right]\Bigg\} , \end{aligned} \tag{78}$$

where

$$\ell_{qq}^{rs,r's'} = \lim_{x_q \to 1} \mathcal{L}_{qq}^{rs,r's'} \quad . \tag{79}$$

We now take the step of replacing λ_q in Eq. (75) by the experimental thermal conductivity of pure component q. The final result is thus equivalent to the Hirschfelder-Eucken formula for mixtures plus a correction term. These are the working equations to be used for comparisons with experiment.

IV. COMPARISON WITH EXPERIMENT

A. Data Needed

Quite a few experimental quantities are required to calculate the thermal conductivity of even a binary mixture. In this subsection we will enumerate what they are and the various choices of evaluating them that are open to us at the present time. Eight properties of pure components are needed: λ_1, λ_2, η_1, η_2, $\mathcal{D}_{1int,1}$, $\mathcal{D}_{2int,2}$, $(c_{1,int}/\zeta_{11})$, and $(c_{2,int}/\zeta_{22})$, of which the first six are needed even for the Hirschfelder-Eucken approximation. However, it is common practice to approximate the internal diffusion coefficients by self-diffusion coefficients, and often to calculate these from the viscosities by the relation

$$\mathcal{D}_{qq} = \frac{6}{5}\left(\frac{\eta_q}{n\, m_q}\right) A^*_{qq} , \qquad (80)$$

using a theoretical value for A^*_{qq}. If resonant exchange collisions are believed to be important, a correction may be applied according to Eq. (15).

Seven mixture properties are required. Three are needed for the Hirschfelder-Eucken approximation: A^*_{12}, B^*_{12}, and $\mathcal{D}_{12}$, the last being necessary to calculate λ(mon). A^*_{12} is usually calculated theoretically for some central-field intermolecular force model; the value of B^*_{12} is often obtained the same way, although it would probably be better to determine it from the temperature dependence of $\mathcal{D}_{12}$ according to Eq. (66) if good diffusion data are at hand. The value of $\mathcal{D}_{12}$ is best obtained experimentally. A number of apparent anomalies in mixture thermal conductivities are probably due to the use of inaccurate values of $\mathcal{D}_{12}$ that were obtained from semi-empirical combination rules.[16] The values of $\mathcal{D}_{1int,2}$ and $\mathcal{D}_{2int,1}$ are also needed for the Hirschfelder-Eucken approximation, but are usually both approximated by $\mathcal{D}_{12}$. This is similar to the procedure adopted for $\mathcal{D}_{1int,1}$ and $\mathcal{D}_{2int,2}$ except that in this case it is not clear as to how to apply a correction for exchange collisions. The only inelastic mixture quantities needed are thus ζ_{12} and ζ_{21}.

The only new data not needed for the Hirschfelder-Eucken approximation are the four relaxation times. The four internal diffusion coefficients were really needed previously, as shown implicitly in Hirschfelder's derivation, but the present treatment emphasizes that these can be markedly different from the corresponding ordinary diffusion coefficients if exchange collisions are probable. With the exception of this last very special type of inelastic effect or of very special models, the effect of inelastic collisions on the internal diffusion coefficients is unknown. This question will be taken up again in the last section. In principle, numerical values of the four relaxation times can be obtained from sound absorption measurements in mixtures, as outlined in Sec. IIIA; in practice such information is seldom available. Values of ζ_{11} and ζ_{22} are often known from experiment, and in the absence of that may always be estimated from measurements of λ_1 and λ_2. Data on ζ_{12} and ζ_{21}, however, are almost completely lacking. For some time to come we will be forced to make educated guesses on their values, based on the values of ζ_{11} and ζ_{22}.

B. Specific Systems

To test the theoretical formulas, a number of systems were selected that represent different general types and for which a reasonable amount of experimental data is available. We consider a mixture of a monatomic plus a nonpolar diatomic gas (He-O_2), mixtures of two nonpolar polyatomic gases (N_2-CO_2 and N_2-H_2), mixtures of a nonpolar and a polar gas (O_2-H_2O, N_2-NH_3, and H_2-NH_3), a ternary mixture (N_2-H_2-NH_3), and mixtures of isotopic polar gases (H_2O-D_2O and HCl-DCl).

The data used are summarized in Tables I and II, together with their sources. Direct experimental data were used as far as possible. Internal diffusion coefficients have had to be approximated by ordinary coefficients of mutual and self-diffusion, and some of the latter had to be calculated from viscosities according to Eq. (80). An exchange correction to the internal diffusion coefficient has been made for the most part only for the case of exact resonance in polar gases, as in Eq. (15). The exception is an ad hoc assumption applied to the H_2O-D_2O interaction. The values of A^*_{12} and B^*_{12} have been calculated from the (12-6) or the (12-6-3) potential functions; this may produce errors of several percent in these quantities, and the final result often does not seem to be very sensitive to these inaccuracies. However, there seem to be special cases in which it is necessary to use the correct B^*_{12}. Potential parameters for the pure components are those listed by Mason and Monchick.[17] The mutual interaction parameters were obtained from these by a simple combining rule.[17] Where good diffusion data were available, empirical values of B^*_{12} were evaluated according to Eq. (66). These are listed in Table II along with the theoretical values. In most cases, thermal conductivites were calculated from the empirical B^*_{12}. These will be discussed below, but are not shown in those graphical or tabular correlations where they did not differ very much from the more naive calculation. The inelastic collision numbers are the most uncertain pieces of data; in many cases the numbers used are only educated guesses. In most cases, we have set ζ_{12} equal to ζ_{11}.

Calculations were carried out both for the present linearized formula, Eqs. (74)-(79), and for the Hirschfelder-Eucken formula where all $\zeta \to \infty$. For some systems we have tried the effect of varying the ζ's and $\mathcal{D}$'s a bit, but without any attempt to produce a "best fit." With some of the polar gases we have tried the effects of resonant collisions and inelastic collisions independently of each other. The details for the individual systems are discussed below. It will be noted that consistent values of ζ_{11} for a given gas were not used for different calculations. It was not found necessary to do this because the shapes of the curves were not too sensitive to the values of ζ.

1. He-O_2

In this particular system of a rare gas and a polyatomic gas, we are fortunate in that all the relaxation times have been measured in the temperature range of interest.[18] This is the only system for which this is true. All the other quantities, with the exception of the self-diffusion coefficient of He, have also been measured. Since He is a monatomic gas whose internal degrees of freedom can be ignored, a value of $\mathcal{D}_{11}$ calculated from the viscosity and a (12-6) value of A^*_{11} should be fairly accurate. From Fig. 1 it is seen that both the Hirschfelder-Eucken and the inelastic formula agree with the experimental data to within 2%. The thermal conductivity was also calculated with the empirical value of B^*_{12} but differed at most by 1% from the curve calculated with a (12-6) value of B^*_{12}. Some additional numerical experimentation showed that the inelastic formula was very insensitive to the particular values of the relaxation numbers. This seemed to be a common feature of all nonpolar gas mixtures.

2. N_2-CO_2 and N_2-H_2

In both of these systems the calculations carried out with the theoretical value of B^*_{12} only are shown since the theoretical value differed only slightly from the empirical. At the two lowest temperatures the N_2-CO_2 data seem to be fitted equally well, within experimental uncertainty ($\approx$ 2%), by the Hirschfelder-Eucken or the various inelastic curves. Numerical experimentation, shown in more detail in Fig. 2, demonstrated that this system was more sensitive to the ζ's than the He-O_2 system, but that the total variation was less than the experimental error. The deviation at 1000°K is probably due to experimental error. Recent measurements of the self-diffusion coefficients of CO_2[19] indicate a rather larger value of $\mathcal{D}_{11}$ than would be estimated from the viscosity data. At 1000°K the data of Ember, Ferron and Wohl[19] indicate a value of $\mathcal{D}_{11} = 1.246$, whereas the viscosity indicates $\mathcal{D}_{11} = 0.962$. However, the values of A^*_{11} required if these data are valid seem much too high.

A calculation was made with Ω_{11} increased by $\approx$ 3%, but the curves were lowered only by 0.7%. It was also ascertained that the N_2-CO_2 curves were very insensitive to B^*_{12}.

Much less numerical experimentation was carried out on the N_2-H_2 system, as shown in Fig. 3. The calculations were carried out only for the (12-6) value of B^*_{12}. Gray and Wright[20] indicate that a value of B^*_{12} = 1.17 would move the Hirschfelder-Eucken curves up to fit the data better, but the experimental diffusion data seem to indicate a value of 1.078, which would make the fit even worse.

3. Polar-Nonpolar Gas Mixtures: N_2-NH_3, H_2-NH_3, O_2-H_2O

In Figs. 4 and 5 are plotted the thermal conductivities of N_2-NH_3 and H_2-NH_3 mixtures.[21] As is seen from Table II the empirical values of B^*_{12} differ widely from the theoretical. The thermal conductivities were calculated with both values of B^*_{12}. In the N_2-NH_3 case the difference was too small to be seen graphically and only the thermal conductivity calculated with the theoretical value of B^*_{12} is shown. Good agreement was obtained at 298.5°K, but at 348°K the agreement is as poor as in the N_2-H_2 case. For the H_2-NH_3 mixture a significant improvement was obtained by using the empirical value of B^*_{12}.

In Table III the calculated values of the ternary mixture H_2-N_2-NH_3 are tabulated. The parameters used are the same as those used in the binary cases and the general fit with experiment is similar.

In the O_2-H_2O system shown in Fig. 6 the two values of B^*_{12} differed at most by 3%, but in the final calculations with the two values of B^*_{12}, λ differed only by a fraction of a percent. This seemed to be a general feature of all the systems investigated. A system where the molecular weights were very different was much more sensitive to the value of B^*_{12} than a system where the masses were comparable in magnitude. As shown by Mason and Monchick[3] the resonant correction to $\Omega_{1int,1}$ is very important for polar molecules. In the present system this correction was applied independently of the inelastic correction. It was observed that the general effect of the resonant correction was both to move the curves upward and to change the magnitude of the inelastic correction. The first effect had already been anticipated by Baker and Brokaw,[22] who predicted that since the diffusion cross section for unlike collisions should be less than that for like collisions if resonant exchange is probable, the rate of transfer of internal energy should increase initially as the mole fraction is varied. The second effect is a relatively minor one. The inelastic correction may move the curves up or down and it is not possible to predict the direction a priori, because $\Delta\lambda$ as given by Eq. (78) is made up of many terms and a large amount of partial cancellation takes place. The Hirschfelder-Eucken formula seems to be preferable at the two temperatures shown. At 1000°K all approximations seem to be equally good.

4. Polar Gas Mixtures: H_2O-D_2O, HCl-DCl

We chose two systems to investigate. The H_2O-D_2O system has been investigated by Baker and Brokaw[22] but unfortunately it now seems[23] that hydrogen-deuterium exchange takes place and this system is really a ternary mixture of H_2O, HDO, and D_2O whose exact composition is not known. Furthermore, because H_2O and D_2O are not symmetric tops the exact magnitude of the resonant correction is not known. Following Baker and Brokaw's suggestion,[22] we used values of δ_{11} and δ_{22} roughly ½ the ones previously used.[3] The calculations were carried out as if the system were really the binary mixture H_2O-D_2O in order to see the effect of various assumptions. As in the previous calculations, the resonant correction applied only to like interactions bows the curves upward. In this case the inelastic effect is appreciably altered by the resonant correction. Following the suggestion of Baker and Brokaw[22] that perhaps easy exchange also takes place between H_2O and D_2O, we assumed that

$$\mathcal{D}_{1\mathrm{int},2} = \mathcal{D}_{2\mathrm{int},1} = \mathcal{D}_{12}/(1 + \delta_{12}),$$

and that $\delta_{12} = \frac{1}{2}(\delta_{11} + \delta_{22})$. This procedure is inconsistent with the foregoing derivation which neglected all complex collisions for unlike molecules. In another sense, however, the equations become more consistent in that they would now give the correct result for the mixture of a polar gas with itself. The results are shown in Fig. 7. Curve (a) is the result for the Hirschfelder-Eucken approximation with exchange corrections in all the internal diffusion coefficients, and is indistinguishable from λ_{HE} with no exchange corrections. Curve (c) is the corresponding inelastic curve and we see that the inelastic effect has actually been changed in sign by introducing a non-zero δ_{12}.

The HCl-DCl system should be a much more clear-cut one to study. Both molecules are linear dipoles for which the resonant exchange correction can be calculated with much more confidence. A sample calculation is shown in Fig. 8 in the hope that someday this system will be investigated experimentally. There is one complicating feature: there is evidence that rotational energy exchange takes place in HCl-DCl collisions.[24] This is due to the fact that the moment of inertia of DCl is almost twice that of HCl and so almost resonant dipole interactions can take place.

V. DISCUSSION

The general conclusion that may be drawn from these calculations, and others that have been carried out but not presented, is that for nonpolar gases or a mixture of a nonpolar and a polar gas, the thermal conductivity is rather insensitive to the exact values of the collision numbers. For these cases, the inelastic correction is small, generally less than experimental uncertainty, and the Hirschfelder-Eucken mixture formula seems to be satisfactory. As shown by the sensitivity of the results to the exchange correction, it is important in both approximations to use the correct values of $\mathcal{D}$. The results are also sensitive to errors in B^*_{12}, very much so if there is a large disparity in the molecular weights of the two gases. The inelastic correction may be positive or negative and moves the curve a little bit up or down but does not change the shape much. Only in half of the systems investigated does the change seem to be in the right direction. The reason for this apparent insensitivity of λ_{mix} to inelastic effects is that we have forced agreement with the pure component end points. Had the calculations been made on a completely theoretical basis, the inelastic effects would have appeared to be much more important. The pure component thermal conductivity is much more sensitive to the relaxation times. Thus the easiest way to calculate mixture thermal conductivities from scratch, if the pure component thermal conductivities are not known, is to use the fully corrected formulas for the pure component thermal conductivities and then to use these in the Hirschfelder-Eucken formula.

Some of the experimental data seems to deviate from theory by amounts outside the quoted experimental error. Gray and Wright[20] have suggested that changes of 6% in $\mathcal{D}_{12}$ or 9% in B^*_{12} could explain these deviations in the N_2-H_2 system. It is possible that the diffusion measurements might be that much in error, but it is also possible that our approximations for $\mathcal{D}_{iint,j}$ and B^*_{ij} might be inaccurate. The following crude treatment to examine the effect of inelastic effects on $\mathcal{D}_{1int,1}$ is put forward not as a proposed correction, but as a plausible argument that this is an area to be investigated more closely.

First, we rewrite Eq. (1) as

$$(c_{int}/k)\ \Omega^{(1,1)}_{int} = \langle((\epsilon_i - \bar{\epsilon})\ (\epsilon_i - \epsilon_j)\ (\gamma^2 - \gamma\gamma'\cos\chi\rangle$$

$$- \langle((\epsilon_i - \bar{\epsilon})\ (\Delta\epsilon - \Delta\epsilon_1)\ \gamma\gamma'\cos\chi\rangle. \qquad (81)$$

Assuming the existence of inverse collisions[3] and neglecting complex collisions, we can write this as

$$(c_{int}/k)\ \Omega_{int}^{(1,1)} \approx \langle(\epsilon_i - \bar{\epsilon})\ (\epsilon_i - \epsilon_j)\ (\gamma^2 - \gamma\gamma'\cos\chi)\rangle + \tfrac{1}{4}\ \langle(\Delta\epsilon)^2\ \gamma\gamma'\cos\chi\rangle$$

$$\approx (c_{int}/k)\ \Omega^{(1,1)} + \tfrac{1}{4}\ \langle(\Delta\epsilon)^2\ \gamma\gamma'\cos\chi\rangle. \qquad (82)$$

To procede further an explicit model is needed to evaluate the last integral. Except for an isotropic differential scattering pattern for the inelastic channels, the last term will not vanish in general. The neglect of complex collisions excludes resonant collisions which also introduce a large correction into $\mathcal{D}_{1int,1}$. The correction term in Eq. (82), therefore, includes types of collision other than complex collisions.

To evaluate the correction term approximately it is convenient to introduce the differential scattering cross section for diffuse scattering of rigid spheres for all inelastic channels. For this model[25]

$$\langle\gamma\gamma'\cos\chi\rangle_{diff} = -\ (4/9)\ \langle\gamma^2\rangle_{el}\quad . \qquad (83)$$

where the suffixes diff and el refer to diffuse and elastic rigid sphere scattering. Assuming the same relation for real molecule scattering and that

$$\langle\gamma^2\ (\Delta\epsilon)^2\rangle \approx \frac{3}{2}\ \langle\Delta\epsilon^2\rangle \quad , \qquad (84)$$

we have finally that

$$\mathcal{D}_{1int,1} \approx \mathcal{D}_{11}\left[1 - \frac{16}{15\pi}\ \frac{A^*_{11}\ c_{1,rot}}{c_{1,int}\ \zeta_{11}}\right]^{-1} \quad . \qquad (85)$$

For N_2 at 300°, the correction amounts to 8%. A definite possibility exists, therefore, that the angular dependence of the inelastic scattering channels must also be taken into account in order to obtain the last few percent in the calculation of transport properties. This has already been observed in the special cases of resonant collisions of polar molecules,[3] the thermo-mechanical effect in dusty gases,[25,5] and the rough sphere model.[4] The foregoing use of the diffuse rigid sphere scattering model should not be taken too seriously. In the case of real molecules, it is probable that the correction to be added to $\mathcal{D}_{int}$ may be positive or negative, depending on the dominant molecular interaction. A similar correction may be derived for $\mathcal{D}_{qint,q'}$. $B^*_{qq'}$ may be investigated in the same manner, but several additional questionable assumptions must be made along the way and so no results will be reported here except to say that we feel that B^*_{12} may also have a small correction due to inelastic effects.

Table I. Pure component properties.

Gas	T °K	$10^5\ \lambda$ cal/cm-sec-°K	$10^5\ \eta^g$ g/cm-sec	$\mathcal{D}_{11}$ (1 atm) cm²/sec	δ_{11}	ζ_{11} collisions
H_2	298.5	42.1[a]	8.92	1.425[h]	0	200
	348.0	46.9[a]	9.917	1.871[h]	0	200
He	303.2	36.37[b]	19.545	1.681[i]	0	∞
	318.2	37.68[b]	20.249	1.812[i]	0	∞
N_2	298.5	6.20[a]	17.77	0.212[j]	0	4.0
	348.0	6.99[a]	19.92	0.277[j]	0	4.0
	300	6.13[c]	17.86	0.211[j]	0	5.41
	500	9.16[c]	25.73	0.299[i]	0	7.42
	1000	15.70[c]	40.15	1.620[i]	0	10.5
O_2	303.2	6.442[b]	20.88	0.213[j]	0	4.0
	318.2	6.688[b]	21.63	0.232[j]	0	4.0
	450	9.00[d]	27.80	0.424[i]	0	4.0
	700	12.70[d]	37.66	0.892[i]	0	7.5
CO_2	300	3.93[c]	14.93	0.117[k]	0	1.84, 2.5
	500	7.80[c]	23.70	0.526[i]	0	2.5
	1000	16.80[c]	39.70	0.962[i]	0	3.84
				0.992[l]	0	∞
NH_3	298.5	5.82[a]	9.99	0.187[i]	0.149	2.0
	348.0	7.10[a]	11.00	0.244[i]	0.118	2.0
H_2O	450	7.35[d]	15.22	0.409[i]	0.70, 0.31	4.0
	700	13.90[d]	24.25	1.019[i]	0.16	4.0
	478.0	7.95[e]	16.40	0.481[i]	0.287	2.3
D_2O	478.0	8.00[e]	16.90	0.456[i]	0.083	1.2
HCl	295.0	3.29[f]	14.40	0.1254[m]	0.487	3.0
DCl	295.0	3.27[f]	14.59	0.1238[m]	0.179	1.582

[a] P. Gray and P. G. Wright, Proc. Roy. Soc. (London) A263, 161 (1961).

[b] B. N. Srivastava and A. K. Barua, J. Chem. Phys. 32, 427 (1960).

[c] A. A. Westenberg and N. de Haas, Phys. Fluids 5, 266 (1962).

[d] A. A. Westenberg and N. de Haas, Phys. Fluids 6, 617 (1963).

[e] C. E. Baker and R. S. Brokaw, J. Chem. Phys. 40, 1523 (1964).

[f] E. U. Franck, Z. Elektrochem. 55, 636 (1951).

[g] Taken from a number of experimental sources, as listed by E. A. Mason and W. E. Rice, J. Chem. Phys. 22, 522, 843 (1954).

[h] P. Harteck and H. W. Schmidt, Z. physik. Chem. B21, 447 (1933).

[i] Calculated from viscosity and a theoretical A^*_{11}.

[j] E. B. Winn, Phys. Rev. 80, 1024 (1950); E. R. S. Winter, Trans. Faraday Soc. 47, 342 (1951).

[k] I. Amdur, J. W. Irvine, E. A. Mason, and J. Ross, J. Chem. Phys. 20, 436 (1952).

[l] Explained in the text.

[m] H. Braune and F. Zehle, Z. physik. Chem. 49B, 247 (1941).

Table II. Mixture properties.

System	T °K	$\mathcal{D}_{12}$ (1 atm) cm²/sec	$\delta_{12} \approx \delta_{21}$	ζ_{12}[h] Collisions	ζ_{21}[h] Collisions	B^*_{12} Theor.	B^*_{12} Empirical
He-O_2	303.2	0.756[a]	0	∞	7.5[i]	1.092	1.115[j]
	318.2	0.825[a]	0	∞	7.5[i]	1.092	1.115[j]
N_2-CO_2	300	0.147[b]	0	5.41	1.84	1.150	1.122[k]
				10.0, 1.84	5.0, 1.84		
	500	0.440[b]	0	7.42	2.5	1.097	1.100[k]
	1000	1.450[b]	0	10.5	3.84	1.092	1.092[k]
O_2-H_2O	450	0.579[c]	0	4.0	4.0	1.124	1.093[k]
	700	1.217[c]	0	7.5	4.0	1.103	1.092[k]
N_2-H_2	298.5	0.784[d]	0	4.0	200	1.093	1.078[j]
	348.0	1.000[d]	0	4.0	200	1.092	1.078[j]
N_2-NH_3	298.5	0.230[d]	0	4.0	2.0	1.134	1.265[j]
	348.0	0.316[d]	0	4.0	2.0	1.122	1.265[j]
H_2-NH_3	298.5	0.780[d]	0	200	2.0	1.107	1.200[j]
	348.0	1.057[d]	0	200	2.0	1.102	1.200[j]
H_2O-D_2O	478.0	0.469[e]	0, 0.19[g]	2.3	1.35	1.255	
HCl-DCl	295.0	0.1246[f]	0	3.0	1.582	1.215	

[a] R. Paul and I. B. Srivastava, Indian J. Phys. 35, 465 (1961).

[b] R. E. Walker and A. A. Westenberg, J. Chem. Phys. 29, 1147 (1958); actual values used were obtained from the best Lennard-Jones fit of the experimental diffusion data.

[c] R. E. Walker and A. A. Westenberg, J. Chem. Phys. 32, 436 (1960); see remark under b.

[d] R. E. Bunde, University of Wisconsin Naval Research Laboratory Rept. No. CM-850 (August 1955).

[e] Calculated from the (12-6-3) potential.

[f] H. Braune and F. Zehle, Z. physik. Chem. 49B, 247 (1941).

[g] Average of δ_{11} and δ_{22}.

[h] Estimated from ζ_{11} and ζ_{22}, or else varied arbitrarily.

[i] R. Holmes, G. R. Jones, N. Pusat, and W. Tempest, Trans. Faraday Soc. 58, 2342 (1962).

[j] Estimated from Eq. (66).

[k] Estimated from the best Lennard-Jones fit of the experimental diffusion data; see R. E. Walker, L. Monchick, A. A. Westenberg, and S. Favin, in *Physical Chemistry in Aerodynamics and Space Flight* (Pergamon Press, Oxford, 1961), pp. 221-227.

Table III. Thermal conductivity of the mixture N_2-NH_3-H_2.

x_{N_2}	x_{NH_3}	$10^5\ \lambda_{HE}$ cal/cm-sec-°K	$10^5\ \lambda_{inel}$ cal/cm-sec-°K	$10^5\ \lambda_{expt}$ cal/cm-sec-°K
		T = 298.5°K		
0.572	0.195	10.68	10.82	11.40 11.05
0.376	0.176	16.05	16.21	16.80
0.086	0.6365	11.83	12.15	12.50
0.151	0.291	19.85	20.19	20.85
0.389	0.5335	7.68	7.79	8.74
0.230	0.5975	9.51	9.70	9.95
0.6305	0.234	8.75	8.87	9.16
0.6185	0.120	11.22	11.32	12.00
0.1020	0.471	15.81	16.24	16.70
0.493	0.159	13.32	13.46	14.00
0.2955	0.159	19.09	19.22	19.95
0.244	0.384	14.21	14.52	14.80
0.282	0.133	20.39	20.47	22.10
0.091	0.353	19.90	20.34	21.15
0.238	0.130	22.16	22.22	21.20
0.238	0.0895	23.64	23.58	24.80
0.117	0.112	28.30	28.28	31.20
0.1215	0.226	23.32	23.60	24.65
		T = 348.0°K		
0.390	0.221	16.58	16.75	17.90
0.568	0.156	13.21	13.34	14.90
0.4265	0.105	18.56	18.61	20.50
0.3145	0.442	13.12	13.35	13.60
0.326	0.124	21.60	21.64	23.70
0.152	0.570	14.02	14.31	15.10
0.177	0.333	20.36	20.70	20.85
0.135	0.450	17.93	18.31	18.70
0.1675	0.2685	22.99	23.27	24.70
0.687	0.167	10.24	10.34	11.30
0.271	0.1685	22.29	22.40	24.10
0.558	0.300	10.42	10.55	11.30
0.419	0.4405	10.54	10.67	11.25
0.2805	0.569	10.80	10.94	11.25

Figure Captions

Fig. 1. He-O_2. Experiment: 303.2°K, ○; 318.2°K, ●. Theoretical: Hirschfelder-Eucken (HE), ——; inelastic, - - -.

Fig. 2. N_2-CO_2. Experiment: 300°K, ○; 500°K, ●; 1000°K, ◓. Theoretical: 300°K: HE and inelastic with $\zeta_{11} = \zeta_{12} = 5.41$, $\zeta_{21} = \zeta_{22} = 1.84$, ——; inelastic with $\zeta_{11} = 5.41$, $\zeta_{12} = 10$, $\zeta_{21} = 5$, $\zeta_{22} = 2.5$, - - -; inelastic with $\zeta_{11} = 5.41$, $\zeta_{12} = \zeta_{21} = \zeta_{22} = 1.84$, —-—-. 500°K: HE, ——; inelastic with $\zeta_{11} = \zeta_{12} = 7.42$, $\zeta_{21} = \zeta_{22} = 2.5$, — — —. 1000°K: HE, $\mathcal{D}_{22} = .962$, ——; HE with $\mathcal{D}_{22} = 0.992$, — - — -; inelastic with $D_{22} = .962$, $\zeta_{11} = \zeta_{12} = 10.5$, $\zeta_{21} = \zeta_{22} = 3.84$, — — —.

Fig. 3. H_2-N_2. Experiment: 298.5°K, ○; 348.0°K, ●. Theoretical: HE, ——; inelastic, — — —.

Fig. 4. H_2-NH_3. Experiment: 298.5°K, ○; 348.0°K, ●. Theoretical: HE, ——; inelastic, — — —.

Fig. 5. N_2-NH_3. Experiment: 298.5°K, ○; 348.0°K, ●. Theoretical: HE, ——; inelastic, — — —.

Fig. 6. O_2-H_2O. Experiment: 450°K, ○; 700°K, ●. Theoretical: HE with no dipole resonant exchange correction, ——; inelastic with no dipole resonant exchange correction, — —; HE with dipole resonant exchange correction, —-—-; inelastic with dipole resonant exchange correction, -----.

Fig. 7. H_2O-D_2O. Experiment: 478.0°K, ○. Theoretical: (a) HE with no exchange corrections, and HE with exchange corrections between all molecules; (b) inelastic with no exchange corrections; (c) HE with exchange corrections between like molecules only; (d) inelastic with exchange corrections between like molecules only; (e) inelastic with exchange corrections between all molecules.

Fig. 8. HCl-DCl. Theoretical HE with exchange correction between like molecules only, ——. Inelastic with exchange correction between like molecules only, — — —.

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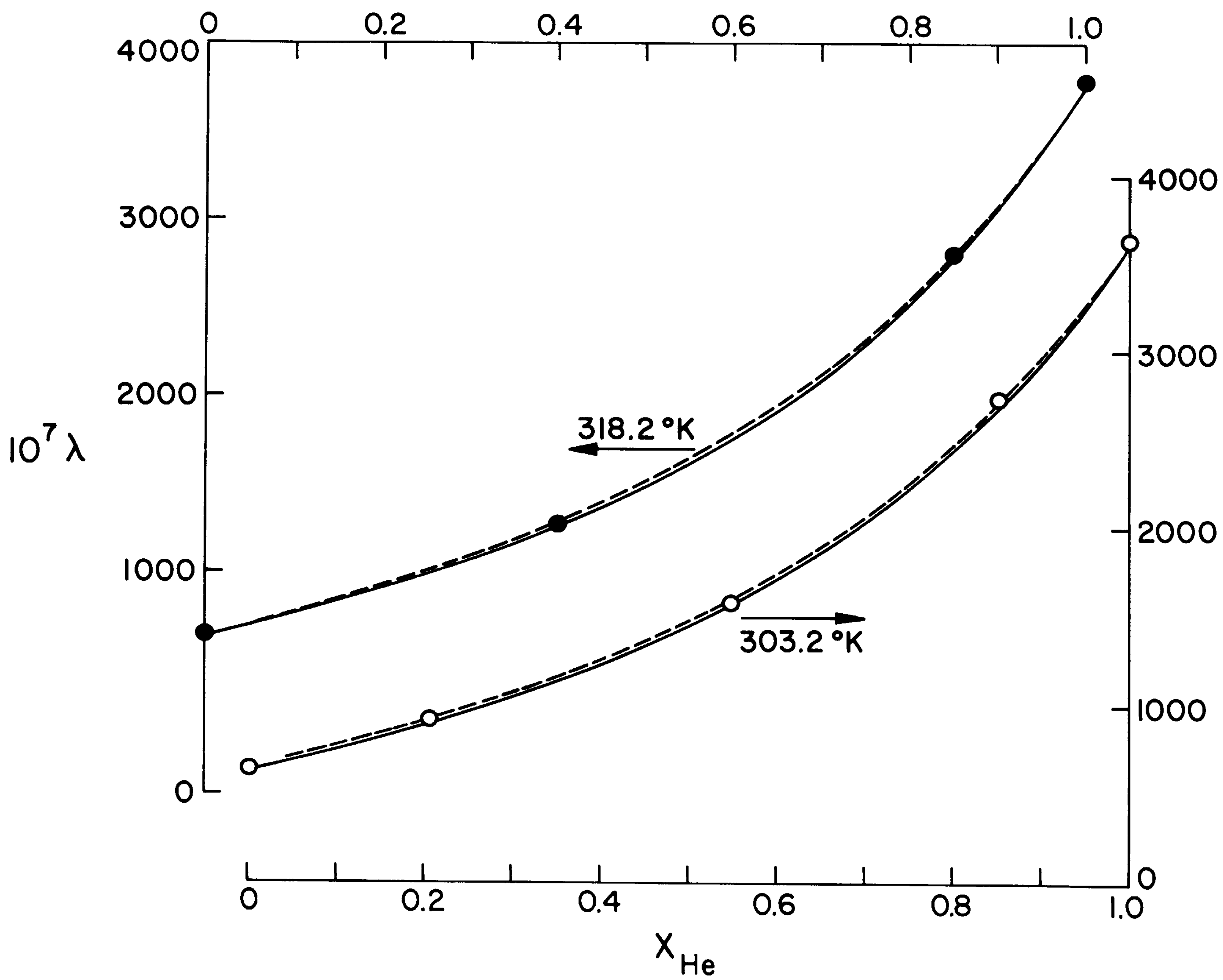
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2000
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0
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0.2
0.4
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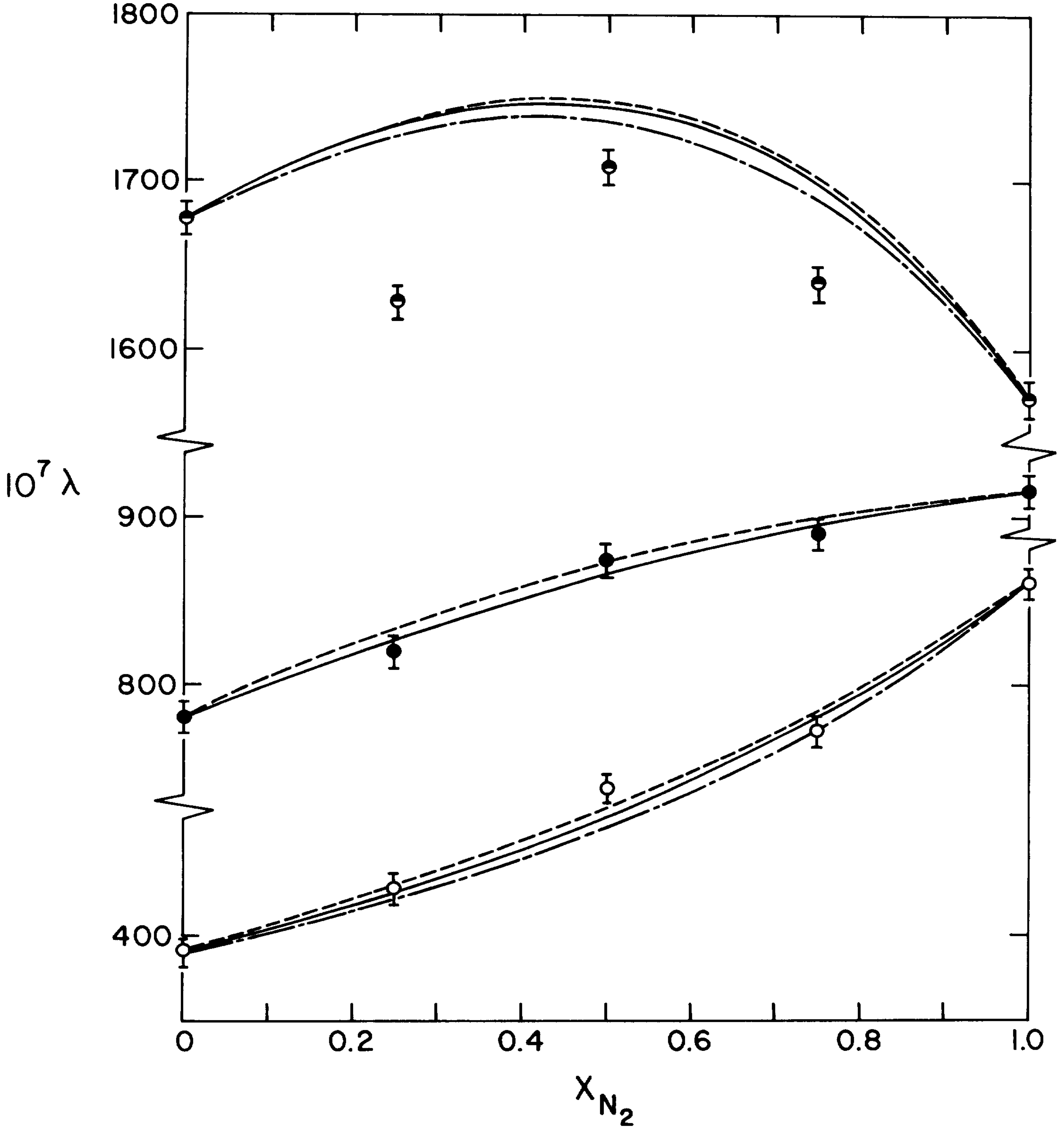
1.0
X_{He}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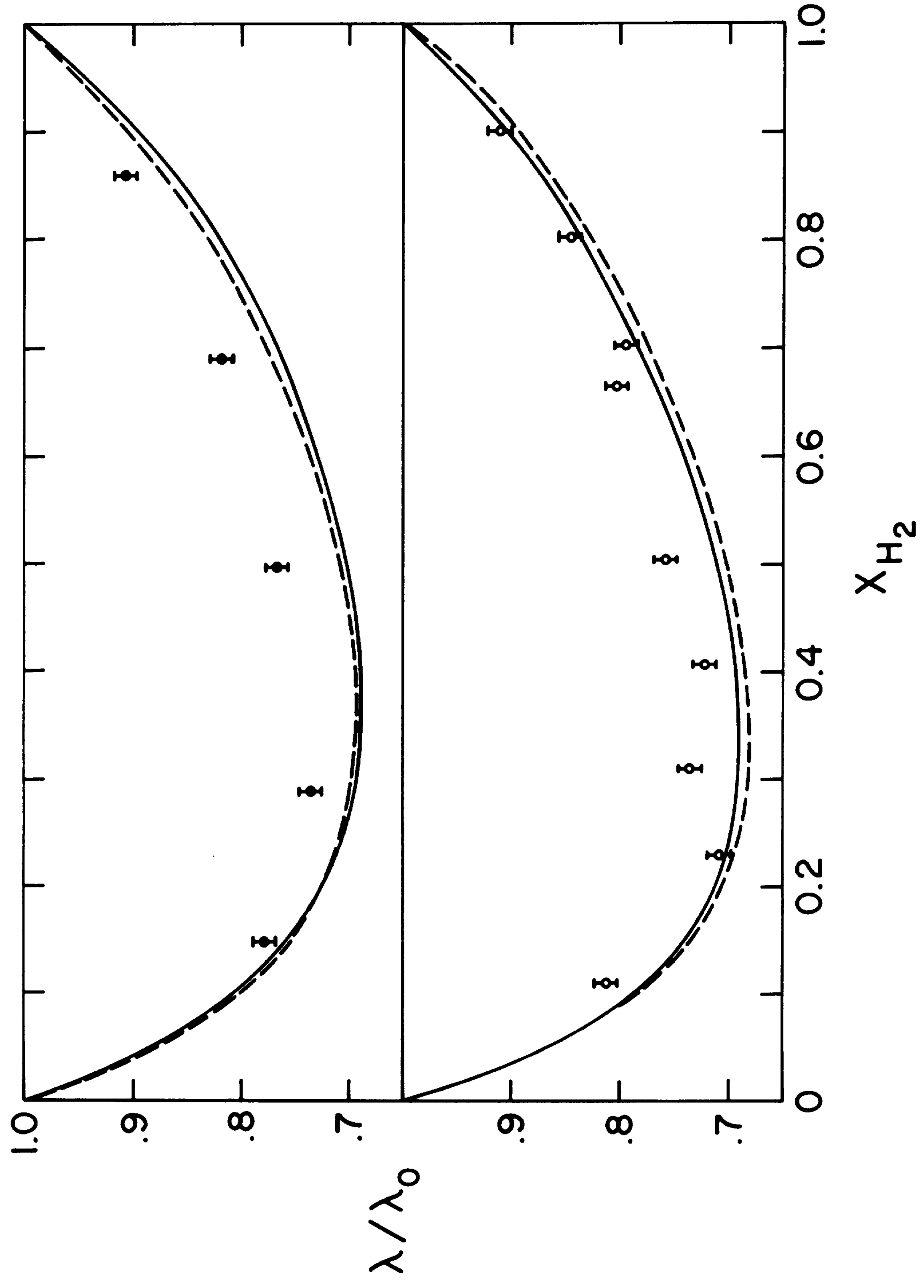

λ/λ₀
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.7
.9
.8
.7
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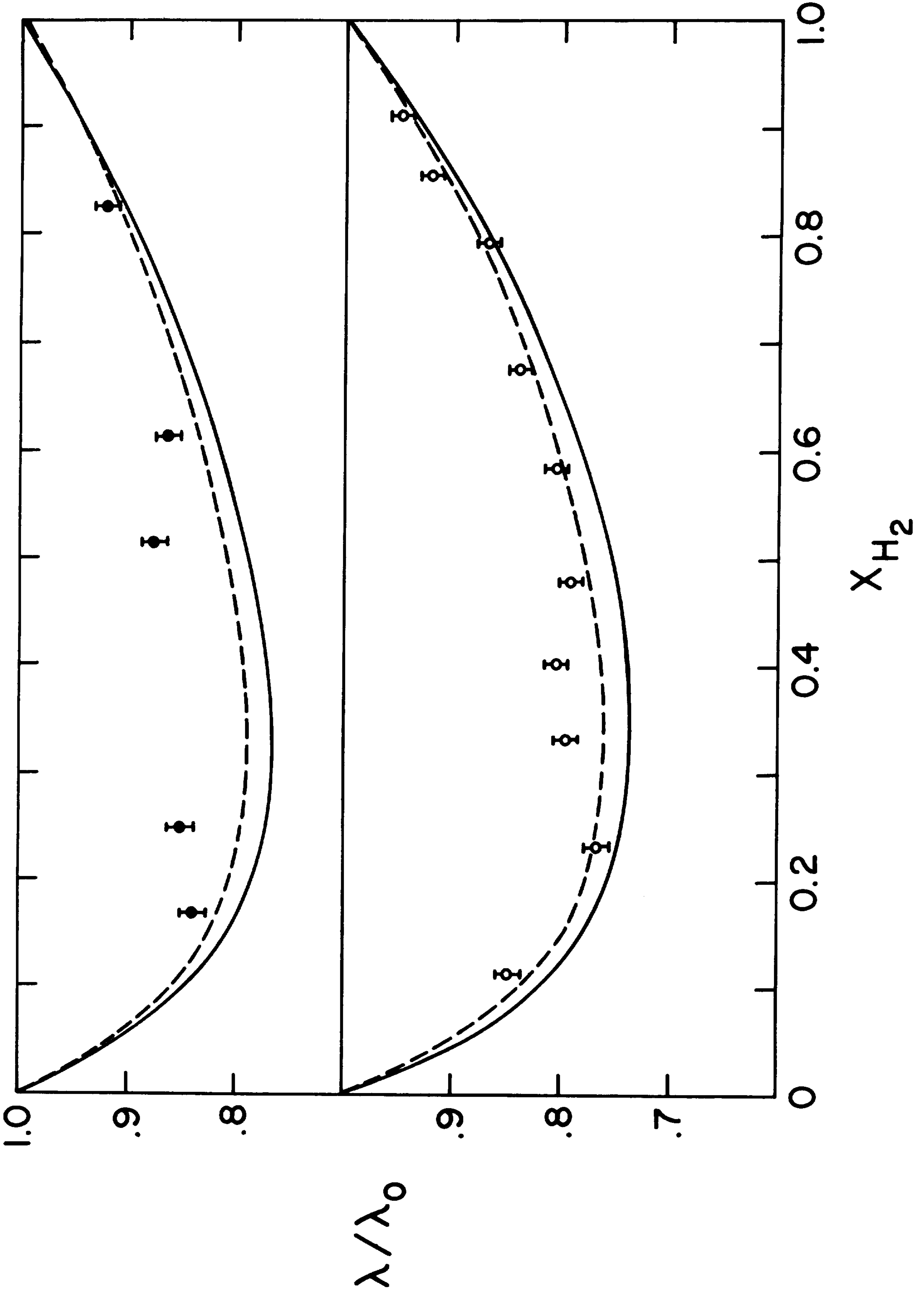
1.0
X_{H_2}



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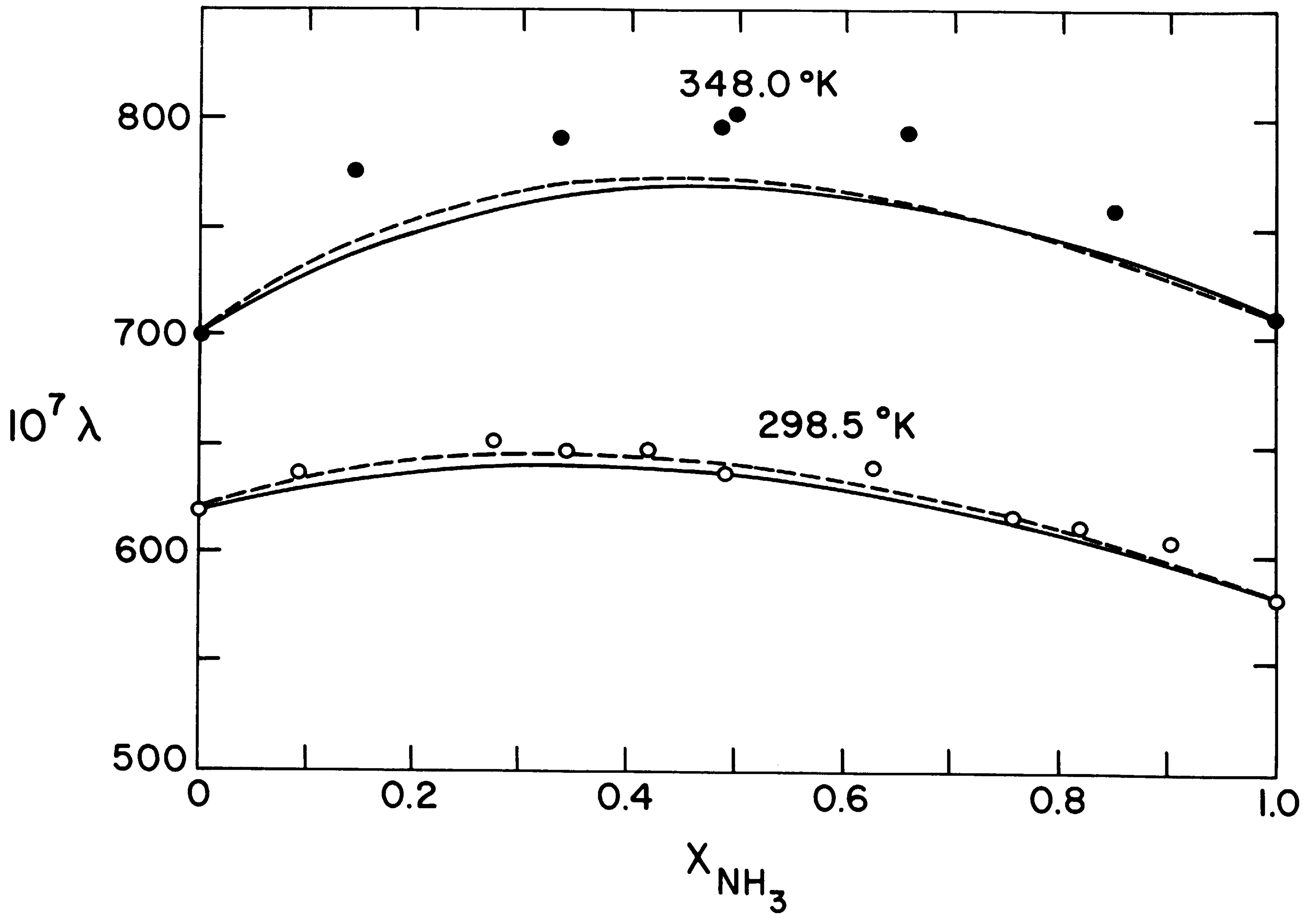
X_{H_2}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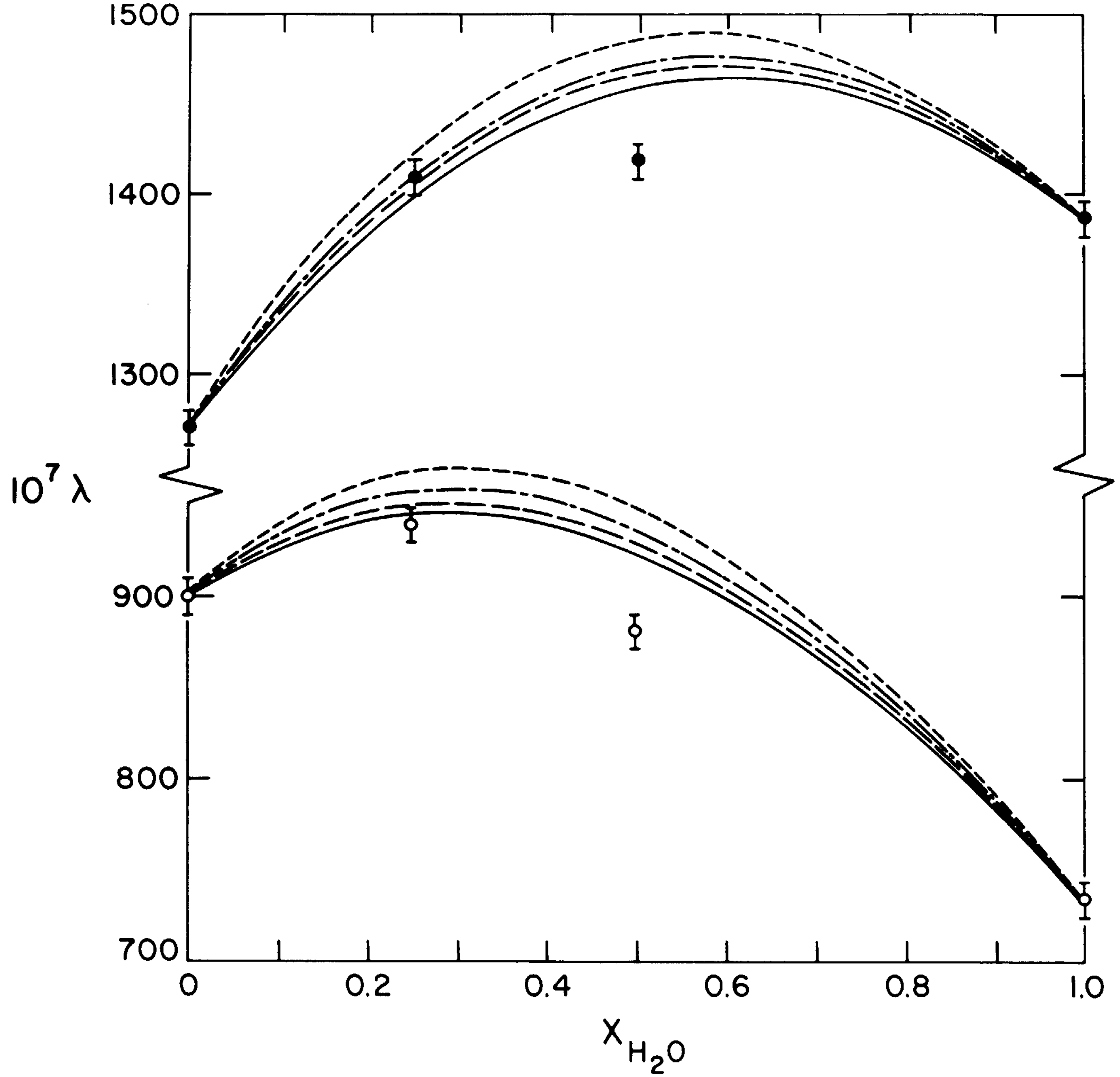
X_{NH_3}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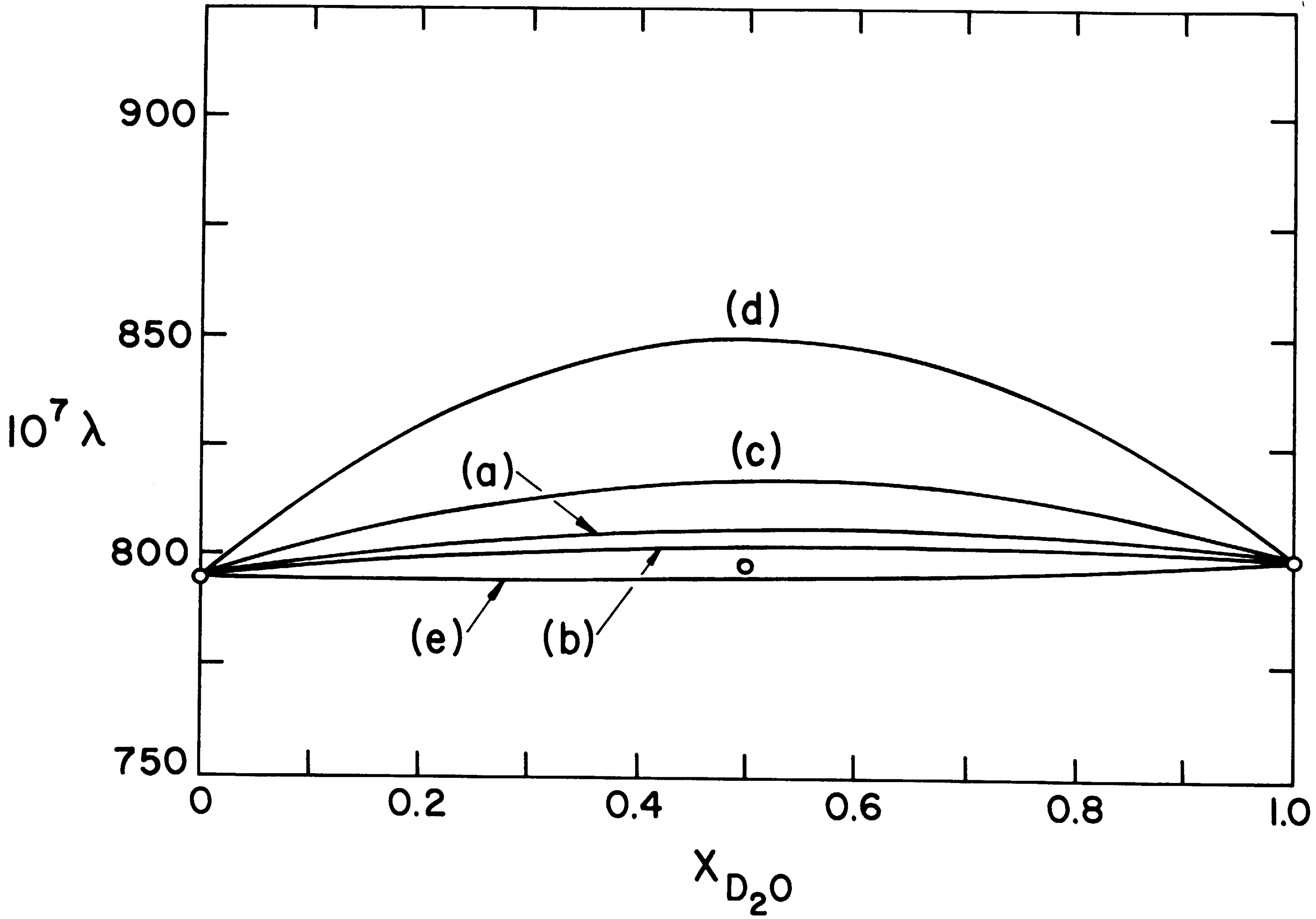
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(d)
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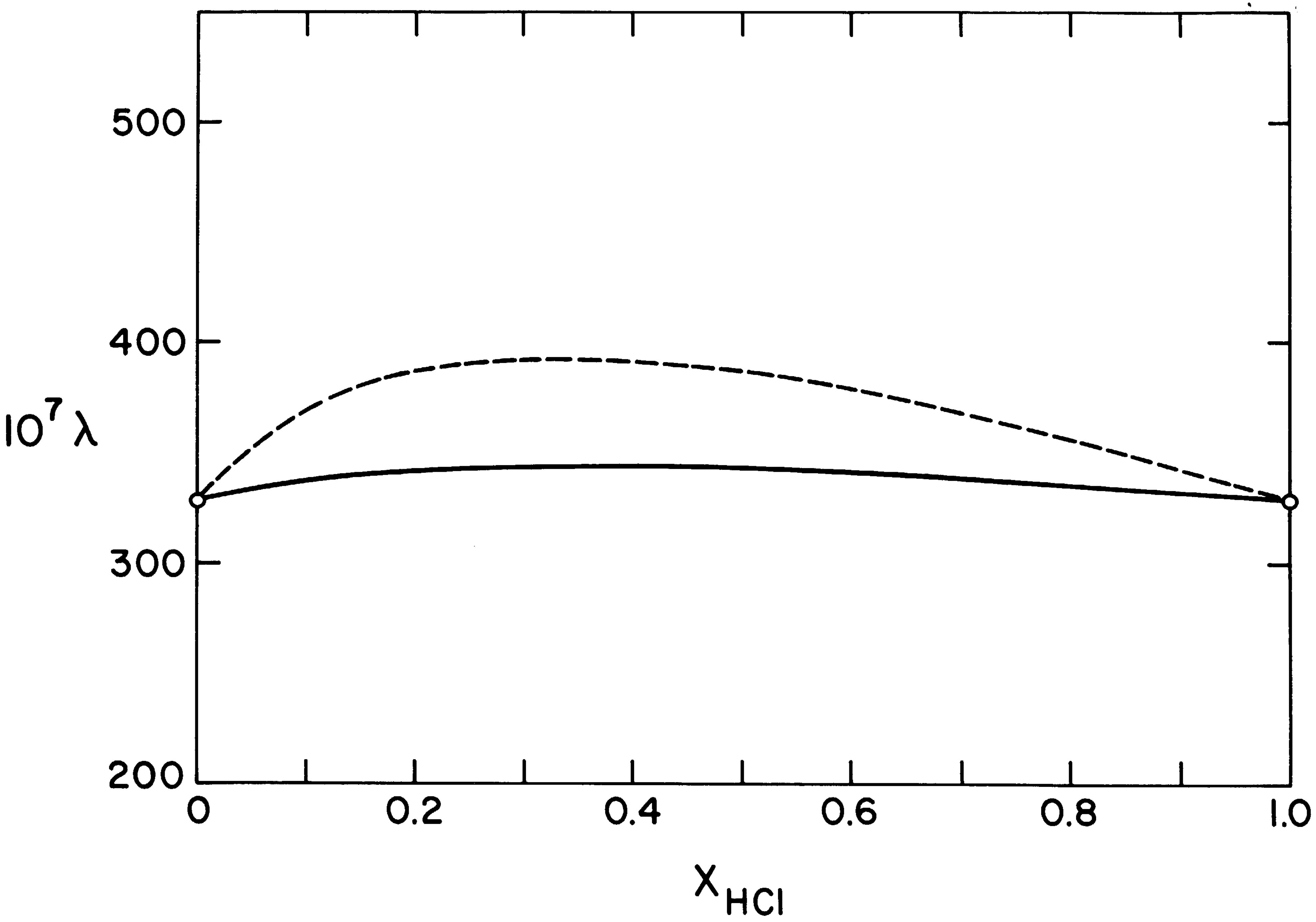
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