

ROTATIONAL RELAXATION IN POLAR GASES

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CHAPTER I

GENERAL REMARKS

At thermal equilibrium, the various molecular energy states in a gas are populated according to Maxwell-Boltzmann statistics. Although energy is continually exchanged between internal and translational degrees of freedom by collisional processes, the various internal states are time invariant, and since individual collisional processes cannot be distinguished experimentally, the rate of energy exchange cannot be measured for a system at thermal equilibrium. However, perturbation of the thermal equilibrium by a sound wave produces heat adiabatically in the compressional phase which is dissipated in the expansion phase. This heat energy is initially in the translational degrees of freedom and is then distributed among the internal degrees of freedom by collisions and this distribution requires time. If the frequency of the sound wave becomes sufficiently high, there may not be enough time in the compressional phase for the heat energy to be transferred to some of the internal degrees. When this happens the effective number of degrees of freedom of the gas has been lowered.

For molecular gases, as the sound frequency is increased from zero, the vibrational modes are the first to fail to keep in equilibrium. As the frequency is further increased the rotational modes are the next which undergo this transition, and when the wavelength of the sound wave becomes approximately the same as the mean-free-path of the

gas molecules, the translational degrees are affected.

Experimental studies of the effects produced by equilibrium perturbation are in general called relaxation studies. The relaxation of the vibrational modes has received the most study both experimentally and theoretically since usually this relaxation occurs at frequencies which are easily obtainable.

Equilibration of the rotational modes has only recently received much study, and good understanding of the energy transfer processes involved has not as yet been achieved either experimentally or theoretically. The rotational modes have proved difficult to study experimentally because of (1) the small equilibration times which are involved, (2) the close unequal spacing of the rotational energy levels dictates a multi-level equilibration process which is difficult to interpret, and (3) translational relaxation often occurs before the absorption peak due to rotation can be attained.

Several classical theoretical calculations have been made for nonpolar gas models⁽¹⁻⁶⁾ and one such calculation has been made for a polar gas model⁽⁷⁾. The nonpolar calculations relate dependence of the equilibration times on the moment inertia of the molecule and the ambient temperature of the system. There has been no general agreement among the nonpolar calculations, and it has been shown that the calculations are extremely dependent upon the potential energy function which is chosen. The calculation for a polar model relates the dependence of the number of collisions necessary for rotational equilibration on the dipole moment and the moment of inertia of the molecule and also to the ambient temperature of the system.

Rotational collision numbers have also been obtained by analysis

of experimental thermal conductivity data; however, there has not been good agreement among the different reports, and it appears that a small error in the experimentally determined thermal conductivities will produce a very large deviation in the subsequent rotational collision numbers.

Some methods other than acoustics and thermal conductivity which have been used to study rotational equilibration are (1) shock waves, (2) jet nozzle techniques, (3) molecular beam scattering, (4) optical spectroscopy, (5) nuclear magnetic resonance. These methods have all been adequately described in several general texts or review articles and will not be discussed here (8-13).

Purpose and Scope.

Rotational equilibration as a function of temperature for most of the common homonuclear diatomic gases and also for several hydrocarbon gases have been reported in the literature (14-15). However, very little data has been reported on rotational equilibration in polar gases and most of the data which has been reported has been derived from thermal conductivity measurements which were performed at low temperatures. From the available data very few conclusions can be drawn as to the dependence of rotational equilibration on dipole moments, moments of inertia, or ambient temperature. One conclusion which has been drawn is that the rotational collision numbers appear to be anomalously low when compared to nonpolar molecules. No conclusion at all can be drawn for the temperature dependence of rotational equilibration since the results of the different experiments which have been performed over a range of temperatures have not been in agreement as to the temperature

dependence of Z_{rot} . In light of these ambiguities it was felt that further study should be made on polar gases.

Gases chosen for this study had to meet the following requirements: (1) appreciable but different dipole moments, (2) small moments of inertia, (3) thermal stability, (4) simple molecular structure, (5) chemically inert to a glass and quartz system, and (6) commercially available. Many gases were examined but most were ruled unacceptable for one or more of the above reasons. Two gases which do meet all of these requirements are HCl and HBr and for this reason these two were chosen for this study.

Ultrasonic absorption and velocity dispersion measurements were made on these gases over a temperature range of 298 °K - 1073 °K. The data obtained has been analyzed both by a one adjustable parameter and a two adjustable parameter technique, and the equilibration times were determined. Comparison has been made to the theoretical calculation for polar gases, and the results are compared to results derived from thermal conductivity studies.

Discussion of Instrument

The measurements were made by use of a high temperature ultrasonic spectrometer which has been described elsewhere⁽¹⁴⁾. Modifications made were as follows: (1) a better bond (Elmer's glue) was used for the receiving transducer, (2) better high pass filters, (3) a slightly larger quartz rod on the receiver, and (4) an additional 20 dB of amplification. These changes improved the frequency range of the instrument somewhat; however, all of the increase in signal was not usable because of the inability of the operator to adequately judge the end of

the standing wave region. Because of the corrosive and poisonous nature of both HCl and HBr the entire apparatus including the gas cylinders were placed under an exhaust hood. A micrometric manometer was also added to the system for determining low pressures with greater accuracy. This allowed for data points to be more closely spaced at high frequencies.

Outline of Balance of Thesis

Chapter II contains a discussion of single relaxation theory, multiple relaxation theory, thermal conductivity theory as related to rotational relaxation and Zeleznik's classical theoretical calculation. In Chapter III previous results for HCl and HBr are presented with the experimental data from this investigation. A discussion of the results is included. Chapter IV is a summary of the results and comparisons are made to both theory and other experiments. Appendix A is a discussion of the instrument and experimental techniques, and Appendix B is a discussion of the best methods of calculating the transport properties and second virial coefficients of polar gases.

CHAPTER II

THEORY

Single Relaxation

When the effective number of degrees of freedom of a gas is decreased by increasing the frequency of a perturbing sound wave, this decrease is accompanied by an increase in the specific heat ratio,

$\gamma = \frac{C_p}{C_v}$, of the gas. The velocity of sound in an ideal gas is given by

$$V = \left(\frac{\gamma RT}{M} \right)^{\frac{1}{2}} \quad (1)$$

where R is the gas constant, T is the temperature, and M is the molecular weight. The specific heats are given by

$$C_v = C_{tr} + C_{rot} + C_{vib} \quad (2)$$

$$C_p = C_v + R$$

where tr , rot , and vib denote translational, rotational, and vibrational respectively. For most diatomic gases the vibrational specific heat relaxes at very low frequencies and for the study of the rotational degrees of freedom in a diatomic gas

$$C_v = C_{tr} + C_{rot} = \tilde{C}_v + C'$$

$$C_p = C_{tr} + C_{rot} + R = \tilde{C}_p + C' \quad (3)$$

where C' indicates the internal or relaxing specific heat.

At frequencies sufficiently high for the vibrational modes to have come to equilibrium but low enough so that the rotational modes have not started to equilibrate, the velocity of sound is given by

$$v_o^2 = \frac{RT}{M} \left(1 + \frac{R}{C_{tr} + C_{rot}}\right) = \frac{RT}{M} \left(1 + \frac{R}{\tilde{C}_v + C'}\right) \quad (4)$$

at higher frequencies, after the rotational degrees have relaxed, the velocity of sound is given by

$$v_\infty^2 = \frac{RT}{M} \left(1 + \frac{R}{C_{tr}}\right) = \frac{RT}{M} \left(1 + \frac{R}{\tilde{C}_v}\right) \quad (5)$$

In the relaxing region the internal or relaxing specific heat is a function of the sound frequency, and the effective specific heat or frequency dependent specific heat of the system is given by⁽¹²⁾

$$\langle C_v \rangle_{\text{eff}} = \tilde{C}_v + \frac{C'}{1 + i\omega\tau} = C_v - \frac{C' i\omega\tau}{1 + i\omega\tau} \quad (6)$$

where τ is the relaxation time of the system. τ is defined by

$$-\frac{dE'}{dt} = \frac{1}{\tau} [E' - E'(T_{tr})] \quad (7)$$

where E' is the momentary value of the internal energy and $E'(T_{tr})$ is the value it would have in equilibrium with the translational degrees of freedom. T_{tr} is the instantaneous value of the translational temperature.

Inserting the effective value of the specific heat into Equation (1) yields

$$v^2 = \frac{RT}{M} + \frac{R^2 T}{M} \left(\frac{1}{C_v - \frac{C' i \omega \tau}{1 + i \omega \tau}} \right) \quad (8)$$

and taking the real part of this gives (11).

$$v^2 = \frac{RT}{M} \left\{ 1 + R \left[\frac{C_v + \tilde{C}_v \omega^2 \tau^2}{C_v^2 + \tilde{C}_v^2 \omega^2 \tau^2} \right] \right\} \quad (9)$$

At low frequencies when $\omega \tau \ll 1$ this reduces to Equation (4) and at high frequencies when $\omega \tau \gg 1$ it reduces to Equation (5).

For diatomic gases it is known from equipartition of energy that $C_{tr} = 3/2 R$ and $C_{rot} = R$ so that

$$C_v = 3/2 R + R = 5/2 R$$

$$C_p = (3/2 R + R) + R = 7/2 R$$

For the discussion of rotation these are the maximum values of C_v and C_p . The minimum values are $C_v = 3/2 R$ and $C_p = 5/2 R$. These are the same values given by Equation (6) in the limits of $\omega \tau \ll 1$ and $\omega \tau \gg 1$.

The frequency at which the inflection point of Equation (9) occurs is related to the relaxation time of Equation (7) by

$$\omega_i = \frac{1}{\tau} \frac{C_v}{\tilde{C}_v}$$

The velocity dispersion region in a molecular gas is accompanied

by a frequency band of absorption greater than that which would be expected from classical sources. If this frequency band lies in the region where normal macroscopic hydrodynamical equations are valid, i.e. the transport properties are not frequency dependent, then it can be safely assumed that the classical absorption and excess absorption are additive.

$$\alpha = \alpha_{cl} + \alpha_{int} \quad (10)$$

where α is the total absorption or the experimentally measured absorption, α_{cl} is the classical absorption, and α_{int} is the internal or molecular absorption. The classical absorption is predicted from the viscosity and heat conductivity of the gas and is given by⁽¹⁰⁾

$$\alpha_{cl} = \frac{\omega^2}{2\rho V^3} \left[\frac{4}{3} \eta + \left(\frac{1}{C_v} - \frac{1}{C_p} \right) \kappa \right] \quad (11)$$

where ρ is the gas density, M is the viscosity, and κ is the heat conductivity. It should be remembered when calculating α_{cl} from Equation (11) that the quantities V , C_p , and C_v are frequency dependent in the excess absorption region, and at high frequencies the classical term can be very large.

The internal or molecular absorption is given by⁽¹⁰⁾

$$\alpha_{int} = \frac{\omega V}{2V_o^2} \left\{ \frac{RC'}{C_v \tilde{C}_p} \frac{\omega \tau'}{1 + \omega^2 \tau'^2} \right\} \quad (12)$$

where τ' is related to the relaxation time defined in Equation (7) by

$$\tau' = \frac{C_p - C'}{C_p} = \frac{\tilde{C}_p}{C_p} \tau \quad (13)$$

It has been common practice to express experimental relaxation times in terms of a collision number Z_{coll} defined as

$$Z_{\text{coll}} = \frac{\tau}{\tau_c} \quad (14)$$

where τ_c is the mean time between collisions usually taken to be

$$\tau_c = \frac{\pi\eta}{4p} \quad (15)$$

Roughly, Z_{coll} is the number of collisions required to interchange a quantum of internal energy with translational energy. For cases where all measurements are normalized to one atmosphere, p has the value of one, and Z_{coll} is then calculated by

$$\frac{1.271 \tau}{\eta} \quad (16)$$

All of the preceding relaxation equations are derived with the assumption that the observed system relaxes exponentially (Equation 7). However, in practice this is not always the case. The equilibration of the rotational degrees of freedom is not a relaxation in the same sense as vibrational relaxation because the return to equilibrium is not exponential with a single time constant. In most cases many rotational levels are excited and each has its own time constant. When one fits the single relaxation theory to experimental data from rotational equilibration, it should be remembered that the relaxation time found

is not a time constant for a true exponential decay but only an averaged time⁽¹⁰⁾.

$$\tau_{av} = \frac{\sum_j C_j \tau_j}{\sum_j C_j} \quad (17)$$

where C_j is the specific heat associated with the j^{th} energy level and τ_j is its relaxation time.

Multiple Relaxation

To adequately describe the experimental data from rotational equilibration experiments one needs some sort of multiple relaxation analysis. Recently several different approaches have appeared in the literature. Holmes and Stott⁽¹⁶⁾ have utilized the absorption and dispersion equations as written by Tanzcos. The relaxation strength and the relaxation time are adjusted to obtain a best fit by least squares criterion so that the sum of the squares of the deviations of the measured points from the theoretical curve is a minimum. The biggest objection to this method is that it requires a copious amount of data to obtain good results.

Raff and Winter⁽⁶⁾ have successfully predicted the temperature dependence of the velocity dispersion in H_2 , D_2 , and N_2 . They have assumed a simple, line of center collision model and from this obtain a set of rate constants which represent the multilevel rotational system. A negative temperature dependence is reported and is attributed to the multilevel character of the system and the fact the adjacent level spacing increases linearly with rotational quantum numbers. The

objections to this method are (1) it is only applicable to linear molecules, (2) it requires many hours of computer time, and (3) as yet it has not been extended to absorption.

Gordon⁽¹⁷⁾ has produced a method which accounts for the absorption due to rotational equilibration in terms of the molecular collisions which occur in a gas. His approach to the problem is to consider the number of successive collisions which a molecule undergoes. To a first approximation his results reduce to the familiar single relaxation relation. This first approximation corresponds physically to keeping only the independent effects of single binary collisions. Higher approximations are obtained which correct for the correlated effects of two, three, ... successive binary collisions. These correlations are present because the final rotational state in one collision becomes the initial state for the next collision. Since the probability for energy transfer in a collision depends on the initial state, two successive collisions in general have a different effect than a pair of uncorrelated collisions. It is also assumed that all of the relaxation effects are contained in a relaxing bulk viscosity. The absorption and dispersion equations as written by Gordon are:

$$\alpha_{\text{int}} = \frac{\omega V_0^2}{2V^3} \left(\frac{2C'}{3C_p} \right) \left(\frac{\omega\tau}{1 + \omega^2\tau^2} \right) \left[1 + \frac{(1 - 3\omega^2\tau^2)}{(1 + \omega^2\tau^2)^2} f_2 + \frac{(1 - 6\omega^2\tau^2 + \omega^4\tau^4)}{(1 + \omega^2\tau^2)^3} f_3 + \dots \right] \quad (18)$$

$$\frac{V}{V_0} = 1 + \left(\frac{2C'}{3C_p} \right) \left(\frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \right) \left[1 + \frac{(3 - \omega^2\tau^2)}{(1 + \omega^2\tau^2)^2} f_2 + \dots \right]$$

where f_2 and f_3 are constants related to the number of second and third

binary collisions. The n^{th} term of the series would contain information about the dynamics of n successive binary collisions.

In private communication Raff has objected to Gordon's method. His main objection is that it is impossible to obtain microscopic information from a macroscopic theory and that there is no method of predicting the temperature dependence of the rotation mechanism. Raff does agree, however, that since Gordon's method has two adjustable parameters it should give a better fit to experimental data.

Thermal Conductivity

Much of the relaxation information on polar gases has been obtained from analysis of experimental thermal conductivity data. There are two separate theories for the thermal conductivity of polyatomic gases⁽¹⁸⁻¹⁹⁾, however, only the theory produced by Mason and Monchick is applicable to polar gases and for that reason it alone will be discussed here.

The heat conductivity of a polyatomic gas, nonpolar as well as polar, is not described satisfactorily by classical kinetic theory. The reason is that the classical theory takes account only of elastic collision and so ignores the internal degrees of freedom of the molecules, which transport an appreciable quantity of energy. Various attempts to patch up the classical theory which consider the transport of internal energy have been made. Most are essentially variations on a suggestion originally made by Eucken⁽²⁰⁾.

In the classical theory

$$\frac{\kappa M}{\eta} = f C_v \quad (19)$$

where κ is the heat conductivity, M is the molecular weight, η is the viscosity, and f is a pure number almost exactly equal to $5/2$. Eucken suggested that this equation could be generalized by writing it as

$$\frac{\kappa M}{\eta} = f_{tr} C_{tr} + f_{int} C_{int}$$

and he set $f_{tr} = 5/2$ and $f_{int} = 1$. This leads to the well known expression for the Eucken factor

$$\frac{\kappa M}{\eta} = f_E \quad (20)$$

where $f_E = 1 + 9/4 R/C_v$.

This expression was found to give reasonable agreement with experiment at low temperatures. However, for polar gases, and for nonpolar gases at elevated temperatures, the Eucken factor was found not to agree well with experiment, and, in fact, for polar gases the observed f_E was often appreciably lower than the Eucken value. This implied that the heat conductivities of polar gases were anomalously low.

Mason and Monchick have developed a modification to the Eucken correction "which is based as nearly as possible upon rigorous kinetic theory results"⁽¹⁸⁾. Such a calculation requires as a starting point a kinetic theory for polyatomic gases which takes into account inelastic collision. In a formal sense such a theory has been developed by Wang Chang and Uhlenbeck for the semiclassical case and by Taxman for the classical case. However, the resulting equations are forbiddingly complicated, and the task of solving the dynamical problem of inelastic molecular collisions is almost hopeless. So as a starting point Mason

and Monchick have initially assumed that only one quantum of internal energy at a time can be exchanged with translation energy on collision (or two quanta for homonuclear diatomic molecules). With this assumption they have neglected all terms involving the change of internal energy, ΔE_{int} , in a collision. When this is done, the formal theory gives the modified Eucken factor.

Proceeding further they then considered the terms involving change in internal energy. The terms appear in the formal kinetic theory in two classes (1) essentially linear in ΔE_{int} and (2) terms involving $(\Delta E_{\text{int}})^2$. Since ΔE_{int} can be either positive or negative the linear terms go to nearly zero on averaging and are neglected. The remaining terms in $(\Delta E_{\text{int}})^2$ are expressed in terms of an additional experimental quantity, the relaxation time or the bulk viscosity. The final results for nonpolar gases is a Eucken-type factor which involves only experimental quantities and introduces one new quantity, the relaxation time. The Eucken-type factors as derived by Mason & Monchick are

$$f_{\text{int}} = \frac{\rho D_{\text{int}}}{\eta} \left[1 + \left(\frac{5}{\pi}\right) \left(1 - \frac{2}{5} \frac{\rho D_{\text{int}}}{\eta}\right) \left(\frac{C_{\text{rot}}}{C_{\text{int}} Z_{\text{rot}}} + \frac{C_{\text{vib}}}{C_{\text{int}} Z_{\text{vib}}} \right) \right] \quad (21)$$

$$f_{\text{tr}} = \frac{5}{2} \left[1 - \left(\frac{10}{3\pi}\right) \left(1 - \frac{2}{5} \frac{\rho D_{\text{int}}}{\eta}\right) \left(\frac{C_{\text{rot}}}{R Z_{\text{rot}}} + \frac{C_{\text{vib}}}{R Z_{\text{vib}}} \right) \right]$$

where D_{int} is an internal diffusion coefficient defined by Mason and Monchick. Since for most cases $Z_{\text{vib}} \gg Z_{\text{rot}}$ the terms involving Z_{vib} may be neglected.

To account for the anomalous behavior of polar gases the resonant exchange of internal energy from one molecule to another without affecting the translational energy is investigated. This is considered prominent for polar gases because in this case the cross section for the resonant exchange of a quantum of rotational energy is very large due to the long-range dipole force. The results of this assumption is again an Eucken-type factor which involves a cross section for exchange of internal energy. This cross section has never been measured, but can be calculated in terms of the dipole moment and moment of inertia of the molecule. For polar molecules Mason and Monchick's equation for the thermal conductivity has been written by Baker and Brokaw as ⁽²¹⁾.

$$\kappa = \frac{\eta}{M} \left[\frac{5}{2} C_{tr} + \frac{\rho D_{int}}{\eta} C_{int} - \frac{2}{\pi} \left(\frac{5}{2} - \frac{\rho D_{int}}{\eta} \right)^2 \frac{C_{rot}}{Z_{rot}} \right]. \quad (22)$$

Here again it has been assumed that $Z_{vib} \gg Z_{rot}$. For resonant collisions

$$D_{int} = \frac{D_{11}}{1 + \delta} \quad (23)$$

where D_{11} is the self diffusion coefficient and δ contains the information about resonant collisions. For linear dipoles

$$\delta = \frac{1.7963 \times 10^3 \mu^2 M^{1/2} \theta_{rot}^{3/2}}{(C_{int}/R) \langle \Omega^{(1,1)*} \rangle \sigma_o^2 T} \quad (24)$$

where μ is the dipole moment, θ_{rot} is the characteristic temperature for rotation, σ_o is the viscosity cross section and $\langle \Omega^{(1,1)*} \rangle$ is a dimensionless collision integral for diffusion. The quantities σ_o and

$\langle \Omega^{(1,1)*} \rangle$ have been given by Monchick and Mason in an earlier paper⁽²²⁾.

A Theory for Polar Gases

Zeleznik⁽⁷⁾ has made a classical calculation for rotational relaxation in polar gases. For the calculation he considers three parameters which could affect the rotational collision number: (1) the magnitude of the permanent dipole moment μ , (2) the mass distribution as characterized by the ratio of the arithmetic mean moment of inertia I to the mass M , and (3) the ambient temperature T . The calculation is essentially a classical perturbation calculation of the change in rotational energy produced by the scattering of permanent electric dipoles. The molecules are constrained to a plane and no out of plane forces are permitted.

Like Parker's⁽⁵⁾ classical calculation for nonpolar molecules dE_R/dt is always positive and therefore only those systems which are initially unexcited $E_R(0) = 0$ can be considered. The resulting equation for the collision numbers of identical colliding molecules for a quasi-three dimensional case is

$$Z_{\text{rot}}^{-1} = \frac{1}{N} \pi^{1/2} \frac{\Gamma(5/2)}{\Gamma(2)} \left(\frac{\mu^2}{\sigma^3 kT} \right) \frac{(T/T_R)}{(\bar{b}/\sigma)^2} \theta_{11}(\zeta^2) \quad (25)$$

where σ is the molecular diameter, k is Boltzman's constant, M is the dipole moment, N is the number of rotational degrees of freedom, T_R is the rotational temperature, T is the ambient temperature, \bar{b} is the maximum impact parameter and $\theta_{11}(\zeta^2)$ is a function of the moment of inertia and is given in tabular form in Zeleznik's paper. If a ratio of

collisional numbers is considered the adjustable impact parameter \bar{b} can be eliminated, and if, in addition, a near equilibrium situation is considered T/T_r may be set equal to unity. This gives

$$\frac{Z_{\text{rot}}(1,T)}{Z_{\text{rot}}(2,T_o)} = \frac{N_1}{N_2} \left(\frac{\mu_2}{\mu_1}\right)^4 \left(\frac{\sigma_1}{\sigma_2}\right)^4 \left(\frac{T}{T_o}\right)^2 \frac{\theta_{11}(\zeta_2^2)}{\theta_{11}(\zeta_1^2)} \quad (26)$$

where $Z_{\text{rot}}(1,T)$ represents the collision number of species 1 at temperature T .

Before the above equation can be compared to experiment the molecular diameter σ and the moment of inertia I must be evaluated. The moment of inertia I is taken to be the arithmetic mean of a molecule's principle moments of inertia. The molecular cross section σ is set equal to the viscosity collision cross section and can be calculated by the relation

$$\sigma^2 = \sigma_\eta^2 = \frac{5}{16} \left[\frac{(\pi M k T)^{1/2}}{\pi \eta} \right]^2 \quad (27)$$

The variable ζ^2 required for the evaluation of θ_{11} is calculated by

$$\zeta^2 = \frac{16}{5} \pi \frac{(I/M) \eta}{(\pi M k T)^{1/2}} \quad (28)$$

For the case of diatomic molecules of the same species, Equation (26) reduces to

$$\frac{Z_{\text{rot}}(1,T)}{Z_{\text{rot}}(1,T_o)} = \left(\frac{T}{T_o}\right)^3 \left(\frac{\eta_1(T_o)}{\eta_1(T)}\right)^2 \frac{\theta_{11}(1,T_o)}{\theta_{11}(1,T)} \quad (29)$$

where equation (27) is used for σ .

According to Equation (26) an increase in dipole moment decreases the collision number. An increase in I causes a decrease in Z_{rot} . Also, an increase in temperature increases Z_{rot} but because of the compensation due to viscosity the increase is at a considerable lower rate than indicated by the explicit T^3 dependence. Based on some typical calculations Zeleznik says that the increase is very nearly linear at lower temperatures but becomes somewhat steeper as the temperature increases.

CHAPTER III

EXPERIMENTAL RESULTS IN POLAR GASES

Previous Work

Breazeale and Kneser⁽²³⁾ have made the only previous acoustic investigation on the rotational equilibration of HCl and apparently no acoustic absorption or dispersion investigations have been reported on HBr. Breazeale and Kneser using an ultrasonic pulse technique at 273 °K over the frequency range 1 MHz - 15 MHz found no velocity dispersion in HCl and making use of the direct relation $\alpha/\alpha_{cl} = 1 + .067 Z_{rot}$ for absorption found $Z_{rot} = 7$. In comparing this to other diatomic molecules they conclude that the collisions between molecules having the same dipole moment are especially effective in exchanging vibrational and rotational energy with translational energy.

Several reports of rotational collision numbers for polar molecules extracted from thermal conductivity measurements have appeared in recent years. Baker and Brokaw⁽²⁴⁾ using an eight cell hot wire thermal conductivity apparatus have reported results for HCl over the temperature range 300 °K to 475 °K. They find Z_{rot} to decrease from 6.2 at 300 °K to 3.0 at 471 °K.

Barua, Manna, and Mukhopadhyay⁽²⁵⁾ using a similar type thermal conductivity apparatus over the temperature range 273 °K to 473 °K have also found Z_{rot} for HCl to decrease from 6.6 at 273 °K to 2.2 at 473 °K.

They have concluded on the basis of their measurements on H_2S , HCl , and NH_3 that excepting very low temperatures the decrease of Z_{rot} with increase of temperature is a common feature of polar gases.

Mason and Monchick⁽¹⁸⁾ treating Z_{rot} as a disposable constant have used a value of 3.0 for both HCl and HBr to adequately describe thermal conductivity data. They have also assumed Z_{rot} to be independent of temperature as a first approximation.

Experimental Method and Data Analysis

In this investigation ultrasonic absorption and velocity dispersion measurements have been made on the two polar gases HCl and HBr . The measurements were made over the temperature range $298^\circ K$ to $1073^\circ K$ and over the approximate frequency range $1\text{ MHz/atm} - 100\text{ MHz/atm}$. The gases were purchased from the Matheson Company with stated minimum purities of 99.0% for HCl and 99.8% for HBr . No further purification was attempted. The HBr had approximately 0.2% HCl as an impurity and this small amount proved to be very bothersome due to the unequal vapor pressures of the two gases. To insure that the gas used had not reacted with part of the apparatus a sample of gas was taken and analyzed on a mass spectrometer after each different temperature.

To analyze the data, the classical absorption must first be subtracted from the experimental absorption to obtain the excess absorption which in this case is attributed to rotational equilibration. Two mistakes which appear to have been common practice in the past were detected in this procedure: (1) assuming that the classical absorption is independent of the equilibration of the internal modes by using

frequency independent values of C_p and C_v in Equation (11) rather than a frequency dependent specific heat as in Equation (6); (2) using specific heats which contain contributions due to vibrational modes which have already relaxed. The effects of these mistakes can produce rather large errors in the internal absorption, particularly at frequencies greater than the frequency of maximum absorption. Inspection of Equation (11) also reveals that using frequency dependent specific heats in the classical absorption equation makes the thermal conductivity term become more important at high frequencies. Figure (1) shows plots of the classical absorption as a function of frequency dependent specific heats and as a function of steady state specific heats along with the experimental data for HCl at 1073 °K for comparison purposes. Figure (2) shows the internal absorption for HCl at 1073 °K when the classical absorption is calculated using steady state values of the specific heats and Figure (6) show the same data when frequency dependent specific heats are used.

The values for the viscosity were calculated as outlined by Monchick and Mason⁽²²⁾, and the thermal conductivity values were calculated by use of the Eucken factor. The accuracy of the viscosity data by this method of calculation agrees within experimental error when compared with available data; however, the Eucken factor gives values for thermal conductivity for polar gases which are consistently high. These high values of thermal conductivity tend to make the classical absorption too large at high frequencies. Appendix B contains the procedure for these calculations. The experimental velocity was corrected for non-ideality by use of second virial coefficients and the method for this calculation is also contained in Appendix B.

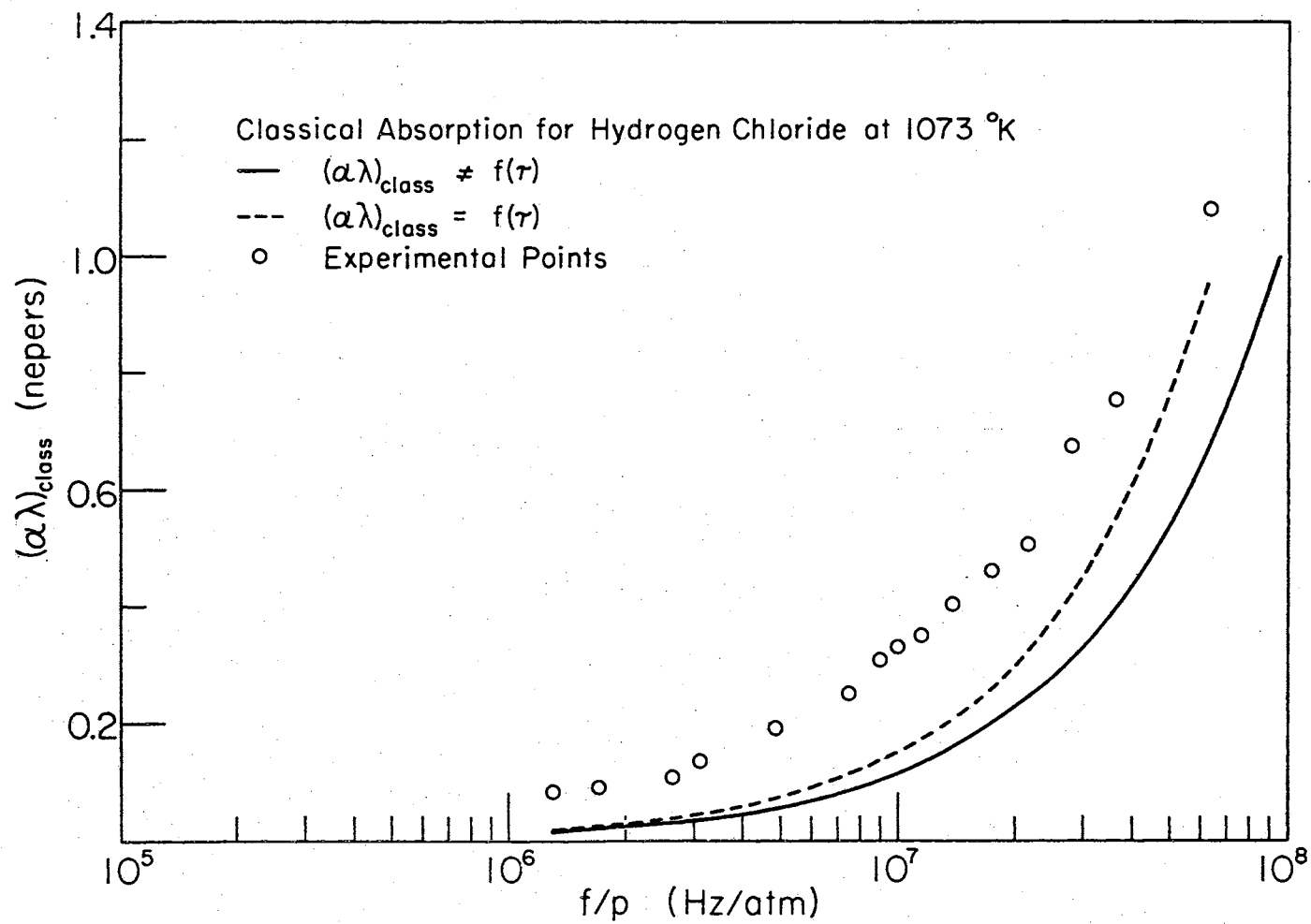


Figure 1. Experimental Data and Classical Absorption Calculated With Both Frequency Dependent and Frequency Independent Specific Heats for Hydrogen Chloride at 1073 °K.

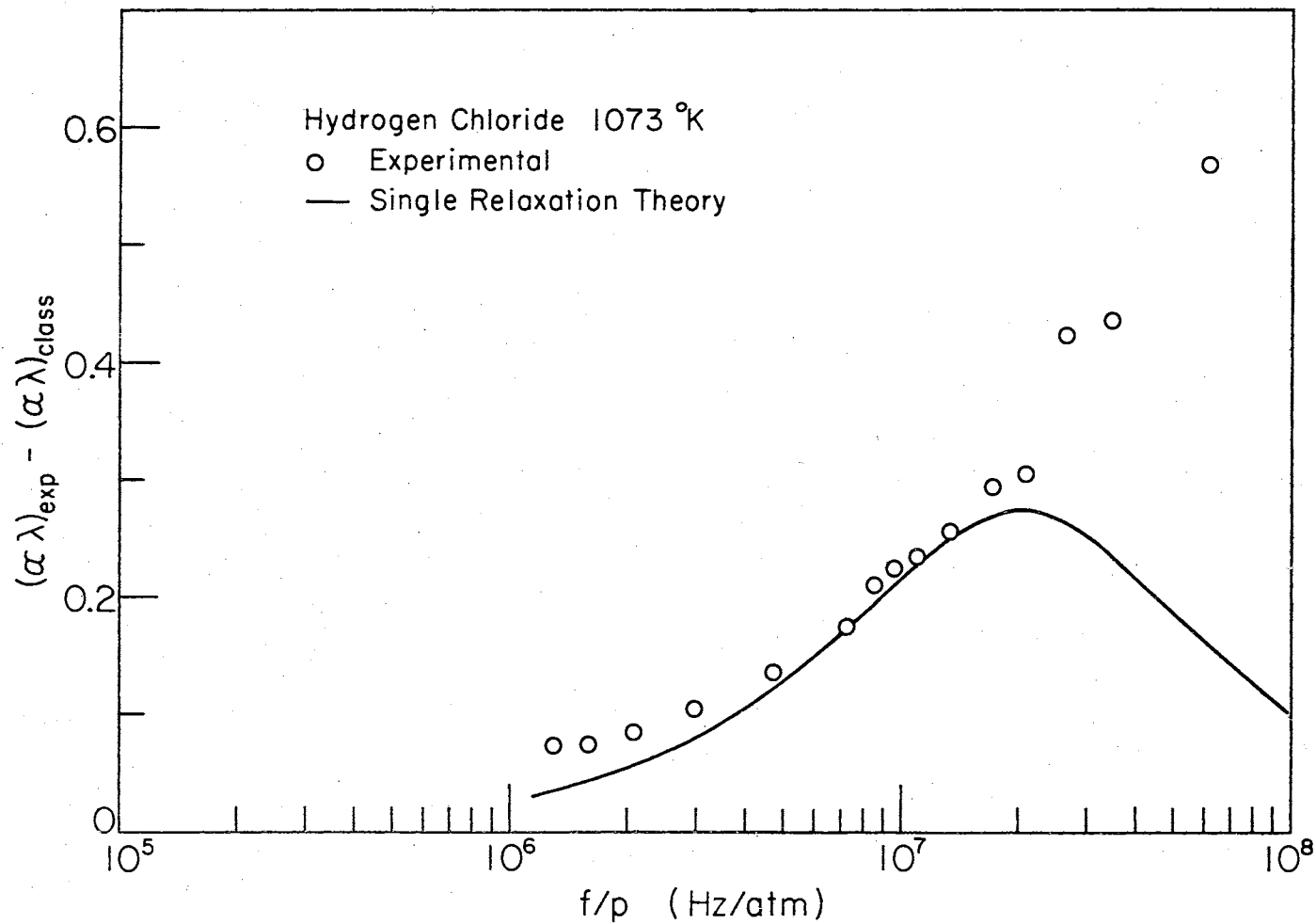


Figure 2. Internal Absorption for Hydrogen Chloride at 1073 °K When the Classical Absorption is Calculated Using Frequency Independent Specific Heats.

The absorption data is presented as plots of $(\alpha\lambda)_{int}$ vs (f/p) with the best fit obtained by both single relaxation theory and Gordon's multiple relaxation theory shown as solid lines. The single relaxation analysis and the multiple relaxation analysis are shown on different plots because of the difference in the internal absorption caused by the difference in $(\alpha\lambda)_{cl}$ chosen for the two different cases.

The velocity data is shown on the same page as the absorption data as plots of V^2 vs $(\frac{f}{p})$. The solid curves have been calculated by use of the relaxation times obtained from the absorption data at that temperature. No attempt has been made to obtain relaxation times from the velocity data.

Hydrogen Chloride

Figures 3-6 depict the absorption and velocity data along with the single relaxation theory drawn for a relaxation time which gives a least squares best fit to the experimental data for HCl at the four temperatures 298 °K, 573 °K, 793 °K, 1073 °K. The data is fitted to the theory by first choosing a τ and calculating the classical absorption using frequency dependent specific heats. This classical absorption is then subtracted from the experimental data, and $(\alpha\lambda)_{int}$ is calculated from theory. Next the sum of the squares of the deviation of $(\alpha\lambda)_{int}$ and experiment is calculated. The relaxation time is then incremented some small amount and the procedure is repeated over the chosen range of τ 's. The τ which produces the smallest deviation is then chosen as the relaxation time of the system. If the τ which is picked by this procedure is equal to either the upper or lower limit of

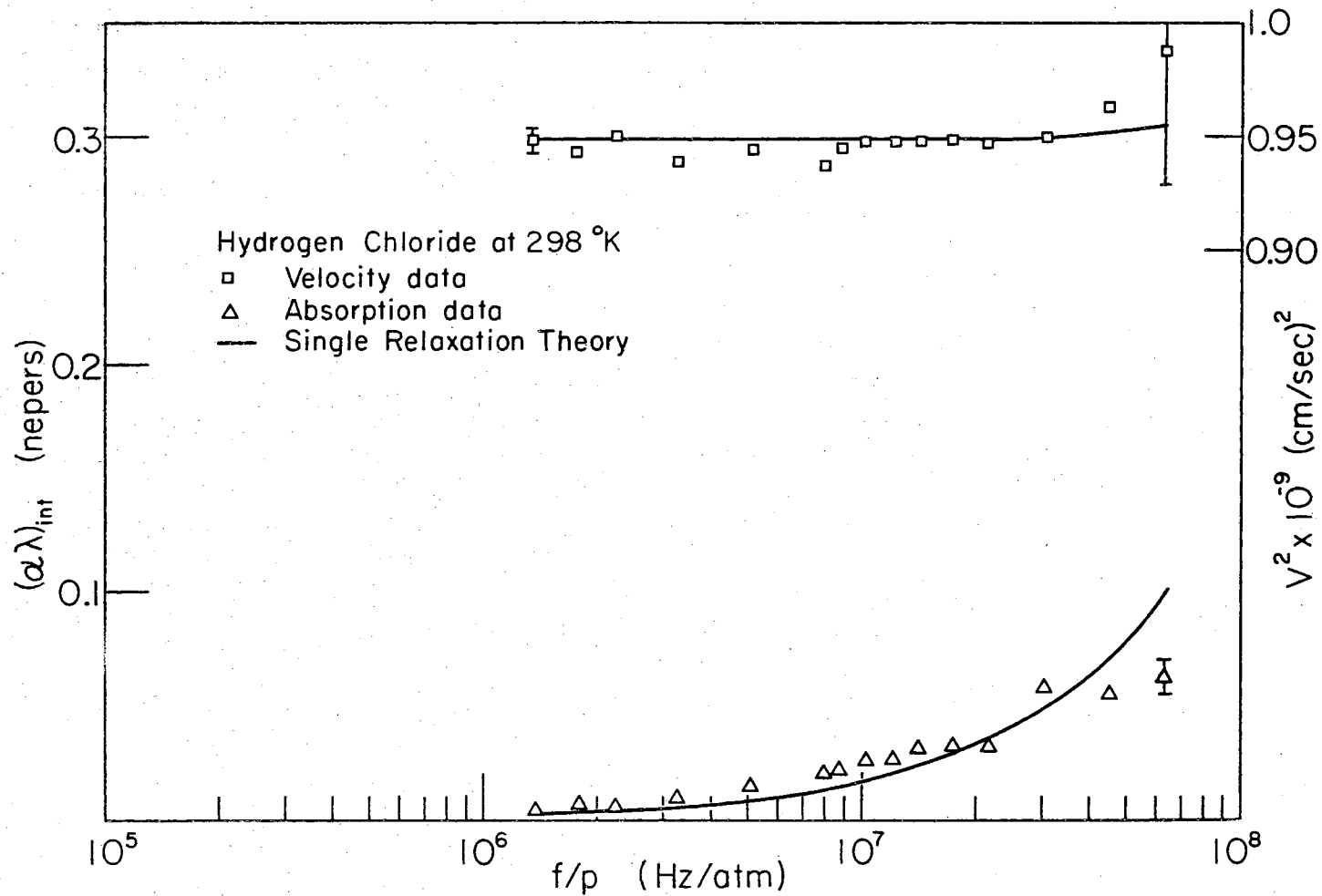


Figure 3. Dispersion and Absorption in Hydrogen Chloride at 298 °K With Single Relaxation Curves.

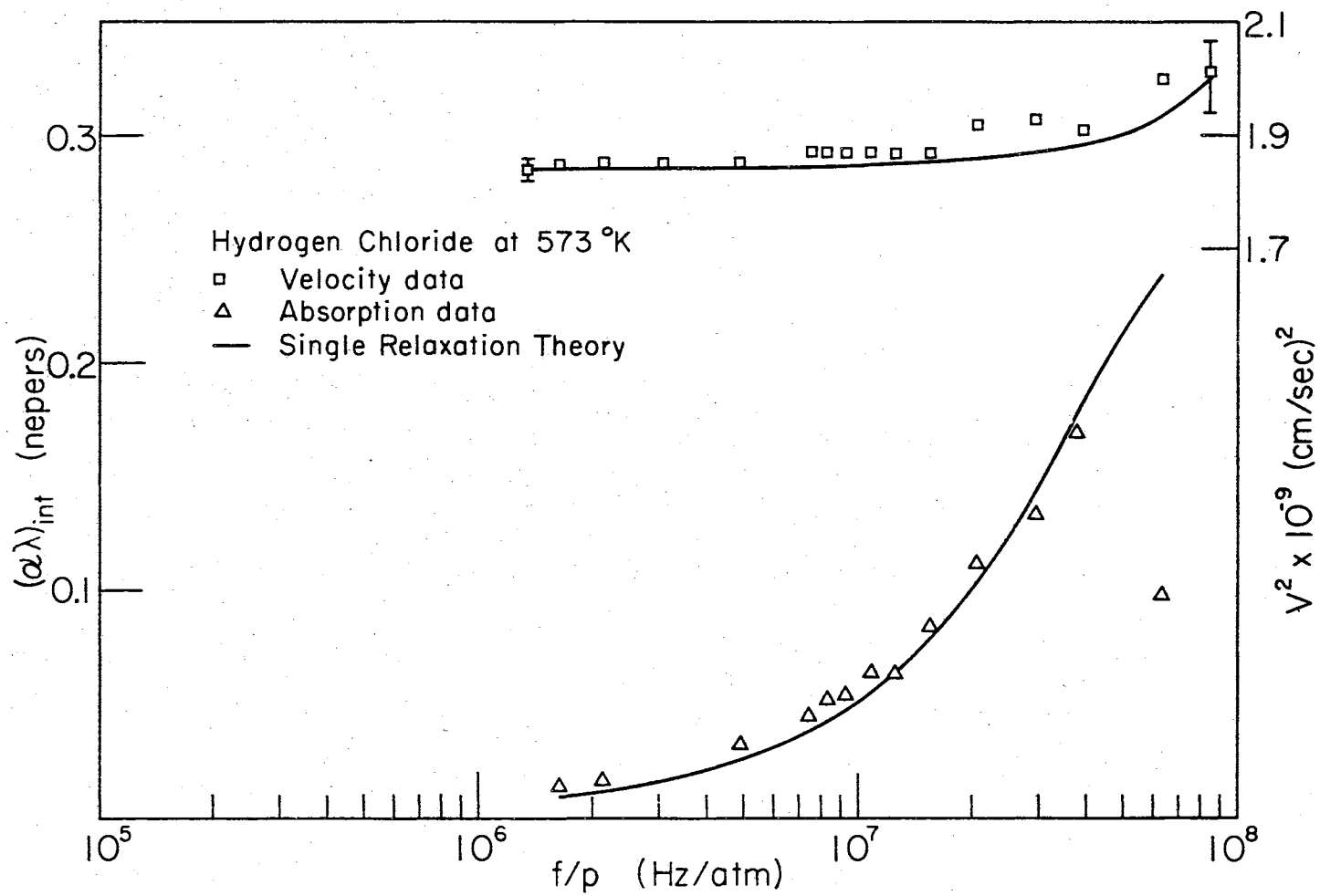


Figure 4. Dispersion and Absorption in Hydrogen Chloride at 573 °K With Single Relaxation Curves.

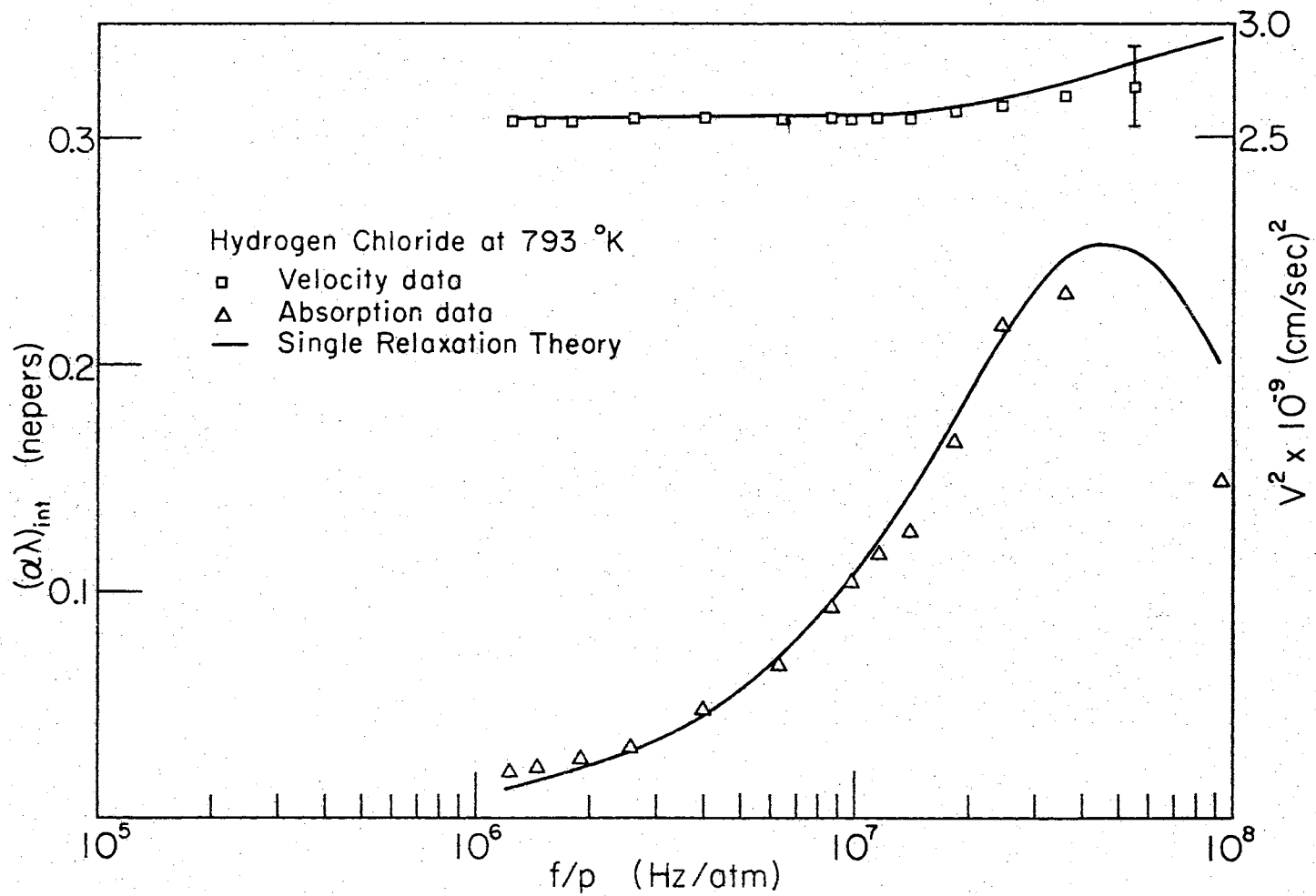


Figure 5. Dispersion and Absorption in Hydrogen Chloride at 793 °K With Single Relaxation Curves.

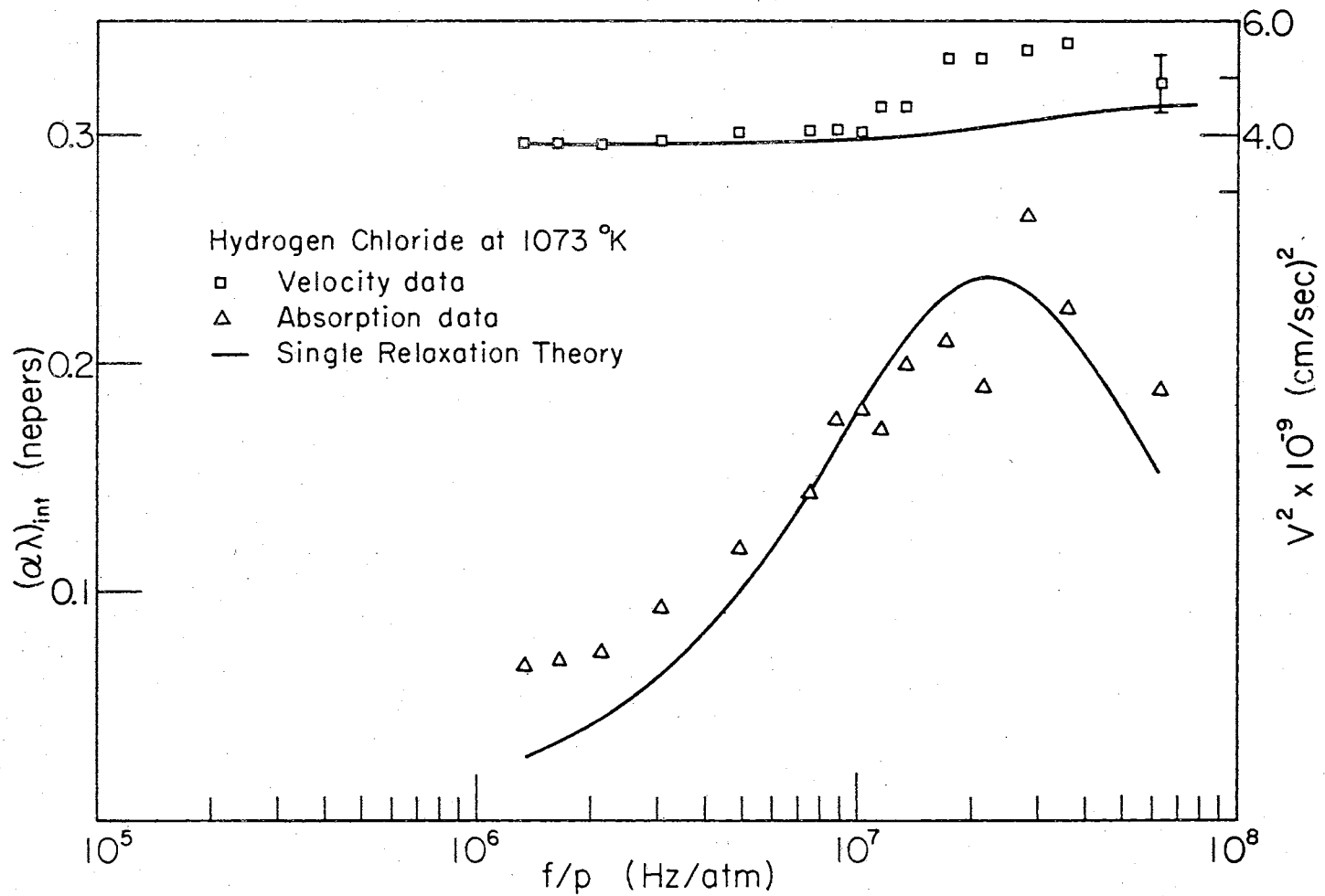


Figure 6. Dispersion and Absorption in Hydrogen Chloride at 1073 °K With Single Relaxation Curves.

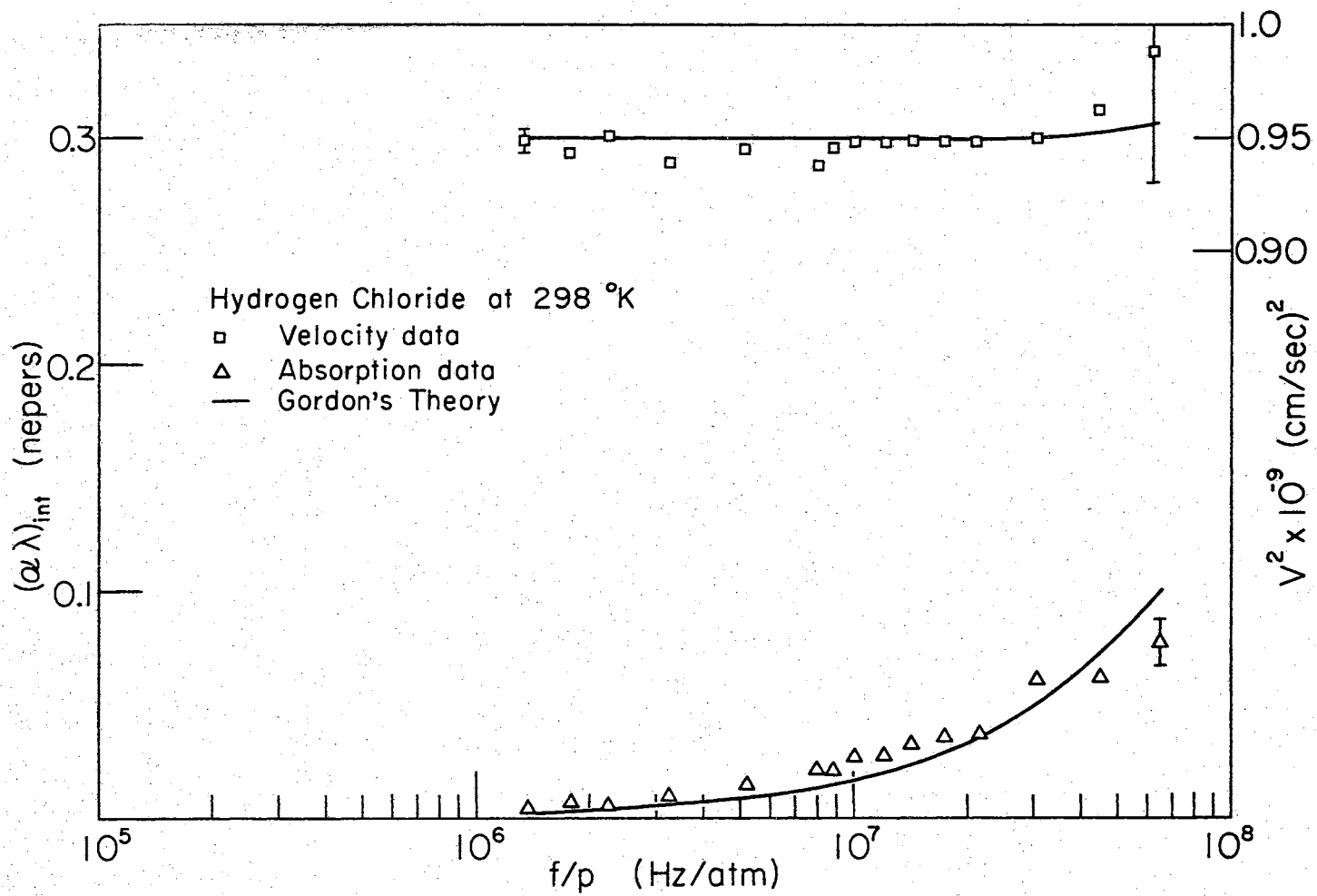


Figure 7. Dispersion and Absorption in Hydrogen Chloride at 298 °K With Gordon's Multiple Relaxation Curves.

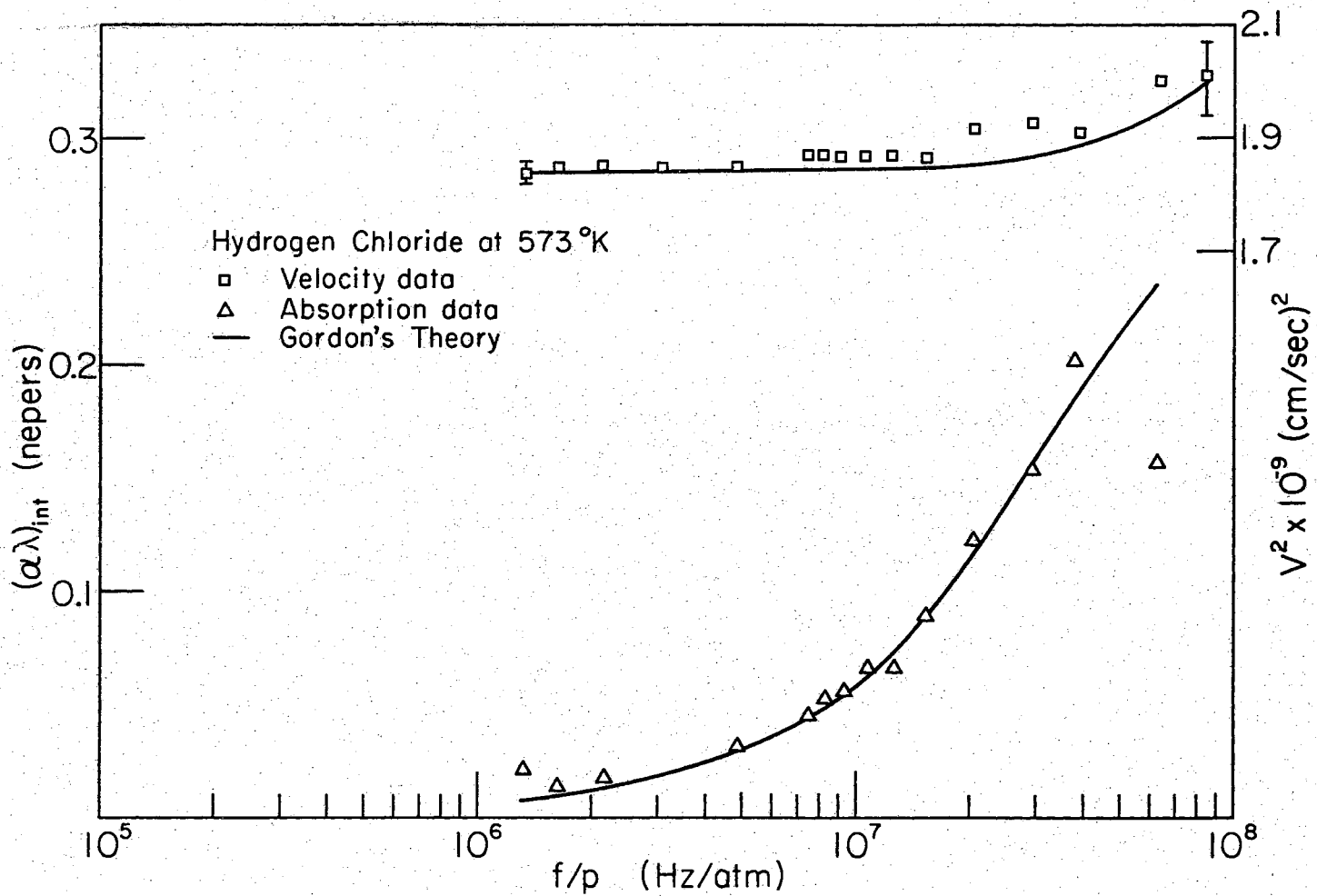


Figure 8. Dispersion and Absorption in Hydrogen Chloride at 573 °K With Gordon's Multiple Relaxation Curves.

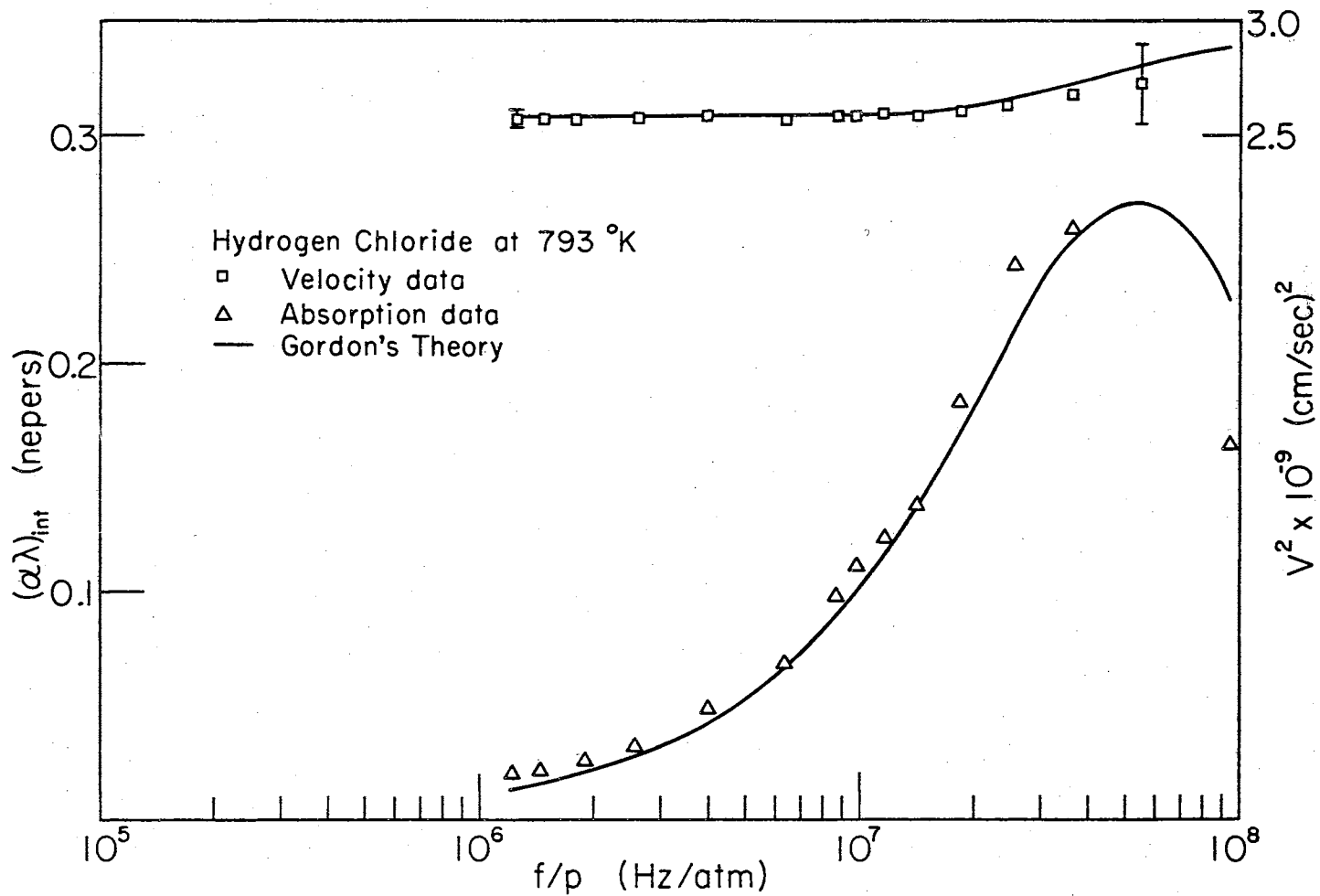


Figure 9. Dispersion and Absorption in Hydrogen Chloride at 793 °K With Gordon's Multiple Relaxation Curves.

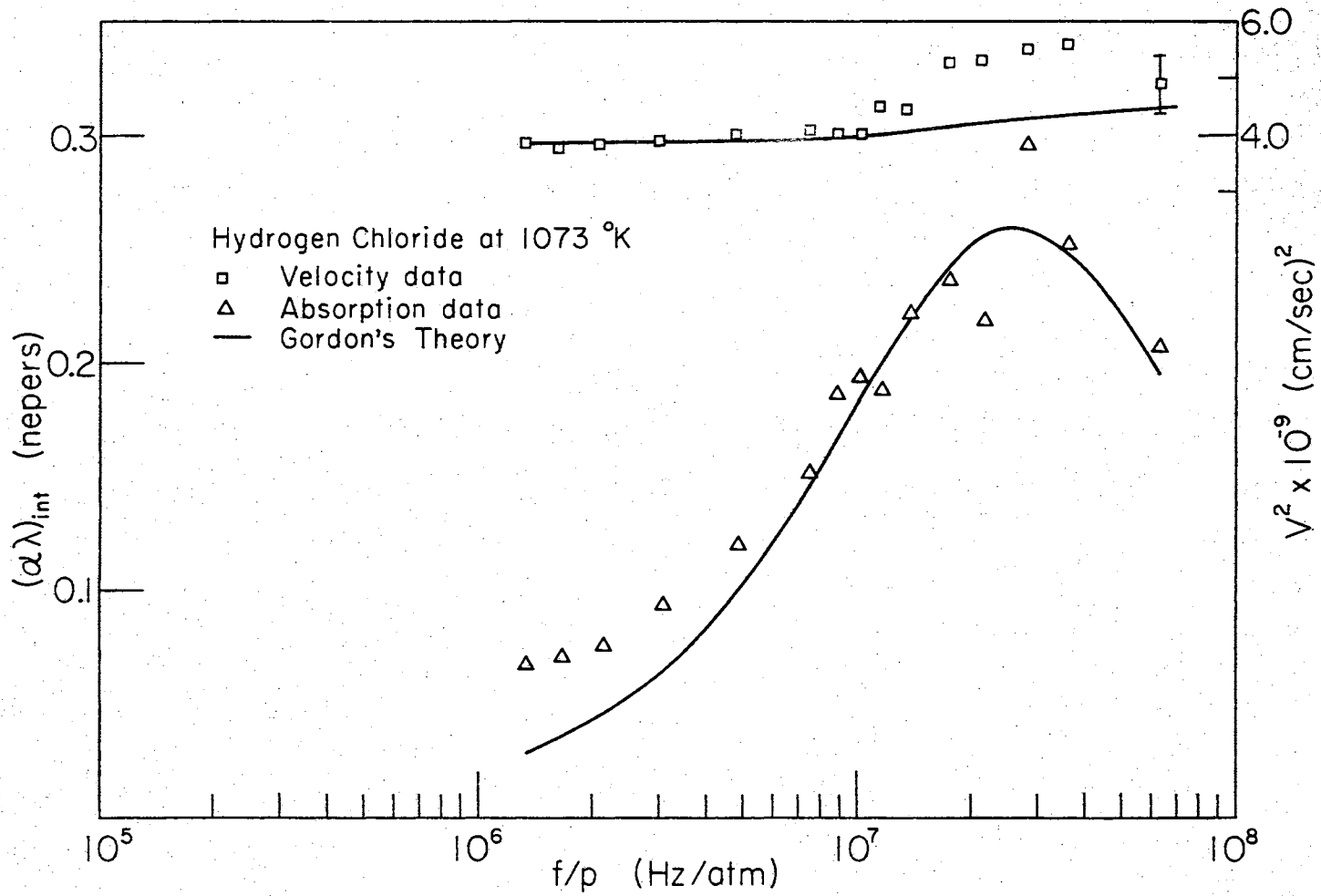


Figure 10. Dispersion and Absorption in Hydrogen Chloride at 1073 °K With Gordon's Multiple Relaxation Curves.

the range of τ then the range is adjusted accordingly and the entire process is repeated.

The same data analyzed in a similar manner by Gordon's multiple relaxation theory are shown in Figures 7-10. In the use of Gordon's method only the term f_2 in the brackets of equation (18) is considered. The analysis procedure for Gordon's method is the same as for single relaxation except that for each incremented f_2 , a τ has to be chosen. This is done by choosing a range for f_2 and incrementing the range. This means, that for each incremented f_2 , τ is calculated over the entire range of chosen values. This process is repeated over the entire f_2 range until a least value determined by least squares criterion is found.

In comparing the results for the two different methods, Gordon's method seems to fit the experimental data somewhat better than single relaxation theory; however, this is to be expected since it contains two adjustable parameters. There is no apparent trend in the f_2 's which are chosen at the different temperatures.

Hydrogen Bromide

The experimental data for hydrogen bromide at the temperatures 298 °K, 573 °K, 773 °K, are shown in Figures 11-16. The single relaxation analysis is shown in the first three figures and Gordon's method is shown in the last three. Before measurements were made on HBr a micrometric manometer was added to the system which allowed for data points to be more closely spaced at high frequencies (low pressure). The sharp fall off of the absorption data at the higher frequencies at

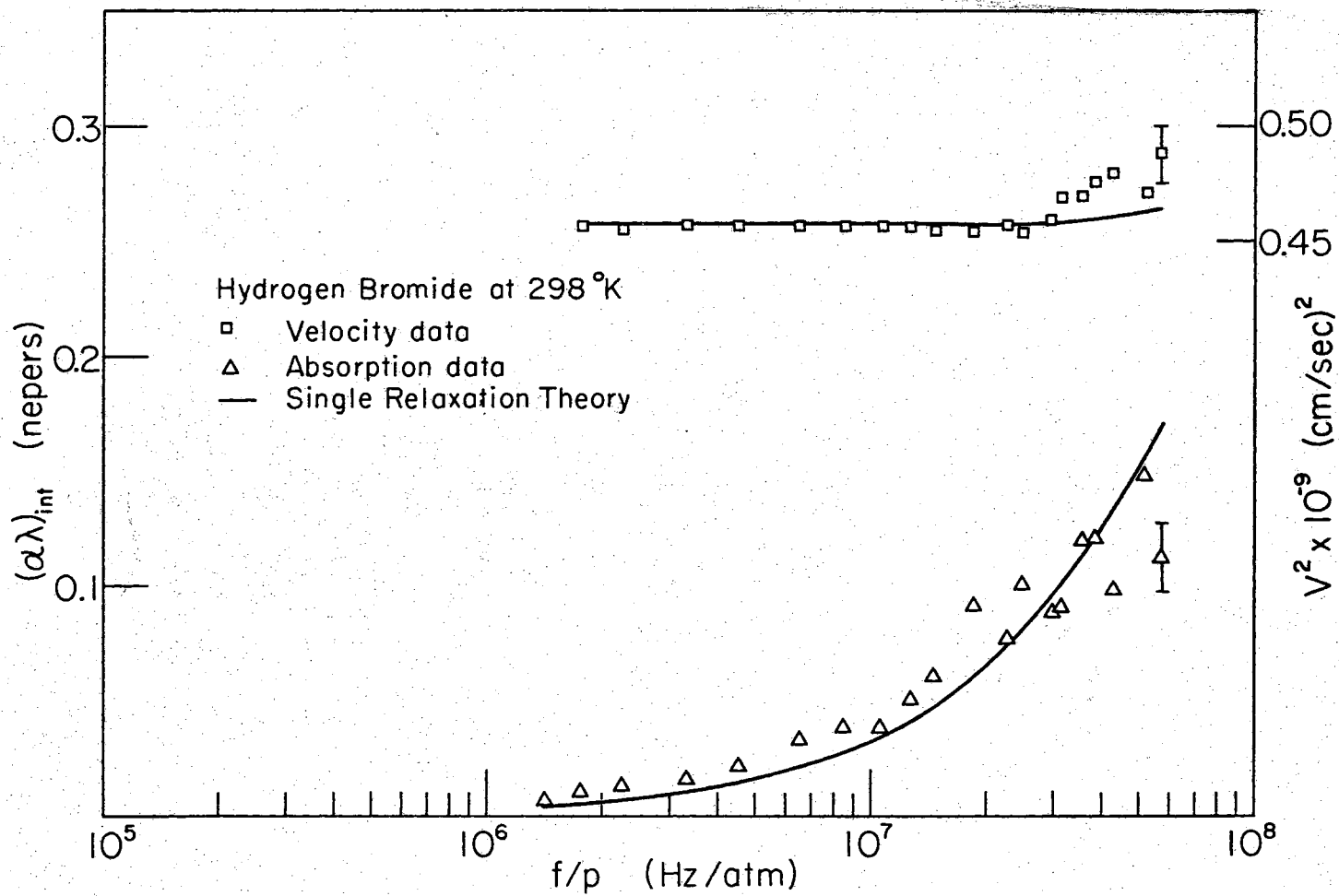


Figure 11. Dispersion and Absorption in Hydrogen Bromide at 298 °K With Single Relaxation Curves.

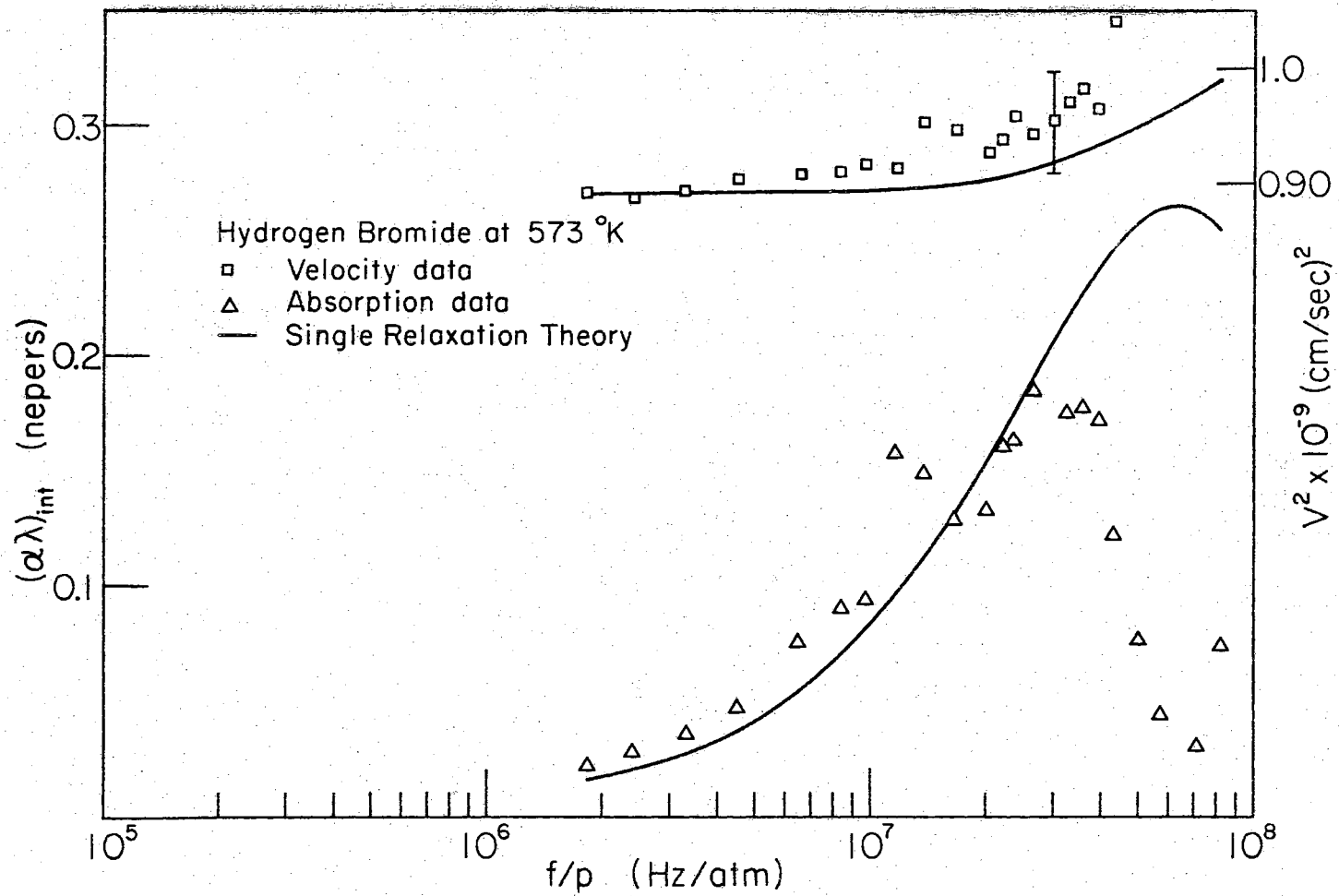


Figure 12. Dispersion and Absorption in Hydrogen Bromide at 573 °K With Single Relaxation Curves.

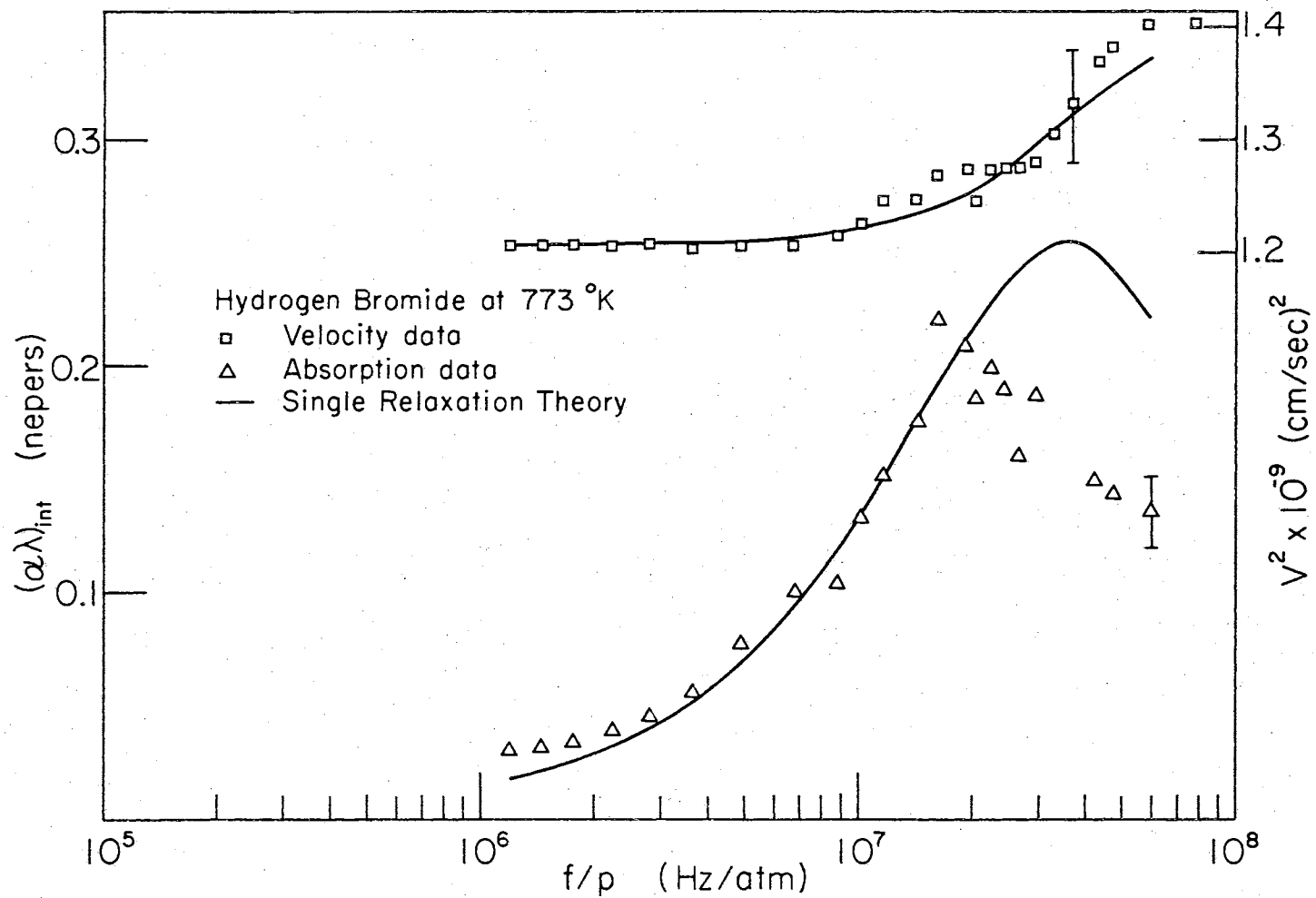


Figure 13. Dispersion and Absorption in Hydrogen Bromide at 773 °K With Single Relaxation Curves.

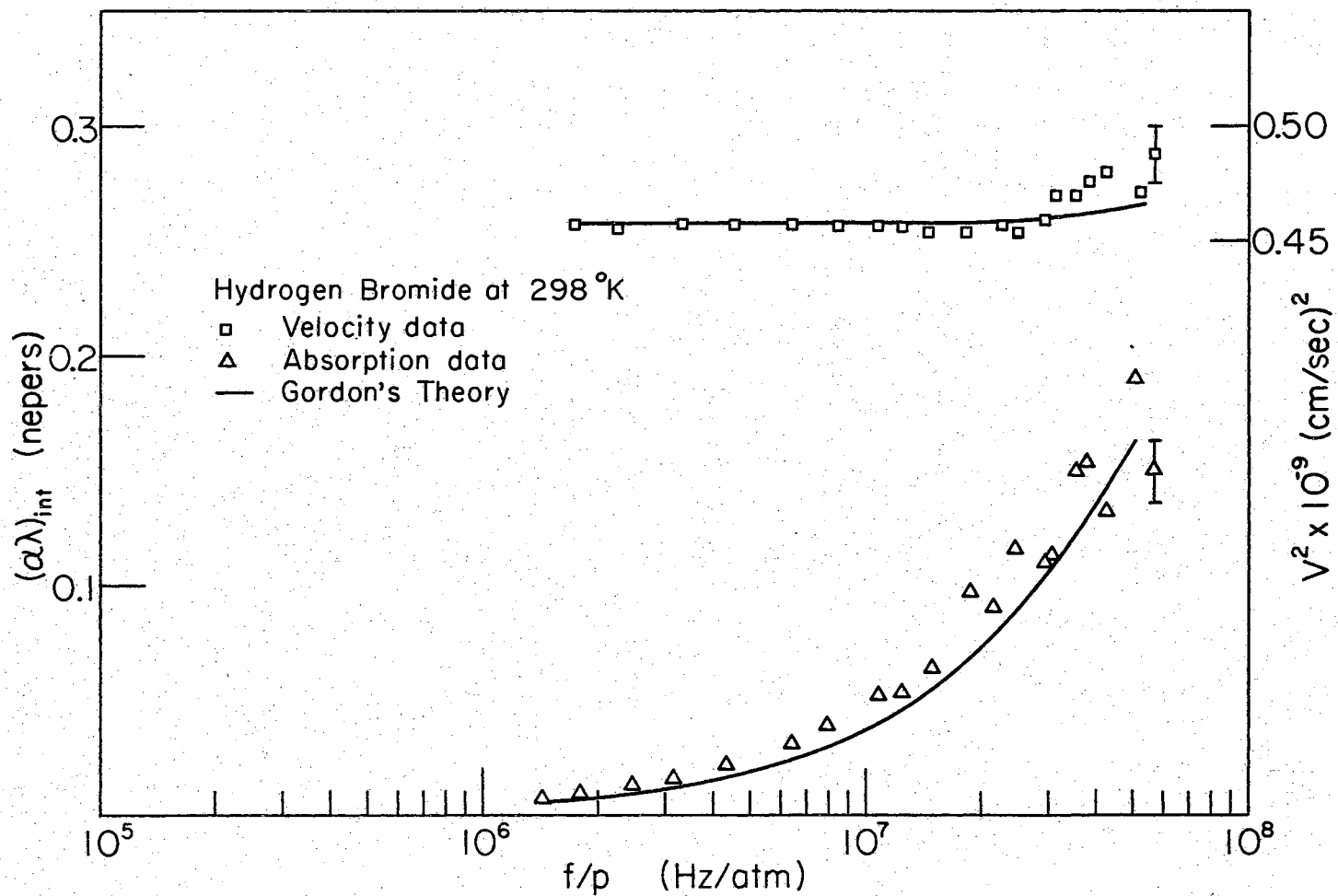


Figure 14. Dispersion and Absorption in Hydrogen Bromide at 298 °K With Gordon's Multiple Relaxation Curves.

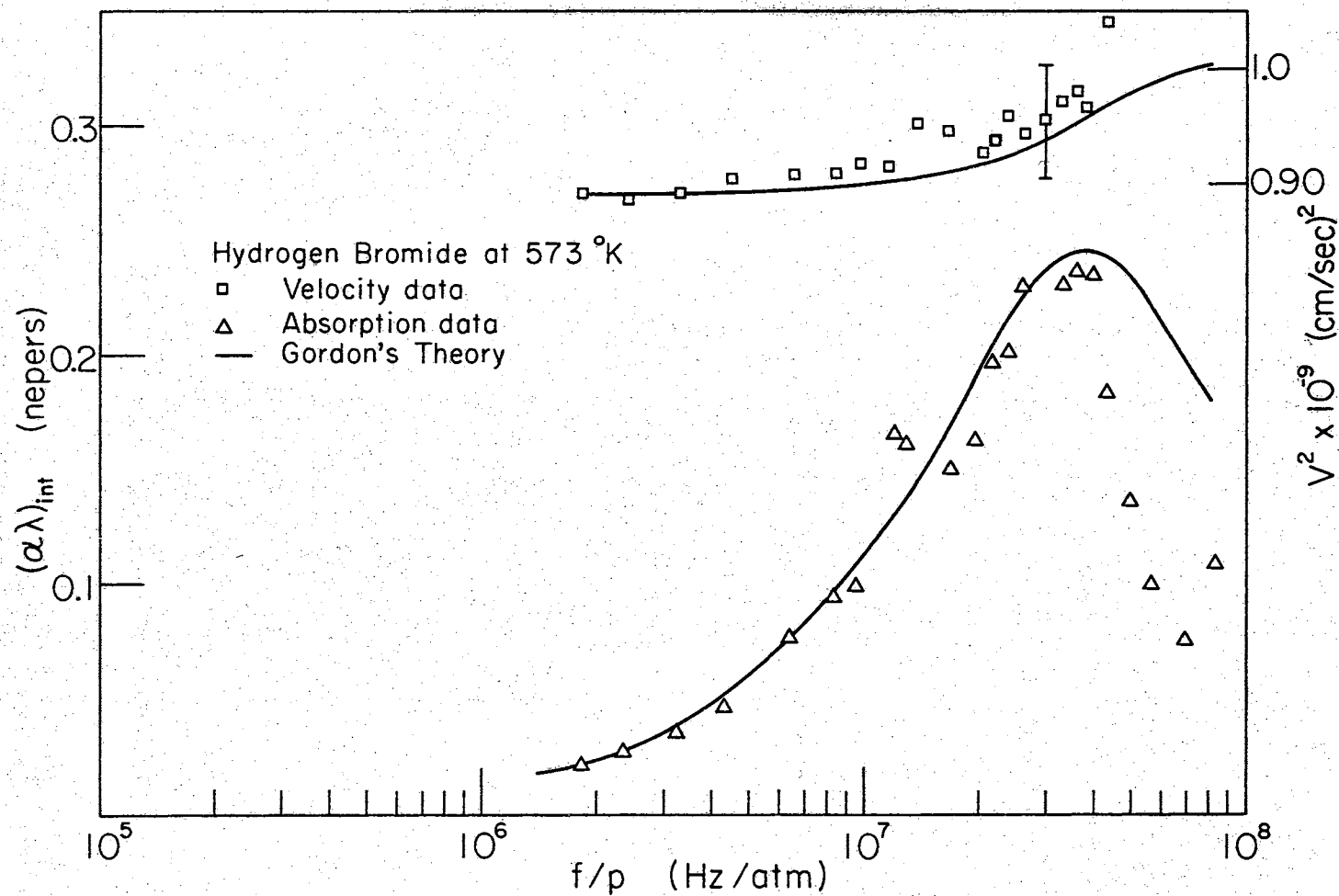


Figure 15. Dispersion and Absorption in Hydrogen Bromide at 573 °K With Gordon's Multiple Relaxation Curves.

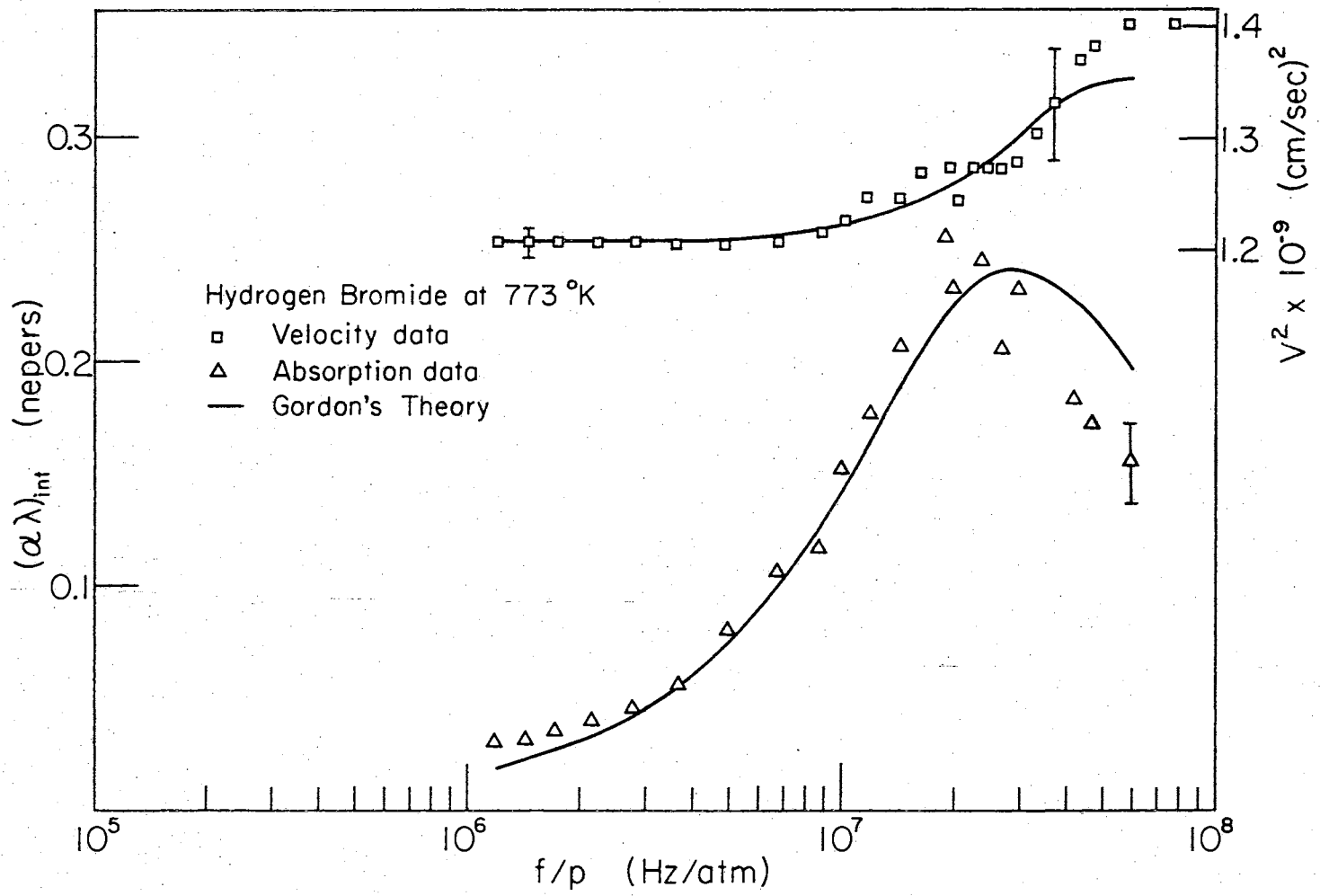


Figure 16. Dispersion and Absorption in Hydrogen Bromide at 773 °K With Gordon's Multiple Relaxation Curves.

573 °K and 773 °K can be attributed to the fact that the thermal conductivities were calculated using Eucken's factor which gives high values in polar gases. Measurements were not made on HBr at 1073 °K because the HBr reacted with the experimental apparatus.

In each case for HBr Gordon's method appears to give a better fit to the experimental data than the fit obtained by single relaxation theory; however, again there does not appear to be a trend in the f_2 's which were chosen.

Discussion of Results

The relaxation times and collision numbers obtained in this investigation are presented in Table I. The relaxation times in the single relaxation column correspond to the relaxation time defined by Equation (7) and the times in the multiple relaxation column correspond to the time in Gordon's multiple relaxation equations. No attempt has been made to adjust the values obtained by Gordon's method so that they would be comparable to the single relaxation values, so care should be exercised in making direct comparison. Table I also contains values for the masses M , characteristic temperatures $\theta_r = \frac{h^2}{2Ik}$, and the dipole moments μ .

Visual inspection of the data plots reveals: (1) that the absorption peaks are lower than that predicted by single relaxation theory, (2) that the velocity dispersion is somewhat greater than predicted by single relaxation theory, (3) that the absorption peaks for both HCl and HBr are shifting to lower frequencies with increase in temperature, (4) that the absorption peak of HCl, which has a higher rotational characteristic temperature, at 298 °K lies at a higher frequency than

the peak for HBr, (5) the shift of the absorption peak appears to be faster for HCl than for HBr.

TABLE I
COMPARISON OF RESULTS FROM SINGLE AND MULTIPLE RELAXATION ANALYSES

Hydrogen Chloride					
M = 36.47 gm/mole; $\theta_r = 15.02$ °K; $\mu = 1.08$ Debye					
T °K	Single Relaxation		Multiple Relaxation		
	τ sec $\times 10^9$	Z_{rot}^*	τ sec $\times 10^9$	Z_{rot}^*	f_2
298	0.52	6.4	0.35	3.0	0.29
573	2.4	11.3	1.1	5.3	0.45
793	5.3	19.1	2.8	10.0	0.02
1073	12.3	30.8	5.2	14.7	0.11

Hydrogen Bromide					
M = 80.93 gm/mole; $\theta_r = 12.03$ °K; $\mu = 0.80$ Debye					
T °K	Single Relaxation		Multiple Relaxation		
	τ sec $\times 10^9$	Z_{rot}^*	τ sec $\times 10^9$	Z_{rot}^*	f_2
298	1.5	10.1	0.77	4.9	0.36
573	3.9	13.9	1.9	6.7	0.74
773	6.3	18.9	2.9	7.8	0.48

* Calculated by Equation (15)

CHAPTER IV

SUMMARY OF RESULTS

Comparison with Other Experiments

In comparing the results of this work with other experiments Table I reveals that $Z_{rot} = 6.4$ at 298°K for HCl agrees very well with the value $Z_{rot} = 7$ found by Breazeale and Kneser at 273°K ⁽²³⁾. Agreement also appears to be good with the lowest temperature values in both thermal conductivity studies ⁽²⁴⁻²⁵⁾; however, again great care should be taken in making direct comparisons of values obtained by different analyses. The temperature dependence found for Z_{rot} in this investigation is in direct opposition to that found in both of the thermal conductivity studies. In this study Z_{rot} was found to increase with temperature. A reason for this discrepancy may be the apparent sensitivity of Z_{rot} to small errors in the measured thermal conductivity. Srivastava and Das Gupta ⁽²⁶⁾ have pointed out that a change of only 3% in their experimental thermal conductivity data for NH_3 would have reversed the shift of Z_{rot} with temperature. Another reason could be that some deficiency exists in Mason and Monchick's theory for extracting Z_{rot} from thermal conductivity measurements.

Comparison with Theory

Zeleznik has considered the effect of (1) dipole moment, (2) moment of inertia, and (3) ambient temperature in his theoretical calculation for polar gases. To compare the experimental results with Zeleznik's calculation the following two ratios must be found:

$$(1) \frac{Z(1,T)}{Z(1, 298^{\circ}K)} \quad \text{where 1 represents either HCl or HBr and (2)}$$

$\frac{Z(\text{HBr},T)}{Z(\text{HCl},T)}$. The first ratio gives a comparison of the change of Z_{rot} with temperature and the second ratio gives an indication of the shift of Z_{rot} due to dipole moment and moment of inertia. The first ratio does not reveal the true temperature dependence since the ratio also depends somewhat on the moment of inertia. The values of the ratios for the experimental data along with the theoretical values are in Table II. The values for the first ratio are calculated from equation (29), and the second ratio is calculated from equation (26) with $T = T_0$ and $N_1 = N_2$. The cross sections are again calculated by Equation (27).

Inspection of Table II reveals that theory and experiment are in excellent agreement as to the temperature dependence, and the general shift is the same for the dipole moment and moment of inertia dependence. Zeleznik says that the general predictions of the theory are as follows: (1) an increase in dipole moment decreases the collision number, (2) an increase in moment of inertia causes a decrease in Z_{rot} , and (3) an increase in temperature also causes Z_{rot} to increase.

According to Zeleznik's theory since the characteristic temperature of HCl is larger than that of HBr, HCl should have a larger Z_{rot} at a given temperature; however, comparison of the dipole moments indi-

cates HCl should have a smaller Z_{rot} . Inspection of Equation (26) shows that the dipole term has a fourth power dependence while the moment of inertial dependence while not immediately obvious is somewhat less. This indicates that Z_{rot} for HCl should be less than Z_{rot} for HBr. Table II reveals that this is the case at 298 °K, and 573 °K; however, the collision numbers are approximately the same at 773 - 793 °K. The shift of Z_{rot} with temperature also agrees with the theory not only qualitatively but quantitatively as well.

The excellent agreement of the numerical values between theory and experiment is felt to perhaps be fortuitous. The theory is based on a two dimensional model with no out of plane forces allowed and considers only those transitions from zero rotational energy to some excited state while the ultrasonic experiment measures the time for equilibration from one Boltzman distribution to another Boltzman distribution. Karplus and Raff⁽²⁷⁾ have detected considerable differences between two and three dimensional results in Monte Carlo calculations.

Inspection of Table II also shows that taking ratios of collision numbers may be a better way to compare results from analyses which do not predict the same relaxation times. Very good agreement exists between the ratios of single relaxation collision numbers to the ratios of those predicted by Gordon's method even though the relaxation times are not the same.

Summary

The purpose of this investigation was to make ultrasonic absorption measurements on polar gases and to determine the temperature de-

pendence of the apparent relaxation times and collision numbers. The temperature dependence of the rotational equilibration in hydrogen chloride and hydrogen bromide have been investigated.

The apparent relaxation times and collision numbers obtained by both single relaxation theory and Gordon's multiple relaxation method are collected in Table I. Comparison of the experimental results to Zeleznik's theoretical calculations are summarized in Table II.

The important discoveries produced by this investigation about rotational equilibration in polar gases are as follows: (1) the apparent relaxation times for HCl and HBr increase with increasing temperature, (2) the absorption and dispersion curves are not accurately described by single relaxation theory, (3) Gordon's multiple relaxation analysis fits the data as well as single relaxation theory in each case and much better in several cases, (4) a larger dipole moment leads to a smaller Z_{rot} at low temperatures, (5) the rate of shift of the absorption peak depends upon both the characteristic temperature and dipole moment of a molecule, (6) the temperature behavior of Z_{rot} is in excellent agreement with Zeleznik's theory and the moment of inertia and dipole moment dependence agrees qualitatively, and (7) the classical absorption should be calculated with frequency dependent specific heats.

Results (1) and (2) agree with the results Winter and Hill⁽¹⁴⁾ found for homonuclear diatomic molecules and result (5) shows that their results for the speed of the shift of the relaxation time as a function of characteristic temperature does not necessarily hold when a dipole moment is also involved. Result (4) agrees with the results

of Breazeale and Kneser that molecules with like dipole moments are very efficient collision partners.

TABLE II
 COMPARISON OF EXPERIMENTAL RESULTS TO ZELEZNIK'S THEORY

$Z(1,T)/Z(1,298\text{ }^\circ\text{K})$			
<u>Hydrogen Chloride</u>			
$T\text{ }^\circ\text{K}$	Single Relaxation	Multiple Relaxation	Zeleznik's Theory
298	1.0	1.0	1.0
573	1.77	1.77	1.89
793	3.0	3.33	2.68
1073	4.8	4.9	3.95
<u>Hydrogen Bromide</u>			
$T\text{ }^\circ\text{K}$	Single Relaxation	Multiple Relaxation	Zeleznik's Theory
298	1.0	1.0	1.0
573	1.38	1.37	1.67
773	1.88	1.59	1.90
$Z(\text{HBr},T)/Z(\text{HCl},T)$			
$T\text{ }^\circ\text{K}$	Single Relaxation	Multiple Relaxation	Zeleznik's Theory
298	1.58	1.63	7.8
573	1.23	1.26	6.0
773-793	0.99	0.78	5.9

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APPENDIX A

EXPERIMENTAL APPARATUS AND TECHNIQUES

Apparatus

The experimental apparatus used in this investigation was essentially the same as that described by Winter and Hill⁽¹⁴⁾. A more detailed description is given by Hill⁽²⁸⁾ in his Ph.D. dissertation. The changes which were made in the apparatus are listed in Chapter I and will not be discussed further.

The procedures outlined by Hill in his Ph.D. thesis for disassembly and reassembly of the apparatus should be strictly followed, particularly the procedure for removing and replacing the quartz rods. One change which has been made in the procedure is that flats to accommodate a torque wrench have been machined on the chucks which hold the quartz rods. These chucks should be tightened to 20 lb-ft.

When the apparatus is disassembled it is convenient to be able to check the signal strength of the acoustic signal; however, Hill's criterion of 20 dB of signal at 20 mm Hg pressure is somewhat ambiguous and is impossible to apply at atmospheric pressure. A list of settings for the best signal obtained at atmospheric pressure is as follows:

- (1) 60 dB of in line attenuation, (2) rods separated one inch, (3) high voltage of the pulse generator set at 35% of maximum, (4) the 460 AR amplifier at maximum amplification, (5) the 465 A amplifier set on 20 dB amplification, and (6) the vertical amplifier of the oscilloscope

set at 0.05 volts/cm. With these conditions the signal height on the oscilloscope was 2 cm.

Several difficulties were encountered due to the nature of the gases which were used in this investigation. Measuring the ambient temperature of the system proved difficult since the apparatus was originally designed for a bare thermocouple to be placed directly in the hot zone. Most thermocouples will react in a reducing atmosphere at high temperature and give spurious temperature readings. To alleviate this problem the temperature was measured when the system was under vacuum and when opened to the atmosphere. The thermocouple was then removed from the system while measurements were being made. For future use it is suggested that a feedthrough to accommodate an encapsulated thermocouple be added to the system or that the system be calibrated with Argon and the temperature found from $V^2 = \gamma RT/M$.

Another difficulty encountered was gas purity. There is always the possibility of outside contamination when working with any gas and when using chemically active gases there is the possibility of the gas reacting with the system. One way of detecting a reaction or dissociation is to watch for an unexplained change in the gas pressure; however, this is useful only when working on a static gas system. This was the method used to detect the reaction of HBr with the system at 1073°K.

To check for gas contamination a gas sample was taken from the gas used in each different set of measurements and analyzed on a mass spectrometer. This method detected a large percentage of HCl in some of the HBr samples. The reason for this large percentage of HCl appears to be due to the unequal vapor pressures of HCl and HBr. Both gases

are supplied as vapors over liquid under their own vapor pressure. The HBr contained 0.2% HCl and apparently after the cylinder had been unused for several days the vapor head over the liquid would contain a larger percentage of HCl than the specified 0.2%. When a large amount of gas was evacuated from the cylinder, and then the purity checked, the stated purity was found. So, when making measurements on a gas which is stored under its own vapor pressure be sure to first bleed the gas bottle.

Mass Spectrometer

A mass spectrometer is located in the Biochemistry Department. The instrument was originally designed to analyze solid organic samples and no provisions were made to introduce gases directly into the system. To modify the instrument to accept gas samples directly a probe was designed which could be inserted directly into the ion source through a high vacuum feedthrough. A very fine metering valve was attached to the probe to meter the flow of incoming gas from the sample. The glass shop supplied gas sample tubes which could be sealed by applying a flame. The sample tubes also had a fragile glass seal which could be broken in order to let the sample into the mass spectrometer.

Errors

The errors in the measured velocity and absorption are given by Hill at low frequencies; however, the error increases as the frequency increases. Hill states the probable error for absorption to be 5% over most of the frequency range and becoming somewhat larger at high fre-

quency to pressure ratio's. Above 50 M Hz/atm the error is approximately 10-15% depending upon the gas used and the ambient temperature of the system. The low frequency velocity probable error is given by Hill as 0.5% at low frequency. At frequencies in which the velocity measurements are made using less than the full width of the oscilloscope face the probable error increase. For example, the probable error in HBr at 773^oK at 74.5 MHz/atm is approximately 15%.

APPENDIX B

METHODS USED FOR CALCULATING TRANSPORT PROPERTIES AND SECOND VIRIAL COEFFICIENTS

Introduction

Certain physical properties of gases such as the equation of state and the transport properties are closely connected with the law of force between the individual molecules. The basic theory for the relationship between the transport properties was initially developed by Chapman and Enskog. Chapman and Cowling⁽²⁹⁾ have expressed the transport coefficients in terms of a set of integrals called collision integrals. Once the collision integrals are evaluated for a molecular model in which the laws of interaction are realistic, it is possible to determine values of the physical properties under conditions for which experimental data do not exist, e.g. at elevated temperatures. This is possible because the potential energy of interaction between molecules is temperature independent.

For simple non-polar gases the Lennard-Jones⁽³⁰⁾ potential has proved satisfactory in explaining the equation of state and the transport phenomena:

$$\phi(r) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^6 \right]$$

In this equation r is the separation between the molecules, σ_0 is the

low velocity collision diameter, and ϵ_0 is the maximum energy of attraction.

For polar gases this equation has been modified by Stockmayer⁽³¹⁾ to account for the dipole moment.

$$\phi(r) = 4\epsilon_0 \left[\left(\frac{\sigma_0}{r}\right)^{12} - \left(\frac{\sigma_0}{r}\right)^6 \right] - \left(\frac{\mu_1\mu_2}{r^3}\right) \psi$$

where $\psi = 2 \cos \theta_1 \cos \theta_2 - \sin \theta_1 \sin \theta_2 \cos \chi$

and μ_1 and μ_2 are the dipole moments of the two interacting molecules, θ_1 and θ_2 the angles of inclination of the dipoles to the line joining the centers of the molecules, and χ is the azimuthal angle between them.

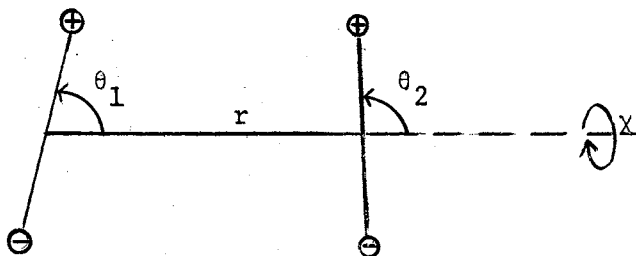


Figure 17. The Coordinates Describing the Mutual Orientation of Two Polar Molecules.

Monchick and Mason⁽²²⁾ have calculated the collision integrals for the Stockmayer potential and have tabulated the values.

Coefficient of Viscosity

The coefficient of viscosity as given by Monchick and Mason is

$$\eta = \frac{5}{16} \left(\frac{mkT}{\pi} \right)^{\frac{1}{2}} \frac{f_{\eta}}{\sigma_0^2 \langle \Omega^{(2,2)*} \rangle}$$

where $\langle \Omega^{(2,2)*} \rangle$ is a dimensionless collision integral averaged over all relative orientations and f_{η} is a correction factor resulting from higher kinetic theory approximations which differs from unity at most by a few percent and is given by

$$f_{\eta} = 1 + \frac{3}{196} [8 \langle E^* \rangle - 7]^2.$$

$\langle E^* \rangle$ is defined to be

$$\langle E^* \rangle \equiv \frac{\langle \Omega^{(2,3)*} \rangle}{\langle \Omega^{(2,2)*} \rangle}.$$

Values of σ_0 as determined from low temperature viscosity data are given by Monchick and Mason for most simple polar gases. The collision integrals are tabulated as functions of two parameters: (1) the reduced temperature $T^* = T/\epsilon_0/k$ and (2) a function of the dipole moment δ . Values of δ and ϵ_0/k are also given by Monchick and Mason for most simple polar gases.

Monchick and Mason have indicated that the viscosity values obtained by this method are in general as accurate as values obtained for non-polar gases by use of the Lennard-Jones potential.

Thermal Conductivity

The procedure for calculating the thermal conductivity from Eucken factors is described by Hirschfelder, Curtiss, and Bird⁽³²⁾. For poly-

atomic gases the thermal conductivity is given approximately by

$$\kappa = \frac{15}{4} \frac{R}{M} [\eta] \left(\frac{4}{15} \frac{C_v}{R} + 3/5 \right)$$

and if $C_p = C_v + R$, then

$$\kappa = \frac{\eta}{M} (C_p + 3/4 R)$$

and since $R = 1.987 \text{ cal/mole } ^\circ\text{K}$

$$\kappa = \frac{\eta}{M} [C_p + 1.49]$$

Velocity Correction

To correct the experimentally measured values for the velocity of sound in a gas for effects due to non-ideality one may assume the equation of state for the gas to be

$$pv = RT + Bp$$

where B is the second virial coefficient. The velocity of sound for a gas may be written as

$$V^2 = \gamma \left(\frac{\partial p}{\partial \rho} \right)_T$$

This may be rewritten as

$$V^2 = \gamma \left(\frac{\partial p}{\partial v} \right)_T \left(\frac{\partial v}{\partial \rho} \right)_T$$

Since the density $\rho = m/v$ and $\partial v / \partial \rho = -v^2/m$ the above equation may be

written as

$$v^2 = -\gamma \left(\frac{\partial p}{\partial v} \right)_T \frac{v^2}{M} .$$

Now from the virial equation of state

$$\left(\frac{\partial p}{\partial v} \right)_T = - \frac{RT}{(v - B)^2}$$

and expanding the denominator in a binomial expansion and keeping only the first two terms gives

$$\left(\frac{\partial p}{\partial v} \right)_T = - \frac{RT}{v^2} \left(1 + \frac{2B}{v} \right) .$$

Putting this into the velocity equation and setting $v = RT/p$ gives

$$v^2 = \frac{\gamma RT}{M} \left(1 + 2 \frac{Bp}{RT} \right) .$$

Now if the velocity of sound for an ideal gas is given by

$$v_{id}^2 = \gamma_{id} \frac{RT}{M}$$

then

$$\frac{v^2}{v_{id}^2} = \frac{\gamma}{\gamma_{id}} \left(1 + \frac{2Bp}{RT} \right) .$$

The second virial coefficients are tabulated by Hirschfelder, Curtiss, and Bird⁽³²⁾. The coefficient B is defined as

$$B = B^* b_0 = B^* \left(\frac{2}{3} \pi N \sigma_0^3 \right)$$

where N is Avogadro's number. The values of B^* are tabulated as func-

tions of the reduced temperature T^* and a dipole dependent term

$t^* = 8^{-1/2} \mu^*$ where $\mu^* = \mu / \sqrt{\epsilon_0 \sigma_0^3}$. The dipole term t^* is related

to the δ term used by Monchick and Mason by

$$t^* = 2^{1/2} \delta .$$

Unfortunately values for ϵ_0 and σ_0 derived from low temperature virial coefficients were not available so the viscosity values were employed.

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