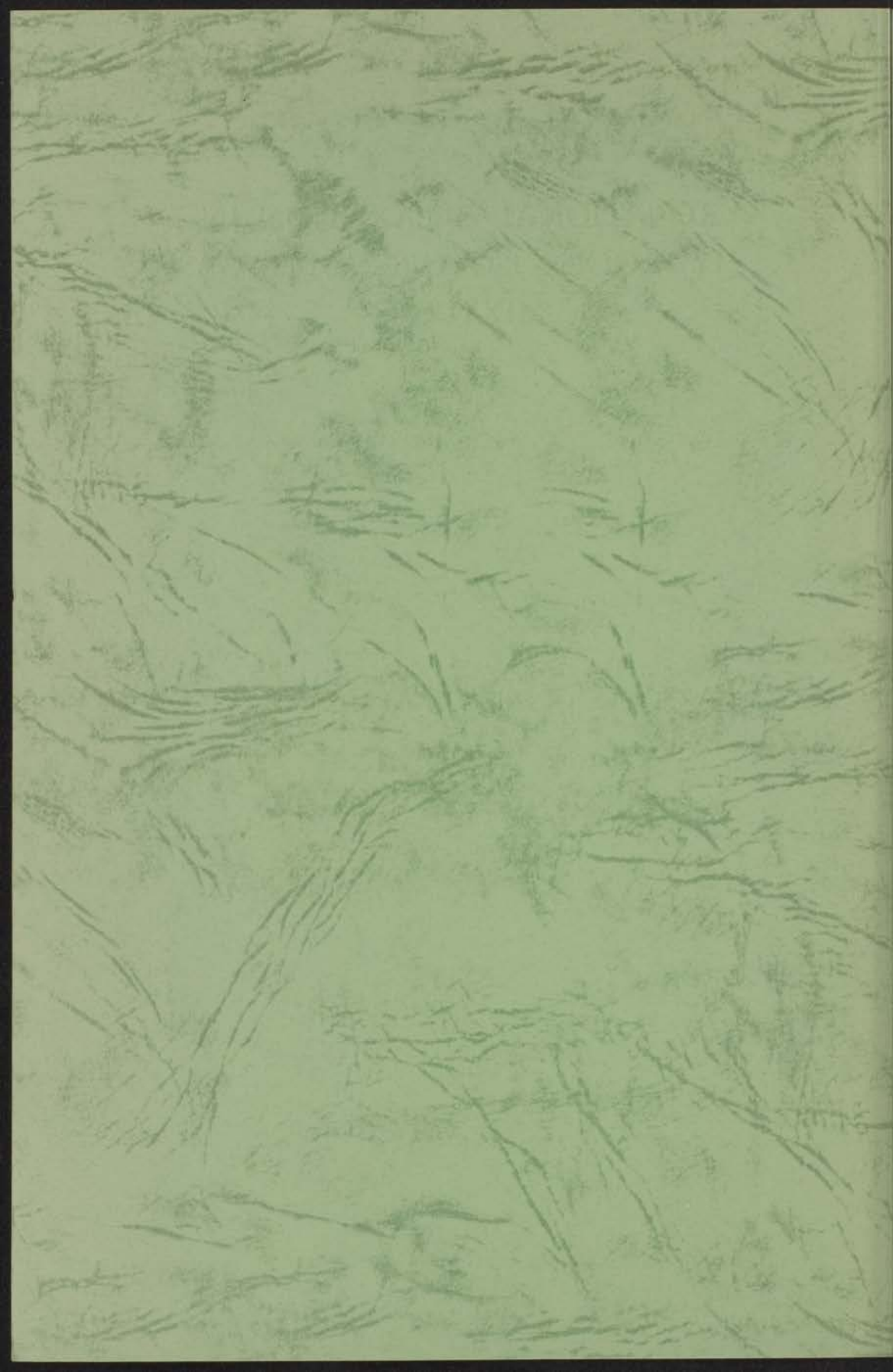


ROTATIONAL RELAXATION IN
HYDROGEN ISOTOPE-NOBLE GAS
MIXTURES

INSTITUUT LORENTZ
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2 OKT. 1967

ROTATIONAL RELAXATION IN
HYDROGEN ISOTOPE-NOBLE GAS
MIXTURES

PROEFSCHRIFT

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DE WISKUNDE EN NATUURWETENSCHAPPEN AAN DE
RIJKSUNIVERSITEIT TE LEIDEN, OP GEZAG VAN DE
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DRUCO DRUKKERIJBEDRIJVEN N.V. - LEIDEN

ROTATIONAL RELAXATION IN
HYDROGEN BROMIDE-
MIXTURES

PROLOGUE

The present work is a contribution to the study of the rotational relaxation of hydrogen bromide in mixtures with various gases. The results are compared with those obtained for other diatomic molecules and with theoretical predictions. The experimental method used is the microwave absorption technique.

Promotor: Prof. Dr. J.J.M. Beenakker

ROBERT HARTMANN JONKMAN
DEPARTMENT OF PHYSICS

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Dit werk vormt een onderdeel van het onderzoek programma van de Stichting voor Fundamenteel Onderzoek der Materie en is mogelijk gemaakt door financiële steun van de Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek.

Präsident: Prof. Dr. J. J. B. ...

Das ist ein ...
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I N T R O D U C T I O N

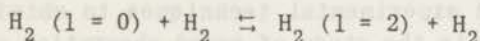
In this thesis we will study rotational translational relaxation in gaseous binary mixtures of the hydrogen isotopes with the noble gases. Rotational relaxation processes deal with the equilibration of the occupation of the rotational quantum states in a non-equilibrium system. Hence the relaxation times describing these processes are of interest for widely different fields of research dealing with such systems. From a microscopic point of view the relaxation times are related to the inelastic scattering cross sections for the process involved. For rotational transitions these cross sections are dependent on the interaction potential and in particular on the non-spherical part of it. So the relaxation times provide a means to obtain information about the anisotropy of the intermolecular potential. Especially for this reason the molecular physics group of the Kamerlingh Onnes Laboratory decided in 1962 to investigate rotational translational relaxation times experimentally and theoretically.

One of the commonly used experimental techniques to obtain rotational relaxation times is the study of sound-absorption or -dispersion due to relaxation processes¹⁾²⁾³⁾. Since also other mechanisms like viscous friction, heat conduction and diffusion play a role in sound propagation, we evaluate in chapter I⁴⁾ expressions for the sound-absorption and -dispersion in the considered relaxing mixtures. In these mixtures the sound absorption coefficient α , can be very large and therefore sound velocity measurements will be rather unreliable. For this reason sound absorption measurements as a function of frequency and pressure seem to be a better tool to obtain relaxation times. From the experimental data of α these relaxation times can be obtained in a reliable way if only one relaxation time is involved, which is the case e.g. for a two level system. Since we are interested in rotational transitions, the hydrogen isotopes parahydrogen (pH_2) and orthodeuterium (oD_2) in which gases only the rotational levels $l = 0$ and $l = 2$ are occupied in a fairly extended temperature range seem to be a good choice.

As a part of this program S l u i j t e r, K n a a p and

Beenakker published in 1964 a series of papers⁵⁾⁶⁾⁷⁾ on rotational-translational relaxation times in pure gaseous pH_2 and oD_2 at several temperatures. The results were related to the inelastic scattering cross sections for the process involved, yielding a value for the asymmetry parameter, β , in the interaction potential. These inelastic scattering cross sections for rotational transitions, $Q_{1,1}$, in hydrogen isotopes are calculated by several authors⁸⁾⁹⁾¹⁰⁾. In such calculations one must take into account the orientations of both colliding molecules. This complication does not arise, however, in a hydrogen-noble gas interaction so that for such a pair the calculation of the inelastic scattering cross section will be simpler. Hence, as an extension of the work of Sluiter et al. we decided to investigate rotational transitions in hydrogen isotopes induced by the various noble gas atoms obtaining at the same time another check on the consistency of the theory.

The relaxation time of pH_2 or oD_2 colliding with noble gas atoms only can be experimentally obtained by performing measurements in hydrogen-noble gas mixtures as a function of concentration. These experiments are described in chapters II¹¹⁾ and III¹²⁾, dealing with pH_2 - and oD_2 -mixtures respectively. In such mixtures the following reactions will occur:



Since these reactions are parallel we see directly³⁾ that the process can again be described with a single relaxation time, $\tau_{\text{VT mix}}$:

$$(\tau_{\text{VT mix}})^{-1} = x_{\text{H}_2} (\tau_{\text{VT H}_2\text{-H}_2})^{-1} + x_{\text{n.g.}} (\tau_{\text{VT H}_2\text{-n.g.}})^{-1} \quad (1)$$

Hence a plot of $(\tau_{\text{VT}})^{-1}$ versus concentration should be a straight line. This indeed has been verified experimentally. Extrapolation to $x_{\text{n.g.}} = 1$ gives the relaxation time of a system of hydrogen molecules, colliding with noble gas atoms only. In chapter IV¹³⁾ this value of $(\tau_{\text{VT}})_{\text{H}_2\text{-n.g.}}$ is compared with the results of calculations on averaged inelastic scattering cross sections, $Q_{02}(T)$ based on the modified wave approximation in the distorted wave method as used by Takayanaagi⁸⁾.

Apart from this program in chapters II and III also relaxation times in mixtures of pH_2 and oH_2 at 77°K and in mixtures of oD_2 and pH_2 at 45°K are reported. At these temperatures oH_2 and pH_2 are completely in rotational states $l = 1$ and $l = 0$ respectively and behave like inert collision partners. Therefore in these mixtures too we expect eq. (1) to be valid. The difference between $(\tau_{VT})_{\text{pH}_2-\text{pH}_2}$ and $(\tau_{VT})_{\text{pH}_2-\text{oH}_2}$ will inform us about the influence

of the rotational state of the collision partner on the relaxation process. The results obtained in the case of the deuterium-hydrogen mixtures give indications of the occurrence of the quasi resonance reaction:



as predicted theoretically by Van Kranendonk¹⁴⁾.

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CHAPTER I

EXPRESSIONS FOR SOUND ABSORPTION AND -DISPERSION IN BINARY MIXTURES OF A RELAXING GAS WITH NOBLE GASES DERIVED FROM IRREVERSIBLE THERMODYNAMICS.

1. Introduction

Inelastic collision cross-sections of molecules are a point of common interest for widely different fields of research, such as astrophysics and chemical kinetics. Therefore it is not surprising that during the last years several authors¹⁾²⁾³⁾ presented results of calculations on rotational transitions of hydrogenic molecules, colliding with noble gas atoms. It is worthwhile to study these systems experimentally also. Determination of acoustic relaxation times provides us an experimental means to obtain the rate constants of the reaction, which can be shown⁴⁾ to be weighted averages of the inelastic collision cross-sections. The relaxation times can be obtained from sound absorption and sound velocity measurements in mixtures as a function of frequency, pressure and concentration⁵⁾. Both techniques have their specific difficulties.

From the frequency dependence of the absorption due to the relaxation process the relaxation time can be obtained. This approach is complicated however by the fact that in addition to this relaxation absorption other losses occur, due to friction, heat-conduction, thermal-diffusion and diffusion. An expression for this absorption has been given by K o h l e r⁶⁾ already in 1941. This expression is experimentally verified by P e t r a l i a⁷⁾. For mixtures of molecules of which the masses differ appreciably the diffusion contribution can be comparable in magnitude with the relaxation absorption and must be known rather accurately in order to obtain reliable relaxation times. In sound dispersion measurements on the other hand the large non-relaxation absorption makes measurements at high values of ωT rather inaccurate. The

reason is that it becomes difficult to measure over a distance of more than one wavelength; see e.g. the work of Bose¹⁸⁾. So, in our opinion, absorption measurements are to be preferred.

Since in the expression for the non-relaxation absorption specific heats occur, which are in these systems known to be complex functions of $\omega\tau$ ⁵⁾, one feels intuitively that also this absorption mechanism becomes dependent on the relaxation time. In view of the complexity of the situation we decided to derive an expression for the total sound absorption in this type of gaseous mixtures, using non-equilibrium thermodynamics. We essentially followed a formalism, outlined already in 1943 by Meixner⁸⁾ for the general case of a mixture of n components, each of which is subjected to chemical reactions. Our final results will be expressed in kinetic coefficients which can in principle be measured directly.

Apart from the symbols as defined in the text we use the following notation:

- c_i concentrations of component i in moles per gram,
- \vec{D}_i diffusion current of component i in the center of mass system,
- M_i molecular weight of component i ,
- P pressure,
- R gas constant per mole,
- T temperature,
- U_i internal energy of component i per mole,
- \vec{v} center of mass velocity,
- \vec{W} energy current in center of mass system,
- x_i mole fraction of component i ,
- Γ_i production of component i by chemical reactions in gram/cm³.s,
- γ specific heat ratio,
- η shear viscosity,
- η_v bulk viscosity,
- μ_i chemical potential of component i per gram,
- ρ mass density.

2. Theory

As usual in treatments like this we will start from the rate-of-change equations. As in a sound field the amplitudes are small, we linearize by taking partial derivatives in stead of substantial ones and we assume that $\text{rot } \vec{v} = 0$:

$$\frac{\partial \rho}{\partial t} + \rho \operatorname{div} \vec{v} = 0 \quad (1)$$

$$\rho \frac{\partial c_i}{\partial t} + \operatorname{div} \vec{D}_i = \Gamma_i \quad (i = 1, \dots, n) \quad (2)$$

$$\rho \frac{\partial \vec{v}}{\partial t} = -\operatorname{grad} P + \left(\frac{4}{3}\eta + \eta_v\right) \Delta \vec{v} \quad (3)$$

$$\frac{\partial}{\partial t} \sum_i \frac{c_i U_i}{M_i} = \frac{P}{\rho^2} \frac{\partial \rho}{\partial t} - \frac{1}{\rho} \operatorname{div} \vec{W} \quad (4)$$

The corresponding phenomenologic equations read

$$\vec{D}_i = \sum_k a_{ik} (-T \operatorname{grad} \frac{\mu_k}{T}) + b_i (-\operatorname{grad} \ln T) \quad (i = 1, \dots, n) \quad (5)$$

$$\vec{W} = \sum_k b_k (-T \operatorname{grad} \frac{\mu_k}{T}) + c (-\operatorname{grad} \ln T) \quad (6)$$

$$\Gamma_i = \sum_k A_{ik} \mu_k \quad (i = 1, \dots, n) \quad (7)$$

where the chemical potential per gram of component i , μ_i , is defined by:

$$M_i \mu_i = f_i(T) + RT \ln \rho c_i ; \frac{\partial}{\partial T} \left(\frac{f_i}{T} \right) = \frac{-U_i}{T^2} \quad (8)$$

As the fluxes are defined in the center of mass system, one has: $\sum_i \vec{D}_i = 0$; and also $\sum_i \Gamma_i = 0$. In this way we obtain the following

relations between the phenomenologic coefficients:

$$\begin{aligned} \sum_i a_{ik} &= 0 \\ \sum_i b_i &= 0 \\ \sum_i A_{ik} &= 0 \end{aligned} \quad (9)$$

For the set of equations (5) the Onsager-relations have the following simple form

$$a_{ik} = a_{ki} ; \quad A_{ik} = A_{ki} \quad (10)$$

Finally the equation of state reads

$$P = \frac{RT\rho}{M} \quad (11)$$

where the average molecular mass, M , is given by $M = \sum_1 x_1 M_1$.

The time and space dependent quantities ρ, c_i, \vec{v}, T and P , which characterize the system, fluctuate around their equilibrium values, indicated with a subscript "0". Following De Groot and Mazur⁹ we proceed at this point by making a Fourier transform of the deviations from the equilibrium value; e.g.

$$\rho(\vec{r}, t) - \rho_0 = \left(\frac{1}{2\pi}\right)^4 \int_{-\infty}^{+\infty} \int \hat{\rho}(\vec{K}, \omega) \exp i(\vec{K} \cdot \vec{r} - \omega t) d\vec{K} d\omega \quad (12)$$

with:

$$\hat{\rho}(\vec{K}, \omega) = \int_{-\infty}^{+\infty} \int \{ \rho(\vec{r}, t) - \rho_0 \} \exp i(-\vec{K} \cdot \vec{r} + \omega t) d\vec{r} dt \quad (13)$$

By calculation of grad ρ with (12) it is easily seen that

$$\int_{-\infty}^{+\infty} \int (\text{grad } \rho) \exp i(-\vec{K} \cdot \vec{r} + \omega t) d\vec{r} dt = i\vec{K} \hat{\rho}(\vec{K}, \omega) \quad (14)$$

and analogical

$$\int_{-\infty}^{+\infty} \int \left(\frac{\partial \rho}{\partial t}\right) \exp i(-\vec{K} \cdot \vec{r} + \omega t) d\vec{r} dt = -i\omega \hat{\rho}(\vec{K}, \omega) \quad (15)$$

The above treatment is still correct, under suitable conditions, if \vec{K} is the complex vector $\vec{K} = \vec{k} + i\vec{\alpha}$, \vec{k} being the wave vector. Inserting a scalar for ρ in (14) shows that \vec{k} and $\vec{\alpha}$ are parallel vectors so that we can write $\vec{k} = k \vec{u}$ and $\vec{\alpha} = \alpha \vec{u}$, \vec{u} being a unit vector; α is the absorption coefficient. Clearly $\rho(\vec{r}, t)$ can be looked upon as a superposition of damped partial waves with amplitude $\hat{\rho}(\vec{K}, \omega) \exp(-\vec{\alpha} \cdot \vec{r})$. Similar arguments hold for c_i, \vec{v}, T and P .

Fourier transformation of (1) - (4) and (11) gives after elimination of \vec{v} and \hat{P} the following relations for \hat{c}_i, \hat{T} and $\hat{\rho}$:

$$(m + \frac{4}{3}\eta + \bar{\eta}_v - 1)\hat{\rho} - \hat{T} - \sum_1 x_1 \hat{c}_1 = 0 \quad (16)$$

$$x_i \hat{c}_i + \sum_k (\bar{A}_{ik} - \bar{a}_{ik}) \left(\frac{U_k}{RT} \hat{T} - \hat{\rho} - \hat{c}_k\right) + \bar{b}_i \hat{T} = 0 \quad (i=1, \dots, n) \quad (17)$$

$$C_v \hat{T} + \sum_i \frac{U_i}{RT} x_i \hat{c}_i - \hat{\rho} - \sum_i \bar{b}_i \left(\frac{U_i}{RT} \hat{T} - \hat{\rho} - \hat{c}_i \right) + \bar{c} \hat{T} = 0 \quad (18)$$

The following shorthand notation has been used:

$$\begin{aligned} m &= \frac{\omega^2}{\bar{K} \cdot \bar{K}} \frac{\rho}{P} & ; & & \bar{c} &= \frac{i\omega\rho}{P^2} \frac{c}{m} & ; \\ \bar{\eta} &= \frac{i\omega}{P} \eta & ; & & \bar{b} &= \frac{i\omega}{P} \frac{b_i M}{M_i m} & ; \\ \bar{\eta}_v &= \frac{i\omega}{P} \eta_v & ; & & \bar{a}_{ik} &= \frac{i\omega}{\rho} \frac{a_{ik} M^2}{M_i M_k m} & ; \quad (19) \\ \bar{A}_{ik} &= \frac{P}{i\omega\rho^2} \frac{A_{ik} M^2}{M_i M_k} & ; & & U_i &= U_{i0} + C_v T & ; \end{aligned}$$

C_v = total molar specific heat minus the contribution of the relaxing degree of freedom. m can be considered as a frequency dependent complex specific heat ratio, as follows directly from the definition of m and the expression $\omega^2/(\bar{K} \cdot \bar{K}) = \gamma(\omega) P/\rho$.

We will now confine ourselves to the special case of a mixture of a two level system with a noble gas. Examples of such two level systems are pH_2 at temperatures $70 < T < 200^\circ \text{K}$, oD_2 at $35 < T < 90^\circ \text{K}$ and HD at $20 < T < 50^\circ \text{K}$, where only the two lowest rotational levels are occupied and e.g. the electronic transition ${}^2\Pi_{3/2} \rightleftharpoons {}^2\Pi_{1/2}$ occurring in $\text{NO}^{(10)}$. In this derivation we treat the system as a three component mixture. This means that the excited molecule is to be considered to behave like a separate chemical species. We assume that the lifetime of this excited molecule is long compared to the mean time between collisions, τ_c . This assumption is the same as the one that is used in the Eucken-treatment for the heat conductivity⁽¹¹⁾. In a more advanced treatment correction terms of the order $Z^{-2} = (\tau_c/\tau)^2$ occur in our final results. Identifying species 1 and 2 with the ground and excited state and 3 with the noble gas, we have: $M_1 = M_2$; $U_1 = U_3 = C_v T$; $U_2 = C_v T + \epsilon/N$, where ϵ is the energy separation of the two levels and N is Avogadro's number. Remark furthermore that according to the definition $A_{31} = 0$ which leads to $A_{11} = A_{22} = -A_{12} = -A_{21} = A$. To introduce explicitly the relaxation time into our

problem we observe that the relaxation equation is given by:

$$\Gamma_2 = -\rho \frac{(x_2 - x_{2eq})}{\tau_{VT}} + \frac{M_2}{M} \quad (20)$$

Using the equilibrium condition $\Gamma_2 = 0$ for $x = x_{eq}$ (7) leads to :

$$\bar{A} = A \frac{P}{\rho} \left\{ \ln \frac{x_1}{x_{1eq}} - \ln \frac{x_2}{x_{2eq}} \right\} \frac{M}{M_2}$$

$$\approx -i\omega\rho \bar{A} (x_2 - x_{2eq}) \left(\frac{x_{1eq} + x_{2eq}}{x_{1eq} x_{2eq}} \right) \frac{M_2}{M}$$

Combination of these results yields a relation between \bar{A} and τ_{VT} :

$$\bar{A} = \frac{x_1 x_2}{(x_1 + x_2) i\omega \tau_{VT}} \quad (21)$$

The contribution to the specific heat of the relaxing degree of freedom, C' , can easily be shown to be

$$C' = R \left(\frac{\epsilon}{kT} \right)^2 \frac{x_1 x_2}{(x_1 + x_2)} \quad (22)$$

In the case x_3 vanishes C' reduces to the well known Schottky specific heat of a two level system.

The five linear homogeneous equations (16), (17) and (18) for the five unknown quantities $\hat{\rho}$, \hat{T} and \hat{c}_1 , must be simultaneously fulfilled. This can only be the case if the coefficient-determinant vanishes (23). Here we put for short $C_V^* = C_V/R$; $\epsilon^* = \epsilon/kT$ and $m = (M_1 - M_3)/M_3$. Our task is to obtain m from this expression in terms of the coefficients, i.e. $m = m(\eta, \eta_v, a_{ik}, b_i, c, A, x_i)$.

It is easy to show⁸⁾ that η, η_v, c, b_i , and a_{ik} are of the order $\omega\tau_c$ and hence small compared to 1 at frequencies $\omega \ll \tau_c^{-1}$.

$m - 1 + \frac{4}{3}\bar{\eta} + \bar{\eta}_v$	-1	$-x_1$	$-x_2$	$-x_3$
$-1 + \bar{b}_3 m$	$C_v^* - C_v^* \bar{b}_3 m - \bar{b}_2 \epsilon^* + \bar{c}$	$x_1 C_v^* + \bar{b}_1$	$x_2 C_v^* + \epsilon^* x_2 + \bar{b}_2$	$x_3 C_v^* + \bar{b}_3$
$m \bar{a}_{31}$	$-m C_v^* \bar{a}_{31} - \epsilon^* \bar{a}_{21} + \bar{b}_1 - \epsilon^* \bar{A}$	$x_1 - \bar{A} + \bar{a}_{11}$	$\bar{A} + \bar{a}_{12}$	\bar{a}_{13}
$m \bar{a}_{32}$	$-m C_v^* \bar{a}_{32} - \epsilon^* \bar{a}_{22} + \bar{b}_2 + \epsilon^* \bar{A}$	$\bar{A} + \bar{a}_{21}$	$x_2 - \bar{A} + \bar{a}_{22}$	\bar{a}_{23}
$m \bar{a}_{33}$	$-m C_v^* \bar{a}_{33} - \epsilon^* \bar{a}_{23} + \bar{b}_3$	\bar{a}_{31}	\bar{a}_{32}	$x_3 + \bar{a}_{33}$
$= 0 \quad (23)$				

Let us first look for a zero order solution, m_0 , of (23), where we will neglect $\bar{\eta}$, $\bar{\eta}_v$, \bar{c} , \bar{b}_i and \bar{a}_{ik} . With (21) and (22) one obtains immediately:

$$(m_0 - 1) = (C_v^* + \mathcal{R} C'^*)^{-1} \quad (24)$$

where

$$C'^* = \frac{C'}{R} \text{ and } \mathcal{R} = (1 - i \omega \tau_{VT})^{-1} \quad (25)$$

Remembering the definitions of m and \vec{K} , (14, 19)

$\vec{K} \cdot \vec{K} = k^2 - \alpha^2 - 2 i k \alpha = \omega^2 \rho / m P$, the well known⁵⁾ expressions for the sound dispersion and absorption in relaxing gases follow directly by separating real and imaginary parts:

$$\left(\frac{k}{k_0} \right)^2 = 1 - e \frac{\omega^2 \tau_{PS}^2}{1 + \omega^2 \tau_{PS}^2} + \frac{\alpha^2}{k_0^2} \quad (26)$$

$$\frac{\alpha}{k} \left(\frac{k}{k_0} \right)^2 = \frac{1}{2} e \frac{\omega \tau_{PS}}{1 + \omega^2 \tau_{PS}^2} \quad (27)$$

with e given by
$$e = \frac{RC'}{C_p(C_v + C')} ; \quad (28)$$

τ_{PS} and τ_{VT} are related by
$$\tau_{PS} = \frac{C_p}{C_p + C'} \tau_{VT} \quad (29)$$

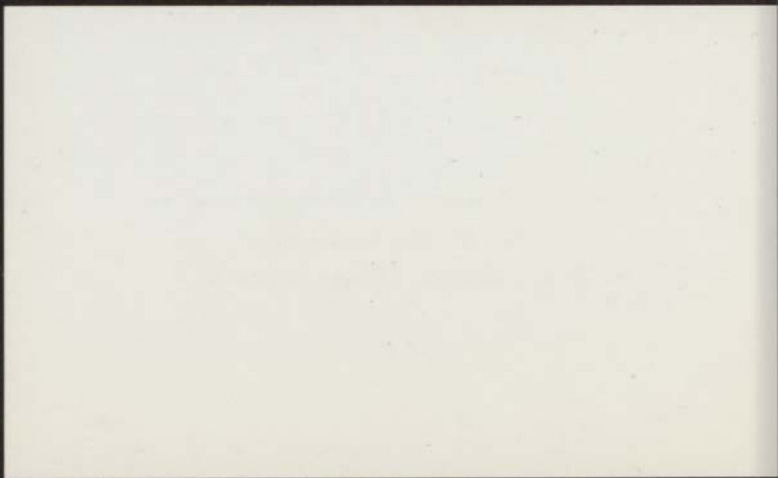
and the subscript "0" means = "in the limit of zero frequency". The contribution $(\alpha/k_0)^2$ to the dispersion is small in most cases and therefore normally neglected.

To obtain the combined effect of relaxation and losses from the other irreversible phenomena we look for the higher approximation by substituting in (23) $m = m_0 + \delta$. By our choice of m_0 it is then possible to construct one row in the determinant which completely consists of first order terms in δ , $\bar{\eta}$, $\bar{\eta}_v$, \bar{c} , \bar{b}_i and \bar{a}_{ik} . To obtain a first order solution to the problem it is then sufficient to neglect all first order contributions occurring in the rest of the determinant. In this way we find after some calculation:

$$\delta = - \left[\frac{1}{2} \bar{\eta} + \bar{\eta}_v + (C_v^* + \mathcal{R} C'^*)^{-2} \left\{ \bar{c} - 2 \bar{b}_2 (1 - \mathcal{R}) \epsilon^* + 2 \bar{b}_3 \mathcal{R} B + \bar{a}_{22} (1 - \mathcal{R})^2 \epsilon^{*2} - 2 \bar{a}_{32} \mathcal{R} C'^* (1 - \mathcal{R}) \epsilon^* B + \bar{a}_{33} \mathcal{R}^2 B^2 \right\} \right] \quad (30)$$

De promotie vindt plaats in het Groot-Auditorium, en
is voor een ieder toegankelijk.

Na afloop receptie in het Academiegebouw.



where we put for short $B = \frac{1 - \gamma}{\epsilon^* x_1} + \gamma$

Proceeding in the same way as in the case of the zero order solution would yield an expression for the sound absorption and dispersion in terms of \bar{a}_{ik} , \bar{b}_i and \bar{c} . Since we prefer to express our results in directly observable quantities we must find a relation between \bar{a}_{ik} , \bar{b}_i and \bar{c} and heat conductivities, thermal-diffusion coefficients and diffusion coefficients, all defined in a three component mixture in the usual way:

$$\frac{\partial x_i}{\partial t} + (\vec{\phi} \cdot \text{grad } x_i) = \text{div} (D_{T_i} \text{ grad } \ln T + \sum_k D_{ik} \text{ grad } x_k) \quad (i = 1, 2, 3) \quad (31)$$

$$\rho C_p \frac{\partial T}{\partial t} - \frac{\partial p}{\partial t} = \text{div} (\kappa \text{ grad } T + p \sum_i D_{T_i} \text{ grad } \ln x_i) \quad (32)$$

When our reference frame moves with the average particle velocity, $\vec{\phi}$, in an isobaric system, then in both equations the second term at the left hand sides vanishes. Meixner¹²⁾ gives the following relations, expressing the kinetic coefficients in (31) and (32) in the coefficients occurring in (5) and (6):

$$T\kappa = c - 2 \sum_k b_k h_k + \sum_i \sum_k a_{ik} h_i h_k \quad (33)$$

$$D_{T_i} = \frac{M}{\rho} \left[\frac{1}{M_i} (b_i - \sum_k a_{ik} h_k) - x_i \sum_j \frac{1}{M_j} (b_j - \sum_k a_{jk} h_k) \right] \quad (i = 1, 2, 3) \quad (34)$$

$$D_{ik} = \frac{T^2}{p x_k} \left[\frac{a_{ik}}{M_i M_k} - x_i \sum_j \frac{a_{jk}}{M_j M_k} \right] \quad (35)$$

Here the specific enthalpies per gram are given by

$$h_k = M_k^{-1} (C_p^* + \delta_{2k} \epsilon^*) RT$$

where δ_{ij} is the Kronecker symbol. To invert these expressions we observe that from the summation properties of a_{ik} and b_i follows:

$$\sum_i D_{T_i} = 0 \quad (36) \quad \text{and} \quad \sum_i D_{ik} = 0 \quad (37).$$

Furthermore the Onsager relations read now:

$$x_k (D_{ik} - x_1 \tilde{M} D_{3k}) = x_1 (D_{ki} - x_k \tilde{M} D_{3i}) \quad (38)$$

$$\text{with } \tilde{M} = \frac{M_3 - M_1}{M}.$$

Using these relations we are able to invert (33) to (35):

$$\bar{c} = \frac{i\omega M}{mPR} \left(\kappa + 2(\bar{b}_3^* m C_P^* + \bar{b}_2 \epsilon^*) - \left\{ \bar{a}_{33}^* (m C_P^*)^2 + 2 \bar{a}_{32}^* m C_P^* \epsilon + \bar{a}_{22}^* (\epsilon^*)^2 \right\} \right) \quad (39)$$

$$\bar{b} = \frac{i\omega M}{mTR} (D_{T_1} - x_1 \tilde{M} D_{T_3}) + \bar{a}_{i3}^* m C_P^* + \bar{a}_{i2}^* \epsilon^* \quad (i = 1, 2, 3) \quad (40)$$

$$\bar{a}_{ik} = \frac{i\omega M x_k}{mTR} (D_{ik} - x_1 \tilde{M} D_{3k}) \quad (i, k = 1, 2, 3) \quad (41)$$

We can now express m in three thermal diffusion coefficients and nine diffusion coefficients. Let us first consider the three thermal diffusion coefficients. Between them (36) holds. At this point we observe that the transport coefficients are determined by the molecular masses and the intermolecular potential, which is known to be nearly the same for the ground state and the excited state. So it is sensible to assume that the difference in transport coefficients between these states can be neglected. From this assumption follows directly the following relation for the particle flows of component 1 and 2 in the laboratory system, \vec{J}_1 and \vec{J}_2 :

$$x_2 \vec{J}_1 = x_1 \vec{J}_2$$

$$\text{From } \frac{dx_i}{dt} = -\text{div } \vec{J}_i = \text{div } D_{T_i} \text{ grad } \ln T.$$

we find a second relation between the thermal-diffusion coefficients:

$$x_1 D_{T_2} = x_2 D_{T_1} \quad (42)$$

In this way we treat the mixture as being effectively a two component mixture as far as interaction between the chemical reacting molecules and the inert gas is concerned. It is then reasonable,

in view of (42) to choose D_{T_3} as the independent coefficient.

$$D_{T_i} = -\left(\frac{x_1}{x_1 + x_2}\right) D_{T_3} \quad (i = 1, 2) \quad (43)$$

Between the nine diffusion coefficients, D_{ik} , the six relations (37) and (38) hold. An extra relation can again be obtained by the assumption of a quasi binary mixture. Let us apply to the system a concentration gradient, $\text{grad } x_3$, keeping temperature and pressure uniform. The assumption means, that the quotient (x_2/x_1) has anytime and anywhere its equilibrium value.

So $\text{grad } x_1 = \{-x_1/(x_1 + x_2)\} \text{grad } x_3$ ($i=1, 2$).
By setting the particle flows proportional to the concentrations we get in a way similar to the deduction of (42):

$$-x_1 x_2 D_{11} - x_2^2 D_{12} + x_2 (x_1 + x_2) D_{13} = -x_1^2 D_{21} - x_1 x_2 D_{22} + x_1 (x_1 + x_2) D_{33} \quad (44)$$

There are now 7 relations for the 9 coefficients D_{ik} . So we can choose two independent ones. For the first one we proceed as in the case of a binary mixture. We define \mathcal{D} as:

$$\frac{dx_3}{dt} = -\text{div } \mathcal{D} \text{ grad } x_3 \quad (45)$$

Note that this coefficient is the one effectively measured by a detection system that does not distinguish between the different quantum states of the molecules¹³). (31) with (45) leads to

$$\mathcal{D} = -D_{31} \left(\frac{x_1}{x_1 + x_2}\right) - D_{32} \left(\frac{x_2}{x_1 + x_2}\right) + D_{33} \quad (46)$$

The second independent coefficient, \mathcal{D}' , we want to define according to the following picture. We keep x_3 constant and vary the ratio (x_2/x_1) , e. g. by applying a temperature gradient. The resulting diffusion flow of excited molecules will give rise to the contribution of the internal degrees of freedom to the heat conductivity. Therefore we define: $dx_2/dt = -\text{div } \mathcal{D}' \text{ grad } x_2$.

This coefficient is the one measured by a detection system that does distinguish between the different states of the reacting

molecule. According to our assumption of equal transport coefficients for these different states any type of labeling in the reacting mixture will give the same resulting diffusion coefficient \mathcal{D}' . So \mathcal{D}' corresponds to the diffusion coefficient measured in these mixtures by spin echo techniques applied to the reacting molecules. If x_3 vanishes, \mathcal{D}' reduces to the self-diffusion coefficient of the relaxing gas.

By virtue of $\text{grad } x_1 + \text{grad } x_2 = 0$ the next expression for \mathcal{D}' follows directly:

$$\mathcal{D}' = D_{22} - D_{21} \quad (47)$$

We are now able to express \bar{a}_{ik} , \bar{b}_1 and \bar{c} in the independent quantities κ , D_{T_3} , \mathcal{D} and \mathcal{D}' :

$$\left. \begin{aligned} \bar{c} &= \frac{i\omega}{mTR} \left[\frac{M\kappa T}{P} - 2 \left\{ \tilde{M}M C_P^* - \frac{\epsilon^* x_2}{x_1 + x_2} \right\} D_{T_3} + M c' \mathcal{D}' + \right. \\ &\quad \left. + M x_3 (1 - x_3) \left\{ \tilde{M} C_P^* + \frac{M_3 x_2 \epsilon^*}{M(1 - x_3)} \right\}^2 \mathcal{D} \right], \\ \bar{b}_2 &= \frac{i\omega}{mTR} \left[\frac{-x_2}{x_1 + x_2} M_3 D_{T_3} + M \epsilon^* \frac{x_1 x_2}{x_1 + x_2} \mathcal{D}' + x_2 x_3 M_3 \left(\tilde{M} C_P^* + \right. \right. \\ &\quad \left. \left. + \frac{M_3 \epsilon^* x_2}{M(1 - x_3)} \right) \mathcal{D} \right], \\ \bar{b}_3 &= \frac{i\omega}{mTR} \left[M_1 D_{T_3} - M_1 x_3 (1 - x_3) \left\{ \tilde{M} C_P^* + \frac{M_3 \epsilon^* x_2}{M(1 - x_3)} \right\} \mathcal{D} \right], \\ \bar{a}_{22} &= \frac{i\omega}{mTR} \frac{M x_2}{(1 - x_3)} \left\{ x_1 \mathcal{D}' + x_2 x_3 \left(\frac{M_3}{M} \right)^2 \mathcal{D} \right\}, \\ \bar{a}_{23} &= \frac{-i\omega}{mTR} \frac{M_1 M_3}{M} x_2 x_3 \mathcal{D}, \\ \bar{a}_{33} &= \frac{i\omega}{mTR} \frac{M_1}{M} x_3 (1 - x_3) \mathcal{D}. \end{aligned} \right\} \quad (48)$$

Inserting these results in (30) gives

$$\begin{aligned}
 -\frac{P\delta}{i\omega} = & \frac{4}{3} \eta + \eta_v + \frac{M\kappa}{C_{v\text{eff}}^* C_{p\text{eff}}^* R} + \frac{\mathcal{R}^2 C'^* \rho \mathcal{D}}{C_{v\text{eff}}^* C_{p\text{eff}}^*} + \\
 & + \frac{C_{p\text{eff}}^* x_3 (1-x_3) \tilde{M}^2 \rho \mathcal{D}}{C_{v\text{eff}}^*} - \frac{1}{2C_{v\text{eff}}^*} \tilde{M} D_{T_3} \quad (49)
 \end{aligned}$$

where we introduced $C_{v\text{eff}}^* = C_v^* + \mathcal{R}C'^*$ and $C_{p\text{eff}}^* = C_p^* + \mathcal{R}C'^*$. Completely analogical to the treatment in the zero order solution case we now get, neglecting higher powers of δ/m_0 :

$$\left(\frac{k}{k_0}\right)^2 - \left(\frac{\alpha}{k_0}\right)^2 - 2i \frac{\alpha}{k_0} \left(\frac{k}{k_0}\right) = \frac{\gamma_0}{m_0} \left(1 - \frac{\delta}{m_0}\right)$$

from which follows finally by separating the real and imaginary parts neglecting higher powers of ϵ in the perturbation term δ (this is allowed since always $\epsilon < 0.2$) and introducing the specific heat ratio

$$\gamma_\omega = C_{p\text{eff}} / C_{v\text{eff}} \quad \text{and the thermal diffusion ratio, } \alpha_T,$$

defined as $\alpha_T = D_{T_3} \left\{ \frac{x_3}{3} (1-x_3) \mathcal{D} \right\}^{-1}$

$$\begin{aligned}
 \left(\frac{k}{k_0}\right)^2 - \left(\frac{\alpha}{k_0}\right)^2 = & \epsilon \frac{\omega^2 \tau_{PS}^2}{1 + \omega^2 \tau_{PS}^2} \left[1 + \frac{1}{\tau_{PS} P \gamma_\omega} \left\{ \frac{8}{3} \eta + 2\eta_v - \frac{(3 - \gamma_\omega)(\gamma_\omega - 1) M\kappa}{\gamma_\omega R} + \right. \right. \\
 & \left. \left. 2 \frac{\gamma_0 - 1}{\gamma_\omega - 1} \frac{\rho \mathcal{D}}{1 + \omega^2 \tau_{PS}^2} + x_3 (1 - x_3) \gamma_\omega \tilde{M}^2 \rho \mathcal{D} \left(1 + 2 \frac{(2 - \gamma_\omega) \alpha_T}{\gamma_\omega \tilde{M}} \right) \right\} \right] \quad (50)
 \end{aligned}$$

$$\begin{aligned}
 \frac{2\alpha k}{k_0^2} = & \frac{\omega \gamma_0}{P \gamma_\omega^2} \left[\frac{4}{3} \eta + \eta_v + \frac{(\gamma_\omega - 1) M\kappa}{\gamma_\omega R} + x_3 (1 - x_3) \gamma_\omega \tilde{M}^2 \rho \mathcal{D} \left(1 - 2 \frac{(\gamma_\omega - 1) \alpha_T}{\gamma_\omega \tilde{M}} \right) \right] + \\
 & + \epsilon \frac{\omega \tau_{PS}}{1 + \omega^2 \tau_{PS}^2} \left[1 + \frac{1}{\tau_{PS} P \gamma_\omega} \left\{ \frac{8}{3} \eta + 2\eta_v - \frac{(3 - \gamma_\omega)(\gamma_\omega - 1) M\kappa}{\gamma_\omega R} + \right. \right. \\
 & \left. \left. + \frac{\gamma_0 - 1}{\gamma_\omega - 1} \frac{\rho \mathcal{D}}{1 + \omega^2 \tau_{PS}^2} + x_3 (1 - x_3) \gamma_\omega \tilde{M}^2 \rho \mathcal{D} \left(1 + 2 \frac{(2 - \gamma_\omega) \alpha_T}{\gamma_\omega \tilde{M}} \right) \right\} \right] \quad (51)
 \end{aligned}$$

In practice one measures α as a function of frequency and pressure. Therefore it is often more convenient to have an expression for the directly measured quantity α/ω . This is given by:

$$\begin{aligned} \frac{\alpha}{\omega} = & \frac{\omega}{2PV_{\infty}\gamma_{\infty}} \left[\frac{4}{3} \eta + \eta_v + \frac{(\gamma_{\infty} - 1)^2}{\gamma_{\infty}} \frac{M\kappa}{R} + \right. \\ & \left. + x_3(1-x_3) \gamma_{\infty} \tilde{M}^2 \rho \mathcal{D} \left(1 - 2 \frac{(\gamma_{\infty} - 1) \alpha_T}{\gamma_{\infty} \tilde{M}} \right) \right] + \\ & + \frac{\gamma_{\infty}}{2V_{\infty}\gamma_0} e^{\frac{\omega\tau_{PS}}{1+\omega^2\tau_{PS}^2}} \left[1 - \frac{\gamma_{\infty} e}{2\gamma_0(1+\omega^2\tau_{PS}^2)} + \frac{1}{\tau_{PS}P\gamma_{\infty}} \left\{ 2\eta + \frac{3}{2}\eta_v - \right. \right. \\ & - \frac{(5-\gamma_{\infty})(\gamma_{\infty}-1)M\kappa}{2\gamma_{\infty}R} + \frac{(\gamma_0-1)\rho\mathcal{D}}{\gamma_{\infty}-1} \frac{1-\omega^2\tau_{PS}^2}{1+\omega^2\tau_{PS}^2} + \\ & \left. \left. + x_3(1-x_3) \gamma_{\infty} \tilde{M}^2 \rho \mathcal{D} \left(\frac{1}{2} + \frac{(3-\gamma_{\infty})}{\gamma_{\infty}} \frac{\alpha_T}{\tilde{M}} \right) \right\} \right] \quad (52) \end{aligned}$$

The first term between square brackets gives the asymptotic behaviour of the absorption in the system at high frequencies and is as such measured. It corresponds, as is to be expected, to the "Kohler" absorption, $\alpha_{n.r.}/\omega$, in a non-(i.e. no longer) reacting mixture. For the excess absorption $\alpha' = \alpha - \alpha_{n.r.}$ one can now write an expression similar to (51):

$$\begin{aligned} \frac{2\alpha'k}{k_0^2} = & e^{\frac{\omega\tau_{PS}}{1+\omega^2\tau_{PS}^2}} \left[1 + \frac{1}{\tau_{PS}P\gamma_0} \left\{ 2\eta + \frac{3}{2}\eta_v - \frac{(5-\gamma_{\infty})(\gamma_{\infty}-1)M\kappa}{2\gamma_{\infty}R} + \right. \right. \\ & \left. \left. + \frac{(\gamma_0-1)\rho\mathcal{D}}{\gamma_{\infty}-1} \frac{1-\omega^2\tau_{PS}^2}{1+\omega^2\tau_{PS}^2} + x_3(1-x_3) \gamma_{\infty} \tilde{M}^2 \rho \mathcal{D} \left(\frac{1}{2} + \frac{(3-\gamma_{\infty})\alpha_T}{\gamma_{\infty} \tilde{M}} \right) \right\} \right] \quad (53) \end{aligned}$$

3. Discussion

We mentioned already that the behaviour at high frequencies corresponds to the Kohler expression for a non-reacting mixture.

To obtain an expression for the asymptotic behaviour at low frequencies it is better not to use expression (50) seq. because of our approximation of neglecting terms with e^2 in δ . From (49) one obtains directly in the low frequency limit for $x_3 = 0$ the Kirchhoff-Stokes absorption with the modified Eucken expression for the heat conductivity, $\kappa_E = \kappa + C' \rho \mathcal{D}' / M$ corresponding to our approximation $Z^{-2} \ll 1$. (49) yields also an expression for the frequency dependence of κ_E :

$$\kappa_E(\omega) = \kappa + \frac{C' \rho \mathcal{D}'}{M(1 + \omega^2 \tau_{PS}^2)^2} \quad (54)$$

The frequency dependence of (54) is directly related to (22) that is characteristic for a two level system. (54) differs from the result obtained by Monchick¹⁴⁾¹⁵⁾ who used a kinetic approach. His expression lacks the square in the denominator.

In general we can conclude from (52) that we can separate the total sound absorption in two parts:

- a) A "Kohler" absorption with for $\gamma(\omega)$ and $\kappa(\omega)$ the values corresponding to the high frequency limits. This is the first term between square brackets in (52).
- b) A relaxation absorption which now also contains the relaxing part of the absorption due to viscous, heat and diffusion losses. If we first neglect the \mathcal{D}' contribution, we see, that the resultant absorption has the normal Debye frequency dependence with the relaxation time τ_{PS} , but with a slightly modified scale factor e . Since the \mathcal{D}' term vanishes at $\omega \tau_{PS} = 1$ it does not contribute to the maximal value. To make an estimate of the change in e we observe that the transport coefficients are all proportional to $\tau_c P = (1/\pi\omega^2)(\pi\mu k l/8)^{1/2}$. Therefore one obtains $e_{eff} = e(1 + \xi_1/Z)$ where ξ_1 is a numerical constant dependent on molecular weights and concentrations. In the case of large mass differences ξ_1 is mainly determined by the diffusion contribution. In a rather extreme case like a 50% H_2 -Xe mixture one has $\xi_1 = 40$ and $Z = 400$ which leads to $\xi_1/Z = 0.1$. The term $\rho \mathcal{D}'$ contains an extra frequency dependence that will shift the position of the maximum of $(\alpha'/k)(k/k_0)^2$. For small values of $\rho \mathcal{D}' / \tau_{PS} P \gamma_\infty = \xi_2/Z$ one can easily show that the maximum occurs at $\omega \tau_{PS} = 1 - \xi_2/Z$. As the numerical constant, ξ_2 , is of the order 1 this correction is negligible for large values of Z .

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CHAPTER II

EXPERIMENTAL DETERMINATION OF ROTATIONAL RELAXATION TIMES IN PARAHYDROGEN- NOBLE GAS MIXTURES.

1. Introduction

In this chapter we will at first describe the experimental techniques, used to obtain the relaxation times. These relaxation times are for the considered two level case inversely proportional to the rate constants of the reaction¹⁾. In the pH_2 -noble gas mixtures investigated the following reactions will occur:



Since these reactions are parallel we deal, like in the case of pure pH_2 in the temperature range chosen, with a single relaxation process with the relaxation time $\tau_{VT \text{ mix}}$, given by:

$$(\tau_{VT \text{ mix}})^{-1} = x_{H_2} (\tau_{VT}^{pH_2-H_2})^{-1} + x_{N.G.} (\tau_{VT}^{pH_2-N.G.})^{-1}. \quad (1)$$

$(\tau_{VT})_{pH_2-H_2}$ is the relaxation time that is measured in pure pH_2 at the given temperature. The other quantity $(\tau_{VT})_{pH_2-N.G.}$ is the relaxation time that should be measured in a hypothetical gas, in which only H_2 -noble gas collisions cause the transition. Experimental values for this relaxation time can be obtained from the experimental data for $(\tau_{VT \text{ mix}})^{-1}$ as a function of concentration by extrapolation to zero H_2 concentration, $x_{H_2} = 0$.

We investigated in the same way mixtures of pH_2 and oH_2 at 77°K. Since at this temperature oH_2 is completely in rotational state $l = 1$, it behaves like an inert gas and eq. (1) should again be valid. From this experiment we hope to get information about the

influence of the rotational state of the collision partner to the relaxation process.

2. Experimental method

We employed essentially the same apparatus that Sluiter et al.²⁾ used for the pure hydrogen isotopes. The original apparatus consisted of two condenser-type sound transducers (see fig. 1).

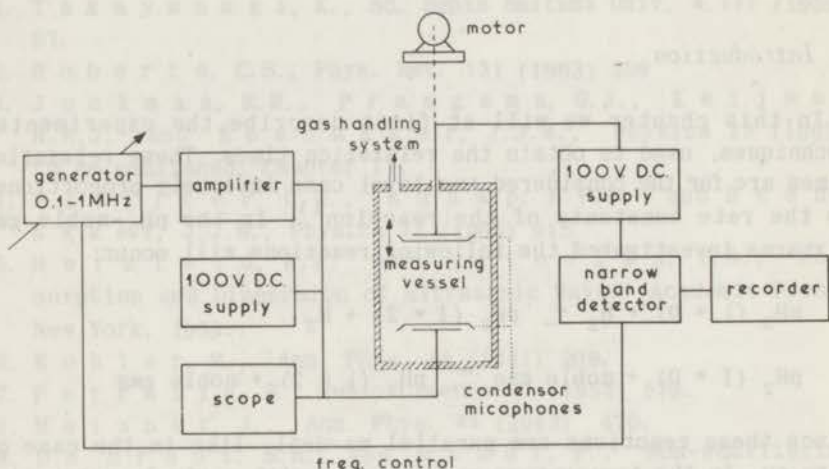


Fig. 1. Schematic diagram of the experimental set-up.

While one microphone transmits at a steady rate the other detects the intensity of the sound field as it moves at a constant speed relative to the first. The received signal decreases exponentially with increasing distance. This signal is amplified and plotted against time by a logarithmic level recorder so that a straight line is obtained. From the slope of this line the absorption coefficient, α , can be determined.

Since, however, in mixtures the sound absorption coefficient (eq. 2) is much larger than in pure gases due to diffusion effects, we had to alter the apparatus slightly. If α is large the intensity of the sound field decreases rapidly with distance. This means that we had to be able to perform measurements with the transducers very close to each other. By slowing down the travel speed and altering the microphones slightly we could measure from

the point where the microphone foils were in mutual contact. The detection of smaller sound intensities, however, caused some difficulties. We detect an acoustic signal as well as a small electric signal which penetrates into the receiver circuit through the slightly transparent microphone foils. If these two signals are comparable in intensity an interference pattern arises because the acoustic signal varies in phase and the electric pick-up signal does not. Following a suggestion of Meyer and Sessler³⁾ the condenser paper was covered with an evaporated aluminium film to reduce the transparency. We had to cover the paper when mounted, since otherwise this extra evaporated film would crack when the paper stretched into the microphones. During the evaporation process we had troubles with excessive outgassing of the original polystyrene insulation in the microphones; this difficulty was overcome by replacing the original insulation by glass. In fig. 2 a cross-section of the new microphone is shown.

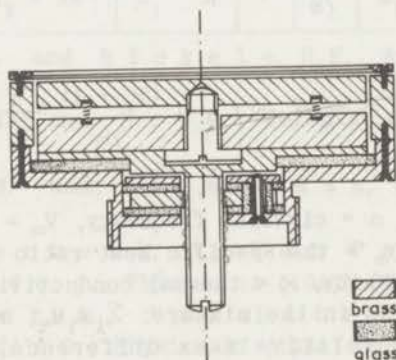


Fig. 2. Cross-section of a condenser microphone.

Under the improved conditions the electric cross-talk is less than 2.5 dB when compared with the noise of the receiver.

The measurements were performed at 77.3, 90.5, 111.5 and 170° K, using liquid N₂, O₂, CH₄ and C₂H₄ at atmospheric pressure as refrigerant. The temperatures which were measured with a platinum resistance thermometer were chosen in such a way as to deal always with a two-level system. The parahydrogen was prepared by condensing normal hydrogen in a vessel filled with an iron oxide catalyst. This parahydrogen (pH₂) was not used for more than three days even though the amount of orthohydrogen was then still less than 1% according to N.M.R. investigations. Purification of the

noble gases was achieved by cryogenic methods, thus obtaining a better than 99.5% purity.

3. Evaluation of relaxation times

In chapter I⁴⁾ we deduced an expression for the sound absorption coefficient in binary mixtures of noble gases with a two-level-system gas. Using this expression we obtain the relaxation time from the measured absorption coefficients by proceeding in a manner given below. First we calculate the difference $\alpha' = \alpha_{\text{meas}} - \alpha_{\text{n.r.}}$ with $\alpha_{\text{n.r.}}$ given by:

$$\frac{\alpha P}{\omega^2} = \frac{1}{2V_{\infty}\gamma_{\infty}} \left[\frac{4}{3}\eta + \frac{(\gamma_{\infty} - 1)^2}{\gamma_{\infty}} \frac{M\kappa}{R} + \right. \quad (2)$$

$$\left. x_{\text{N.G.}} (1 - x_{\text{N.G.}}) \gamma_{\infty} \tilde{M}^2 \rho \mathcal{D} \left(1 - 2 \frac{(\gamma_{\infty} - 1)}{\gamma_{\infty}} \frac{\alpha_T}{M} \right) \right]$$

Here P = pressure, ω = circular frequency, V_{∞} = sound velocity in the limit $\omega \rightarrow \infty$, γ_{∞} = the specific heat ratio in the same limit, η = the shear viscosity, κ = thermal conductivity, M is the average molecular mass in the mixture: $\sum_1 x_1 M_1$, x_1 are the molar fractions, \tilde{M} the relative mass difference, defined as $\tilde{M} = (M_{\text{N.G.}} - M_{\text{H}_2})/M$, ρ the mass density, \mathcal{D} the coefficient of mutual

diffusion and α_T the thermal diffusion factor. In order to calculate $\alpha_{\text{n.r.}}$ we used experimental values for the transport coefficients if they were available in the literature. If not, they were calculated with the formulae 8.2 - 20, 22, 41 and 44 given by Hirschfelder, Curtiss and Bird⁵⁾. See table I for the origin of the data. An impression of the order of magnitude of the non-relaxation absorption can be obtained from fig. 3 where $\alpha_{\text{n.r.}} P/f^2$ is plotted versus concentration for the various mixtures at 170° K. As can be seen from fig. 4 the calculated $\alpha_{\text{n.r.}}/f$ joins the experimental α/f curve at high frequencies, providing an experimental proof of the high frequency limit of eq. (52) in chapter I⁴⁾.

TABLE I

Literature sources for the transport coefficients, used to calculate to classical sound absorption.

system	η	κ	\mathcal{D}	α_T
H ₂ - ³ He	*	*	*	*
H ₂ - ⁴ He	c), d), e)	*	h)	k)
H ₂ - Ne	c), d), i)	*	h)	f)
H ₂ - Ar	a), i)	*	h)	f)
H ₂ - Kr	*	*	j)	j)
H ₂ - Xe	b)	*	h)	g)

- a) Trautz, M. and Binkelle, H.E., Ann. Phys. 5 (1930) 561
 b) Trautz, M. and Heberling, R., Ann. Phys. 20 (1934) 118.
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 f) Grew, K.E. and Ibbes, T.L., Thermal Diffusion in Gases, (Cambridge 1953).
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 k) Van Ee, H., Thesis (Leiden 1966);
 Van Ee, H., Knaap, H.F.P. and Beenakker, J.J.M., Physica 33 (1967) to be published.

*Calculated

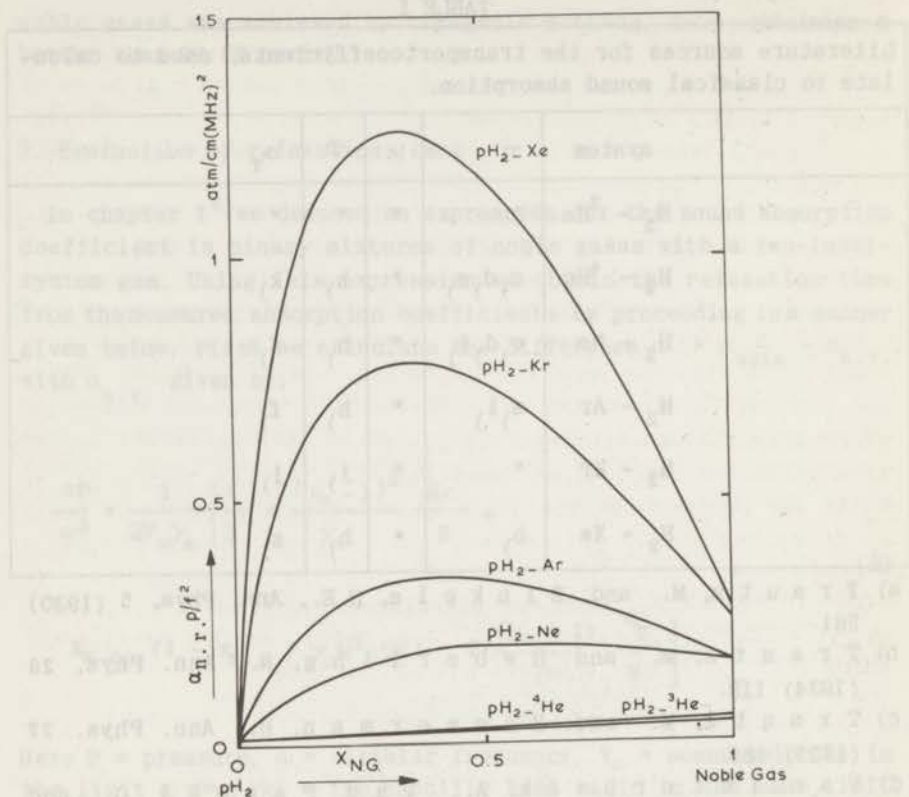


Fig. 3. Classical absorption factor, $\alpha_{n.r.} P/f^2$ vs. concentration, for p_{H_2} -noble gas mixtures at 170° K.

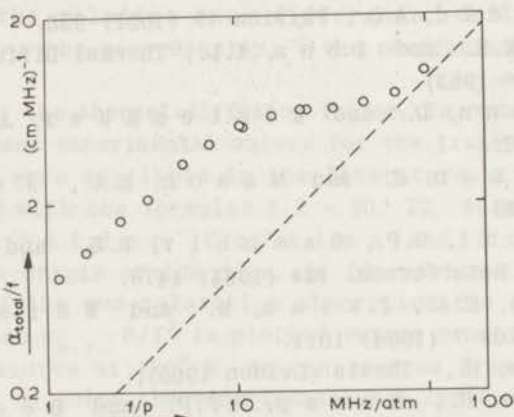


Fig. 4. $\ln(\alpha_{total}/f)$ vs. $\ln(f/P)$ for a p_{H_2} -Ne mixture; $x = 0.0928$, $T = 170^\circ$ K with the theoretical curve for the classical sound absorption (eq. 1).

As deduced in chapter I α' is given by the following equation:

$$\frac{2\alpha'k}{k_0^2} = e \frac{\omega\tau_{PS}}{1 + \omega^2\tau_{PS}^2} \left[1 + \frac{1}{\tau_{PS} P \gamma_0} \left\{ 2\eta - \frac{(5 - \gamma_\infty)(\gamma_\infty - 1)}{2\gamma_\infty R} M\kappa + \frac{(\gamma_0 - 1)}{(\gamma_\infty - 1)} \frac{1 - \omega^2\tau_{PS}^2}{1 + \omega^2\tau_{PS}^2} \rho \mathcal{D}' \right. \right. \quad (3)$$

$$\left. \left. x_{N.G.} (1 - x_{N.G.}) \gamma_\infty \hat{M}^2 \rho \mathcal{D}' \left(\frac{1}{2} + \frac{(3 - \gamma_\infty)}{\gamma_\infty} \frac{\alpha_T}{\hat{M}} \right) \right] \right]$$

where k is the wave number, e is given by $C'R/C_p(C_v + C')$ and \mathcal{D}' is a diffusion coefficient describing the self diffusion of the H_2 in the presence of the noble gas. The term with \mathcal{D}' is known to be rather small. This means that in practice the frequency dependence of $\alpha'k/k_0^2$ has the simple form $\omega\tau_{PS}/(1 + \omega^2\tau_{PS}^2)$. Hence, in order to obtain τ_{PS} from our experiments we firstly calculated (V_0/V) with $(V_0/V)^2 = 1 - e \omega^2\tau_{PS}^2/(1 + \omega^2\tau_{PS}^2)$, using a provisional value for τ_{PS} . Next $\alpha'k/k_0^2$ was calculated with

$$\alpha'k/k_0^2 = \alpha'/\omega \cdot V \cdot (V_0/V)$$

and plotted versus f/P on a double logarithmic scale. With a transparent of the form $y = x / (1 + x^2)$ we obtained by means of a shifting procedure the value of f/P where $\omega\tau_{PS} = 1$ together with the maximum value of $\alpha'k/k_0^2$ (see fig. 5). This maximum value

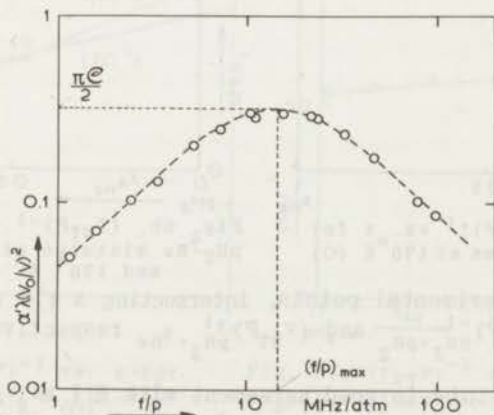


Fig. 5. $\ln(\alpha'k/k_0^2)$ vs. $\ln(f/P)$ for a pH-Ne mixture $x = 0.0928$, $T = 170^\circ K$ with the theoretical curve $y = x/(1+x^2)$.

always agreed within experimental error with the theoretical value $RC'/4 C_p(C_v + C')$, where $C' = x_{H_2} C'_{H_2}$ calculated with C'_{H_2} taken from spectroscopic data⁶). Apart from a small correction term related to \mathcal{D}' , τ_{PS} is found from $(f/P)_{\omega T=1} = (2\pi P \tau_{PS})^{-1}$.

Since the linear relation (1) holds for the isochoric isothermal relaxation time, τ_{VT} , this quantity is now calculated with $\tau_{VT} = (1 + C'/C_p) \tau_{PS}$.

4. Results

In figs. 6^{a-g} $(\tau_{VT} P)^{-1}$ is plotted against concentration for binary mixtures of pH_2 with ${}^3\text{He}$, ${}^4\text{He}$, Ne, Ar, Kr, Xe and oH_2 . $(\tau_{VT} P)^{-1}$ is always found to vary linearly with concentration within measuring accuracy, thus providing an experimental proof of eq. 1. This linearity was tested more thoroughly for the system $pH_2 - {}^4\text{He}$, where a large set of measurements were performed (see fig. 6^b). Using the method of least squares we fitted a straight

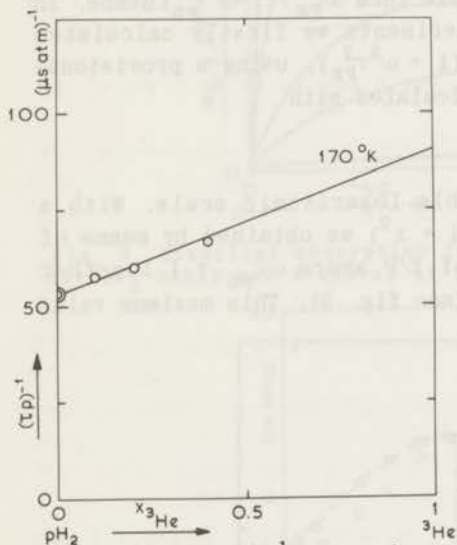


Fig. 6a. $(\tau_{VT} P)^{-1}$ vs. x for pH_2 - ${}^3\text{He}$ mixtures at 170°K (O)

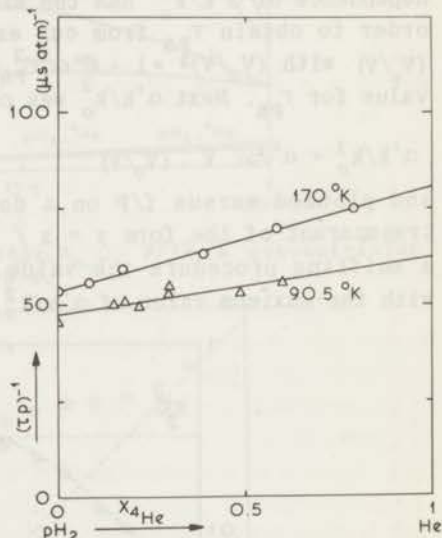


Fig. 6b. $(\tau_{VT} P)^{-1}$ vs. x for pH_2 - ${}^4\text{He}$ mixtures at 90.5°K (Δ) and 170°K (O)

line to the experimental points, intersecting $x = 0$ and $x = 1$ at the values $(\tau_{VT} P)^{-1}_{pH_2-pH_2}$ and $(\tau_{VT} P)^{-1}_{pH_2-{}^4\text{He}}$ respectively. The first

value was found to be in good agreement with Sluiter's^{2,7)} results. The other quantity $(\tau_{VT} P)^{-1}_{pH_2-{}^4\text{He}}$, is the relaxation time

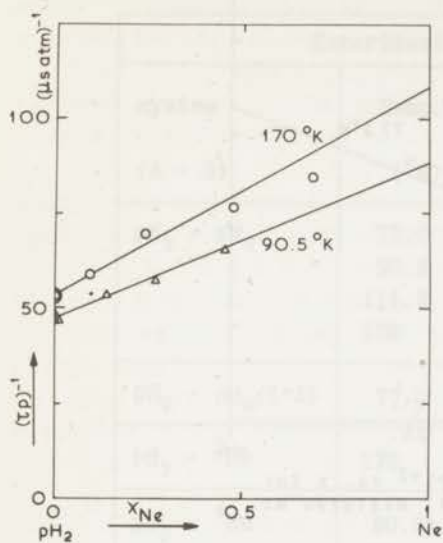


Fig. 6c. $(\tau_{VT}P)^{-1}$ vs. x for pH_2 -Ne mixtures at 90.5°K (Δ) and 170°K . (O)

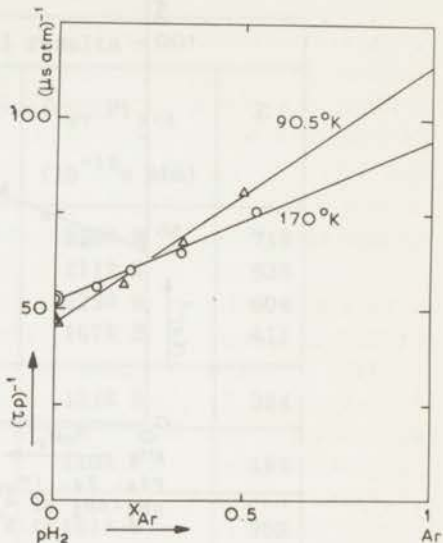


Fig. 6d. $(\tau_{VT}P)^{-1}$ vs. x for pH_2 -Ar mixtures at 90.5°K (Δ) and 170°K . (O)

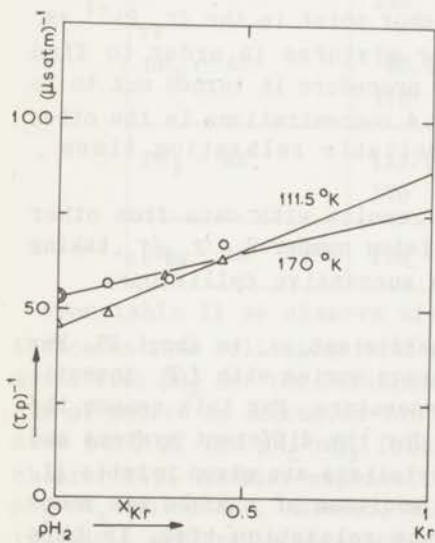


Fig. 6e. $(\tau_{VT}P)^{-1}$ vs. x for pH_2 -Kr mixtures at 111.5°K (Δ) and 170°K . (O)

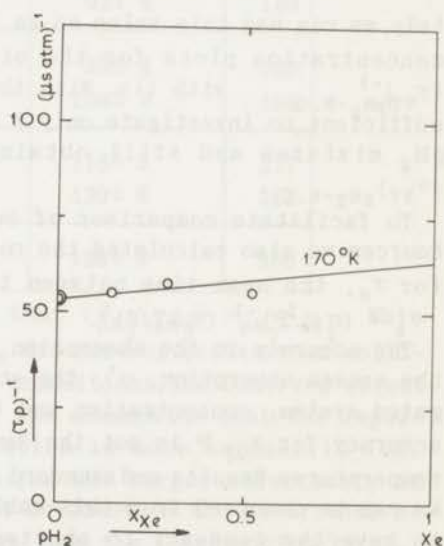


Fig. 6f. $(\tau_{VT}P)^{-1}$ vs. x for pH_2 -Xe mixtures at 170°K . (O)

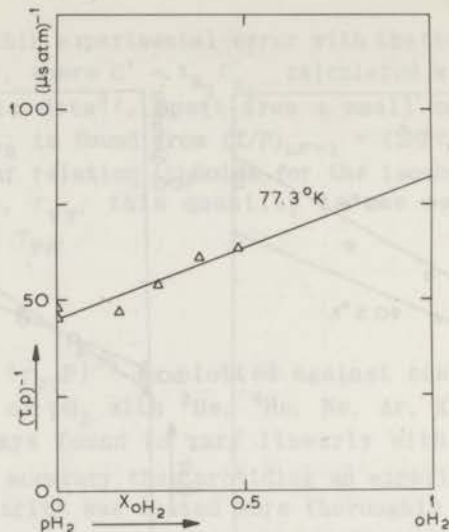


Fig. 6g. $(\tau_{VT} P)^{-1}$ vs. x for pH_2 - oH_2 ($1 = 0.1$) mixtures at 77.3°K .

that results when the hydrogen molecules undergo collisions with ^4He molecules only. Since $(\tau_{VT} P)^{-1}_{\text{pH}_2-\text{pH}_2}$ is now known very accurately,

we can use this value as an anchor point in the $(\tau_{VT} P)^{-1}$ vs. concentration plots for the other mixtures in order to find $(\tau_{VT} P)^{-1}_{\text{pH}_2-\text{N.G.}}$ with (1). With this procedure it turned out to be sufficient to investigate only 3 or 4 concentrations in the other pH_2 mixtures and still obtain reliable relaxation times, $(\tau_{VT} P)^{-1}_{\text{pH}_2-\text{N.G.}}$.

To facilitate comparison of our results with data from other sources we also calculated the collision number $Z = \tau_{VT} / \tau_c$, taking for τ_c , the mean time between two successive collisions:

$$\tau_c = (\pi \sigma^2 P)^{-1} (\pi \mu k T / 8)^{1/2}$$

The accuracy in the absorption coefficient, α , is about 5%. For the excess absorption, α' , the accuracy varies with f/P , investigated system, concentration and temperature. For this reason the accuracy for $\tau_{VT} P$ is not the same for the different systems and temperatures. Results and standard deviations are given in table II. As can be observed from this table addition of a noble gas seems to have the tendency to shorten the relaxation time. In this respect argon turns out to be the most effective. An interpretation of these results on a microscopic basis will be given in chapter IV⁸).

TABLE II

Experimental results			
system (A - B)	Temp. (°K)	$(\tau_{VT} P)_{A-B}$ (10^{-10} s atm)	Z
pH ₂ - pH ₂	77.0	220± 8	715
	90.5	211± 2	635
	111.5	223± 4	604
	170	187± 2	411
pH ₂ - oH ₂ (l=1)	77.0	121± 5	394
pH ₂ - ³ He	170	110± 5	194
pH ₂ - ⁴ He	90.5	161± 8	369
	170	124± 2	207
pH ₂ - Ne	90.5	113± 4	235
	170	92± 4	140
pH ₂ - Ar	90.5	88± 4	225
	170	106± 3	198
pH ₂ - Kr	111.5	115± 8	277
	170	130± 8	253
pH ₂ - Xe	170	158± 8	356

From table II we observe also that $\tau_{\text{pH}_2-\text{pH}_2} > \tau_{\text{pH}_2-\text{oH}_2}$. This indicates that collisions with oH₂ are more effective than collisions with pH₂ for the rotational transitions. The observed effect can of course be accounted for by the assumption that the repulsive part of the pH₂-oH₂ interaction is more asymmetric (cf. chapter IV). Another explanation for the larger effectivity of pH₂-oH₂ collisions, however, might be found in the occurrence of inelastic collisions, at which apart from the l-transition in pH₂, also the magnetic quantum number, m, of oH₂ is changed. This provides a new reaction mechanism leading also to shorter relaxation times.

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CHAPTER III

EXPERIMENTAL DETERMINATION OF ROTATIONAL RELAXATION TIMES IN ORTHO-DEUTERIUM-NOBLE GAS MIXTURES.

1. Introduction

In chapter II¹⁾ rotational-translational relaxation times in mixtures of parahydrogen (pH_2) with the noble gases and orthohydrogen (oH_2) were reported. In chapter IV²⁾ these data will be compared with averaged inelastic scattering cross-sections. As one more check on the theoretical calculations we decided to investigate also the orthodeuterium (oD_2)-noble gas mixtures. oD_2 behaves like a two level system at temperatures $30 < T < 100^\circ$ K. Since in this temperature range the vapour pressures of the noble gases Kr and Xe are too low, only mixtures of oD_2 with 4He , Ne and Ar were investigated. Below 55° K pH_2 is completely in the rotational state $l = 0$ and was therefore expected to behave as an inert gas atom. For this reason we also measured the rotational relaxation time in oD_2 - pH_2 mixtures at 45° K.

2. Experimental method

We could use the experimental setup described in chapter II¹⁾. Since, however, no liquids are available which could be used as a refrigerant at temperatures between 30 and 77° K, we had to develop a thermostat in order to measure in that range. The measuring vessel was for this purpose mounted above a liquid hydrogen bath. The vessel was cooled by the cold hydrogen vapour that flew along it when we evaporated the hydrogen. A heating coil around the vessel heated it if necessary. A carbon thermometer mounted at the outside of the vessel was used as a sensor. The temperature of the gas was measured with a platinum resistance thermometer, in thermal contact with the mounting frame of one of the micro-

phones. This thermometer was calibrated by means of sound velocity measurements in pure gaseous helium.

The sound absorption coefficients were treated as described in chapter II¹⁾, in order to obtain the relaxation times. For the deuterium mixtures no experimental data for the transport coefficients were available. Therefore these coefficients were calculated with the formulae given in the book of H i r s c h f e l d e r, C u r t i s s and B i r d. Since we again expected a linear relationship between τ_{VT}^{-1} and concentration, we plotted the inverse relaxation time versus the molar concentration in figs. 1-4.

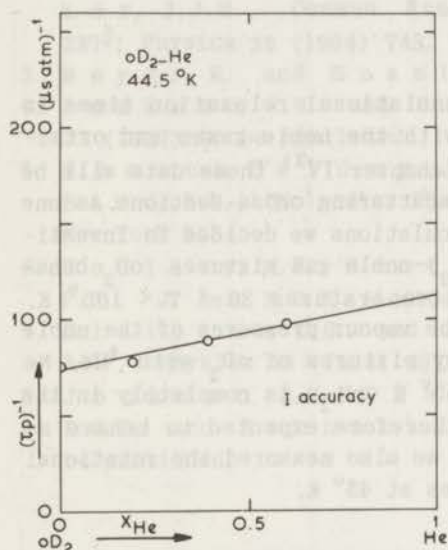


Fig 1a. $(\tau_{VT}P)^{-1}$ vs. x for $\text{oD}_2 - {}^4\text{He}$ mixtures at 44.5°K .

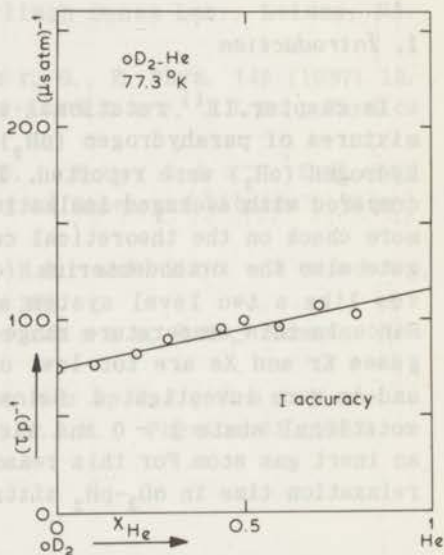


Fig. 1b. $(\tau_{VT}P)^{-1}$ vs. x for $\text{oD}_2 - {}^4\text{He}$ mixtures at 77.3°K .

3. Results

For all the noble gas mixtures the expected linear relationship between $(\tau_{VT}P)^{-1}$ and concentration was found within experimental error. A straight line was fitted through the measuring points, the intersection of this line with $x_{\text{NG}}=0$ agreeing with S l u i j t e r s⁴⁾ results at 77 and 90°K . The value at $x_{\text{NG}}=1$ is the inverse relaxation time in a hypothetical gas, in which only oD_2 -noble gas collisions cause the reaction. These relaxation times are presented in table I, together with the standard deviations

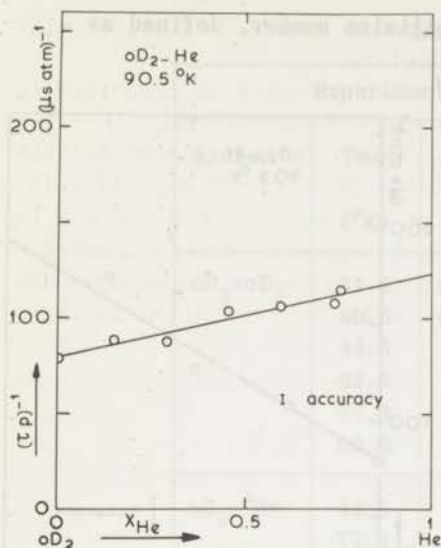


Fig. 1c. (τ_{VTP})⁻¹ vs. x for oD₂-⁴He mixtures at 90.5°K.

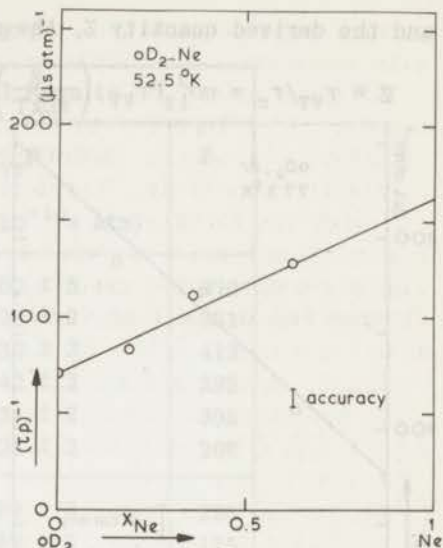


Fig. 2a. (τ_{VTP})⁻¹ vs. x for oD₂-Ne mixtures at 52.5°K.

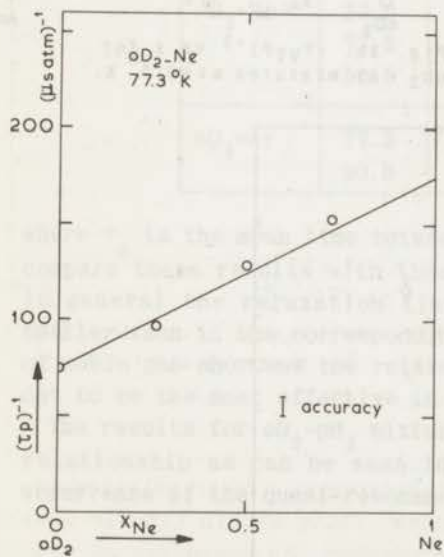


Fig. 2b. (τ_{VTP})⁻¹ vs. x for oD₂-Ne mixtures at 77.3°K.

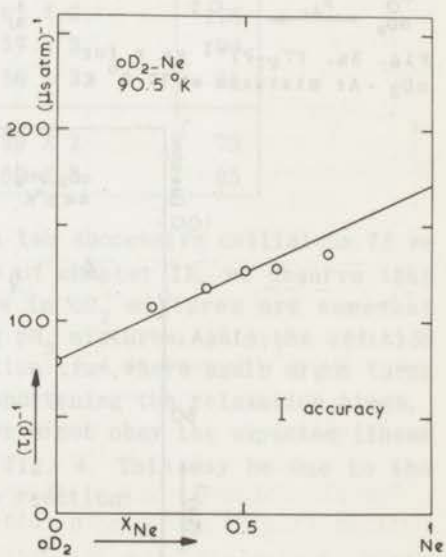


Fig. 2c. (τ_{VTP})⁻¹ vs. x for oD₂-Ne mixtures at 90.5°K.

and the derived quantity Z , the collision number, defined as

$$Z \equiv \tau_{VT}/\tau_c = \pi \sigma_{12}^2 P \tau_{VT} \left(\frac{8}{\pi \mu k T} \right)^{1/2}$$

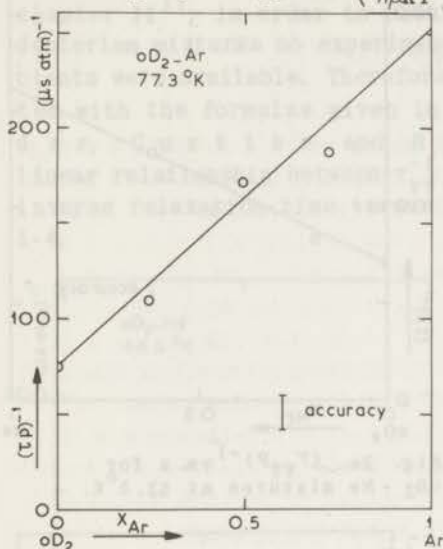


Fig. 3a. $(\tau_{VT}P)^{-1}$ vs. x for oD_2 -Ar mixtures at 77.3°K .

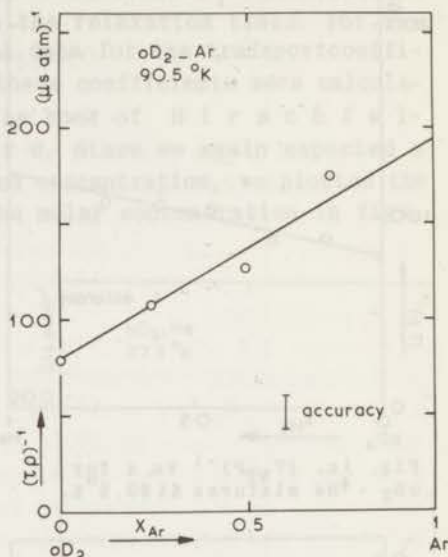


Fig. 3b. $(\tau_{VT}P)^{-1}$ vs. x for oD_2 -Ar mixtures at 90.5°K .

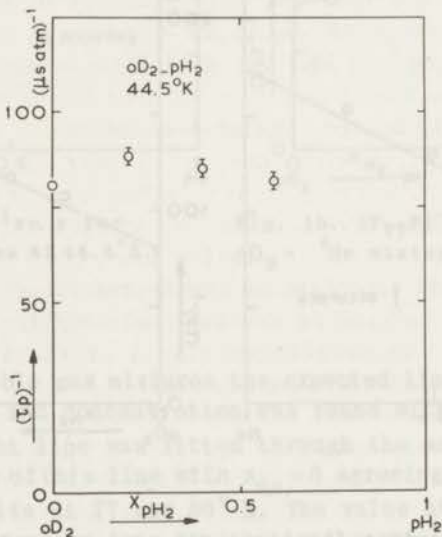


Fig. 4 $(\tau_{VT}P)^{-1}$ vs. x for oD_2 - $\text{pH}_2(l=0)$ mixtures at 44.5°K .

TABLE I

Experimental Results			
system	Temp (°K)	$\tau_{VT}P$ (10^{-10} s atm)	Z
oD ₂ -oD ₂	31.2	102 ± 5	370
	40.6	120 ± 2	381
	44.5	136 ± 2	413
	52.5	142 ± 2	399
	77.3	134 ± 2	308
	90.5	126 ± 2	268
oD ₂ - ⁴ He	44.5	89 ± 3	238
	77.3	86 ± 3	175
	90.5	81 ± 3	152
oD ₂ -Ne	52.5	62 ± 3	126
	77.3	57 ± 3	96
	90.5	58 ± 3	91
oD ₂ -Ar	77.3	39 ± 2	79
	90.5	52 ± 3	95

where τ_c is the mean time between two successive collisions. If we compare these results with those of chapter II, we observe that in general the relaxation times in oD₂ mixtures are somewhat smaller than in the corresponding pD₂ mixtures. Again the addition of noble gas shortens the relaxation time, where again argon turns out to be the most effective in shortening the relaxation times.

The results for oD₂-pD₂ mixtures do not obey the expected linear relationship as can be seen in fig. 4. This may be due to the occurrence of the quasi-resonance reaction:



Theoretical indications for the occurrence of this type of reaction were reported by Van Kranendonk.⁵⁾ This problem is the subject of further investigations.

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The results for ω_2 mixtures do not obey the expected linear relationship as can be seen in Fig. 4. This may be due to the occurrence of the dark-resonance reaction.

$$\omega_2(1.0) + \omega_2(1.2) = \omega_2(1.2) + \omega_2(1.0)$$

Theoretical indications for the occurrence of this type of reaction were reported by A. M. K. A. A. & J. J. M. Beenakker in the subject of further investigations.

CHAPTER IV

THEORETICAL ANALYSIS OF THE RESULTS OBTAINED IN CHAPTERS II AND III.

1. Introduction

In order to interpret the results of chapter II¹⁾ and III²⁾ we want to relate the obtained relaxation times to inelastic scattering cross sections for rotational transitions induced by noble gas atoms. As far as we know, computations of these cross sections are only performed for the reaction $l = 0 \rightarrow 2$ of parahydrogen induced by helium. (R o b e r t s³⁾). T a k a y a n a g i⁴⁾ derived, under certain simplifying assumptions, a closed formula for rotational transition probabilities in hydrogen isotopes. As a result of his approximations he treats essentially the transition probability in a collision between a reacting H_2 molecule and a non-reacting, spherical collision partner. In this respect his formula will certainly be more adapted to the problem of H_2 - noble gas collisions. In view of the success obtained by S l u i j t e r⁵⁾ in applying T a k a y a n a g i's results in his treatment of relaxation times in pure H_2 , it seemed interesting to investigate the possibilities of employing this approach also with respect to our data for hydrogen-noble gas mixtures.

To facilitate the comparison of theory and experiment we will first outline T a k a y a n a g i's treatment (section 2). Since the large mass difference between H_2 and the heavier noble gases may lead to complications due to correlation effects we treat separately (in section 3) the way in which one arrives at the relaxation times from the inelastic scattering cross sections. Finally, the comparison with experimental data reported in chapter II and III will be given in the last section.

2. Inelastic scattering cross sections

The treatment of Takayanagi is based on the distorted wave method (see e.g. Mott and Massey⁶). This method is known to be a good approximation if the transition probabilities are small. This restriction seems to give no problems in our case where the collision number Z is never smaller than 80 (see chapter II and III). In this approach one treats the non-spherical part of the interaction potential as a perturbation term in the total Hamiltonian. Hence one has first to know the wave-functions of the unperturbed system; i.e. of the elastic scattering problem with the radial Schrödinger equation (atomic units are used throughout);

$$\left\{ \frac{d^2}{dr^2} - \frac{j(j+1)}{r^2} + k^2 + 2\mu V_0(r) \right\} \phi_{\text{coll}}(k, j) = 0$$

We will first confine ourselves to S-wave scattering ($j = 0$) and take for $V_0(r)$ the Morse potential:

$$V_0(r) = \epsilon [\exp \{ -2\alpha_M(r-r_0) \} - 2 \exp \{ -\alpha_M(r-r_0) \}]$$

Here ϵ is the depth of the potential well, r_0 the position of the minimum and α_M a steepness parameter. For this potential Strachan⁷ was able to obtain exact expressions for the wave functions, $\phi_{\text{coll}}(k, j = 0)$, of the system. The total eigenfunction for the pair of molecules is now given by

$$\psi(l, k, j = 0) = \psi_{\text{H}_2}(l) \cdot \psi_{\text{noble gas}} \cdot \phi_{\text{coll}}(k, j = 0).$$

The real interaction between the two particles will also be a function of the orientation of the hydrogen molecule, characterized by the angle θ ; see fig. 1. If we develop this dependence in Legendre polynomials we see that, according to the symmetries of the system, the coefficient of the first Legendre polynomial, P_1 ,

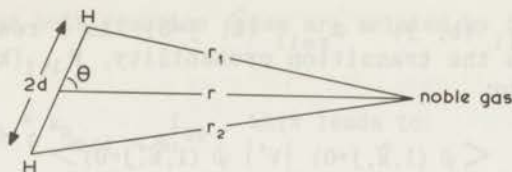


Fig. 1. Geometry of the hydrogen-noble gas interaction.

will vanish. Therefore we choose for the interaction potential $V = V_0 + V'$ with $V' = \beta \epsilon \exp \{-2\alpha_M(r - r_0)\} P_2(\cos \theta)$ (1)

V' will be the perturbation term in the Hamiltonian of the system. Since for the considered transition the repulsion plays the dominant role, V' is limited to a repulsive contribution only. The transition probability for rotational transitions $l' \rightarrow l$ for a given k' and j' (primes refer to the situation before the collision) is proportional to the square of the matrix element

$$\langle \psi(l, k, j) | V' | \psi(l', k', j') \rangle$$

At this point already we observe that the transition probability and thus the reaction rate will be proportional to β^2 . Since, however, j and j' will in general differ from zero we need to know the unperturbed wave-functions also for the case of non-S-wave scattering. Takayanagi overcame this difficulty in the following way. He first neglected the influence of the change of j' by inelastic collisions on the radial part of the matrix element. Since $\Delta j = 0, \pm 2$ this approximation is reasonable for $j \gg 1$. Moreover he observed that the transitions will in general occur when the molecules are at a distance r_c , approximately the hard core diameter. Since at this distance, for not too large values of j' , the local variation of the centrifugal term in the Hamiltonian is small compared to the variations of the potential term, he replaced the centrifugal term $j(j+1)/r^2$ by $j(j+1)/r_c^2$. Furthermore, he combined the kinetic and centrifugal terms by the introduction of the new quantity, \tilde{k} , the modified wave number defined as $\tilde{k}^2 = k^2 - j(j+1)/r_c^2$.

The problem is now formally reduced to the $j = 0$ case and the Schrödinger equation reads:

$$\left\{ \frac{d^2}{dr^2} + \tilde{k}^2 + 2\mu V_0(r) \right\} \phi_{coll}(\tilde{k}, j=0) = 0$$

and thus $\phi_{\text{coll}}(k, j) = \phi_{\text{coll}}(\tilde{k}, j=0)$. As a result of these manipulations the transition probability, $F_{1,1}(k', j')$, is now proportional to:

$$\langle \psi(1, \tilde{k}, j=0) | v' | \psi(1, \tilde{k}', j=0) \rangle^2$$

T a k a y a n a g i obtained the following relation:

$$F_{1,1+2}(k', j') = F_{1,1+2}(\tilde{k}') = \frac{3\pi^2}{40} \frac{(1+1)(1+2)}{(21+1)(21+3)} \frac{\text{sink}2\pi q \text{ sink}2\pi q'}{(\cosh 2\pi q + \cosh 2\pi q')^2} \beta^2 (\Delta q^2)^2 \{(1+\delta)\phi + (1-\delta)\phi^{-1}\} \quad (2)$$

with $q = \tilde{k}/\alpha_M$; $q' = \tilde{k}'/\alpha_M$; $\Delta q^2 = q^2 - q'^2 = 2\mu \Delta E / \alpha_M^2$:

ΔE = the energy separation of the rotational levels l and l' ;

$$d = \frac{(2\mu E)^{1/2}}{\alpha_M} ; \phi = \left| \Gamma\left(\frac{1}{2} - d + iq\right) \right| / \left| \Gamma\left(\frac{1}{2} - d + iq'\right) \right| \text{ and } \delta = 2d/\Delta q^2.$$

Summation over j' yields the inelastic scattering cross section as a function of k' :

$$Q_{1,1}(k') = \frac{\pi}{k'^2} \sum_{j'=0}^{k' r_c} F(k', j') (2j'+1) \approx \frac{2\pi}{k'^2} \int_0^{k' r_c} F(k', j') j' dj'.$$

The upper limit for j' is given by the restriction that the centrifugal energy is not allowed to exceed the available kinetic energy.

3. Evaluation of relaxation times.

The isochoric isothermal relaxation time for our process can, according to H e r z f e l d and L i t o v i t z⁸⁾, be expressed in terms of the rate constants $f_{1,1}$ as

$$\tau_{VT}^{-1} = f_{02} + f_{20}. \quad (3)$$

Since, however, both reaction rates are related by the equilibrium condition,

$x_{H_2(1=0)} f_{02} = x_{H_2(1=2)} f_{20}$, this leads to:

$$(\tau_{VT})^{-1} = \left\{ 1 + \frac{g_0}{g_2} \exp\left(\frac{\Delta E}{kT}\right) \right\} f_{02}, \quad (4)$$

where g_0 and g_2 are the statistical weights of the rotational levels $l = 0$ and $l = 2$. We have yet to express f_{02} in terms of $Q(k')$. The normal procedure is to assume that the relative motion of the colliding particles follows a Maxwell distribution, yielding for f_{02} in a parahydrogen-noble gas mixture:

$$f_{02} = \sum_{i=1,2} x_i n \int_0^{\infty} Q_{02}^i(k') \frac{k'}{\mu_i} (2\pi\mu_i kT)^{-3/2} \exp(-k'^2/2\mu_i kT) 4\pi k'^2 dk' = \quad (5)$$

$$= \sum_{i=1,2} x_i P \left(\frac{8}{\pi\mu_i kT} \right)^{1/2} Q_{02}^i(T) \quad (6)$$

where the superscripts $i = 1$ and 2 of Q_{02}^i denote the H_2 - H_2 and H_2 -noble gas interactions respectively, x_1 and x_2 the mole fractions of H_2 and the noble gas, μ_i the reduced masses for the considered interactions, n = particle density and P = pressure. Here we have introduced the mean cross section $Q_{02}^i(T)$, defined as:

$$Q_{02}^i(T) = 2(2\mu_i kT)^{-2} \int_0^{\infty} k'^3 \exp(-k'^2/2\mu_i kT) Q_{02}^i(k') dk' = \frac{\pi r_c^2}{(2\mu_i kT)^2} \int_0^{\infty} dk'^2 \int_0^{\infty} d\left(\frac{j'}{r_c}\right)^2 \exp(-k'^2/2\mu_i kT) F_{02}^i(k', j') \quad (7)$$

In the last step we assumed r_c to be independent of k' . To evaluate these integrals we make the orthogonal transformation

$$\tilde{k}^2 = k^2 - (j/r_c)^2; \quad (\tilde{j}/r_c)^2 = k^2 + (j/r_c)^2.$$

In terms of these new variables, $Q_{02}^i(T)$ can be expressed as:

$$\begin{aligned}
 Q_{02}^i(T) &= \frac{\pi r_c^2}{2(2\mu_1 kT)^2} \int_0^\infty d\tilde{k}'^2 \int_{\tilde{k}'^2}^\infty d\left(\frac{\tilde{j}'}{r_c}\right)^2 \exp\left(\frac{-\tilde{k}'^2 - (\tilde{j}'/r_c)^2}{4\mu_1 kT}\right) F_{02}^i(\tilde{k}') = \\
 &= \frac{\pi r_c^2}{2\mu_1 kT} \int_0^\infty d(\tilde{k}')^2 \exp(-\tilde{k}'^2/2 \mu_1 kT) F_{02}^i(\tilde{k}') \quad (8)
 \end{aligned}$$

For a pure gas, expressions (4), (6) and (8) also follow from a more rigorous treatment using the Chapman - Enskog theory in the first Sonine approximation⁹⁾. There is, however, some question whether this approach is still correct in the case of reacting mixtures of molecules with widely different masses.

Let us first consider the case of a small amount of a heavy relaxing gas diluted in a light noble gas. Then nearly all the relative velocity at collisions of a pair of unlike molecules originates from the noble gas atom velocity in the laboratory system. Thus, if we follow the reacting molecule on its path, all successive collisions are completely uncorrelated with respect to their relative velocities. Consider on the other hand the opposite case; a mixture of a small concentration of a light reacting gas with a heavy noble gas. In this case the relative momenta at successive collisions of a reacting gas molecule are correlated.

In the calculation of the relaxation time, or what amounts to the same, the volume viscosity, a correlation method can be used¹⁰⁾. In this type of calculations the probability that a reacting molecule has suffered n collisions up to time t , $N(n, t)$, plays an important role. In the first example this quantity is given by the Poisson distribution:

$$N(n, t) = \frac{1}{n!} \left(\frac{t}{\tau_c}\right)^n \exp\left(-\frac{t}{\tau_c}\right) \text{ with } \tau_c = (P\pi\sigma^2)^{-1} \left(\frac{\pi_1 kT}{8}\right)^{1/2}$$

This procedure leads to the results given by eqs. (3).....(8). In the second example, however, this type of counting is no longer correct and the persistence of velocities must be taken into account. This will lead to serious errors if one still calculates τ using Poisson counting.

Our experimentally obtained relaxation times are all measured within the concentration range $0.3 < x_{H_2} < 1$. At these concentrations still on the average at least one out of three successive

collisions is a hydrogen-hydrogen encounter, which will disturb the persistence. Since this equilibration process of the translational degrees of freedom is much faster than the relaxation process studied in these mixtures a possible influence of this persistence is very small. Hence we expect eqs. (3)....(8), to hold in the above concentration range. From eqs. (4) and (6) we deduce:

$$(\tau_{VT})^{-1} = \sum_{i=1,2} x_i (\tau_{VT}^i)^{-1} \quad (9)$$

$$\text{with } (P\tau_{VT}^i)^{-1} = \left\{ \exp\left(\frac{-\Delta E}{kT}\right) + \frac{g_0}{g_2} \right\} \left(\frac{8}{\pi\mu_1 kT}\right)^{\frac{1}{2}} \pi r_c^2 \int_0^{\infty} (\mu_1 kT)^{-1} \exp(-\tilde{k}^2/2\mu_1 kT) F_{02}^i(\tilde{k}) \tilde{k} d\tilde{k}$$

Here we made use of the transformation $\tilde{k}' \rightarrow \tilde{k}$ with the relation:

$$(\tilde{k}')^2 = \tilde{k}^2 + 2\mu_1 \Delta E$$

Note that (9) is identical to eq. (1) in chapter II; its linearity in the concentration range considered is confirmed by the experiments, providing evidence in favour of the above assumptions.

For the systems investigated in our experimental work¹⁾²⁾ we evaluated (2) using the potential parameters given in table I. The Morse potential parameters for the hydrogen isotopes were taken as in the calculations of Takayana⁴⁾ and Davison¹¹⁾. For the noble gases neon and argon we used the parameters given by Konowalow and Hirschfelder¹²⁾ and we used the combination rules deduced by Saxena and Gambhir¹³⁾ to obtain the parameters for the interaction H₂-noble gas: ϵ_{12} , α_{12} and $(r_0)_{12}$.

For the other noble gases no Morse potential parameters were available in literature, so we calculated them by matching the Morse potential with the Lennard-Jones 6-12 potential in the energy range of interest. The Lennard-Jones parameters were taken from the table given by Hirschfelder et al.¹⁴⁾, using the normal combination rules. The complex gamma functions were interpolated from¹⁵⁾. Results of the calculations are shown in fig. 3 for two typical examples.

TABLE I.

Morse potential parameters used in order to calculate the rotational transition probabilities with eq. (2)		
System	α_M	ϵ
	a. u.	10^{-3} a. u.
$\text{pH}_2 - \text{pH}_2$	0.935	0.110
$\text{pH}_2 - {}^3\text{He}$	0.998	0.0667
$\text{pH}_2 - {}^4\text{He}$	0.998	0.0667
$\text{pH}_2 - \text{Ne}$	0.953	0.125
$\text{pH}_2 - \text{Ar I}$	0.856	0.226
$\text{pH}_2 - \text{Ar II}$	1.000	0.213
$\text{pH}_2 - \text{Ar III}$	1.167	0.213
$\text{pH}_2 - \text{Kr I}$	0.871	0.255
$\text{pH}_2 - \text{Kr II}$	0.969	0.255
$\text{pH}_2 - \text{Xe I}$	0.903	0.290
$\text{pH}_2 - \text{Xe II}$	0.940	0.290
$\text{oD}_2 - \text{oD}_2$	0.935	0.110
$\text{oD}_2 - {}^4\text{He}$	0.998	0.0667
$\text{oD}_2 - \text{Ne}$	0.953	0.125
$\text{oD}_2 - \text{Ar I}$	0.856	0.213
$\text{oD}_2 - \text{Ar II}$	0.856	0.226

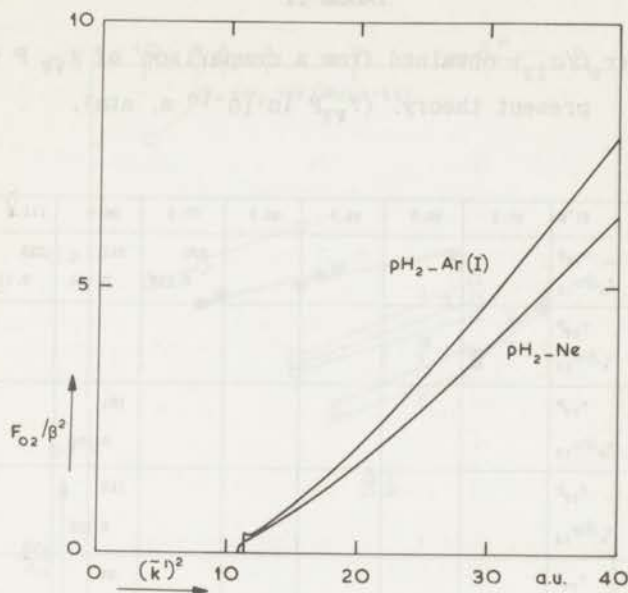


Fig. 2. F_{O_2}/β^2 versus $(\tilde{k}')^2$ for p_{H_2} - Ne and p_{H_2} - Ar interactions, calculated with eq. (2).

4. Discussion

Using eq. (10) the quantity $r_c^2 \beta^2 \tau_{VT}$ was calculated numerically. We did not use the analytic procedure of S l u i j t e r⁵⁾ and J o n k m a n¹⁶⁾ because this turned out to be less accurate at lower temperatures. Division of $r_c^2 \beta^2 \tau_{VT} P$ by the experimental values for $\tau_{VT} P$ from chapters II and III yields values for $r_c \beta$. To compare the different systems, we normalized r_c with σ_{12} for the combination considered. Values of $\tau_{VT} P$ and $r_c \beta / \sigma_{12}$ are given in table II. The last quantity turns out to be markedly dependent on temperature contrary to what one might expect. Our data give the impression that $r_c \beta / \sigma_{12}$ is a function of $T^* = kT / \epsilon_{12}$. This is concluded from figs. 3 and 4 where the logarithm of $r_c \beta / \sigma_{12}$ is plotted versus T^{*-1} . This corresponds to an incorrect prediction of the temperature dependence of τ_{VT} by the T a k a y a n a g i approach. The observed dependence on T^* suggests that the reason for the failure of the T.-approach arises from the neglect of the non-sphericity in the attractive part of the

TABLE II

Values of $(r_c \beta / \sigma_{12})$ obtained from a comparison of τ_{VT}^P with the present theory. (τ_{VT}^P in 10^{-10} s. atm).

System	T(°K)	31.2	40.6	44.5	52.5	77.3	90.5	111.5	170.0
pH ₂ -pH ₂	τ_{VT}^P					220	211	223	187
	$r_c \beta / \sigma_{12}$					0.123	0.124	0.119	0.116
pH ₂ - ³ He	τ_{VT}^P								110
	$r_c \beta / \sigma_{12}$								0.189
pH ₂ - ⁴ He	τ_{VT}^P						161		124
	$r_c \beta / \sigma_{12}$						0.196		0.184
pH ₂ -Ne	τ_{VT}^P						113		92
	$r_c \beta / \sigma_{12}$						0.225		0.201
pH ₂ -Ar	τ_{VT}^P						88		106
	$r_c \beta / \sigma_{12}$	$\begin{cases} \text{I} \\ \text{II} \\ \text{III} \end{cases}$					0.188		0.142
							0.175		0.138
							0.165		0.134
pH ₂ -Kr	τ_{VT}^P							111	130
	$r_c \beta / \sigma_{12}$	$\begin{cases} \text{I} \\ \text{II} \end{cases}$						0.146	0.120
								0.135	0.114
pH ₂ -Xe	τ_{VT}^P								158
	$r_c \beta / \sigma_{12}$								$\begin{cases} 0.092 \\ 0.089 \end{cases}$
oD ₂ -oD ₂	τ_{VT}^P	102	120	136	142	134	126		
	$r_c \beta / \sigma_{12}$	0.137	0.129	0.120	0.117	0.113	0.112		
oD ₂ - ⁴ He	τ_{VT}^P			89		86	81		
	$r_c \beta / \sigma_{12}$			0.188		0.176	0.171		
oD ₂ -Ne	τ_{VT}^P				62	57	58		
	$r_c \beta / \sigma_{12}$				0.204	0.194	0.182		
oD ₂ -Ar	τ_{VT}^P					39	52		
	$r_c \beta / \sigma_{12}$	$\begin{cases} \text{I} \\ \text{II} \end{cases}$				0.173	0.143		
						0.169	0.139		

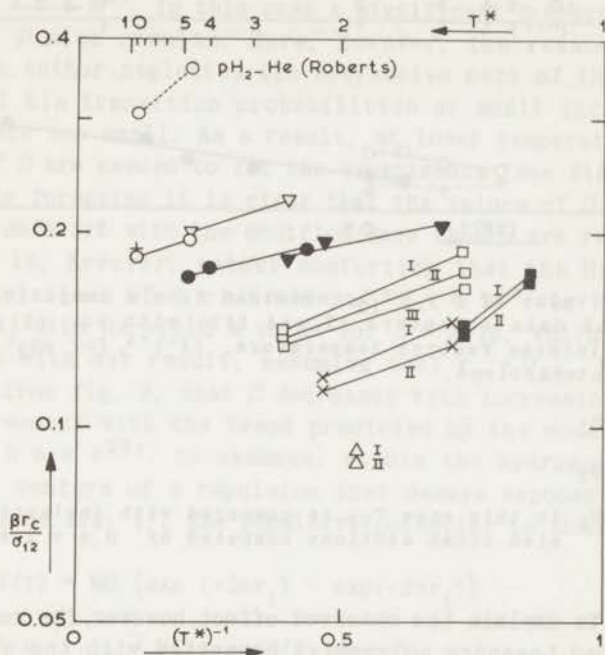


Fig. 3. The value of $\beta r_c / \sigma_{12}$, obtained from a comparison of the experimental data (chapters II and III) with eq. (2), plotted versus the inverse reduced temperature, $(T^*)^{-1}$, for hydrogen isotope-noble gas interactions.

- + $pH_2 - {}^3He$
- $pH_2 - {}^4He$
- ▽ $pH_2 - Ne$
- $pH_2 - Ar$ for the three sets of potential parameters given in table I.
- × $pH_2 - Kr$ for two sets of potential parameters.
- △ $pH_2 - Xe$ for two sets of potential parameters.
- $oD_2 - {}^4He$
- ▼ $oD_2 - Ne$
- $oD_2 - Ar$ for two sets of potential parameters.

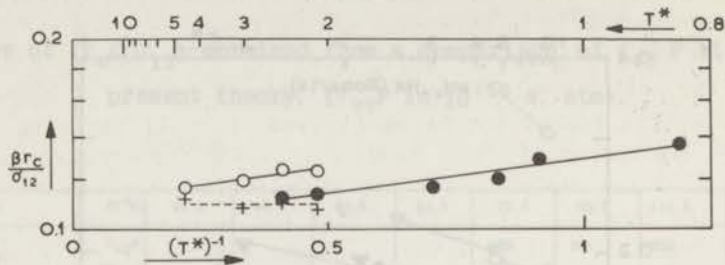


Fig. 4. The value of $\beta r_c / \sigma_{12}$, obtained from a comparison of the experimental data (chapters II and III) with eq. (2), plotted versus the inverse reduced temperature, $(T^*)^{-1}$, for $pH_2 - pH_2$ and $oD_2 - oD_2$ interactions.

○ $pH_2 - pH_2$

● $oD_2 - oD_2$

+ $pH_2 - pH_2$ In this case τ_{VT} is compared with inelastic collision cross sections computed by Davis¹¹.

potential. To explain the observed effect, however, the coefficient of the second Legendre polynomial connected with the attractive part must have the opposite sign to β . This would correspond to a polarisability tensor with $\alpha_{\perp} > \alpha_{\parallel}$, which contradicts, however, the experimental and theoretical results¹⁴⁾¹⁷⁾. Also the use of the Morse potential instead of a more realistic one cannot be the cause of the breakdown of the theory, as can be seen as follows. Davis¹¹) computed the inelastic scattering cross sections for rotational transitions in $pH_2 - pH_2$ interactions with a distorted wave approximation given by Arthur and Dalgaro¹⁸⁾, using both the Morse and the Buckingham exp-6 potentials. In each case his results were in fair agreement with the experiments of Sluiter et al.⁵⁾, while in this case the temperature dependence of τ_{VT} predicted by Takayanagi is again incorrect (fig. 4). Also different values for the potential parameters cannot explain the wrong temperature dependence: variation of α_{12} changes the absolute value of β but the influence in the temperature dependence is small as can be seen in fig. 3, where we plotted the results of calculations for e.g. $H_2 - Ar$ for three different values of α_M . So the reason for the discrepancy must be inherent in the modified wave approximation. It is, however, difficult to pinpoint the exact place where the theory breaks down.

We have tried to fit our data for $H_2 - {}^4He$ with the calculations of Robert s³). In this case a significant temperature dependence of β also results. Here, however, the reason is clear; since the author neglected the attractive part of the spherical potential his transition probabilities at small incoming wave-numbers are too small. As a result, at lower temperatures larger values of β are needed to fit the experiments (see fig. 3).

From the foregoing it is clear that the values of $\beta r_c/\sigma_{12}$ that follow from a fit with the Modified Wave theory are rather uncertain. It is, however, rather comforting that the Hartree-Fock type calculations of Krauss and Mie s¹⁹) on the interaction of H_2 with He yield a value for $\beta = 0.18$, which is in fair agreement with our result, assuming that $r_c = \sigma_{12}$. We can also conclude from fig. 3, that β decreases with increasing σ_{12} . This is in agreement with the trend predicted by the model suggested by de Boer²⁰). He assumes, within the hydrogen molecule, two point centers of a repulsion that decays exponentially with distance (see fig. 1). The repulsive potential is then given by:

$$V(r) = \frac{1}{2}D \{ \exp(-2ar_1) + \exp(-2ar_2) \}$$

Since $d \ll r$, $r_{1,2} \approx r (1 \pm (d/r) \cos \theta)$,

This leads to $V(r) = D \exp(-2ar) \{ 1 + \alpha^2 d^2 \cos^2 \theta \}$

Comparison with (1) yields $\beta = \frac{2}{3} \alpha^2 d^2$.

From the behaviour of the Buckingham exp-six potential we know that α is roughly proportional to σ_{12}^{-1} . So, we expect β to be proportional to σ_{12}^{-2} .

Furthermore we observe that β for $pH_2 - {}^4He$ and $pH_2 - {}^3He$ are equal within the claimed accuracy. Finally from fig. 3 it appears that the combinations with D_2 have smaller asymmetries than the corresponding pH_2 combinations. In our opinion it is however too early to draw more than qualitative conclusions until new computational work on the inelastic cross sections becomes available.

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SAMENVATTING

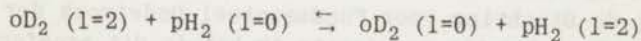
In dit proefschrift worden acoustische metingen van rotatie-translatie relaxatietijden in waterstof-edelgas mengsels beschreven en geïnterpreteerd. Genoemde relaxatietijden beschrijven de energie-uitwisseling tussen de uit- en inwendige vrijheidsgraden van de waterstof-moleculen. Aangezien deze uitwisseling slechts bij moleculaire botsingen tot stand kan komen is direct in te zien dat de relaxatietijd omgekeerd evenredig is met de dichtheid en dus ook met de druk. Tevens kan men hieruit afleiden, dat de reciproke waarde van de isochoor- isotherme relaxatietijd, τ_{VT} , een lineaire functie van de edelgas-concentratie zal zijn. Dit is experimenteel geverifieerd voor mengsels van parawaterstof met ^3He , ^4He , Ne, Ar, Kr en Xe bij temperaturen tussen 77 en 170° K. In dit temperatuurgebied zijn slechts de rotatieniveaux $l = 0$ en $l = 2$ van waterstof bezet. Een analoge serie metingen werd uitgevoerd aan orthodeuterium, gemengd met ^4He , Ne en Ar in het temperatuurgebied $55 < T < 90^\circ \text{K}$, waarin OD_2 een twee-niveaux systeem is. Ook in dit geval bleken bovengenoemde verbanden te gelden.

Door extrapolatie van $(\tau_{VT}P)^{-1}$ naar $x_{\text{edelgas}} = 1$ werd een relaxatietijd bepaald welke zou optreden in een hypothetisch gas, waarin slechts waterstof-edelgas botsingen plaats zouden hebben. Deze relaxatietijd is voor theoretische interpretatie op microscopische basis toegankelijk. Ze is verwant aan de overgangswaarschijnlijkheid van de waterstof-moleculen voor het proces $l = 0 \rightarrow 2$, geïnduceerd door botsingen met edelgas-atomen. Deze kan worden berekend als functie van de onderlinge snelheid der deelnemende moleculen, mits een uitdrukking voor de energetische wisselwerking van deze moleculen als functie van afstand en orientatie gegeven is. Voor het geval het bolronde deel van de wisselwerking gegeven is door de z.g. Morse-potentiaal en het hoek-afhankelijk deel gemoduleerd wordt door een 2^e Legendre-polynoom, $P_2(\cos \theta)$, heeft T a k a y a n a g i een formule afgeleid voor genoemde overgangswaarschijnlijkheid. Met behulp van deze relatie werd voor alle hier onderzochte systemen de overgangswaarschijnlijkheid berekend.

Integratie van deze overgangswaarschijnlijkheden over de relatieve snelheden tenslotte, leidde tot numerieke waarden voor de grootte $\beta^2 \tau_{VT}$, waarin β de asymmetrie-parameter in de interactie-potentiaal is. Het bleek dat de temperatuurafhankelijkheid van deze grootte afweek van die welke experimenteel gevonden werd. Het vermoeden lijkt gerechtvaardigd dat deze discrepantie het gevolg is van de door T a k a y a n a g i gebruikte benaderingsmethode.

Ondanks het falen van de theorie op dit punt is het toch mogelijk een aantal kwalitatieve conclusies te trekken aangaande de waarde van β voor de gekozen waterstofisotoop-edelgas combinaties. Het blijkt, dat β afneemt met toenemend moleculairgewicht van het edelgas. Verder zijn de waarden van β voor de deuterium-combinaties altijd kleiner dan die van de overeenkomstige waterstof-combinaties.

Naast het reeds besproken werk aan waterstof-edelgas combinaties zijn metingen verricht aan de volgende mengsels: a) pH_2 - oH_2 mengsels bij 77° K. Bij deze temperatuur bevindt oH_2 zich vrijwel uitsluitend in rotatietoestand $l = 1$. Om deze reden kan men in principe verwachten dat ook in dit geval $(\tau_{VT}P)^{-1}$ een lineair verloop met de concentratie zal vertonen. Dit blijkt inderdaad het geval. De door extrapolatie verkregen relaxatietijd voor één molecule pH_2 in een oH_2 omgeving blijkt kleiner te zijn dan de relaxatietijd in zuiver pH_2 bij dezelfde temperatuur. Dit zou kunnen wijzen op overgangen van het magnetisch quantumgetal in oH_2 , simultaan met de l -overgangen in pH_2 . b) oD_2 - pH_2 mengsels bij 45° K. In dit geval is pH_2 vrijwel geheel in de grond-toestand ($l = 0$). Om dezelfde reden als in geval a) verwachten wij ook voor dit mengsel weer een lineair verloop van $(\tau_{VT}P)^{-1}$ met de concentratie. De meetnauwkeurigheid in aanmerking genomen blijkt het onmogelijk een rechte door de meetpunten aan te brengen. Het ziet er naar uit dat behalve de $l = 0 \rightarrow 2$ overgang van het deuterium met onveranderde botsingspartner ook de "quasi-resonance" reactie optreedt, welke reeds op theoretische gronden voorspeld werd door V a n K r a n e n d o n k



Door de symmetrie van de rotatietoestanden zou deze reactie een grote waarschijnlijkheid hebben, leidend tot kortere relaxatietijden bij een mengverhouding van 50-50%. Dit werd experimenteel waargenomen.

Teneinde te voldoen aan het verzoek van de faculteit der Wetenschappen en Natuurwetenschappen volgt hier een kort overzicht van mijn studie.

In 1954 werd het eindexamen H.B.S.-B afgelegd als afsluiting van mijn opleiding van de Mathenesser H.B.S. in Rotterdam. Hierna was ik tot 1957 als fysisch-chemisch analist werkzaam in het Unilever Research Laboratorium in Zwijndrecht en later in Vlaardingen. Hier verrichtte ik onder meer een calorimetrisch onderzoek naar de smelteigenschappen van eetbare oliën en vetten. In deze periode behaalde ik de diploma's "Leerling Analyst" en "Candidaat Technisch Chemicus P.B.N.A.". In 1957 begon ik met mijn studie in de natuurkunde aan de Rijksuniversiteit te Leiden waar mij in nov. 1961 het candidaatsexamen studieletter a' werd afgenomen. In deze periode werkte ik in de academische vakanties als research-medewerker in het Unilever Research Laboratorium; nu echter aan de bestudering van rheologische eigenschappen van grenslagen onder leiding van Dr. M. van de Tempel.

Na mijn candidaatsexamen werd ik opgenomen in de groep moleculaire natuurkunde van het Kamerlingh Onnes Laboratorium. Aanvankelijk assisteerde ik Dr. G.C.F.F.M. S c o l e s in het beginstadium van de experimenten betreffende de invloed van magnetische velden op de transportgrootheden van gassen. Hierna heb ik deelgenomen aan een onderzoek naar het verschil in polariseerbaarheid tussen de waterstofisotopen in hun ortho- en para-modificaties. Gedurende de zomer van 1963 werkte ik enkele maanden op het Laboratorium voor Lage Temperaturen en Technische Physica in Leuven onder leiding van Prof. Dr. A. v a n I t t e r b e e k aan metingen van de warmtegeleiding van koper bij zeer lage temperaturen. Vanaf oktober 1963 assisteerde ik Dr. C.G. S l u i j t e r bij de afronding van zijn onderzoek aan rotatie-relaxatie in de zuivere waterstof-isotopen, beschreven in zijn proefschrift. Dit was tevens de aanloop van mijn promotie-onderzoek. In 1962 werd ik assistent op het prae-candidaten practicum. Na mijn doctoraal examen experimentele natuurkunde met bijvak wiskunde in oktober 1964 werd ik aangesteld als wetenschappelijk medewerker in gewoon verband bij de Stichting voor Fundamenteel Onderzoek der Materie, F.O.M. In deze functie verrichtte ik het in dit proefschrift beschreven onderzoek in de werkgroep voor moleculaire natuurkunde, waarvan in Leiden de leiding berust bij Prof. Dr. K.W. T a c o n i s en bij mijn promotor, Prof. Dr. J.J.M. B e e n a k k e r.

De discussies met Prof. Dr.P. M a z u r, Dr.H.F.P. K n a a p en Dr.A. L e v i waren een belangrijke steun bij het volbrengen

van dit promotie-onderzoek, waarbij ik verder geassisteerd werd door Dr. I. Ertas, Dr. R.A. Aziz, Drs. G.J. Prangsm a, S. Emid, R.A.J. Keijser en J.P.J. Heemskerk. Technische hulp had ik in bijzonder van de heren J.M. Verbeek, C. Le Pair, J. de Vinken en T. Nieboer. Ik heb een dankbaar gebruik gemaakt van het uitgebreide literatuur-documentatiesysteem van de groep molecuulfysica, dat onder de leiding van Dr. A.O. Rietveld regelmatig wordt aangevuld. De tekeningen zijn van de hand van de heer W.F. Tegelaar, het typewerk werd op voortreffelijke wijze verzorgd door mej. A.M. Aschoff en Dr. F.R. McCourt heeft bijgedragen tot de leesbaarheid van dit proefschrift door een aantal taalkundige correcties aan te brengen. Ik maak van deze gelegenheid gebruik al diegenen te bedanken die hebben meegewerkt aan het tot stand komen van dit proefschrift.

Utrecht, den 15de April 1967

De Voorzitter van de Promotiecommissie, Dr. A.O. Rietveld

DE PROMOTIE

De zijne wetenschap en de wetenschap van de experimentele fysica in hun theoretische en experimentele verband, te weten het verband van de wetenschap van de fysica.

Utrecht, den 15de April 1967

De wetenschappelijke kennis van de natuurkunde is de wetenschap van de natuurkunde, te weten de wetenschap van de natuurkunde.

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STELLINGEN

1. Gezien de resultaten van dit proefschrift is het wenselijk de berekeningen van Davison voor rotatie-overgangswaarschijnlijkheden in waterstof-waterstof interacties uit te breiden met die in waterstof-edelgas interacties.

W.D. Davison, Disc. Farad. Soc. 33 (1962) 71.

2. Bij de interpretatie van geluidsdispersie metingen in een relaxerend gas moet men bedenken dat de correctie, welke optreedt door inwerking van het relaxatieproces op de absorptie ten gevolge van viscositeit, warmtegeleiding en diffusie, en de gebruikelijk aangebrachte correctie, veroorzaakt door de totale geluidsabsorptie, van gelijke orde-grootte zijn.

Dit proefschrift hoofdstuk I.

3. De wijze waarop Durbin en Kobayashi de experimentele condities in hun diffusie experimenten variëren, leidt niet tot verhoogde betrouwbaarheid van hun resultaat.

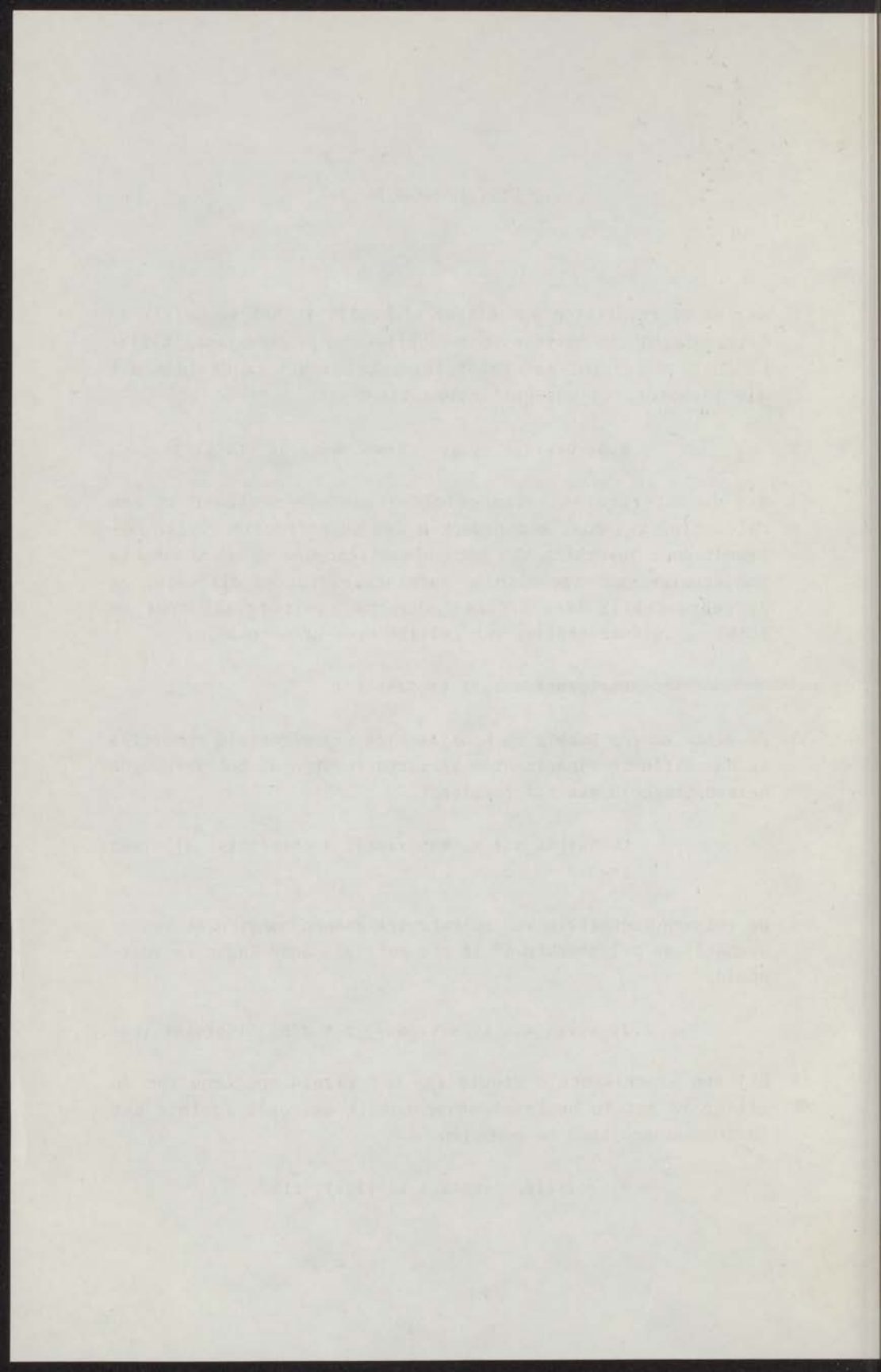
L. Durbin and R. Kobayashi, J.chem.Phys. 37 (1962) 1643.

4. De volumenviscositeit van meeratomige gassen hangt niet van de magnetische veldsterkte af in die mate als door Kagan is voorspeld.

J. Kagan and L. Maksimov, Z.E.T.F. 51 (1966) 1893.

5. Bij een experimentele studie van het geluidsspectrum van de gitaar is het in beginsel onverstandig om zoals Jovicic het instrument apojando te bespelen.

J. Jovicic, Acustica 18 (1967) 113.



6. Het is gebruikelijk Hall-spanningen te meten met behulp van een preparaat uitgevoerd met 3 spanningscontacten in een potentiometer-schakeling. Bij het meten van Hall-spanningen in supergeleiders van de 2^e soort verdient het echter de voorkeur het preparaat uit te voeren met twee vaste spanningscontacten.
7. De argumenten die Winter aanvoert om te bewijzen dat de spin-rooster relaxatietijden van de kernmomenten van ¹⁹F in LiF in belangrijke mate worden bepaald door "kernspin-diffusie" zijn onjuist.

J. Winter, C.R. Acad. Sci. 249 (1959) 2192
A. Abragam, Princ. of Nucl. Magn., chapter IX, Oxford Univ. Press 1961.

8. De bewering van Flippen, dat de verlaging van de kritische veldsterkte H_{c2} in supergeleiders van de 2^e soort in pulsvelden bij toenemende stijgsnelheid van het magneetveld door onomkeerbare warmteproductie veroorzaakt kan worden, is aan twijfel onderhevig.

R.B. Flippen, Phys. Rev. 137 (1965) A 1822.

9. Uit metingen van de dempingscoëfficiënt van oppervlakte-rimpels verkrijgen Davies en Vose relaxatiefrequenties voor de uitwisseling van oppervlakteactieve moleculen tussen oppervlak en oplossing. Deze interpretatie is aanvechtbaar.

J.T. Davies en R.W. Vose, Proc. Roy. Soc. A 286 (1965) 218.

10. Uit hydrostatische overwegingen verdient voor de behandeling van hydrocephalus internus communicans bij volwassenen de atrio-ventriculaire shunt met klepmechanisme de voorkeur boven de lumbo-peritoneale drainage.
11. De conclusies gegeven in het "verslag van een enquête in april 1967 gehouden onder de eerste jaars wis-, natuur- en sterrekunde te Leiden" volgen niet logisch uit de enquête-resultaten.
12. De beroepskleding van uitvoerende musici is in het algemeen bijzonder ondoelmatig.

1. Het is gebruikelijk half-geconcentreerd te spreken met bedoel van een halfgeconcentreerd met 2 spanningsniveaus in een halfgeconcentreerd systeem. Dit halfgeconcentreerd is een halfgeconcentreerd systeem van de 2^o soort waarbij het aantal de voorkeur wordt gegeven dit te spreken met twee spanningsniveaus.

2. De argumenten die worden aangevoerd om te bewijzen dat de halfgeconcentreerde spanningsniveaus van de spanningsniveaus van de 1^o in 1/2 in de halfgeconcentreerde spanningsniveaus door "spanningsniveaus" zijn bedoeld.

3. Volgens C. A. van der Vliet, 1952 (1952) 200
4. Volgens van der Vliet, 1952 (1952) 200
5. Volgens van der Vliet, 1952 (1952) 200

6. De besetting van vijfde, dat de verdeling van de halfgeconcentreerde spanningsniveaus van de 2^o soort te spreken met de halfgeconcentreerde spanningsniveaus van de 1^o in 1/2 in de halfgeconcentreerde spanningsniveaus door "spanningsniveaus" zijn bedoeld.

7. Volgens van der Vliet, 1952 (1952) 200

8. Uit wetgeving van de halfgeconcentreerde spanningsniveaus van de halfgeconcentreerde spanningsniveaus van de 2^o soort te spreken met de halfgeconcentreerde spanningsniveaus van de 1^o in 1/2 in de halfgeconcentreerde spanningsniveaus door "spanningsniveaus" zijn bedoeld.

9. Volgens van der Vliet, 1952 (1952) 200

10. Dit hydrodynamische overwegingen verschillen voor de behoudende van hydrodynamische interactie communicatie bij verandering van de halfgeconcentreerde spanningsniveaus van de 2^o soort te spreken met de halfgeconcentreerde spanningsniveaus van de 1^o in 1/2 in de halfgeconcentreerde spanningsniveaus door "spanningsniveaus" zijn bedoeld.

11. De conclusies worden in het "artikel" van een artikel in 1952 (1952) 200

12. De beschrijving van de halfgeconcentreerde spanningsniveaus van de halfgeconcentreerde spanningsniveaus van de 2^o soort te spreken met de halfgeconcentreerde spanningsniveaus van de 1^o in 1/2 in de halfgeconcentreerde spanningsniveaus door "spanningsniveaus" zijn bedoeld.

