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The Velocity of Sound in an Absorptive Gas

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The theory of velocity propagation in a gas as conditioned by internal energy exchanges is considered in detail for the simplest case in which the "lags" may be different—namely, the model with three sets of states. This "second order" theory is required for the interpretation of experimental results where the wave period is of the order of the lag for some states. Assuming the first vibration state of CO_2 to have the largest lag in accordance with Kneser's interpretation of his recent experiments, the necessary approximations are given explicitly and the results are directly applicable to CO_2. The apparent lag as measured in sound velocity experiments is not the simple stationary state mean "collision life" nor the mean life of the energy quantum except under special conditions and then for only one of the states. The velocity increment in the "resonance" region is given more accurately in terms of transition probabilities and is not described completely by the specific heats as might be expected from the "first order" theory. Contrary to the indications of the simple theory with an empirical constant the external energy is always merely the translation term. The status of the assumed lag assignment in CO_2 is discussed in the light of the results and underlying theory of this paper.

IN TWO earlier papers[1] the author has presented a theory of the propagation of sound in a gas and gas mixtures which deals directly with the fundamental kinetic and atomic qualities of the system. The problem of a gas whose rate of adjustment to fluctuation in translational energy is the same for all internal states was taken up as a special case, or first approximation, under this theory. It was pointed out that this special case corresponded to the macroscopic theory of Herzfeld and Rice.[2] Recently O. Kneser[3] in discussing his important experimental results has used essentially this macroscopic theory and has tried 'to utilize the ideas of transition probabilities, etc., in connection with it. Such a procedure is artificial and seems limited to "first order" approximations—any more thorough investigation must proceed on some such lines as those pursued in I and II and the present paper.

Because of the highly suggestive nature of Kneser's data and the increasing interest in the field of supersonics, it was felt desirable to refine the pertinent formulae in the same measure as the increase in experimental technique. In the interest of the general reader that part of the theory of I and II germane to the present discussion is briefly reviewed in section I. In section II the problem of a gas model with three internal states is taken up in some detail and the calculations are developed with special reference to Kneser's[4] research on CO_2.

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[1] D. G. Bourgin, Nature **122**, 133 (1928); Phil. Mag. **7**, 821 (1929); Phys. Rev. **34**, 521 (1929). (These last will be referred to as I and II, respectively.)

[2] K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).

[3] O. Kneser, Ann. d. Physik **11**, 761, 779 (1931).

[4] Kneser's remark in a footnote that the writer's developments "nicht zu experimentalle

SECTION I

The principle of detailed balancing yields at equilibrium[5]

$$(\Delta N_i)_T = 0 = \{N_i^2(\bar{f}_{ij} - f_{ij}) + NN_if_{ij}\} - \{N_j^2(\bar{f}_{ji} - f_{ji}) + NN_jf_{ji}\}. \quad (1.00)$$

If we disturb equilibrium

$$\begin{aligned}\Delta N_i = &- \sum \delta N\{N_if_{ij} - N_jf_{ji}\} + \delta N_i\{2N_i(\bar{f}_{ij} - f_{ij}) + Nf_{ij}\} \\ &- \delta N_j\{2N_j(f_{ji} - f_{ji}) + Nf_{ji}\} + N_i^2\{\delta(\bar{f}_{ij} + f_{ij})\} + NN_i\delta f_{ij} + . \quad (1.01)\end{aligned}$$

We introduce

$$R_{ij} = [2N_i(\bar{f}_{ij} - f_{ij}) + Nf_{ij}]/N. \quad (1.02)$$

Suppose the effective temperature for the state i is $\omega_i\delta T + T_0$, i.e., the number of molecules in state i may be considered to be that corresponding to this temperature at equilibrium, then the change in N_i due to increase of the temperature of this state to $\omega_i\delta T$ is

$$\delta N_i = (\delta NN_i + N\dot{N}_i\omega_i\delta K)/N \quad (1.03)$$

where $K = (3/2)kT$ and $\dot{N}_i = dN_i/dK$ and the first term corresponds to a density increase.

We now observe that if $\omega_r \equiv 1$ then the ΔN_i of Eq. (1.01) is the difference between the number of molecules leaving state i at temperatures T_0 and $T_0 + \delta T$ because of collisions. Since for each fixed temperature $(\Delta N_i)_T = 0$, therefore ΔN_i for $\omega_r \equiv 1$.

If the first term of Eq. (1.03) were alone active we should have (neglecting the effect of variation of N on f_{ij} for the moment)

$$(\Delta N_i)_T, f = (\delta N/N)[(\Delta N_i)_T] = 0. \quad (1.011)$$

Accordingly we may neglect all terms in Eq. (1.01) with δN. Collecting the remaining terms and bearing in mind

$$\begin{aligned}(\Delta N_i)_{\omega_i \equiv 1} = 0 = &\sum_j N(\delta N_iR_{ij} - \delta N_jR_{ji}) \\ &+ (NN_i - N_i^2)\delta f_{ji} + N_i^2\delta f_{ij} - \cdots. \quad (1.012)\end{aligned}$$

We may therefore replace the sum of the terms in δf (where δf_{ij} involves δN and δK) by

$$- N[\delta N_iR_{ij} - \delta N_jR_{ji}]_{N, \omega_r \equiv 1}.$$

Prüfung dürften" must be ascribed to insufficient acquaintance with the contents of I and II. In fact on adopting the expression for ω given in I, p. 831 footnote, the resulting formula for V^2, cf. Eq. (2.02) and reference 6 of this paper, is (except for one important point of difference taken up in section II) Kneser's main equation. Even the present paper which provides a more solid basis for interpretation of Kneser's experiments is again only a special case of I.

[5] If $N^2\gamma/2$ be the number of collisions per unit time in a gas at temperature T then the number involving $N_i - N_i$ meetings is $N_i^2\gamma/2$ (where N_i is the number of molecules per unit volume in state i). The number involving $N_i - N_j$ meetings is $N_i(N - N_i)\gamma$. If $\bar{f}_{ij}^1$ and f_{ij}^1 are the probabilities of $i \rightarrow j$ transition correlated with each type of collision and if $\bar{f}_{ij} = f_{ij}^1\gamma/2$ and $f_{ij} = f_{ij}^1\gamma$, then there results Eq. (1.00).

Eq. (1.01) becomes

$$\Delta N_i = -\left\{ N \sum_j \dot{N}_i R_{ij}(\omega_i - 1) - \dot{N}_j R_{ji}(\omega_j - 1) \right\} \delta K. \qquad (1.013)$$

The change of energy due to collision is defined as

$$\Delta K = - \sum \Delta N_i \epsilon_i. \qquad (1.04)$$

The equation of continuity is

$$\partial N/\partial t = -(\partial/\partial x) N v \qquad (1.05)$$

where v equals the x component of the mass velocity.

Also

$$(\partial \dot{N}_i/\partial t) = -(\partial/\partial x) N_i v + \Delta N_i \qquad (1.06)$$

$$(\partial/\partial t) m N v = -(2/3)(\partial K/\partial x) N \qquad (1.07)$$

$$(\partial K/\partial t) N = -(5/3)(\partial/\partial x) K N v + \Delta K. \qquad (1.08)$$

Assume a plane wave in the gas then

$$\delta N = |\delta N| \, e^{-j(\nu t - x/\lambda)}$$

where ν is frequency and λ is wave-length, and $j = (-1)^{\frac{1}{2}}$

$$\delta T = |\delta T| \, e^{-j(\nu t - x/\lambda)}$$

$$\delta v = |v| \, e^{-j(\nu t - x/\lambda)}.$$

In the undisturbed gas clearly v is 0.

For small amplitude waves v is so small that $v\delta N$ and $v\delta T$ may be neglected. From Eq. (1.05) we have

$$j\nu |\delta N| = jN |v| /\lambda. \qquad (1.051)$$

From Eq. (1.06) we get, on referring to Eq. (1.02),

$$j\nu \{ \dot{N}_i \omega_i \delta K + |\delta N| N_i/N \} = j v N_i/\lambda + \Delta N_i. \qquad (1.061)$$

Eq. (1.061) yields

$$j\nu \dot{N}_i \omega_i = - N \sum_j \dot{N}_i R_{ij}(\omega_i - 1) - \dot{N}_j(\omega_j - 1). \qquad (1.062)$$

These are a set of n non-homogeneous equations in the n quantities ω_i with a unique solution for, because of the presence of $j\nu$ on the diagonal, the determinant will not vanish, i.e., the coefficient of the ii term is $j\nu N_i + N\Sigma_j N_i R_{ij}$ and is the only term in the ith row containing ν.

The elimination of the moduli of K, N and v, leads to one of the key formulae of I and II, namely:

$$j\nu \left[\frac{3mV^2 - 10K/3}{3mV^2 - 2K} \right] = \sum_i (\omega_i - 1)(\Delta K)_i \qquad (1.10)$$

where $(\Delta K)_i$ is $N_i A_i \epsilon_i$ V is the complex velocity of sound, and

$$A_i = \sum_j (\dot{N}_i R_{ij} - \dot{N}_j R_{ji})/\dot{N}_i. \tag{1.11}$$

SECTION II

Before taking up the second order calculation which is the primary object of this paper it seems appropriate to make some preliminary remarks having a direct bearing on Kneser's paper. First we exhibit in slightly more detail than given in I the special case

$$\omega \underset{i}{\equiv} \omega_i.$$

It follows immediately from Eq. (1.062) that

$$\omega \equiv NA_i/j\nu + NA_i. \tag{2.00}$$

We remark that, with E the internal energy,

$$\begin{aligned} \sum_j \dot{N}_i \epsilon_i &= dE/dK \\ &= NC_i/(3/2)k \end{aligned} \tag{2.01}$$

where C_i is the internal specific heat pro molecule.

Thus

$$V^2 = \frac{K}{3m}\left[\frac{(5/2)k + C_i + j\nu(5k/2)A_iN}{(3/2)k + C_i + j\nu(3k/2)A_iN}\right]. \tag{2.02}$$

This is essentially the equation derived in I expressed in experimentally meaningful terms.[6] It is the same as Kneser's except in the one respect that the external energy (Kneser's notation C_a) is here given explicitly as $3k/2$ while it is left undetermined in Kneser's formula and is indeed finally given a value greater than that corresponding to the translational energy.

It will be shown in this paper, however, that it is physically inaccurate to assume that the external energy differs from $3/2k$—the apparent departure is due to the deficiency of the simple $\omega \equiv \omega_i$ theory. In order to avoid repetition the $\omega \equiv \omega_i$, or Herzfeld-Rice, Kneser theory will be referred to under the properly descriptive head, first order theory, to distinguish it from the second order theory of this section.

Kneser has shown by straightforward, detailed computations that the dispersion formula used by him as well as that of Lorentz and Herzfeld-Rice, yields an inflection point with respect to log ν. Since Eq. (2.02) is, with the exception mentioned, the precise analogue of Kneser's formula, it is clear that properties of this sort hold for Eq. (2.02) also. However, the existence of an inflection point is immediately evident without calculation for a wide class of formulae including the extremely general case taken up in I on the basis of the most simple considerations. One observes merely that for all natural dispersion formulae $r.p. V^2$ is a function of ν^2 finite together with its first derivatives at the end points of the interval $0 \leqq \nu \leqq \infty$ and continuously differ-

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[6] The only difference is that Eq. (2.02) involves the full expression for ω whereas I employs the first terms only of the series expansion.

entiable twice on this range. Rolle's theorem is all else that is needed (for with these restrictions $r.p.dV^2/d\nu=0$ for $\nu=0$ and $\nu=\infty$).

For a very general case $r.p.V^2$ is a rational function of ν^2 with poles not on the real axis. Since the poles of the derivatives of a rational function are at the same points as the poles of the function and all the derivatives of V^2 are rational functions, it follows that this satisfies the conditions stated. For exhibiting the data, it may be convenient to introduce $z=f(\nu)$ which, generally, will be some simple[7] functional relation. Accordingly the conditions just stated in terms of ν are as easily applied with z.

It is worth while to point out that if $n-1$ states have the same ω then $\omega_n=\omega$ also. Hence one cannot talk about a two state gas model having different ω values.[8] The proof is immediate and involves the assumption that v is very small.

From Eq. (1.061) we derive:

$$j\nu\sum_i \dot{N}_i\omega_i = \sum_i(\Delta N_i) = \Delta N. \tag{2.03}$$

Manifestly, ΔN the change in N due to collisions is 0. We observe next that

$$\sum_i \dot{N}_i = dN/dK = 0. \tag{2.04}$$

Therefore if $\omega_i=\omega$ for $i=n, \cdots$ n, we have

$$\dot{N}_1\omega_1 = -\omega\sum_2^n \dot{N}_i$$
$$= \omega\dot{N}_i$$

or

$$\omega_1 = \omega.$$

Accordingly the next simplest gas model consists of three states (or classes of states) correlated with different ω values.

In order to maintain symmetry, Eqs. (2.03) and (2.04) are not used in what follows now.

Eq. (1.061) yields:

$$\begin{aligned} \dot{N}_i(j\nu + Ns_1)\omega_1 - N\dot{N}_2R_{21}\omega_2 - N\dot{N}_3R_{31}\omega_3 &= N\dot{N}_1A_1 \\ \cdot \qquad\qquad + \dot{N}_2(j\nu + Ns_2)\omega_2 - \quad \cdot &= N\dot{N}_2A_2 \\ \cdot \qquad\qquad\qquad \cdot \qquad\qquad\qquad \cdot &= N\dot{N}_3A_3 \end{aligned} \tag{2.031}$$

where $s_i=\Sigma_jR_{ij}$. The constant term in the determinant of the equations vanishes and there results

$$\omega_i = \frac{j\nu NA_i + N^2S}{(j\nu)^2 + j\nu N\sum s_i + N^2S} \tag{2.05}$$

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[7] It is therefore of perfunctory interest only to state sufficient conditions on $z=f(\nu)$ to insure finite inflection points in z and dependent on the parameters of $V(\nu)$ when there are inflection points in ν.

[8] This is not clear in some recent papers.

and accordingly

$$\omega_i - 1 = -\frac{j\nu[j\nu - N(A_i - \sum s_i)]}{(j\nu)^2 + j\nu N \sum s_i + N^2 S} \tag{2.051}$$

where

$$2S = \sum_i^3 \sum_j^3 s_i s_j - R_{ij}R_{ji},\ i \neq j.$$

Eq. (2.051) allows of direct physical interpretation. $NA_i\dot{N}_i\delta K$ expresses the change in N_i due to collisions in unit time. The difference in value of N_i for T_0 and $T_0+\delta T$ is $\dot{N}_i\delta K$. Hence the fictitious time required at constant rate to attain the new equilibrium value would be the ratio of these two quantities or $(A_iN)^{-1}$. This is the "static" lag.[9] Since increase of the $K.E.$ changes N_i and ΔN_i in the same direction it follows from Eq. (1.013) that $A_i>0$. Although for the first order theory the important low-frequency term for ω_i-1 is just this static lag the corresponding lag term in the second order theory is $N(A_i-\Sigma s_j)/N^2S$. The important point to notice is that the order of the states according to lags is the same as that given by this last formula. This follows from the fact that $\Sigma s_j>A_i$. While in some instances, because of the approximation that may be made, the lag for state i is closely the mean life of the ith quantum of energy, nevertheless the strict value of this latter life[10] is, of course, $(s_iN)^{-1}$.

In order to make close contact with Kneser's experimental work let us make assumption A

$$\text{(a)}\quad A_2, A_3 \gg A_1 \qquad (b)\quad \epsilon_1 \gg \epsilon_2, \epsilon_3.$$

Furthermore we assume that $(c)\dot{N}_2R_{21}+\dot{N}_3R_{31}/\dot{N}_1$ is negligible. The implication of this last condition will perhaps be better apprehended by writing

$$\dot{N}_2R_{21} + \dot{N}_3R_{31} \sim (N_1\dot{N}_2/N_2)R_{12} + (N_1\dot{V}_3/N_3)R_{13}. \tag{2.06}$$

From

$$N_i = Ne^{-\epsilon_i/kT}/\sum_j e^{-\epsilon_j/kT} \tag{2.07}$$

(where possible degeneracy has been remoted by the familiar artifice of a small electrostatic field) one finds $N_1\dot{N}_2/\dot{N}_1N_2=(\bar{\epsilon}-\epsilon_2)/(\bar{\epsilon}-\epsilon_1)$ with $\bar{\epsilon}$ the average internal energy (c) at temperature T_0. Assumption (c) is satisfied if

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[9] As pointed out in II, the $j\nu$ term is the in the "phase" term and hence the word lag is here used with a different connotation from that employed in II where it characterizes the $(\nu)^2$ term. We remark also that it is the combination A_iN, and likewise s_iN and N^2S that is independent of N. In the notation of I our present A_i is $A_i/\dot{N}_i$ and $B=\sum_i N_iA_i\epsilon_i$. For the $\omega\equiv\omega_i$ case, $(AN)^{-1}$ corresponds to $2\beta/3B$ of I.

[10] The impression seems to persist that radiation "lives" generally are of the order of the atomic ones, namely, 10^{-8} to 10^{-10} seconds and that the collision lives are much longer. (Cf. Kneser, p. 779, ibid. and Henry, Nature, Feb. 6, 1932), Actually the radiation "lives" will most likely be the longest. In the case of HCl for instance, both theory and experiment indicate a life for the first vibration state as long as 10^{-2} seconds. D. G. Bourgin, Phys. Rev. **29**, 794 (1927) and Phys. Rev. **32**, 237 (1928).

$$\left| \bar{\epsilon} - \begin{matrix}\epsilon_2 \\ \\ \epsilon_3\end{matrix} \right| \ll \left| \bar{\epsilon} - \epsilon_1 \right| \tag{2.08}$$

which carries with it $N_1 < N_2$, N_3. With these assumptions $S = s_1(s_2 + s_3)$, $A_1 = s_1$ and as may easily be verified,

$$\omega_1 - 1 = -j\nu/j\nu + Ns_1. \tag{2.052}$$

We remark now that

$$N \sum_i \Bigl(A_i - \sum_j s_j \Bigr) (\Delta K)_i = NS \sum_i \dot{N}_i \epsilon_i .$$

Hence on substituting Eq. (2.051) in Eq. (1.10) and using A one finds:

$$V^2 = \frac{2K}{3m} \left[1 + \frac{\frac{2}{3}}{1 + \left\{ \sum_i \dot{N}_i A_i \epsilon_i j\nu + NS\dot{N}_i \epsilon_i/(j\nu)^2 + j\nu N \sum s_i + N^2 S \right\}} \right. \tag{2.09}$$

for determining the inflection point we need only the second term in the bracket. The real part is expressible as

$$\frac{\nu^4 + \nu^2 \{ N^2 [\sum s_i (\sum s_i + \sum \dot{N}_i A_i \epsilon_i / N) - S - S [1 + (C_i/(3k/2)] + N^4 S^2 (1 + C_i/(3k/2)}{\nu^4 + N^2 \nu^2 [(\sum s_i + \sum \dot{N}_i A_i \epsilon_i / N)^2 - 2S[1 + (C_i/(3k/2)] + N^4 S^2 (1 + C_i(3k/2))^2} \cdot \tag{2.091}$$

For comparison with Kneser's result we find the inflection point with reference to log $\nu = z$. To a fair approximation[11] the abscissa of the lowest inflection point is:

$$\nu_0 = \frac{Ns_1(3k/2 + C_i)}{(3/2)k - (4s_1/s_2 + s_3)((3k/2) + C_i)} \cdot \tag{2.10}$$

The first order theory yields in this notation:

$$\nu_0 = [Ns_1(3k/2 + C_i)]/(3/2)k. \tag{2.101}$$

The subsequent discussion uses V^2 with the sense of the real part of the squared velocity and the subscripts 0, μ distinguish between the low and the intermediate frequency velocities. Our immediate concern is the magnitude of the increment $V_\mu^2 - V_0^2 = \Delta V^2$ through the resonance region. Kneser obtains numerical agreement with his experimental data by assuming that the external energy is not simply the translational energy but includes[12] the rotational energy as well while the total specific heat remains unaltered. This statement is not correct physically. In fact for the "first approximation" theory involved in Kneser's formulae, one may reason on altogether general grounds as follows. Under assumption A it is clear that at high frequencies

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[11] In this approximation the next higher order terms are retained till the end.

[12] It is again to be pointed out that we are assuming tentatively with Kneser that the vibration states are the large lag states but the substance of the discussion is independent of this special circumstance.

the vibrational transitions will play a negligible role because of their large lags. Hence one would expect as an approach to the truth that the apparent total specific heat would omit these terms though C_a as always remains the translational energy. Kneser's mistake arises from the fact that his presentation of the simple theory is not really descriptive in that first the shorter lag states are neglected and then the resulting formula is analyzed with respect to behavior in a range where just these states are dominant.

On going to the second approximation it develops that the statements just made are in need of modification and it is evident how a more precise estimate of ΔV^2 is to be arrived at; namely, one needs to determine the value of V_μ^2 for s_2^2, $s_3^2 > (\nu/N)^2 \gg s_1^2$. We shall use Eq. (2.091) for this purpose. Neglecting ν^4 terms restricts the validity of this equation to the low-frequency region. For high frequencies the constant term in the quotient may be omitted and there is obtained thus a sort of asymptotic approximation. In both these extreme cases V^2 (real) is a quotient of monomials in ν^2 in formal analogy with the first approximation problem. The low-frequency equation corresponds to Eq. (2.02) with the important difference that the coefficient of ν^2 is no longer C_a. V_μ^2 lies in the intermediate region of validity of both subsidiary equations. Unless $1 \gg s_1/s_i$ $i=2$, 3 a good approximation will not[13] be obtained if either the constant or ν^4 terms are neglected. However, in the interest of analytic simplicity we shall consider the ν^2 term as alone being of consequence.

This implies

$$S^2/(s_2+s_3)\nu^2 \doteq 0$$

$$\omega_i - 1 \doteq +\left(-j\nu + N\left(A_i - \textstyle\sum_j s_j\right)/j^\nu + N \textstyle\sum_j s_j\right) \quad i = 2, 3. \tag{2.11}$$

If, besides, terms in S are dropped then

$$V_\mu^2 = \frac{2K}{3m}\left[1 + \frac{k}{(3k/2 + \sum A_i \epsilon_i dN_i/dT/N(s_2+s_3)}\right]. \tag{2.092}$$

The first order approximation discussed above indicated a relationship of the form

$$V_\mu^2 = \frac{2K}{3m}\left[1 + \frac{k}{3k/2 + C_i - \left(\dfrac{dN_1}{dT}\epsilon_1/N\right)}\right]. \tag{2.021}$$

Eq. (2.092) and Eq. (2.021) differ except under special supplementary conditions. (For instance if $(dN_1/dT)A_1\epsilon_1/s_2+s_3$ is negligible then we should require the special relation $A_1=A_2=s_2+s_3$.)

We now turn to the question of deriving transition probabilities information from sound velocity and absorption experiments. All our approximations in this paper have been on the assumption that the vibrational energy has, associated, the larger lag. The assumption is, however, not altogether certain even in the case of CO_2. The correct argument for such an assignment as a

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[13] This remark is to be kept in mind in any comparison of Eq. (2.091) with the experimental data.

working hypothesis is the agreement of Eq. (2.021) with Kneser's experimental data. The fortunate coincidence that his assumption leads to the same numerical value here is explained by the fact that there are only two terms of importance in C_i (the two rotational states are lumped in the symbol $C_R = k$). With additional terms in C_i the Kneser postulate yields a result at variance with Eq. (2.021). In order to maintain the agreement one should be led to the bizarre conclusion that all the internal energies, save the one vibrational term, are included in the external energy. More explicitly, for the model considered in this paper Eq. (2.02) yields the rigorous value

$$V_\mu^2 = (1 + k/(3/2)k)2K/3m.$$

Kneser's procedure amounts to arbitrarily replacing the $(3/2)k$ term by $(3/2)k + C_R$. This modified V_μ^2 has just the value given by Eq. (2.021) as is evident on observing that the vibrational energy denoted by

$$C_S = dN_1/dT\,\epsilon_1/N \quad \text{and} \quad C_i = C_R + C_S.$$

For confirmation[14] it is necessary now to use the more accurate Eq. (2.092) and then the analogous second order formula that would result from the supposition that the low energy states[15] (2, 3) have the large lags.[16] The assumption that all rotation states have one type of lag and all vibrational states another may be wide of the truth, in which case a theory is required in which both rotational and rotation-vibrational states exist characterized by the same lag value. Such modifications in the hypothesis may be taken account of by suitably varying the approximations in a treatment like the present one. Then too it may be remarked that the data points in Kneser's figure do not continue into the critical intermediate region, and besides, the experimental accuracy is least here. It seems desirable to supplement and extend the experimental results to higher frequencies by varying the CO_2 percentage in a mixture with a non-masking gas.[17]

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[14] Conversely if the lag assignment be adopted the experimental data yield estimates of the A_i and C_i combinations occurring in Eqs. (2.10) and (2.092).

[15] Kneser's use of the ratio of the squared velocities in CO_2 and Ar may be expected to minimize viscosity, conductivity, etc., corrections.

[16] Without going into details here, Kneser's attempted "a posteriori" justification for expecting larger lags for the vibration state is inadequate in the writer's opinion if only for the reason of the lack of satisfactoriness in the present day treatments of the circumstances of energy transfer in collision.

[17] The theory of gas mixtures may be developed along lines similar to that presented in this paper. Cf. the footnote in a forthcoming publication of the writer in the Jour. Acoust. Soc. where an error in Eq. (1.2) of II is corrected. The work in II is what I have called here a first order theory—incidentally Eq. (7) of II is the theoretical basis for computing humidity effects, etc., and provides the validation for Reid's empirical formula. Reid, Phys. Rev. **35**, 814 (1930). A form of Eq. (7) more convenient to use is

$$\frac{\delta V}{V} = \tfrac{1}{2}\overline{\sum}_w \frac{\delta N_\omega}{N}\left[\frac{C_{n\omega}}{\overline{C}_n} - \frac{C_{v\omega}}{\overline{C}_v} - \frac{m_\omega}{\overline{m}}\right]$$

where the notation is self-explanatory.

The second order treatment of the absorption may be made to parallel the development of this section by taking the imaginary part of V^2 in Eq. (2.09) and very likely other than lag influences may probably be neglected if the ratio with a rare gas is taken (in accordance with Kneser's suggestion).

An experimental study of the temperature effect seems likely to yield important evidence—the theoretical aspect is clearly outlined, namely, the dependence of R_{ij} (and $\dot{N}_j$) on T in connection with the variation in collision frequency and average collision energy. In a way this provides a means for isolating the effects of various groups of states; for instance, the inequalities of (cf. Eq. (2.08)) c valid for sufficiently low temperatures but may actually be reversed if the gas be raised to a very high temperature.

In order to make a close contact with Kneser's experimental work let us make assumption A

$$\text{(a) } A_2, A_3 \gg A_1; \quad (b) \ \epsilon_1 \gg \epsilon_2, \epsilon_3.$$

Furthermore we assume that (C) $\dot{N}_2 R_{21} + \dot{N}_3 R_{31}/\dot{N}_1$ is negligible. The conditions implied in this last assumption are indicated clearly on writing

$$\dot{N}_2 R_{21} + \dot{N}_3 R_{31} = N_1 \dot{N}_2 R_{12}/N_2 + \dot{N}_1 N_3 R_{13}/N_3. \tag{2.06}$$

From

$$N_i = N e^{-\epsilon_i/kT} / \sum_j e^{-\epsilon_i/kT} \tag{2.07}$$

one finds

$$N_1 \dot{N}_2 / \dot{N}_1 N_2 = (\bar{\epsilon} - \epsilon_2)/(\bar{\epsilon} - \epsilon_1) \tag{2.08}$$

with $\bar{\epsilon}$ the average internal energy at temperature T_0.