Acoustical Studies. II. The Behavior of a Gas with Several Independent Internal Energy States

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The method founded by Einstein for the description of the acoustical behavior of a dissociating gas has been extended to cover a nondissociating gas in which five groups of internal energy states have different relaxation times. Since the resulting expressions are unwieldly, approximations based on them, which permit the rough description of experiment, have been given. The study of the variation of the velocity of sound with frequency demonstrates differences in the relaxation times of the various states. The variation of the velocity of sound with pressure shows in addition effects due to three-body collisions or to radiation from optically active states. It has been suggested to treat the temperature coefficient of the kinetic relaxation time by the introduction of an empirical quantity which may be called "the activation energy of collision." By this means a rough kinetic analysis of the transition probability is possible. In gaseous mixtures, the relative spatial and energetic effectiveness of various types of collisions in exciting internal energy may be compared.

INTRODUCTION

GREAT progress has been made during the past few years in the measurement of the velocity of sound in gases. Because of the invention of the sonic interferometer by Pierce[3] it is now possible to determine this quantity in a gas of any desired purity with an accuracy of 0.1 percent from audible frequencies to frequencies somewhat above a million cycles per second. There is every reason to suppose that, with sufficient incentive, even this accuracy may be considerably improved. Similarly, interferometric absorption measurements, particularly owing to the investigations of Hubbard,[4] are rapidly becoming capable of exact interpretation. It is worth while, therefore, to discuss in detail the information which may be expected to become available from extremely accurate acoustical measurements.

Two methods have been used to describe the propagation of sound in acoustically dispersive gases. The first of these evaluates the absorption and dispersion by calculating as a function of frequency the number of molecules making the transition between two given energy states under the influence of the adiabatic acoustical cycle. It was founded by Einstein,[5] who considered the case of a dissociating gas, and has recently been extended by Kneser[6] and by Rutgers[7] to include nondissociating gases. The second method uses the conception of the fictional temperature of an energy state or group of energy states, and calculates as a function of frequency the relation between this fictional temperature and the temperature of the translational terms in the acoustical cycle. It was first published by Herzfeld and Rice[8] and was generalized immediately thereafter by Bourgin[9] to cover gaseous mixtures and effects due to radiation. The two methods are equivalent descriptions of the same process, and with similar postulates must yield similar conclusions. They have converged upon

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[1] It is considered that the communications of Richards and Reid, J. Chem. Phys. 1, 114,737 (1933), are Parts I and Ia of this series.

[2] Fellow of the John Simon Guggenheim Memorial Foundation.

[3] Pierce, Proc. Am. Acad. Sci. 63, 1 (1928).

[4] Hubbard, Phys. Rev. 41, 833 (1932), and earlier papers there cited.

[5] Einstein, Sitz. Ber. Akad. 380 (1920).

[6] Kneser, Ann. d. Physik 11, 761 (1931); 16, 337 (1933).

[7] Rutgers, Ann. d. Physik 16, 350 (1933).

[8] Herzfeld and Rice, Phys. Rev. 31, 691 (1928). Among the numerous and important conclusions reached in this paper is included a demonstration that absorption due to viscosity and heat conduction plays a minor rôle if a heat capacity effect is also present. This is formal justification for disregarding this quantity in using Einstein's method.

[9] Bourgin, Nature 122, 133 (1928); Phil. Mag. 7, 821 (1929); Phys. Rev. 34, 521 (1929) and 42, 721 (1932).

expressions for the velocity and absorption of sound which are practically identical, and are suitable for the description of experiment if the dispersion is produced by the gradual disappearance from the heat capacity at high frequencies of the transition from the zero point energy state of a vibration to its first excited state.

The purpose of the following discussion is to amplify these expressions to include as many transitions as may practically be necessary. The criterion of practical necessity is the calculation of the velocity of sound at very low frequency within limit of experimental error from the same relationship which is used to describe the dispersion. The method of Einstein has been used in preference to that of Herzfeld-Rice-Bourgin because of its greater simplicity. It must again be emphasized that either method is suitable for the purpose, and that the description of cases of any desired complexity is merely a matter of industry. Sections 1, 2, 3 and 4 of the following study are devoted to the development of expressions for the velocity and absorption of sound suitable for use with gases of increasing numbers of frequency dependent internal energy terms. Section 5 considers the bearing of the earlier sections on experiment, and shows how suitable measurements may lead to an increased knowledge concerning collisions of the first and second kinds. An effort has been made to make Section 5 intelligible to a reader who does not wish to follow the mathematical detail of the earlier Sections. Finally, in Section 6, gaseous mixtures and more complex transitions in pure gases are briefly considered.

1. THE METHOD OF EINSTEIN

If we consider the propagation of sound in a pure nondissociating gas which has a molecular heat capacity at constant volume greater than $(3/2)R$, we may expect with increasing frequency one of two alternative types of behavior. Either the rotational and vibrational energy will be brought into equilibrium by each collision, in which case the gas will not become acoustically opaque until frequencies of the order of magnitude of the collision frequency have been reached, or the adjustment of rotational and vibrational energy may be hindered by some spatial or

energetic property of the colliding molecules, in which case it will lag behind the translational adjustments and the gas will become partially opaque at lower frequencies. It is with the second of these possibilities which we are here concerned. If the internal heat capacity is due to changes between many states, each of these changes may be characterized by a separate rate of transition. The method of Einstein may be adapted to supply a quantitative description of the rates of these transition processes.

If π is the excess pressure in an element of volume of the gas at a distance x from the source, and Δ is similarly the density increment of this element, one may write for the time variations of these quantities

$$\pi = \pi_0 e^{i\varphi} e^{i\omega(t-ax)} \qquad (1.1)$$

and

$$\Delta = \Delta_0 e^{i\omega(t-ax)}, \qquad (1.2)$$

where ω is the frequency of sound in radians, and t refers to time. The velocity and absorption of sound are related to a by the expression

$$a = (1/V - i\beta/\omega) \qquad (1.3)$$

if V is the phase velocity $(2\pi V = \omega\lambda)$ and β the absorption coefficient for the amplitude expressed as a reciprocal distance. The propagation of sound in an absorbing medium is therefore in close analogy to the propagation of light in a medium with a complex refractive index. The angle φ expresses the phase lag between pressure and density increments[10] and characterizes both absorption and dispersion. From the real and imaginary parts of (1.1) and (1.2) and the equation of motion of a plane compressional wave it is found that

$$\cos \varphi = (\pi_0/\Delta_0)(1/V^2 - \beta^2/\omega^2) \qquad (1.4)$$

and

$$\sin \varphi = (\pi_0/\Delta_0)(2\beta/\omega V). \qquad (1.5)$$

Einstein has demonstrated that the quantity π/Δ corresponds to the square of a complex velocity of sound, and from this it follows that

$$\text{r.p. } \pi/\Delta = (\partial P/\partial \rho)_{\text{adiab.}} = V^2\mu \qquad (1.6)$$

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[10] Kneser, second reference under footnote 6, has given an illuminating specific picture of this lag and the irreversible energy change it implies.

and that

$$\text{i.p. } \Delta/\pi = -i2\beta/\omega V = -ih/2\pi V^2, \quad (1.7)$$

when h, in (1.7), designates the absorption coefficient for the intensity expressed as a reciprocal number of wave-lengths. The factor μ in (1.6) is

$$\mu = (1 - h^2/16\pi^2)/(1 + h^2/16\pi^2)^2 \quad (1.8)$$

and may be taken as unity except in the neighborhood of the absorption maximum.

In general there will be absorption only when the dispersion $dV/d\omega$ is appreciable.[8] It is difficult, however, to formulate the relation between the two, since it depends upon the characteristics of π/Δ. It is more convenient, therefore, to compare absorption and velocity, which are more simply related as in (1.4). This may be expressed by combining (1.4) with (1.6) to give

$$(\pi_0/\Delta_0)(1 + h^2/16\pi^2) = V^2. \quad (1.9)$$

The complex velocity of sound and the properties of the gas are related by the *characteristic acoustical equation*. This may be written

$$\pi/\Delta = (P/\rho)(1 - \Delta Pv/P\Delta v) \quad (1.10)$$

if P and ρ refer to pressure and density respectively, and ΔPv and $P\Delta v$ are complex energy increments which vary with time about their respective amplitudes by a factor $e^{i\omega t}$, and which are out of phase in the dispersive region of frequency. The problem of calculating the acoustical behavior of a gas is therefore the problem of evaluating ΔPv and $P\Delta v$ in terms of pressure, frequency, temperature, and quantities descriptive of rate of energy adjustment and heat capacity. This is conveniently effected by means of the equation of state and the equation for adiabatic change in the gas, the equation for adiabatic change being related to frequency by means of a series of reaction equations.

In finding ΔPv the gas will be considered ideal, and effects due to departures from ideal behavior later discussed. For an ideal gas the *displaced*

equation of state is

$$\Delta Pv = R\Delta T, \quad (1.11)$$

where R and v are considered gram molecular quantities, and ΔT refers to a temperature displacement of the translational terms. A relation between ΔT and the displacement of the internal energy is given by the *equation for adiabatic change*, which may be written

$$-P\Delta v = (3/2)R\Delta T + E_1 \sum_k k\Delta n_k$$
$$+ E_2 \sum_l l\Delta n_l + \cdots . \quad (1.12)$$

The first term on the right refers to changes in translational energy, and the subsequent terms express energy changes in sets of rotational and vibrational states corresponding to the frequencies $\nu_1 = E_1/hN_A$, $\nu_2 = E_2/hN_A$, etc., h being Planck's constant and N_A Avogadro's number. The symbols n_k, n_l, etc., refer therefore to fractions of gram molecular weights in the kth and lth, etc., states, and are subject to the conditions $\sum_k n_k = 1$, etc., and $\sum_k \Delta n_k = 0$, etc., owing to the law of the conservation of matter. The actual number of molecules per cubic centimeter in the kth state is Nn_k, if N is the total number of molecules per cubic centimeter. If C_1 is the equilibrium heat capacity due to the first set of states, and ΔT_1 its fictional temperature displacement in the sound wave, $E_1 \sum_k k\Delta n_k = C_1\Delta T_1$ where $\Delta T \geq \Delta T_1 \geq 0$. The calculation of the velocity and absorption of sound in a pure gas of given properties follows from an appropriate development of (1.12) on the basis of a reaction equation, and the subsequent substitution of (1.11) and (1.12) in the characteristic acoustical equation (1.10).

In Sections 2, 3, and 4 of this communication the characteristic acoustical equation of the gas will have the form

$$\frac{\pi}{\Delta} = \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + Rx^2 n_0[(a+ib)/(c+id)]}\right\}, \quad (1.13)$$

where C_∞ is that part of the heat capacity which is independent of frequency in the range considered,

$x = E/RT = h\nu/kT$, and the constants n_0, a, b, c, and d vary with the complexity of the internal energy of the gas. According to (1.6), therefore, the velocity is given by

$$V^2\mu = \frac{P}{\rho}\left\{1 + R\frac{(C_\infty + Rx^2 n_0 a/c) + (C_\infty d^2/c^2 + Rx^2 n_0 bd/c^2)}{(C_\infty + Rx^2 n_0 a/c)^2 + (C_\infty d/c + Rx^2 n_0 b/c)^2}\right\} = \frac{P}{\rho}\gamma_\omega, \tag{1.14}$$

where γ_ω may be called the "apparent heat capacity ratio" at the frequency ω, and the dimensionless absorption coefficient, from (1.7) to the first order of small quantities is .

$$h = 2\pi\left\{\frac{(C_\infty + Rx^2 n_0 a/c)(C_\infty d/c + Rd/c + Rx^2 n_0 b/c) - (C_\infty d/c + Rx^2 n_0 b/c)(C_\infty + R + Rx^2 n_0 a/c)}{(C_\infty + Rx^2 n_0 a/c)(C_\infty + R + Rx^2 n_0 a/c) + (C_\infty d/c + Rx^2 n_0 b/c)(C_\infty d/c + Rd/c + Rx^2 n_0 b/c)}\right\}. \tag{1.15}$$

Suitable constants for substitution in (1.14) and (1.15) will now be evaluated.

2. A Gas with Three Sets of Energy States

The simplest case of practical interest is that in which the dispersive region results from a lag in the adjustment of a single quantum transition, as, for example, the transition from the zero point state to the first excited state of a deformation vibration. To describe this various parts of the energy may be considered as contained in three types of energy states. The states E_I are the translational states. The states E_{II} contain in addition all rotational and vibrational states in their equilibrium distribution with the exception of a single mode of vibration, which is considered to have its zero point energy. E_{III} differs from E_{II} in that the single mode of vibration is considered to be in its first excited state. It is then the gradual dropping out of the transition $E_{II}\rightleftarrows E_{III}$ from the effective heat capacity at high frequencies which produces dispersion and absorption. For the equation for adiabatic change (1.12) may then be written

$$-P\Delta v = (3/2)R\Delta T$$
$$+ (\partial(E_{II} - E_I)/\partial T)_v\Delta T + (E_{III} - E_{II})\Delta n_1 \tag{2.1}$$

or, in more abbreviated form,

$$-P\Delta v = C_\infty\Delta T + E\Delta n_1. \tag{2.2}$$

This case will be discussed with pedantic attention to detail in order to illustrate the method of calculation.

In going from (2.1) to (2.2) a step has been taken which is not permissible without further justification. By including in C_∞, which represents the effective heat capacity of the gas at frequencies so high that $\Delta n_1 = 0$, all the heat

capacity except that due to the $E_{III}\rightleftarrows E_{II}$ transition, two assumptions have been made. The first, which supposes that a terminal velocity corresponding to

$$V_\infty = \{(P/\rho)(1 + R/C_\infty)\}^{\frac{1}{2}}$$

may actually be found can, at present, be justified only by experiment. The second, which supposes that, in case all energy states except one are adjusted at a rate much greater than the frequency, their influence on the acoustical behavior of the single slowly adjusted state is negligible, is justified by the more complicated models which are developed in Sections 3 and 4.[9a]

At mitall frequencies of sound the elasticity of the gas has equilibrium value, and (2.2) it becomes

$$-P\Delta v = C_\infty\Delta T + E(\partial n_1/\partial T)_v\Delta T = C_0\Delta T. \tag{2.3}$$

From Boltzmann's principle $n_1/n_0 = e^{-x}$ and $n_0 = (1 + e^{-x})^{-1}$. Hence, in the three-state gas,

$$C_0 - C_\infty = Rx^2 e^{-x}/(1 + e^{-x})^2. \tag{2.4}$$

It is now necessary to relate Δn_0 and Δn_1 to the acoustical frequency. This relation is given by *the reaction equation*, which may be written

$$-dn_0/dt = f_{01}n_0 - f_{10}n_1 \tag{2.5}$$

if t denotes time and n_1, n_0 the fractions of molecules having the energy of the first excited state and the zero point state respectively. The

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[9a] Bourgin (reference 9, 1932 paper) has demonstrated this explicity in his three-state model by carrying all rapidly adjusted states through the entire calculation with specific finite transition probabilities.

symbols f_{01} and f_{10} are used to denote the probabilities of the transitions $0\rightarrow1$ and $1\rightarrow0$ due to any cause; they are taken, for reasons which will later become apparent, as rates of excitation and de-excitation per molecule per second. Thus f_{10} is the mean number of times per second which a molecule in state 1 leaves state 1 for the state 0; it may be expected to depend on pressure and temperature. At equilibrium $f_{10}n_1 = f_{01}n_0$, and therefore $f_{01} = f_{10}e^{-x}$.

Eq. (2.5) is now displaced from equilibrium by small, finite increments of the independent variables, these increments being written Δn_0, ΔT, and ΔN. N as before is the numerical density and ΔT refers, as always, to the temperature of the translational terms. The three partial differential coefficients resulting from the displacement of the left-hand side will not be explicitly written. Since $\bar{n}_0$, the equilibrium value of n_0, has become $\bar{n}_0 + \Delta n_0$ it is sufficient to write

$$d(\bar{n}_0 + \Delta n_0)/dt = d\Delta n_0/dt = i\omega\Delta n_0, \quad (2.6a)$$

the evaluation of the time derivative following from the fact that Δn_0 varies about its amplitude according to a factor $e^{i\omega t}$. The displacement of the right-hand side involves three sets of partial coefficients. Displacement with respect to n_0 gives, if f_{01} and f_{10} are independent of n_0,

$$\left(\frac{\partial(f_{01}n_0 - f_{10}n_1)}{\partial n_0}\right)_{TN} \Delta n_0 = -(f_{10} + f_{01})\Delta n_1, \quad (2.6b)$$

because in this case $\Delta n_0 + \Delta n_1 = 0$. The displacement with respect to T gives, in close analogy to the van't Hoff isochore,

$$(\partial(f_{01}n_0 - f_{10}n_1)/\partial T)_{n_0 N}\Delta T = (f_{10}n_1 x/T)\Delta T. \quad (2.6c)$$

The result of the change $N = \bar{N} + \Delta N$ may be represented in functional form, or some relation between f_{01}, f_{10} and pressure may be assumed. It is more convenient to take the latter course, and to assume that

$$f_{01}/N = k_{01} \quad \text{and} \quad f_{10}/N = k_{10}, \quad (2.7)$$

where k_{01} and k_{10} correspond to the bimolecular rate constants of the reaction $N_0 + N \rightleftharpoons N_1 + N$. It is supposed, therefore, that the excitation of vibrational energy takes place solely because of a double collision of the first kind, and that its de-excitation is the result solely of a double

collision of the second kind. It is further supposed that any molecule is equally capable of causing these transitions whether or not it is itself excited. This assumption can hardly be in strict accord with fact, and a divergence between the predicted and the experimental variation of the acoustical properties of the gas with pressure must therefore be expected. The interpretation of this discrepancy is touched on in Section 5. On the assumption (2.7) the pressure displacement yields

$$(\partial(f_{01}\Delta n_0 - f_{10}\Delta n_1)/\partial N) \, \tau n_0\Delta N$$
$$= (\Delta N/N)(f_0 n_0 - f_{10}n_1) = 0. \quad (2.6d)$$

The displaced equation follows from (2.6a, b, c and d) and gives the result

$$E\Delta n_1 = Rx^2 n_1\left(\frac{\Delta T}{1 + e^{-x} + i\omega/f_{10}}\right) \quad (2.8)$$

and the constants for substitution in (1.14) and (1.15) are evidently $a = e^{-x}$, $b = 0$, $c = (1 + e^{-x})$, $d = \omega/f_{10}$, $n_0 = (1 + e^{-x})^{-1}$. The velocity of sound of small amplitude as a function of frequency will therefore be given by

$$V^2\mu = \frac{P}{\rho}\left\{1 + R\frac{C_0(f_{10} + f_{01})^2 + C_\infty\omega^2}{C_0^2(f_{10} + f_{01})^2 + C_\infty^2\omega^2}\right\} \quad (2.9)$$

and this expression will also hold for the pressure dependence of the velocity insofar as (2.7) is valid. It is not yet suitable to describe the effect of temperature, since the relation between f_{10} and temperature has not been examined. The absorption of sound is correspondingly

$$h = 2\pi y[(Q^2 - 1)/(1 + Q^2 y^2)] \quad (2.10)$$

to the first order of small quantities if $Q = V_\infty/V_0$ and $y = C_\infty\omega/C_0(f_{10} + f_{01})$. These are essentially the expressions given by Kneser, Bourgin, and several others. Their properties and implications have been widely discussed.[11]

3. A FOUR-STATE GAS

The majority of gases which have been investigated do not conform to (2.9) within 0.1

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[11] In addition to the references already given the papers of Luck, Phys. Rev. **40**, 440 (1932), and of Henry, Proc. Camb. Phil. Soc. **28**, 249 (1932), should be cited, since they deal with aspects of acoustical absorption.

percent. For carbon dioxide, the most popular gas, C_0 at 30°C is 3.435 R cal. deg.$^{-1}$, whereas $C_\infty + 2Rx^2 n_0[e^{-x}/(1+e^{-x})]$ is 3.291 R[12] and $V_{0\text{ calc.}}$ is greater than $V_{0\text{ obs.}}$ by about 0.5 percent. In these cases it is, of course, possible to use (2.9) as an approximation, but the meaning of $f_{01}+f_{10}$ is then obscured. More detailed analysis of π/Δ is needed to make available additional information. This may be exemplified by a model containing four internal energy states, E_I, E_{II} and E_{III} being as before, and E_{IV} being E_{III} plus the energy necessary to raise one gram molecule of the gas from the first to the second excited state of the slowly adjusted vibration.

The equation for adiabatic change is then

$$-P\Delta v = C_\infty \Delta T + E(\Delta n_1 + 2\Delta n_2) \qquad (3.1)$$

if the oscillator which represents the slowly adjusted vibration is harmonic (i.e., $E_{III}-E_{II} = E_{IV}-E_{III}=E$). Two reaction equations are now necessary

$$\left. \begin{aligned} -dn_0/dt &= (f_{01}+f_{02})n_0 - f_{10}n_1 - f_{20}n_2, \\ -dn_1/dt &= (f_{10}+f_{12})n_1 - f_{01}n_0 - f_{21}n_2. \end{aligned} \right\} \quad (3.2)$$

Two assumptions will be made in displacing these from equilibrium. The first, which supposes $f_{01}=Nk_{01}$, $f_{12}=Nk_{12}$, etc., has been discussed at length in Section 2 under (2.7). The second

supposes f_{02} and f_{20} to be much less than the other transition probabilities, and terms containing them consequently to be negligible. In the interpretation of experiment it must be remembered that these assumptions may not conform to fact. The displaced equations, together with the simultaneous equation $\Delta n_0 + \Delta n_1 + \Delta n_2 = 0$, give solutions for Δn_1 and Δn_2 in terms of the exponential factor x and the various transition probabilities. When Δn_1 and Δn_2 are substituted in (3.1) the appropriate form of the characteristic acoustical equation follows at once from (1.10). This has the form of (1.13) above where $n_0 = (1+e^{-x}+e^{-2x})^{-1}$ and

$$\left. \begin{aligned} a &= e^{-x}+4e^{-2x}+e^{-3x}, \\ b &= \omega(e^{-2x}/f_{10}+e^{-x}/f_{21}), \\ c &= 1+e^{-x}+e^{-2x}-\omega^2/f_{10}f_{21}, \\ d &= \omega(1+e^{-x})(1/f_{10}+1/f_{21}). \end{aligned} \right\} \quad (3.3)$$

The velocity and absorption of sound follow from appropriate substitution in (1.14) and (1.15); the resulting equations are so complicated that a glance can hardly suffice to reveal their significance, and it appears therefore purposeless to print them in full. A few of the reductions of the expression for the velocity may, however, be examined with profit. For example, when $\omega \ll f_{10}, f_{21}$

$$V_0^2 = \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + Rx^2 n_0[(e^{-x}+4e^{-2x}+e^{-3x})/(1+e^{-x}+e^{-2x})]}\right\}, \qquad (3.4)$$

which represents the terminal velocity at low frequency. When $\omega \gg f_{10}, f_{21}$

$$V_\infty^2 = (P/\rho)\{1+R/C_\infty\} \qquad (3.5)$$

gives the terminal velocity at the highest frequency for which the model is adapted. This is of course not infinite; the terms in C_∞ are still considered in equilibrium in all parts of the wave. When $f_{21} \ll \omega \ll f_{10}$ an intermediate constant velocity

$$V^2_{f_{21}\doteq 0} = \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + Rx^2 n_0(e^{-x}/(1+e^{-x}))}\right\} \quad (3.6)$$

is reached, and when $f_{10} \ll \omega \ll f_{21}$

$$V^2_{f_{10}\doteq 0} = \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + Rx^2 n_0(e^{-2x}/(1+e^{-x}))}\right\}, \quad (3.7)$$

the alternate intermediate constant velocity, is obtained. A third intermediate constant velocity, due to the complete failure of transitions to and from the 1st state, may of course be imagined, but is considered so unlikely to be realized in practice that it has not been provided for in the four-state model above. It may simply be

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[12] Both these values have been calculated on the basis of fundamental frequencies 667.5, 1285, and 2326 cm^{-1}, as reported by Villars, Chem. Revs. 11, 408 (1932). C_∞ is taken as 2.5085R cal. deg.$^{-1}$ in the second.

evaluated by taking

$$\partial n_2/\partial T = -\partial(n_0 e^{-2x})/\partial T$$

which gives

$$V f_{10} = f_{12} = 0$$

$$= \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + 4Rx_2 n_0(e^{-2x}/(1+e^{-2x}))}\right\}. \quad (3.8)$$

The practical realization of constant velocities corresponding to (3.6), (3.7) and (3.8) does not appear very probable, but the influence of a decided difference between f_{10} and f_{21} may be detected by experiment.
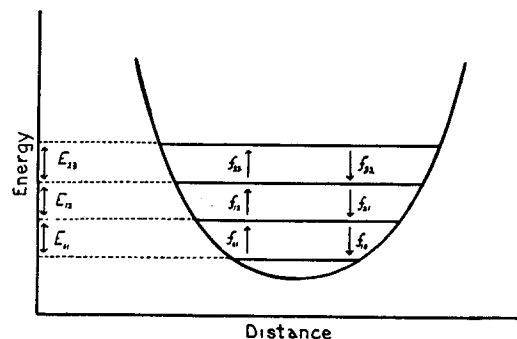

FIG. 1. Diagrammatic representation of the frequency-dependent part of the heat capacity for the five-state model. Transitions involving energy changes greater than $\pm h\nu_0$ have been considered of a low order of probability, and harmonicity of the oscillator has been postulated by setting $E_{01} = E_{12} = E_{23} = h\nu_0$. Where these approximations are permissible the model may be applied to any mode of vibration, whether transverse or longitudinal.

4. A FIVE-STATE GAS

Although the four-state gas model developed in the previous section is adequate to describe the behavior of carbon dioxide at all ordinary temperatures, it cannot be used for gases in which the fundamental vibrational frequency is much lower. It is exactly in these gases, however, that differences in the transition probabilities of the various states may most easily be investigated. It is advisable, therefore, to carry the development of π/Δ one step further, and examine a five-state model. As before the energy states $E_{II} - E_I$ will be considered in equilibrium with the adiabatic cycle at all frequencies. The frequency-variable transitions have been illustrated in Fig. 1, which, with the explanations in the previous sections, gives the model sufficient definition. The development has been carried out exactly as in the previous section with the help of the assumptions that the probabilities are directly proportional to pressure, that all transitions involving an energy change greater than $\pm h\nu$ are so rare as to be negligible, and that the oscillator is harmonic. Three appropriate reaction equations are displaced from equilibrium, and yield, with the equation $\Delta n_0 + \Delta n_1 + \Delta n_2 + \Delta n_3 = 0$

$$\left.\begin{aligned}
\Delta n_0 &= \frac{\Delta n_1 e^x - x n_0 \Delta T/T}{i\omega e^x/f_{10} + 1} \\
\Delta n_1 &= (i\omega/f_{21}+1)\Delta n_2 e^x + (i\omega/f_{21})\Delta n_3 e^x - x n_0 e^{-x}(\Delta T/T) \\
\Delta n_2 &= (i\omega/f_{32}+1)\Delta n_3 e^x - x n_0 e^{-2x}(\Delta T/T)
\end{aligned}\right\}. \quad (4.1)$$

These are solved simultaneously and substituted in the equation for adiabatic change

$$-P\Delta v = C_\infty \Delta T + E(\Delta n_1 + 2\Delta n_2 + 3\Delta n_3) \quad (4.2)$$

to evaluate the constants for substitution in (1.14) and (1.15). These are $n_0 = (1 + e^{-x} + e^{-2x} + e^{-3x})^{-1}$

$$\left.\begin{aligned}
a &= e^{-x} + 4e^{-2x} + 10e^{-3x} + 4e^{-4x} + e^{-5x} - \omega^2(e^{-3x}/f_{10}f_{21} + e^{-2x}/f_{10}f_{32} + e^{-x}/f_{21}f_{32}) \\
b &= \omega[(e^{-x} + 4e^{-2x} + e^{-3x})(e^{-x}/f_{10} + 1/f_{32}) + (e^{-x} + e^{-2x} + e^{-3x} + e^{-4x})/f_{21}] \\
c &= 1 + e^{-x} + e^{-2x} + e^{-3x} - \omega^2(1 + e^{-x})(1/f_{10}f_{21} + 1/f_{10}f_{32} + 1/f_{21}f_{32}) \\
d &= \omega(1 + e^{-x} + e^{-2x})(1/f_{10} + 1/f_{21} + 1/f_{32}) + \omega e^{-x}/f_{21} - \omega^3/f_{10}f_{21}f_{32}
\end{aligned}\right\}. \quad (4.3)$$

Only two of the reductions of the resulting expression for the velocity need be examined. When

$\omega \ll f_{10}, f_{21}, f_{32}$

$$V_0{}^2 = \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + Rx^2[(e^{-x}+4e^{-2x}+10e^{-3x}+4e^{-4x}+e^{-5x})/(1+e^{-x}+e^{-2x}+e^{-3x})^2]}\right\} \tag{4.4}$$

and the low frequency terminal velocity is obtained. The high frequency terminal velocity is identical in form with (3.5). If $f_{32} \ll \omega \ll f_{10}, f_{21}$

$$V^2{}_{f_{32}\doteq 0} = \frac{P}{\rho}\left\{1 + \frac{R}{C_\infty + Rx^2 n_0[(e^{-x}+4e^{-2x}+e^{-3x})/(1+e^{-x}+e^{-2x})]}\right\}, \tag{4.5}$$

which represents a wholly different situation from (3.4) although the two expressions bear a strong superficial resemblance to each other. The other intermediate constant velocities are easily obtained by suitable modifications of the constants given in (4.3). They will not be printed.

5. The Behavior of a Gas with Many Independently Adjusted Energy States

Before proceeding further it will be well to discuss the experimental bearing of what has already been written. This will be undertaken from two viewpoints: first, to discover what fresh information has become available and second, to find reasonably satisfactory approximations which obviate, at any rate during the course of an experimental research, the necessity of calculating from the cumbersome equations resulting from (1.14) and (1.15) with appropriate constants. Since a relation between absorption and velocity is already at hand in (1.19), the velocity of sound will alone be given attention below.

Figs. 2 and 3 illustrate the pressure and frequency dependence of the models developed in Sections 3 and 4, respectively. In each case the ordinates are expressed as the "apparent heat capacity ratio" which is an abbreviation for the apparent ratio of heat capacity at constant pressure to that at constant volume at a particular value of ω. The abscissae scale corresponding values of ω/f_{01} which have, however, been expressed as ω/Nk_{01} since the foregoing exposition is committed to the formal equality of these quantities. This method of plotting describes, therefore, with equal suitability, the behavior of the models at constant frequency and variable pressure, or at constant pressure and variable frequency. Fig. 1 has been obtained by calculating numerically, from the constants (3.3) the cases $f_{10}=f_{21}$, $10f_{10}=f_{21}$, and $100f_{10}=f_{21}$ in a gas for which the exponent $h\nu_0/kT$ is 3.00.

Fig. 3 gives numerical values for the effective heat capacity ratio according to (4.3) in a gas where $h\nu_0/kT$ is 2.00 for the cases $f_{10}=f_{21}=f_{32}$, $100f_{10}=10f_{21}=f_{32}$ and $10^4 f_{10}=10^2 f_{21}=f_{32}$. To avoid ambiguity the slowly adjusted vibration has been considered to have an *a priori* probability of unity, although this will not be the case when
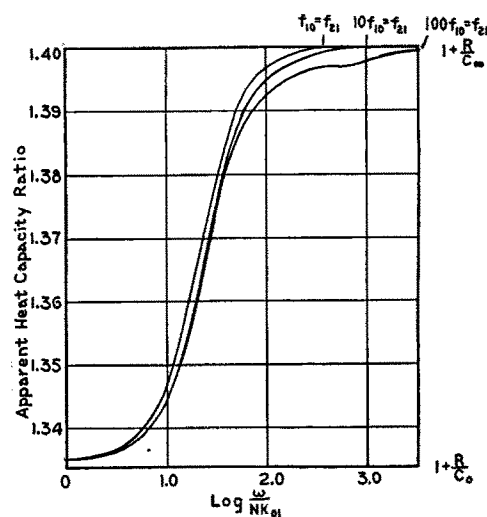

Fig. 2. The acoustical behavior of a model in which the frequency-dependent part of the heat capacity is adequately described by the $0 \rightleftharpoons 1$ and $1 \rightleftharpoons 2$ transitions. The ordinates represent the apparent values of C_p/C_v and consequently indicate also the variations of V^2. The abscissae give corresponding values for log ω/f_{01}, and serve therefore to describe the behavior of the model at constant pressure and variable frequency or, conversely, at constant frequency and variable pressure if the assumption $f_{01}=Nk_{01}$, which has been discussed in the text, is valid. The value of $h\nu_0/kT$ has been chosen as 3.0 for the purpose of plotting, and it has been assumed that the frequency-dependent part of the heat capacity is due to a single valence vibration, the contribution of all other vibrations being negligible.
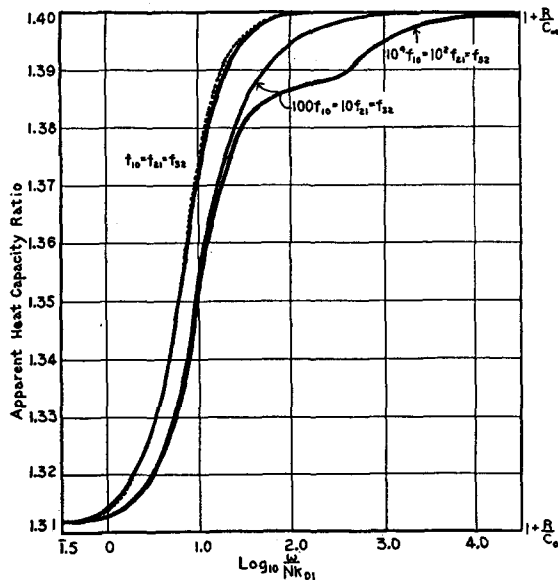
FIG. 3. The acoustical behavior of a model in which the frequency-dependent part of the heat capacity is adequately described by the $0 \rightleftharpoons 1$, $1 \rightleftharpoons 2$, and $2 \rightleftharpoons 3$ transitions of a valence vibration. In the case plotted $h\nu_0/kT$ has been given a value of 2. (This is suitable for comparison with carbon bisulfide at ordinary temperatures if the value of $C_0 - C_\infty$ is doubled throughout.) The graph indicates that differences in the probabilities f_{01} and f_{12} of one order of magnitude should be detectable by measurements at constant frequency and variable pressure or at constant pressure and variable frequency.

the dispersive region is caused by the failure at high frequencies of a degenerate vibration. C_∞ has been uniformly assigned the arbitrary value $2.5R$.

The dependence of the velocity of sound on frequency at constant pressure and temperature

Several conclusions follow from the consideration of Figs. 2 and 3.

I. If the transitions $1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 2 \cdots$ have the same probabilities, the square of the measured velocity of sound plotted as a function of the logarithm of the frequency will conform within experimental accuracy to a symmetrical S-shaped curve. An arbitrary number of energy states cannot of course be treated by the method used above, but there appears to be no danger in making this statement general.

II. Any detectable deviation from a symmetrical S-shaped curve may be attributed to a difference in the transition probabilities f_{10}, f_{21} $\cdots$. Such a difference has been predicted by

Zener,[13] and its direct experimental demonstration should not be difficult by this means. If the higher energy states are more rapidly adjusted than the lower, the high frequency part of the S-curve is flattened; if they are less rapidly adjusted than the lower, the curve is flattened in its low frequency region.

III. If the difference between the rates of adjustment of any two states is greater than about two orders of magnitude, the deformed S-curve becomes irregular, and two or more maxima appear in the variation of the absorption coefficient with frequency. The appearance and separation of these maxima are conditioned by the relative importance of the two energy states in the heat capacity.

IV. If the rate of adjustment of any state is greater than the others by about three orders of magnitude, its contribution to the heat capacity may, from the point of view of experiment, legitimately be incorporated in C_∞ and not assigned a specific rate of adjustment. This is the justification for giving $\partial(E_{II} - E_I)/\partial T$ its equilibrium value throughout the dispersive region in the proceeding sections.

V. If the transitions $2 \rightarrow 0$, $3 \rightarrow 0$, $3 \rightarrow 1$, etc., involving energy changes of two or more quanta are not less frequent than those $1 \rightarrow 0$, $2 \rightarrow 1$, etc., by about two orders of magnitude the low frequency portion of the S-curve may be deformed, and the only legitimate remedy is to describe the situation by a model containing a greater number of transitions. Since, however, the maximum possible contribution to the heat capacity of these transitions is small, their disturbing effect will probably escape experimental detection. The uncongenial task of still further complicating the calculations in this way will be postponed in the fervent hope that experiment may not demand it.

The dependence of the velocity of sound on pressure at constant frequency and temperature

A purely formal consideration of the relationships given in Sections 2, 3 and 4 leads to the conclusion that the increase of the frequency by a certain factor should be exactly balanced by

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[13] Zener, Phys. Rev. **37**, 556 (1931); **38**, 277 (1931).

the decrease of the pressure by the same factor. All the conclusions just stated for the dependence of the velocity of sound on frequency therefore appear to hold in the inverse sense for its dependence on pressure. The correspondence between frequency and pressure is due, however, to the simplifying assumptions and approximations which have been used. In practice the conclusions reached from considering frequency may be applied to pressure only with the following important qualifications.

I. In a real gas the heat capacity at constant volume is not independent of pressure, and pressure and numerical density are not exactly proportional. Although it is always possible to eliminate P/ρ by dividing V_ω by V_0 at any given pressure or frequency, errors due to these causes may become experimentally manifest at high pressures.

II. The assumption that f_{10}, f_{21}, etc., vary directly in proportion to the pressure may be invalid on several grounds. If, for some reason which is not at present clear, triple collisions are more effective than double collisions in adjusting the internal energy $f_{10} \neq N k_{10}$. The mathematical treatment will not seriously be disturbed by this since (2.6d) will vanish for any reasonable functional relationship between f_{10}, etc., and N. A diminution of the pressure will, however, have more effect on the velocity and absorption than a corresponding increase of frequency. If the advantage of triple collisions is marked, this effect should be very strikingly manifest. If only slight, it may escape experimental detection because of the relative infrequency of triple collisions. A correction, if necessary, may be applied to the high-pressure region by expressing each f as the sum of two probabilities, one of which is proportional to the number of double collisions, and one to the number of triple collisions.

III. Again, it is possible that a molecule which is vibrating has an advantage over one which is not vibrating in bringing about energy transformations. Since no example of this is yet known, we need not concern ourselves with a mechanism for it, but merely with its effect on the acoustical behavior of the gas. A more complete statement of the assumption $f_{10} = k_{10} N$ reads $f_{10} = k_{10} N n_0 + k'_{10} N n_1 + k''_{10} N n_2 + \cdots$ where $k_{10} \equiv k'_{10} \equiv k''_{10}$

$\cdots$. If this identity is for any reason invalid, $\partial f_{10}/\partial n_1$ no longer vanishes, and (2.6b) is incorrect. A variation in n_1 may, in a perfect gas, be brought about only by changing the temperature, and this introduces a set of approximations which have not yet been considered. Both for this reason, and because n_1, n_2, etc., are usually small fractions, it seems unlikely that any inequality of k_{10}, k'_{10}, etc., may at present be demonstrated by experiment in pure gases.

The presence of another mode of vibration which, although excited to an appreciable extent, remains in equilibrium with the sound wave throughout the dispersive region, may, of course, cause exactly similar effects. There is some reason to believe, however, that resonance between the two vibrational modes must be close in order for collisions of this type to be effective.

IV. When the dispersive region is produced by the failure of transitions between vibrational states which are optically active, the excited molecules may radiate their energy between collisions. The effect of this will be to cause the mean lifetime of the molecules to increase less rapidly with decreasing pressure than is indicated by the purely kinetic assumption $f_{10} = N k_{10}$. This possibility was first envisaged by Bourgin,[14] who has pointed out that the effect becomes important at low pressures. It has recently been stressed, especially in connection with acoustical absorption, by Kneser.[15] It is not intended to extend the scope of this study to cover radiation effects. It will therefore merely be pointed out that if the relaxation time is written as $\vartheta = 1/[N(k_{10}+k_{01})+1/\tau]$ where τ is a temperature and pressure-independent quantity expressing the radiation lifetime, a rough estimate of τ may be obtained from measurements of the velocity of sound as a function of pressure in the dispersive region. Since the temperature and pressure derivatives of τ vanish, its introduction in this way does not disturb the exposition given in Sections 2, 3, and 4. The radiation lifetimes of molecules are probably so great that it is not to be expected that radiation effects will become appreciable at pressures which are at present suitable for the measurement of the

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[14] Bourgin, reference 9, 1928 papers.
[15] Kneser, reference 6, especially 1933 paper.

velocity of sound. It should be noted, however, that acoustical measurements at very low pressures may ultimately become an effective means of investigating radiation lifetimes.

The dependence of the velocity of sound on temperature at constant frequency and numerical density

The numerical density of a gas increases with decreasing temperature at constant pressure, and it will therefore be convenient to discuss the variation of the velocity of sound with temperature at constant numerical density rather than at constant pressure. Some assumption must now be made concerning the temperature dependence of C_∞ and the f probabilities.

C_∞ will depend on temperature if some of the non-lagging degrees of freedom are not fully excited.[16] In this case $C_\infty = \frac{3}{2}R + p_1 R x_1^2 e^{-x_1}/(1 - e^{-x_1})^2 + \cdots$ if p_1, etc., are the *a priori* probabilities of the degrees of freedom, and x_1, etc., abbreviations for $h\nu_1/kT$, etc.

In discussing the temperature coefficient of the f probabilities only those of the type f_{10}, f_{21}, etc., will be considered, since the relation between these and the f_{01}, f_{12}, etc., probabilities is already known. The simplest assumption is the C_∞ and f_{10}, etc., are independent of temperature. In this case the three, four, and five-energy state models behave similarly: the S-curve is merely compressed as the temperature is lowered. This is roughly described by stating that $(V_\omega^2 - V_\infty^2)/(V_0^2 - V_\infty^2)$ is independent of temperature for a given value of ω. Fig. 4 diagrammatically illustrates this situation.

Such measurements as exist on the temperature dependence[17] of the velocity of sound in the dispersive region indicate that the transition probabilities in several gases are by no means independent of temperature.

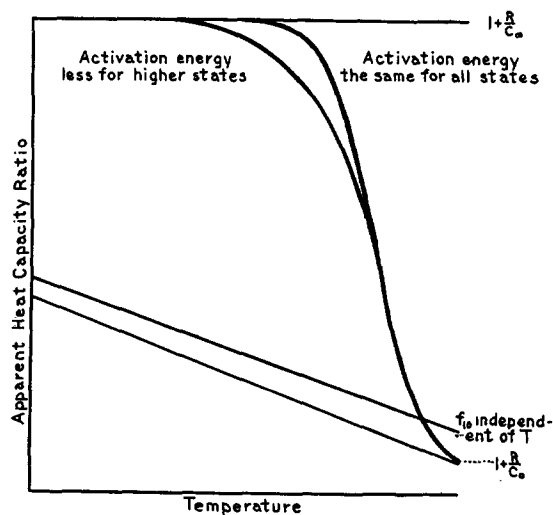To account for this a quantity called the

FIG. 4. Diagrammatic representation of various possibilities for the temperature dependence of the velocity of sound at constant frequency and constant numerical density. In practice f_{10} will depend on the number of collisions per unit time, and the straight line "f_{10} independent of T" is therefore an idealization. Relatively small differences between the activation energies of collision of two states should be experimentally manifest by measuring the temperature coefficient of the velocity at the low frequency and high frequency limits of the dispersive region.

activation energy of collision has already been suggested.[17] This bears an analogy to the activation energy of a chemical reaction in that

$$\frac{\partial f_{10}}{\partial T} = \frac{f_{10}A_{10}}{RT^2}, \quad \frac{\partial f_{01}}{\partial T} = \frac{f_{01}(A_{10}+E)}{RT^2}, \quad \text{etc.}$$

and represents the "threshold kinetic energy" necessary to effect the transitions $1 \rightarrow 0$, etc. Such an impediment to the transference of vibrational to kinetic energy might have several causes. For example Heil,[18] following Oldenberg,[19] has suggested that the dynamics of collisions of the second kind demand that in some cases only molecules of particularly high kinetic energy should be effective. On the other hand, a potential energy barrier of the same general type that found in chemical reactions might be imagined.[17, 20] This possibility will be discussed at slightly greater length in order to make clear

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[16] Kneser and Zühlke, Zeits. f. Physik **77**, 649 (1932), have shown in nitrous oxide that the deformation vibration fails at frequencies lower than the other vibrations. Similar evidence concerning carbon disulphide has recently been obtained in the writers' laboratory in Princeton by Mr. J. A. Reid.

[17] Apparently the measurements of Richards and Reid, Nature **130**, 739 (1932), are the only ones reported present which deal directly with this question.

[18] Heil, Zeits. f. Physik **14**, 31 (1932).

[19] Oldenberg, Phys. Rev. **37**, 194 (1931).

[20] Franck and Eucken, Zeits. f. physik. Chemie **A20**, 460 (1933).

certain characteristics which the activation energy of collision may conceivably possess.

If two molecules approach one another with a given relative kinetic energy they influence increasingly each other's chemical binding energies as they come increasingly into each other's repulsive fields. This process will, with a certain probability, induce a change in the vibrational states of the colliding molecules. A simple though approximate method of calculating the transition probability has been given by Kallmann and London.[21] It may be assumed, in analogy to their mechanism, that the process of approach of the two molecules occupies an extremely short period of time, and that during this time the vibrational wave function remains unchanged. This means that, owing to the mutual "softening" of the chemical bonds,[21a] there is a certain probability that a change will occur in the vibrational quantum numbers of one or both of the colliding molecules. The process of separation is, conversely, considered to be very slow, so that no further change of the vibrational quantum numbers occurs; this must be assumed in order to have a nonvanishing transition probability, since in a rapid separation the wave function would again remain unchanged, and the vibrational quantum numbers would revert to their original values.

During the second, or adiabatic, process the hardening of the bonds as the molecules separate will effect an increase of the vibrational energy. If ν represents the frequency of the original bond, and ν' that of the softened bond, the initial vibrational energy may be increased by a factor, ν/ν'. For a molecule originally in the nth state this excess of energy, which is supplied at the expense of the relative translational energy, will amount to $(\nu/\nu')(n+1/2)h\nu - (n+1/2)h\nu$, and the probability of an excitation will be roughly in proportion to this divided by $h\nu$, or to $(\nu-\nu')/\nu(n+1/2)$. This quantity increases rapidly with increasing values of n, and is three times larger for the second than for the first vibrational state. Thus

when n is small $(\nu-\nu')/\nu$ must be relatively larger, and a greater softening of the bond is necessary to effect an increase of vibrational energy. This can be brought about only by closer approach of the molecules, and consequently by collisions involving greater relative kinetic energies. The difference will be experimentally manifest by larger activation energies of collision for the excitation of the lower than of the higher quantum states.

While the mechanism described above is incorrect in that the rapidity of approach and separation must, in actuality, be of the same order of magnitude, it is believed to represent a plausible picture for the expected relationship $A_{10} > A_{21} > A_{32} \ldots$. It is hoped that a more satisfactory description of energy transitions during collision of the first and second kinds may be obtained from a quite different method of approach, which cannot here be included.

It is not proposed, however, to introduce the activation energy of collision on deductive grounds, but to use it as a purely empirical quantity calculable from the temperature coefficients of f_{10}, f_{21}, etc., according to the expressions derived from (1.14) and (1.15) in appropriate cases. Any reasoning from analogy with the chemical activation energy will be suppressed, since there is at present no convincing reason for believing the activation energy of collision to be independent of temperature over any considerable range. Furthermore, it is not at present possible to predict its order of magnitude. It has been introduced only to facilitate the description of the temperature coefficient of the velocity in terms of experimentally determined quantities, and to permit a rough kinetic analysis of the probabilities f_{10}, f_{21}, etc.

Before proceeding further it must be pointed out that the existence of an activation energy of collision introduces a new approximation into the treatment of the previous sections. If the molecules on the high energy side of the Maxwell-Boltzmann distribution lose translational energy to vibrational energy on every collision, the effective pressure of the gas must also vary somewhat with frequency in the dispersive region. It does not appear possible at present to compute the extent of this approximation, but it is believed to be of small importance.

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[21] Kallmann and London, Zeits. f. physik. Chemie **B2**, 207 (1929).

[21a] The "softening" of the chemical bonds as a forerunner of chemical decomposition has been studied, in connection with Raman spectra, by Cremer and Polanyi, Zeits. f. physik. Chemie, Bodenstein-Festband, 771 (1931).

The effect of an activation energy of collision on the dispersive behavior of the gas is clear. If f_{10}, f_{21}, etc., all have equal activation energies, lowering the temperature will correspond to increasing the frequency, and the gas may be made to pass through its dispersive region by means of temperature changes alone. This case has been diagrammatically represented in Fig. 4; the S-curve is slightly deformed by the variation of C_0 with temperature. The greater the activation energy the more rapidly will the gas pass through its dispersive region as the temperature is lowered. If the activation energies are different for f_{10}, f_{21}, etc., the S-curve will be more greatly deformed. Since it seems probable, on the argument given above, that $A_{10} > A_{21}$, etc., this case has also been diagrammatically represented in Fig. 4. The extreme upper and lower temperature of the dispersive region will in this case show different activation energies of collision, which may be interpreted by means of a gas model containing a suitable number of energy states.

The kinetic analysis of transition probabilities

All modern writers on the dispersion and absorption of sound have used a kinetic mechanism as the basis for their interpretation.[22] If experiment has established the magnitude of the activation energy of collision and the essential importance of double collisions in the excitation process, a little further information may be obtained by subjecting the transition probabilities to a rough kinetic analysis.[17] The results so obtained must not, however, be considered significant in any exact quantitative sense.

The number of double collisions suffered by the molecules in the 0 state per cubic centimeter per second is approximately

$$Z_0 = 4N^2 n_0 \sigma^2 (\pi RT/M)^{\frac{1}{2}}, \qquad (5.1)$$

where N is the total number cc^{-1} and n_0 the fraction of these in the 0 state as before, M is the molecular weight, and σ the distance of nearest approach of the molecules in a double

collision. On the assumption that σ is unaltered by the changes of state $0 \to 1$, $0 \to 2$, etc., similar expressions for Z_1, Z_2, etc., follow. Carrying through the previous assumption that either steric or energetic properties of the molecules may hinder the transformation of kinetic into vibrational energy, the number of collisions cc^{-1} sec.$^{-1}$ which are effective in removing a molecule from the 0 to the 1 vibrational state may be written.

$$z_0 = 4N_2 n_0 \xi_{01} \sigma^2 (\pi RT/M)^{\frac{1}{2}} e^{-A_{01}/RT}, \qquad (5.2)$$

where $2\pi\xi_{01}\sigma^2$ is a steric factor not strongly dependent on temperature, which may be termed the "effective cross section" of the molecule for the transition $0 \to 1$. Since the f probabilities are expressed per molecule per second it is apparent that to find f_{01} z_0 must be divided by Nn_0, the number of molecules in the 0 state cc^{-1}. Thus

$$f_{01} = (4N\sigma^2(\pi RT/M)^{\frac{1}{2}})\xi_{01}e^{-(A_{10}+E)/RT} \qquad (5.3)$$

and

$$f_{10} = (4N\sigma^2(\pi RT/M)^{\frac{1}{2}})\xi_{10}e^{-A_{10}/RT}, \qquad (5.4)$$

from which the equality of the effective cross sections in the two directions is immediately deducible from $f_{01}/f_{10} = e^{-x}$. Similar relations between any pair of transition probabilities $f_{n,\,n+1}f_{n+1,\,n}$ may similarly be written. There is no reason at present for supposing the various ξ values to be equal for different states.

From the comparison of $2\pi\sigma^2\xi_{01}$ with the ordinary kinetic cross section deduced from viscosity, effusion, and the like, it is possible that interesting information concerning the spatial characteristics of the excitation process may be deduced. For example if a triatomic colinear molecule is visualized by the naïf model of three balls connected by springs, a "head on" collision of another molecule with either of the end atoms must be far less effective in exciting the deformation vibration than a "broadside" collision of another molecule with the center atom. The effective solid angle for collisions may in this case be small, and the ordinary cross section far greater than that indicated by acoustical measurements.[23]

It should be noted that if the exponential

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[22] Apparently Jeans (*Dynamical Theory of Gases*, Cambridge (1904)), was the first to take this standpoint. Einstein, Herzfeld and Rice, Bourgin, and others have suggested or stressed a kinetic mechanism.

[23] Heil, reference 18, has shown this from Kneser's measurements on carbon dioxide.

factor in (5.4) is near to unity the effective cross section must be expressed with greater circumspection than has here been considered necessary, since in this case it may dominate the temperature coefficient of the dispersion. The probabilities f_{10}, etc., must also be expected to diminish slightly with temperature owing to the decreased frequency of collisions.

Approximations suitable for orientation in experimental investigations

Since calculation from the four and five-state modifications of (1.14) and (1.15) is a laborious and uncongenial process, two approximations are here given which it is hoped will be useful in orienting the experimenter during the course of his measurements. They are in certain cases also suitable for the final expression of measurements.

To describe the frequency and pressure dependence of the velocity the expression

$$V^2\mu = \frac{P}{\rho}\left\{1+\frac{RC_0+RC_\infty\omega^2\vartheta_N^2}{C_0^2+C_\infty^2\omega^2\vartheta_N^2}\right\}, \quad (5.5)$$

where $\vartheta_N = (e^x+1)/(e^x-1)^2 f_{01}$, is very nearly identical in its behavior to that of the multistate models of Sections 3 and 4 when $f_{10}=f_{21}=f_{32}$. The correspondence with the four state model is so close that no difference is apparent in Fig. 2. The correspondence with the five state model is within all reasonable experimental limits, as the dotted line in Fig. 3 shows. Any experimentally detectable deviation from (5.5) may therefore be attributed to inequality of f_{10}, f_{21}, etc., if the frequency dependence of the velocity is in question. Conversely if f_{10}, f_{21}, etc., have been proved identical by varying the frequency at constant pressure and temperature, deviation from (5.5) may be attributed to radiation or triple collision effects if the pressure dependence of the velocity is receiving attention.

It has been proposed to study the temperature coefficient of the velocity in the dispersive region merely to determine the activation energy of collision for each of the various excitation processes. Since this is given by f_{10}/f'_{10}, etc., corresponding to T and T', an error in the absolute magnitude of f_{10}, etc., is of no importance. It is somewhat better for the determination of the activation energy of collision to use the approximation

$$V^2\mu = \frac{P}{\rho}\left\{1+\frac{RC_0+RC_\infty\omega^2\vartheta_T^2}{C_0^2+C_\infty^2\omega^2\vartheta_T^2}\right\}, \quad (5.6)$$

where $\vartheta_T = 1/f_{10}(1+e^{-x})$ rather than the approximation (5.5). The values of f_{10} so obtained may be noticeably in error, but this will not affect the calculated activation energy. If A_{10} is different from A_{21}, etc., the low and high frequency parts of the S-curve will show different temperature dependence, as illustrated by Fig. 4. The exact significance of the difference can be demonstrated only by a more profound analysis, but its existence may conveniently be demonstrated by (5.6).

Both (5.5) and (5.6) assume a knowledge of the energy levels of the molecule, since they require the value of e^x. Cases may occur where these are not obtainable. A rough analysis may then be made by supposing $C_0 - C_\infty$[24] to be due to the failure of a single vibrational transition involving a suitable quantum jump. This will, of course, lead to more or less erroneous f values, but will give a variation of ϑ_T with temperature which is approximately correct.

6. A Few Further Cases. Gaseous Mixtures

It is believed that the suggestions given in the previous sections are sufficient to interpret the acoustical behavior of all pure gases which have at present been examined experimentally. They by no means suffice, however, to cover all possible cases of interest. These are, indeed, so numerous and diverse that the labor and space required to examine them individually are prohibitive. Since the description of a system of any necessary complexity by the method of Einstein or of Bourgin is a matter of labor rather than of ingenuity, more complicated cases may reasonably be postponed until required by experiment. The purpose of this section is only to give a superficial survey of further territory.

The simultaneous failure of two modes of vibration

Kneser's contention that in gases in which the deformation vibration is excited it is this vibra-

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[24] This must in any case be known in order to identify the energy transitions which are absent at high frequencies.

tion alone which causes the first dispersive region[25] appears to be justified in all cases which have at present been reported. It has nevertheless been noted that chlorine and oxygen, which can have only longitudinal vibrations, show dispersion of sound in the region of frequency which is at present accessible to experiment, and the simultaneous failure of two vibrational modes in the acoustical cycle must therefore be considered as possible. If the excitation and de-excitation of the two modes is due only to the relative kinetic energy of the two molecules on collision, the behavior of the gas will be a composite of two examples of the type already discussed. An approximate description is obtained by writing for the characteristic acoustical equation

$$\frac{\pi}{\Delta} = \frac{P}{\rho}\left\{1 + \frac{R(1+i\omega\vartheta_1)(1+i\omega\vartheta_2)}{C_\infty(1+i\omega\vartheta_1)(1+i\omega\vartheta_2) + C_1(1+i\omega\vartheta_2) + C_2(1+i\omega\vartheta_1)}\right\}, \qquad (6.1)$$

in which, of course, $C_0 = C_\infty + C_1 + C_2$ and ϑ_1 and ϑ_2 are the approximate relaxation times of the vibrational modes k and l, respectively. Serviceable if somewhat inexact expressions for velocity and absorption follow from (6.1) by (1.6) and (1.7). The absorption will show maxima at two frequencies if ϑ_k and ϑ_l differ by about two orders of magnitude.

A more interesting case is provided if vibrational resonance phenomena increase the probability of the exchange of energy between the two modes of vibration. Such a possibility has already been touched on in Section 5, paragraph III of the discussion dealing with the variation of the velocity of sound with pressure. Each transition may then be brought about by one of several means, and it will in general be the most effective of these which determines the position of the dispersive region. The probability f_{01} will, for example, be the sum of the number of times per second which a molecule leaves the 0 state for the first state due to each of the various types of collisions. It is clear that unless a considerable fraction of the molecules are excited the number of transitions per second due to collisions with vibrating molecules will escape detection. It is also clear that, since the rate of transition due to each type of collision cannot be measured separately, a large number of extremely accurate measurements at different temperatures and pressures must be made in order to separate one from the other. It is therefore more likely that information of this type will be obtained from the study of gaseous mixtures than from pure gases.

[25] Kneser, reference 6, 1933 paper.

The behavior of a dissociating gas in which the heat capacity may vary with frequency has been treated at great length in Parts I and Ia of this series. It is perhaps worthy of note that if the conclusions stated above are justified this treatment is adequate for all present purposes.

Binary gaseous mixtures

The discussion of the previous paragraphs immediately suggests a parallel treatment for gaseous mixtures. This branch of acoustical theory has already been comprehensively developed by Bourgin and nothing of importance need here be added to what he has said. The following remarks are primarily to be interpreted as a translation of Bourgin's work into the language of Einstein's theory. The analysis of the transition probabilities is, however, somewhat more specific, and consequently more vulnerable than that which Bourgin has provided, although it is believed to be fully in accord with his intentions.

The simplest dispersive binary gaseous mixture consists of a dispersive gas A and a nondispersive gas B. The heat capacity in equilibrium of gas A is C_{0A} mole^{-1} deg.$^{-1}$, and of this a part $C_{0A} - C_{\infty A}$ is dependent on frequency. The heat capacity of B is C_{0B} at all frequencies which are experimentally considered. The numerical density of A is mN and of $B(1-m)N$. The effective heat capacity at very low frequencies of sound will then be $C_0 = C_{0A}m + C_{0B}(1-m)$ and at high frequencies will be $C_\infty = C_{\infty A}m + C_{0B}(1-m)$. It will probably be sufficient to describe the acoustical behavior of A by a three-state approximation, particularly if measurements are compared at a single frequency in the dispersive region. In this

case the characteristic acoustical equation of the mixture is

$$\frac{\pi}{\Delta} = \frac{P}{\rho_A m + \rho_B(1-m)}\left\{1 + \frac{R(1+i\omega\vartheta)}{C_\infty(1+i\omega\vartheta) + (C_{0A} - C_{\infty A})m}\right\} \qquad (6.2)$$

and expressions for the velocity and absorption follow from (1.6) and (1.7). P in (6.2) is of course the sum of the partial pressures of A and B. The relaxation time ϑ is now, however, a more complicated quantity; collisions of an A molecule with another of the same species or with a B molecule may produce energy transitions, and it is the more effective of these encounters which will dominate the relaxation-time. This may be expressed by writing, for a pressure great enough to exclude radiation effects,

$$\vartheta \cong \text{const.}/(f_{AA} + f_{AB})(1 + e^{-x}), \qquad (6.3)$$

where f_{AA} and f_{AB} are the probabilities per molecule per second of removing vibrational energy from an excited state by collisions of the type AA and AB, respectively. The constant in (6.3) may be taken as unity without losing the significance of the measurements; it will become larger than this if $C_{0A} - C_{\infty A}$ is great. The values of f_{AA} are obtained from measurements on pure A at various temperatures and partial pressures. In this way the activation energy of collision and effective cross section for collisions of the type AA may be evaluated by means of (5.3). Measurement at a certain temperature, frequency, and composition determines the value of ϑ in the binary mixture. The value of f_{AA} at a corresponding partial pressure of pure A is then substituted in (6.3) and f_{AB} is obtained. Since, roughly

$$f_{AB} = 4N(1-m)\sigma_{AB}{}^2\xi_{AB}(\pi RT(M_A + M_B)/M_A M_B)^{\frac{1}{2}}e^{-A_{AB}/RT}, \qquad (6.4)$$

the temperature variation of f_{AB} will permit a comparison of the steric and energetic effectiveness of collisions of the types AA and AB.

The next simplest binary mixture consists of two gases A and B each of which has a dispersive region in the frequency range under observation. If direct transmission of energy from the vibrations of A to those of B is not possible, the characteristic acoustical equation of this mixture will be given by (6.1) if $P = P_A m + P_B(1-m)$,

$$C_1 = (C_{0A} - C_{\infty A})m, \quad C_2 = (C_{0B} - C_{\infty B})(1-m),$$

$$\vartheta_1 = \text{const.}_A/(f_{AA} + f_{AB})(1 + e^{-x})$$

and $\vartheta_1 = \text{const.}_B/(f_{BB} + f_{AA})(1 + e^{-x_B})$ are substituted. In view of what has been said in connection with (6.1) and (6.2) this requires no further discussion.

It should be pointed out, however, that this case provides the best means of investigating advantages due to vibrational resonance effects in collisions between unlike molecules. The probabilities f_{AA} and f_{BB} may be separately determined for the two pure components, and the analysis of measurements on such a mixture will therefore be at a great advantage over

similar measurements in pure gases. By suitably varying the number of molecules in the excited states of the two molecular species with temperature, there appears to be a reasonable chance that significant information concerning vibrational resonance may be obtainable.

The behavior of a gas on illumination

If a gas is illuminated by light of wave-length suitable to raise it to a state of electronic excitation, the velocity of sound may change. The vibrational levels in the excited state will be, of course, quite different from those in the normal state. On radiating the gas may be expected to drop back to those vibrational levels in the normal state which disturb the relative separation of the nuclei as little as possible, in accord with the Franck-Condon principle. These will in general be of higher energy than those excited by collision. An alteration of the heat capacity and a change in the velocity of sound may therefore be expected. The situation so created is, of course, exceedingly complicated, and does not encourage general treatment. The number of molecules raised to the electronic state will also be only a very small fraction of

the total since the absorption coefficient for light is customarily small in gases. Nevertheless it may be possible to find a system which shows the effect of illumination to a marked extent with strong light sources and, in addition, possesses a sufficiently simple energy structure to permit its quantitative study without prohibitive labor. The possibility is mentioned here since experiments which are open to this interpretation have already been reported in the nondispersive region of several gases.[26] The study of a dispersive gas with a high optical absorption coefficient such as bromine might, in the dispersive region, yield valuable results if the optical conditions were quantitatively controlled.

[26] See for example, Kupper, Ann. d. Physik 43, 905 (1912); Trautz, Zeits. f. Elektrochemie 18, 513, 651 (1912).

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It is hoped to make the next two parts of this series a detailed account of the experimental investigations on carbon dioxide, carbon disulphide, and binary mixtures of ethylene with other gases which have already been partially reported.[17]