NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1268

ISENTROPIC PHASE CHANGES IN DISSOCIATING GASES AND THE METHOD OF SOUND DISPERSION FOR THE INVESTIGATION OF HOMOGENEOUS GAS REACTIONS WITH VERY HIGH SPEED

By Gerhard Damköhler

Translation of "Isentropische Zustandsänderungen in Dissoziierenden Gasen und die Methode der Schalldispersion zur Untersuchung sehr Schneller Homogener Gasreaktionen."
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I. INTRODUCTION AND STATEMENT OF THE PROBLEM

In seeking to investigate kinetically those homogeneous gas reactions which proceed at very high speed or at very high temperatures we are frequently led to the field of isentropic changes of state in dissociating gases, a field which as yet has received no detailed theoretical treatment. This is the more remarkable since more than 30 years ago W. Nernst proposed the investigation of very high speed reactions kinetically through measurement of the speed of sound at various frequencies, that is; a method whereby isentropic or approximately isentropic changes of state are impressed on the gas and it is observed whether the reactions corresponding to the equilibrium state can or cannot follow the sound frequency used, the velocity of the sound being different in the two cases[1]. This sound dispersion method, in which moreover instead of the sound velocity the sound absorption can likewise be measured as a function of the frequency, has subsequently often been used, particularly after it was shown by H. O. Kneser[2] that also the transition from the energy of translation into internal molecular energy (primarily energy of vibration) can be kinetically investigated by sound tests of this kind. However it was still impossible to apply the sound dispersion method to cases of more complicated reaction kinetics since the evaluation formulas of such sound tests always assume a knowledge of the kinetic laws[3] (in particular the dependence of the

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*"Isentropische Zustandsänderungen in Dissoziierenden Gasen und die Methode der Schalldispersion zur Untersuchung sehr Schneller Homogener Gasreaktionen." Zeitschrift für Elektrochemie, Bd. 48, Nr. 2, 1942, pp. 62-82. (The conclusion of this paper, sections V to VIII, has been published as NACA TM 1269.)

[1] See dissertation by F. Keutel conducted in the Nernst Laboratory, Berlin 1910.

[2] H. O. Kneser, Ann. Physik 11, 761 (1931).

[3] See A. Einstein, Sitzungsber. Preuss. Akad. Wiss. Berlin, 1920, 380 to 385. H. O. Kneser, Ann. Physik 11, 761 (1931), and H. O. Kneser and O. Gauler, Physikal. Ztschr. 37, 677 to 684 (1936).

reaction velocities on the concentrations) and only the remaining undetermined reaction velocity constants are obtained. Thus the problem still remained of deriving an evaluation formula for such sound tests which is free from any restricting assumptions as regards the unknown reaction velocities.

The knowledge of the isentropics of dissociating gases is also required, however, for the understanding of numerous gas dynamic phenomena in hot combustion gases. Such phenomena can be very well studied in pipes for which purpose several relations of G. Damköhler and Adam Schmidt were recently obtained.[4] In these relations there again always occurs the isentropic exponent which for nondissociating gases agrees with the ratio of the heat capacities $C_p/C_v = \kappa$. This, however, does not hold for dissociating gases. But in this case too it was recently found by G. Damköhler and R. Edse for several examples in as yet unpublished computations that the isentropic can be represented by the general polytropic equation $pV^m = \text{const.}$ (p = pressure, V = volume), even over large pressure intervals. If, for example, the gases of the stoichiometric CO combustion ($CO + \frac{1}{2} O_2$ as the initial mixture) which are assumed initially to be at 40 atm. and 3450° K are expanded isentropically to 6 atm. and then again to 1 atm.[5], the temperatures assume the values 2973 and 2615° K; the total number of moles changes from 1.197 to 1.142 to 1.099 (referred to 1 mole CO + $\frac{1}{2}$ mol O_2 as initial mixture) so that the isentropic exponent m becomes 1.115 in the upper pressure interval and 1.103 in the lower pressure interval. The value of m thus changes by only about 1 percent even in this large interval.

In the following we can therefore restrict ourselves to the treatment of the differential isentropic changes in state in dissociating gases. It will be assumed, however, that several dissociation equilibrium states occur since this is practically always the case for high-temperature reactions. In the dissociation of pure CO_2, for example, we have to take into account both

$$2\ CO_2 \rightleftarrows 2\ CO + O_2 \qquad (1)$$

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[4] Damköhler, G., and Schmidt, A., Ztschr. Elektrochem. 47, 547 to 567 (1941).

[5] Such pressure relations occur for example in the case of detonation heads in pipes.

and

$$O_2 \rightleftarrows 2\ O \qquad (2)$$

In the combustion of hydrocarbons with oxygen we have to consider three additional equilibria

$$2\ H_2O \rightleftarrows 2\ H_2 + O_2, \qquad (3)$$

$$2\ H_2O \rightleftarrows H_2 + 2\ OH, \qquad (4)$$

$$H_2 \rightleftarrows 2\ H \qquad (5)$$

and in the presence of nitrogen, also the reaction

$$N_2 + O_2 \rightleftarrows 2\ NO \qquad (6)$$

In what follows the problem of the differential isentropic changes of state in dissociating gases will be treated quite generally, namely, the attainment of complete equilibrium at each instant on the one hand and on the other the incomplete equilibrium state in the sonic field. A generally valid formula for the reaction-kinetic evaluation of sound dispersion tests is obtained. Almost all physical effects which likewise give rise to sound dispersion and can therefore act as disturbing factors are discussed and quantitatively estimated. General points of view are obtained for the experimental carrying out of sound tests in the high-temperature range.

II. THE DIFFERENTIAL ISENTROPIC EXPONENT m FOR THE CASE OF COMPLETE ATTAINMENT OF CHEMICAL EQUILIBRIUM

We consider a definite quantity of an ideal gas mixture of various kinds of molecules j, among which exist n thermodynamically mutually independent equilibrium conditions. To these correspond n overall reactions, which however can be arbitrarily chosen to some extent.

The following symbols will be used:

T	absolute temperature (°K)
V	volume of gas considered
N_j	number of g-moles of the type j contained in V
$N = \sum^{j} N_j$	total number of g-moles contained in V
M_j	molar weight of the particles of type j
$\rho = \dfrac{\sum^{j} M_j N_j}{V}$	density
$c_j = N_j/V$	g-moles of the type j in unit volume
p_j	partial pressure of particles of type j
$p = \sum^{j} p_j$	total pressure
$\underline{R}$	gas constant = 1.986 cal/mole deg = 8.313×10^7 erg/mole deg
$\underline{C}_{pj}$	molar heat at constant pressure of the molecules of type j
$\underline{C}_{vj} = \underline{C}_{pj} - \underline{R}$	molar heat at constant volume of molecules of type j
H	enthalpy of gas system considered
$H_j = \left(\dfrac{\partial H}{\partial N_j}\right)_{pT}$	partial molar enthalpy of molecule of type j,
$C_p = \left(\dfrac{\partial H}{\partial T}\right)_{pN_j} = \sum^{j} N_j \underline{C}_{pj}$	heat capacity of the gas system considered at constant pressure and constant number of moles N_j
$C_v = \sum^{j} N_j \underline{C}_{vj} = C_p - N\underline{R}$	heat capacity of the gas at constant volume and constant number of moles N_j
$\kappa = C_p/C_v$	
m	exponent in the isentropic pV^m = constant.

The lth overall reaction is assumed to satisfy the stoichiometric equation of the type

$$\begin{aligned} &|\nu_{1l}|X_1 + |\nu_{2l}|X_2 + \ldots \rightleftarrows \\ &\rightleftarrows |\nu_{5l}|X_5 + |\nu_{6l}|X_6 + \ldots + W_l \end{aligned} \tag{7}$$

where

X_j	is the chemical symbol for the molecule of the type j
$\lvert\nu_{jl}\rvert$	the absolute value of the stoichiometric conversion coefficient of the molecules of type j (first index) for the lth reaction (second index); for the reaction going from left to right, corresponding to the Eucken notation[6] we have
$\nu_{jl} > 0$	if the molecule of type j vanishes
$\nu_{jl} < 0$	if the molecule of type j originates
$\nu_{jl} = 0$	if the molecule of type j remains unchanged
$\nu_l = \sum^{j} \nu_{jl}$	
$W_l = \sum^{j} \nu_{jl} H_j$	heat of reaction at constant pressure for the lth chemical reaction

A differential isentropic change in state, indicated by δ, in the gas mixture considered must on the one hand satisfy the first fundamental law, i.e.

$$V\delta p = \delta H = \left(\frac{\partial H}{\partial T}\right)_{pN_j} \delta T + \left(\frac{\partial H}{\partial p}\right)_{TN_j} \delta p + \sum^{j} \left(\frac{\partial H}{\partial N_j}\right)_{pT} \delta N_j \tag{8}$$

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[6] Precisely the opposite sign convention is used by American investigators.

or with the relation $\left(\frac{\partial H}{\partial p}\right)_{TN_j} = 0$ which holds for ideal gases and with the above notation.

$$C_p\delta T - V\delta p + \sum^{j} H_j\delta N_j = 0 \tag{9}$$

On the other hand each of the n independent overall reactions must satisfy the law of mass action, which for the lth reaction assumes the form

$$\sum^{j} \nu_{jl}\ln p_j = \ln K_l \tag{10}$$

where K_l denotes the equilibrium constant which depends only on the temperature. For the differential change in state we have therefore n further determining equations:

$$\sum^{j} \nu_{jl}\frac{\delta p_j}{p_j} = \delta \ln K_l = \frac{W_l}{\underline{R}T^2}\delta T \tag{11}$$

In equations (9) and (11) we now replace the differential changes δT, δp_j, and δN_j by the magnitudes δV, δp, and δz_m where δz_m indicates how often the mth reaction equation (7) for the differential change in state has proceeded from left to right. We have

$$\delta N_j = \sum^{m} -\nu_{jm}\delta z_m \tag{12}$$

$$\delta N = \sum^{m} -\nu_m\delta z_m \tag{13}$$

$$\sum^{j} H_j\delta N_j = -\sum^{m} W_m\delta z_m \tag{14}$$

From

$$pV = N\underline{R}T \tag{15}$$

follows

$$\frac{\delta T}{T} = \frac{\delta p}{p} + \frac{\delta V}{V} - \frac{\delta N}{N} = \frac{\delta p}{p} + \frac{\delta V}{V} + \sum^{m} \nu_m \frac{\delta z_m}{N} \tag{16}$$

and from

$$p_j = \frac{pN_j}{N} \tag{17}$$

there is obtained

$$\frac{\delta p_j}{p_j} = \frac{\delta p}{p} - \frac{\delta N}{N} + \frac{\delta N_j}{N_j} = \frac{\delta p}{p} + \sum^{m} \left(\nu_m - \nu_{jm} \frac{N}{N_j}\right) \frac{\delta z_m}{N} \tag{18}$$

Substituting these expressions in the equations (9) and (11) and using the relation

$$\frac{C_p}{N\underline{R}} = \frac{\sum^{j} N_j \underline{C}_{pj}}{\sum^{j} N_j (\underline{C}_{pj} - \underline{C}_{vj})} = \frac{\kappa}{\kappa - 1} \tag{19}$$

there is obtained as the expression for the first fundamental law:

$$\kappa \frac{\delta V}{V} + \frac{\delta p}{p} + \sum^{m} \left(\kappa \nu_m - [\kappa - 1] \frac{W_m}{\underline{R}T}\right) \frac{\delta z_m}{N} = 0 \tag{20}$$

and the law of mass action of the lth reaction is given by

$$\frac{W_l}{\underline{R}T} \frac{\delta V}{V} + \left(\frac{W_l}{\underline{R}T} - \nu_l\right) \frac{\delta p}{p} + \sum^{m} \left(\frac{W_l}{\underline{R}T} \nu_m + \sum^{j} \nu_{jl} \nu_{jm} \frac{N}{N_j} - \nu_l \nu_m\right) \frac{\delta z_m}{N} = 0 \tag{21}$$

For briefness we write:

$$A_l = \kappa\nu_l - [\kappa - 1]\frac{W_l}{RT} \tag{22}$$

$$B_{lm} = \frac{W_l}{RT}\nu_m + \sum^{j}\nu_{jl}\nu_{jm}\frac{N}{N_j} - \nu_l\nu_m \tag{23}$$

$$C_l = \frac{W_l}{RT} - \nu_l \tag{24}$$

hence

$$\frac{W_l}{RT} = A_l + \kappa C_l \tag{25}$$

and obtain from the 1 + n equations (20) and (21) the system of equations

$$\left.\begin{aligned}
&\frac{\delta p}{p}\frac{V}{\delta V} + A_1\frac{\delta z_1}{N}\frac{V}{\delta V} + A_2\frac{\delta z_2}{N}\frac{V}{\delta V} + \ldots + A_n\frac{\delta z_n}{N}\frac{V}{\delta V} = -\kappa \\
C_1&\frac{\delta p}{p}\frac{V}{\delta V} + B_{11}\frac{\delta z_1}{N}\frac{V}{\delta V} + B_{12}\frac{\delta z_2}{N}\frac{V}{\delta V} + \ldots + B_{1n}\frac{\delta z_n}{N}\frac{V}{\delta V} = -(A_1 + \kappa C_1) \\
C_2&\frac{\delta p}{p}\frac{V}{\delta V} + B_{21}\frac{\delta z_1}{N}\frac{V}{\delta V} + B_{22}\frac{\delta z_2}{N}\frac{V}{\delta V} + \ldots + B_{2n}\frac{\delta z_n}{N}\frac{V}{\delta V} = -(A_2 + \kappa C_2) \\
&\vdots \qquad\qquad\qquad \vdots \qquad\qquad\qquad \vdots \qquad\qquad\qquad\qquad \vdots \\
C_n&\frac{\delta p}{p}\frac{V}{\delta V} + B_{n1}\frac{\delta z_1}{N}\frac{V}{\delta V} + B_{n2}\frac{\delta z_2}{N}\frac{V}{\delta V} + \ldots + B_{nn}\frac{\delta z_n}{N}\frac{V}{\delta V} = -(A_n + \kappa C_n)
\end{aligned}\right\} \tag{26}$$

From the above system of equations the isentropic exponent m can be immediately computed. For, from

$$pV^m = \text{const.} \tag{27}$$

we have

$$\frac{\delta p}{p} + m\frac{\delta V}{V} = 0 \tag{28}$$

and therefore

$$m = \frac{-\delta p}{p}\,\frac{V}{\delta V} = \kappa + \frac{\begin{vmatrix} 0 & A_1 & A_2 & \cdots & A_n \\ A_1 & B_{11} & B_{12} & \cdots & B_{1n} \\ A_2 & B_{21} & B_{22} & \cdots & B_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ A_n & B_{n1} & B_{n2} & \cdots & B_{nn} \end{vmatrix}}{\begin{vmatrix} 1 & A_1 & A_2 & \cdots & A_n \\ C_1 & B_{11} & B_{12} & \cdots & B_{1n} \\ C_2 & B_{21} & B_{22} & \cdots & B_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B_{n1} & B_{n2} & \cdots & B_{nn} \end{vmatrix}} = \kappa + \frac{\Delta_1}{\Delta_2} \tag{29}$$

The isentropic exponent m in dissociating gases is thus referred to the ratio κ of the molar heats and the ratio of two determinants Δ_1 and Δ_2. The dimensionless magnitudes in the latter A_l, B_{lm}, C_l are immediately given as soon as the composition of the gas and the heats of reaction of the n overall reactions are known. In order to avoid any errors in writing the indices it is best to prepare a table of the n overall reactions as we shall see below. The two determinants Δ_1 and Δ_2 are to a large extent symmetrically constructed and contain 1 + n rows corresponding to the first fundamental law and the n mass action laws for the n thermodynamically independent chemical reaction possibilities. It is immaterial in what manner the latter are expressed. If, for example, the original overall reaction ② is replaced by a reaction $\textcircled{\bar{2}}$ which is obtained by the addition of the reaction ① taken x times and the reaction ② taken y times there follows from (22) to (24)

$$A_{\bar{2}} = \kappa(x\nu_1 + y\nu_2) - \left[\kappa - 1\right]\frac{xW_1 + yW_2}{\underline{R}T} = xA_1 + yA_2 \tag{30}$$

$$C_{\bar{2}} = \frac{xW_1 + yW_2}{\underline{R}T} - (x\nu_1 + y\nu_2) = xC_1 + yC_2 \tag{31}$$

$$B_{2m} = \frac{xW_1 + yW_2}{\underline{R}T}\nu_m + \sum^{j}(x\nu_{j1} + y\nu_{j2})\nu_{jm}\frac{N}{N_j} - (x\nu_1 + y\nu_2)\nu_m = xB_{1m} + yB_{2m} \quad \text{for} \quad \textcircled{\bar{2}} \neq \textcircled{m} \tag{32}$$

$$B_{l\bar{2}} = \frac{W_l}{\underline{R}T}(x\nu_1 + y\nu_2) + \sum^{j}\nu_{jl}(x\nu_{j1} + y\nu_{j2})\frac{N}{N_j} - \nu_l(x\nu_1 + y\nu_2) = xB_{l1} + yB_{l2} \quad \text{for} \quad \textcircled{l} \neq \textcircled{\bar{2}} \tag{33}$$

$$B_{2\bar{2}} = \frac{xW_1 + yW_2}{\underline{R}T}(xv_1 + yv_2) + \sum^{j}(xv_{j1} + yv_{j2})^2 \frac{N}{N_j} - (xv_1 + yv_2)^2 = x^2B_{11} + xyB_{12} + yxB_{21} + y^2B_{22} \tag{34}$$

We then have for the determination in the denominator in (29)

$$\bar{\Delta}_2 = \begin{vmatrix} 1 & A_1 & A_{\bar{2}} & \cdots & A_n \\ C_1 & B_{11} & B_{1\bar{2}} & \cdots & B_{1n} \\ C_{\bar{2}} & B_{\bar{2}1} & B_{\overline{22}} & \cdots & B_{\bar{2}n} \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B_{n1} & B_{n\bar{2}} & \cdots & B_{nn} \end{vmatrix} = \begin{vmatrix} 1 & A_1 & (xA_1 + yA_2) & \cdots & A_n \\ C_1 & B_{11} & (xB_{11} + yB_{12}) & \cdots & B_{1n} \\ (xC_1 + yC_2) & (xB_{11} + yB_{21}) & \begin{pmatrix} x^2B_{11} + xyB_{12} \\ + yxB_{21} + y^2B_{22} \end{pmatrix} & \cdots & (xB_{1n} + yB_{2n}) \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B_{n1} & (xB_{n1} + yB_{n2}) & \cdots & B_{nn} \end{vmatrix} \tag{35}$$

The last determinant remains unchanged if we subtract the second row multiplied by x from the third row. There is then obtained:

$$\Delta_2 = \begin{vmatrix} 1 & A_1 & (xA_1 + yA_2) & \cdots & A_n \\ C_1 & B_{11} & (xB_{11} + yB_{12}) & \cdots & B_{1n} \\ yC_2 & yB_{21} & y(xB_{21} + yB_{22}) & \cdots & yB_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B_{n1} & (xB_{n1} + yB_{n2}) & \cdots & B_{nn} \end{vmatrix} \qquad (36)$$

If we now subtract the second column multiplied by x from the third column there is obtained:

$$\bar{\Delta}_2 = \begin{vmatrix} 1 & A_1 & yA_2 & \cdots & A_n \\ C_1 & B_{11} & yB_{12} & \cdots & B_{1n} \\ yC_2 & yB_{21} & y^2B_{22} & \cdots & yB_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B_{n1} & yB_{n2} & \cdots & B_{nn} \end{vmatrix} \qquad (37)$$

Taking the common factors of the third row and the third column outside the determinant we have

$$\bar{\Delta}_2 = y^2\Delta_2 \qquad (38)$$

In a similar manner we have for the new determinant in the numerator

$$\bar{\Delta}_1 = y^2\Delta_1 \qquad (39)$$

so that the quotient becomes

$$\frac{\bar{\Delta}_1}{\bar{\Delta}_2} = \frac{\Delta_1}{\Delta_2} \tag{40}$$

Thus it has been mathematically proven that the expression (29) for the isentropic exponent m is independent of the manner in which the n thermodynamically independent reaction possibilities are expressed by n overall reactions. Physically of course no other result could have been expected.

III. THE INCOMPLETE ATTAINMENT OF CHEMICAL EQUILIBRIUM IN THE PLANE SOUND WAVE (NEGLECTING THE EFFECTS OF HEAT CONDUCTION, FRICTION AND DIFFUSION ON THE SOUND DISPERSION)

If a sound wave is allowed to pass through a gas the latter is subjected to periodic compressions and expansions which, to a first approximation, are isentropic. In the case of a dissociating gas for sufficiently high sound frequencies the chemical reaction velocities are no longer sufficient for the attainment of complete equilibrium and we have the case of sound dispersion. In the theoretical treatment of the latter, which is partly also a problem of flow theory, three conservation laws are to be taken into account: the conservation of mass (continuity equations), the conservation of energy (first fundamental law of thermodynamics) and the conservation of momentum (Euler equation of hydrodynamics).

We consider a definite gas mass, i. e. a volume V, fixed with respect to the flow, of such small dimensions that the same state may be assumed throughout. This volume changes with time by differential amounts in the following manner:

Continuity equations:

$$\frac{dN_j}{dt} = -\sum^{m} \nu_{jm} \frac{dz_m}{dt} \tag{41}$$

$$\frac{dN}{dt} = -\sum^{m} \nu_m \frac{dz_m}{dt} \tag{42}$$

$$\frac{1}{V}\frac{dV}{dt} = \frac{\partial w}{\partial x} \tag{43}$$

where w is the flow velocity at a point fixed in space over which a plane sound wave passes in the positive or negative direction.

Energy equation:

$$\frac{dE}{dt} = -p\frac{dV}{dt} \tag{44}$$

or on substituting the enthalpy $H = E + pV$ and after some computation

$$C_p \frac{dT}{dt} - V\frac{dp}{dt} - \sum^{m} W_m \frac{dz_m}{dt} = 0 \tag{45}$$

Momentum equation:

$$\rho \frac{dw}{dt} = -\frac{\partial p}{\partial x} \tag{46}$$

Equations (41), (42), and (45) agree with the previous equations (12), (13), and (9). Equations (43) and (46) are respectively the hydrodynamic continuity and momentum equation. In equation (46) the added friction term is neglected and in equations (44) and (45) the added heat conduction. The particle interchange through diffusion between the neighboring gas elements is likewise not taken into account.

For a sufficiently small sound intensity all the state variables carry out sinusoidal vibrations about corresponding mean values characterized by the index zero. To a first approximation they agree with the corresponding magnitudes of the equilibrium equations of the medium without sound waves.[7] We may therefore set:

$$\begin{aligned}
p &= p_0 + \delta p & \delta p &= \underline{Re}\left(\underline{p}e^{gx + ht}\right) \\
V &= V_0 + \delta V & \delta V &= \underline{Re}\left(\underline{v}e^{gx + ht}\right) \\
T &= T_0 + \delta T & \delta T &= \underline{Re}\left(\underline{T}e^{gx + ht}\right) \\
\rho &= \rho_0 + \delta \rho & \delta \rho &= \underline{Re}\left(\underline{r}e^{gx + ht}\right) \\
N_j &= N_{j0} + \delta N_j & \delta N_j &= \underline{Re}\left(\underline{N}_j e^{gx + ht}\right) \\
N &= N_0 + \delta N & \delta N &= \underline{Re}\left(\underline{N}e^{gx ++ht}\right) \\
c_j &= c_{j0} + \delta c_j & \delta c_j &= \underline{Re}\left(\underline{c}_j e^{gx + ht}\right) \\
& & \delta z_m &= \underline{Re}\left(\underline{z}_m e^{gx + ht}\right) \\
& & \delta w &= \underline{Re}\left(\underline{w}e^{gx + ht}\right)
\end{aligned} \tag{47}$$

where $\underline{Re}()$ denotes the real part of (). The underlined symbols are complex magnitudes which take into account the phase angles between the various magnitudes and are assumed independent of x and t; g is complex and h is pure imaginary. They depend on the frequency f, the sound velocity a and the damping constant γ for the sound amplitude in the following manner:

$$gx + ht = 2\pi f i\left[t \mp \frac{x}{a}\right] \mp \gamma x \tag{48}$$

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[7] The difference between the mean pressure value p_0 in the sound wave and the pressure in the medium without sound is, for example, of the order of magnitude of the sound radiation pressure. The latter is proportional to the energy density in the sound wave and therefore proportional to the square of the sound amplitude. The above mentioned pressure difference can therefore, for sufficiently small sound amplitudes, be neglected as a small second order magnitude.

or

$$a = \frac{2\pi f}{\left|\underline{\mathrm{Im}}(g)\right|} \qquad {}^{*}\left\{\begin{aligned} &\frac{2\pi f}{a} = \text{imaginary part of } g, \text{ i.e. } \underline{\mathrm{Im}}(g) \\ &\text{since } gx = \mp\left(\frac{i2\pi f}{a} + \gamma\right)x \end{aligned}\right. \tag{49}$$

and

$$\gamma = \left|\underline{\mathrm{Re}}(g)\right| \qquad {}^{*}\left\{ \text{and } \gamma = \text{real part of } g. \right. \tag{50}$$

For the time variation in moving forward with the flow along the path curve dF/dt of any magnitude F in the equations (41) to (46) we can also write

$$\frac{dF}{dt} = \frac{\partial F}{\partial t} + w\frac{\partial F}{\partial x} \tag{51}$$

where $\partial F/\partial t$ and $\partial F/\partial x$ are the partial derivatives at a point of the spatially fixed coordinate system, relative to which the gas particles move periodically with the velocity w. In equation (51) the second term on the right vanishes with decreasing sound intensity more rapidly than the first term on the right because the former is proportional to the second power while the latter is proportional to the first power of the sound amplitude. We may therefore throughout replace the operation d/dt by $\partial/\partial t$ and use it directly on the expression (47).

The magnitude dz_m/dt in the initial equations (41), (42), and (45) indicates how often the mth overall reaction occurs in the volume V of the gas and is thus proportional to the mth reaction velocity. It depends naturally also on the velocities of the individual elementary reactions but these do not enter separately in the final formulas to be derived for the sound dispersion, since they are not contained in the initial equations (41) to (46). Hence only the velocities of the overall reactions can primarily be determined from sound dispersion experiments and not the velocities of the elementary reactions.

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*Added by the NACA reviewer for clarity.

We consider again the lth total reaction

$$|\nu_{1l}|X_1 + |\nu_{2l}|X_2 + \dots \rightleftarrows |\nu_{5l}|X_5 + |\nu_{6l}|X_6 + \dots + W_l, \qquad (7)$$

and denote by

$\overrightarrow{U}_l$ its frequency from left to right per unit of time and volume at a given instant;

$\overleftarrow{U}_l$ its frequency from right to left per unit of time and volume at a given instant,

U_l its corresponding frequency from right to left and left to right in the equilibrium state (state in the medium without sound = mean value of the state in the medium with sound), where $\overrightarrow{U}_l = \overleftarrow{U}_l = U_l$.

For dz_l/dt there is then obtained

$$\frac{dz_l}{dt} = V(\overrightarrow{U}_l - \overleftarrow{U}_l) \qquad (52)$$

The reaction velocities $\overrightarrow{U}_l$ and $\overleftarrow{U}_l$ depend on the temperature T and the various concentrations c_j. Since only very small changes in state are assumed impressed on the gas by the sound wave the magnitudes $\overrightarrow{U}_l$ and $\overleftarrow{U}_l$ differ only by a small amount from the reaction velocity U_l in the sound-free equilibrium state. We may therefore develop the first order to arrive later at more general formulas free from special assumptions: We start not with $\overrightarrow{U}_l$ but with $\ln \overrightarrow{U}_l$:

$$\left.\begin{aligned} \ln \overrightarrow{U}_l &= \ln U_l + \frac{\partial \ln \overrightarrow{U}_l}{\partial T}\,\delta T + \sum^{j} \frac{\partial \ln \overrightarrow{U}_l}{\partial c_j}\,\delta c_j, \\ &\text{or} \\ \ln \frac{\overrightarrow{U}_l}{U_l} &= \frac{\partial \ln \overrightarrow{U}_l}{\partial T}\,\delta T + \sum^{j} \frac{\partial \ln \overrightarrow{U}_l}{\partial c_j}\,\delta c_j \\ &= \ln\left(1 + \frac{\overrightarrow{U}_l - U_l}{U_l}\right) \approx \frac{\overrightarrow{U}_l - U_l}{U_l} \end{aligned}\right\} \qquad (53)$$

and similarly for the right to left reaction

$$\ln \frac{\overleftarrow{U}_l}{U_l} = \frac{\partial \ln \overleftarrow{U}_l}{\partial T} \delta T + \sum^{j} \frac{\partial \ln \overleftarrow{U}_l}{\partial c_j} \delta c_j = \ln\left(1 + \frac{\overleftarrow{U}_l - U_l}{U_l}\right) \approx \frac{\overleftarrow{U}_l - U_l}{U_l} \qquad (54)$$

In the neighborhood of the equilibrium state the velocities $\overrightarrow{U}_l$ and $\overleftarrow{U}_l$ are no longer entirely independent of each other but mathematically must possess such form that in the state of equilibrium itself where $\overrightarrow{U}_l$ and $\overleftarrow{U}_l$ become equal the mass action law applies, i. e. for our reaction (7):

$$\frac{c_1^{|\nu_{1l}|} c_2^{|\nu_{2l}|} \dots}{c_5^{|\nu_{5l}|} c_6^{|\nu_{6l}|} \dots} = \text{const.} \qquad (55)$$

This is possible only if we set:

$$\overrightarrow{U}_l = \overrightarrow{k}_l c_1^{|\nu_{1l}|} c_2^{|\nu_{2l}|} \dots F(T, c_1, c_2, \dots c_j) \qquad (56)$$

and

$$\overleftarrow{U}_l = \overleftarrow{k}_l c_5^{|\nu_{5l}|} c_6^{|\nu_{6l}|} \dots F(T, c_1, c_2, \dots c_j) \qquad (57)$$

In both equations on the right there is the same factor $F(T, c_1, c_2, \dots c_j)$ which otherwise may quite arbitrarily depend on the temperature T and the concentrations c_j. It is not difficult to see that by means of the expressions (56) and (57) all reaction-kinetic laws for the reactions in either direction can be represented, subject to the only restricting condition, namely, that in equilibrium they must lead to equation (55). The magnitudes $\overrightarrow{k}_l$ and $\overleftarrow{k}_l$ in equations (56) and (57) are the reaction velocity constants which depend only on the temperature corresponding to the Arrhenius equation

$$\frac{\partial \ln \overrightarrow{k}_l}{\partial T} = \frac{\overrightarrow{q}_l}{\underline{R}T^2} \qquad (58)$$

and

$$\frac{\partial \ln \overleftarrow{k}_l}{\partial T} = \frac{\overleftarrow{q}_l}{\underline{R}T^2} \tag{59}$$

where $\overrightarrow{q}_l$ and $\overleftarrow{q}_l$ are the heats of activation for the reactions in the corresponding directions. Substituting the expression (56) to (59) in the equations (53) and (54) and then subtracting the two latter from each other there is obtained after brief computation

$$\frac{\overrightarrow{U}_l - \overleftarrow{U}_l}{U_l} = \frac{\overrightarrow{q}_l - \overleftarrow{q}_l}{\underline{R}T} \delta \ln T + \sum^{j} \nu_{jl} \delta \ln c_j \tag{60}$$

The as yet undetermined factor $F(T,c_1,c_2,\ldots c_j)$ in the expressions (56) and (57) dropped out in the subtraction.[8] The stoichiometric coefficients in equation (60) again have the signs corresponding to the Eucken notation given above. In equation (60) there occurs the difference in the heats of activation $\overrightarrow{q}_l - \overleftarrow{q}_l$ which may be expressed in terms of the heat of reaction W_l. From the kinetic equilibrium condition

$$\frac{\overrightarrow{k}_l c_{10}^{|\nu_{1l}|} c_{20}^{|\nu_{2l}|} \ldots}{\overleftarrow{k}_l c_{50}^{|\nu_{5l}|} c_{60}^{|\nu_{6l}|} \ldots} = 1, \text{ or, } \ln \overrightarrow{k}_l - \ln \overleftarrow{k}_l = - \sum^{j} \nu_{jl} c_{j0} \tag{61}$$

and the thermodynamic equilibrium condition

$$\ln K_l = \sum^{j} \nu_{jl} \ln p_{j0} = \sum^{j} \nu_{jl} \left[\ln c_{j0} + \ln \underline{R} + \ln T\right] \tag{62}$$

we have

$$\ln \overrightarrow{k}_l - \ln \overleftarrow{k}_l = - \ln K_l + \nu_l \ln \underline{R} + \nu_l \ln T \tag{63}$$

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[8] At this point it is readily seen why we developed above the Taylor series not for $\overrightarrow{U}_l$ but for $\ln \overrightarrow{U}_l$

or differentiating with respect to the temperature $\underline{T}$ with account taken of (58), (59), and (11)

$$\frac{\overrightarrow{q}_l - \overleftarrow{q}_l}{\underline{R}T} = -\left[\frac{W_l}{\underline{R}T} - \nu_l\right] \tag{64}$$

Finally making use of

$$\delta \ln c_j = -\delta \ln V + \delta \ln N_j = \frac{-\delta V}{V} - \sum^{m} \nu_{jm} \frac{N}{N_j} \frac{\delta z_m}{N} \tag{65}$$

and the previous relation

$$\delta \ln T = \frac{\delta V}{V} + \frac{\delta p}{p} + \sum^{m} \nu_m \frac{\delta z_m}{N} \tag{16}$$

there is obtained from equation (60) after brief computation

$$\frac{\overrightarrow{U}_l - \overleftarrow{U}_l}{U_l} + \left(\frac{W_l}{\underline{R}T}\right)\frac{\delta V}{V} + \left(\frac{W_l}{\underline{R}T} - \nu_l\right)\frac{\delta p}{p} + \sum^{m}\left(\frac{W_l}{\underline{R}T}\nu_m + \sum^{j} \nu_{jl}\,\nu_{jm}\frac{N}{N_j} - \nu_l\,\nu_m\right)\frac{\delta z_m}{N} = 0 \tag{66}$$

The above equations (66), of which there exist as many as there are thermodynamically independent overall reactions, completely correspond to the n previous equations (21) as is seen by comparison of the factors in parentheses. Equation (66) now contains also, however, the reaction velocities $\overrightarrow{U}_l$, $\overleftarrow{U}_l$, and U_l of the lth total reaction, as must be the case in the sound dispersion field. For very small frequencies f or very high reaction velocities U_l equations (66) go over into the previous equations (21). For, from equation (52) there is obtained, using equations (47) and (48)

$$\frac{\overrightarrow{U}_l - \overleftarrow{U}_l}{U_l} = \frac{1}{U_l V}\frac{dz_l}{dt} = \underline{R}e\left\{\frac{2\pi f i N}{U_l V}\frac{\underline{z}_l}{N}e^{gx + ht}\right\} \tag{67}$$

an expression which is proportional to the sound frequency f and inversely proportional to the reaction velocity U_l in equilibrium.

If we introduce the dimensionless magnitudes

$$\varphi_{ll} = \frac{2\pi f N}{U_l V} = \frac{2\pi f \sum^{j} c_j}{U_l} \tag{68}$$

and again use the previous notation

$$A_l = \kappa\nu_l - \left[\kappa - 1\right]\frac{W_l}{\underline{RT}} \tag{22}$$

$$B_{lm} = \frac{W_l}{\underline{RT}}\nu_m + \sum^{j}\nu_{jl}\nu_{jm}\frac{N}{N_j} - \nu_l\nu_m \tag{23}$$

$$C_l = \frac{W_l}{\underline{RT}} - \nu_l \tag{24}$$

and equations (47) there is obtained from equation (45), which leads to the previous equation (20), and from equations (66), after brief computation, the system of equations

$$\left.\begin{array}{lllllll}
\kappa\frac{v}{V} + & \frac{p}{p} + & A_1\frac{z_1}{N} & + \; A_2\frac{z_2}{N} & + \dots + & A_n\frac{z_n}{N} & = 0 \\
(A_1 + \kappa C_1)\frac{v}{V} + & C_1\frac{p}{p} + & (B_{11} + i\varphi_{11})\frac{z_1}{N} + & B_{12}\frac{z_2}{N} & + \dots + & B_{1n}\frac{z_n}{N} & = 0 \\
(A_2 + \kappa C_2)\frac{v}{V} + & C_2\frac{p}{p} + & B_{21}\frac{z_1}{N} & + \; (B_{22} + i\varphi_{22})\frac{z_2}{N} & + \dots + & B_{2n}\frac{z_n}{N} & = 0 \\
\vdots & \vdots & \vdots & & & \vdots & \\
(A_n + \kappa C_n)\frac{v}{V} + & C_n\frac{p}{p} + & B_{n1}\frac{z_1}{N} & + \; B_{n2}\frac{z_2}{N} & + \dots + & (B_{nn} + i\varphi_{nn})\frac{z_n}{N} & = 0
\end{array}\right\} \tag{69}$$

From the above there is obtained for the ratio of the relative pressure changes to the relative density and volume changes respectively, in the sound wave

$$\frac{\underline{p}\rho}{p\underline{r}} = \frac{-\underline{p}V}{p\underline{V}} = \kappa + \frac{\begin{vmatrix} 0 & A_1 & A_2 & \cdots & A_n \\ A_1 & (B_{11} + i\varphi_{11}) & B_{12} & \cdots & B_{1n} \\ A_2 & B_{21} & (B_{22} + i\varphi_{22}) & \cdots & B_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ A_n & B_{n1} & B_{n2} & \cdots & (B_{nn} + i\varphi_{nn}) \end{vmatrix}}{\begin{vmatrix} 1 & A_1 & A_2 & \cdots & A_n \\ C_1 & (B_{11} + i\varphi_{11}) & B_{12} & \cdots & B_{1n} \\ C_2 & B_{21} & (B_{22} + i\varphi_{22}) & \cdots & B_{2n} \\ \vdots & \vdots & \vdots & & \vdots \\ C_n & B_{n1} & B_{n2} & \cdots & (B_{nn} + i\varphi_{nn}) \end{vmatrix}} = \kappa + \frac{\Delta_1'}{\Delta_2'} = me^{i\varphi} \tag{70}$$

Equation (70) goes over into the previous equation (29) if the phase angle[9] in the expression $me^{i\varphi}$ on the right vanishes, i. e. if in the determinants Δ_1' and Δ_2' the

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[9] The phase angle φ indicates by how much the pressure change δp in the sound wave leads the density and volume changes $\delta\rho$ and δV respectively.

imaginary terms $i\varphi_{ll}$ vanish. According to equation (68) this is the case for sufficiently small sound frequencies f or sufficiently high reaction velocities U_l. Thus we have also derived our previous equation (29) by a purely kinetic method.

The determinants Δ_1' and Δ_2' can be obtained from the determinants Δ_1 and Δ_2 respectively of equation (29) by substituting in the latter for the B_{lm} values those values which satisfy the equation

$$\left\| \; B_{lm}' = B_{lm} + i\varphi_{lm} \right. \tag{71}$$

with the added conditions

$$\left\| \; \varphi_{lm} = \begin{cases} \dfrac{2\pi fN}{U_l V} & \text{for} \quad l = m \\ 0 & \text{for} \quad l \neq m \end{cases} \right. \tag{72}$$

The ratio $\underline{p}\rho/p\underline{r}$ given by the expression (70) can also be obtained from the purely hydrodynamic equations (43) and (46) by substituting the expressions (47) and replacing, as before, d/dt by ∂/∂t. We then have from (43)

$$\frac{h\underline{V}}{V} = -\frac{h\underline{r}}{\rho} = g\underline{w} \tag{73}$$

and from (46)

$$\rho h\underline{w} = -g\underline{p} \tag{74}$$

and multiplying the two last equations

$$h^2\underline{r} = g^2\underline{p} \quad \text{or finally} \quad g = \frac{\mp h}{\sqrt{\left(\dfrac{\underline{p}\rho}{p\underline{r}}\right)\dfrac{p}{\rho}}} \tag{75}$$

Substituting in the above equation the expression (70) and setting

$$\frac{p}{\rho} = \frac{pV}{N\overline{M}} = \frac{RT}{\overline{M}} \tag{76}$$

where $\overline{M}$ is the mean molar weight there is obtained

$$g = \frac{\mp h}{\sqrt{\frac{\underline{m}RT}{\overline{M}}e^{\frac{i\varphi}{2}}}} = \frac{\mp 2\pi fi}{\sqrt{\frac{\underline{m}RT}{\overline{M}}}}\left(\cos\frac{\varphi}{2} - i\sin\frac{\varphi}{2}\right) = \mp\left(\frac{2\pi fi}{a} + \gamma\right) \tag{77}$$

Thus the sound velocity a and the damping constant γ are referred to the magnitudes m and φ computable from equation (70). For we have

$$a = \sqrt{\frac{\underline{m}RT}{\overline{M}}}\,\frac{1}{\cos\frac{\varphi}{2}} \approx \sqrt{\frac{\underline{m}RT}{\overline{M}}}\left(1 + \frac{\varphi^2}{8}\right) \tag{78}$$

$$\gamma = 2\pi f\sqrt{\frac{\overline{M}}{\underline{m}RT}}\sin\frac{\varphi}{2} \approx \pi f\sqrt{\frac{\overline{M}}{\underline{m}RT}}\,\varphi\left(1 - \frac{\varphi^2}{24}\right) \tag{79}$$

The damping of the sound wave per wave length $l = a/f$ is given by

$$\gamma l = 2\pi\tan\frac{\varphi}{2} \approx \pi\varphi\left(1 + \frac{\varphi^2}{12}\right) \tag{80}$$

Since physically the damping constant γ enters only as a positive value in the expression (48) it follows from (79) that also the phase angle φ, which always amounts to only a few degrees (see below), is positive. Hence according to equation (70) the pressure change δp leads the volume and density changes δV and $\delta\rho$ respectively. It has already been shown clearly by H. O. Kneser (Ztschr. Techn. Physik 16, pp. 213-219 (1935)) that only in this way is there obtained for periodic changes of state (on the pV-diagram) a closed curve leading to energy absorption.

Equations (70) and (78) and (79) can be ulitized in the following manner for describing the kinetic relations in multiplying dissociating gases: For a constant gas composition, fixed pressure and temperature, definite numerical values are assumed for the n reaction velocities U_l, and m and φ values are computed by equation (70) for various sound frequencies f and from these with the aid of (78) and (79) the sound velocity a or the damping constant γ. There is then determined, in a series of measurements for the same gas composition, the same pressure and the same temperature, the sound velocity or the sound absorption as a function of the frequency. Finally the experimental a-f and γ-f curves are compared with the theoretical curves and it is seen which expression for the assumed U_l values gives best agreement with the test curves. If, in particular, of the n reaction velocities the numerical values of $n - 1$ are known (from other considerations), the last unknown reaction velocity U_n can be given exactly for the chosen test conditions. By systematic variation of the latter in various series of tests in which again the total frequency range is traversed the last reaction velocity U_n can be determined as a function of the concentration c_j and the temperature T, provided that these relations are already known for the remaining $n - 1$ reactions.[10] Hence no special reaction kinetic law is a priori assumed for U_n but the latter can be quite arbitrary and is determined by comparison of the experimental and theoretical curves. The new procedure described for the evaluation of sound dispersion tests thus differs fundamentally from the procedure used thus far since the latter make special assumptions on the kinetic laws of all the individual reactions whereas we now require only a knowledge of the velocities of $n - 1$ total reactions. This will be seen more clearly below.

IV. EXAMPLES FOR THE APPLICATION OF THE NEW FORMULAS

1. Older Cases of the Reaction-Kinetic Sound Dispersion

Before we apply the newly derived equations on the problems of particular importance of high-temperature dissociation it will be shown that naturally all the cases of sound dispersion already considered by other authors are correctly described by the new formulas. We shall restrict ourselves to the case of incomplete attainment of an individual dissociation equilibrium, which was first computed by A. Einstein,[11] and furthermore the incomplete attainment of an energy term (vibration term) in a molecule, as investigated by H. O. Kneser.[12]

Einstein considers only a single dissociation equilibrium in which from a molecule X_1 there arise two equal molecules X_2 so that the reaction equation reads:

$$X_1 \rightleftarrows 2X_2 + W_1 \tag{81}$$

We shall denote it by the 'reaction index' 1.

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[10] This is also superfluous if the sound dispersion is "mainly" brought about by a single total reaction. See the example of the CO_2 dissociation below.

[11] Einstein, A., Sitzungsber. Preuss. Akad. Wiss., Berlin 1920, 380 to 385.

[12] Kneser, H. O., Ann. Physik 11, 761 (1931)

For the doubly indexed stoichiometric coefficients[13] there is obtained

$$\nu_{11} = 1 \quad \nu_{21} = -2$$

and therefore

$$\nu_1 = \sum^{j} \nu_{j1} = -1 \tag{82}$$

Einstein does not make use, as we do, of the heat of reaction W_1 at constant pressure but the dissociation heat D at constant volume so that we obtain

$$W_1 = -(D + \underline{R}T) \tag{83}$$

For the constants (22) to (24) there is therefore obtained

$$A_1 = \kappa\nu_1 - (\kappa - 1)\frac{W_1}{\underline{R}T} = -\kappa + (\kappa - 1)\left(\frac{D}{\underline{R}T} + 1\right) = (\kappa - 1)\frac{D}{\underline{R}T} - 1 \tag{84}$$

$$B_{11} = \frac{W_1}{\underline{R}T}\nu_1 + \sum^{j} \nu_{j1}^2 \frac{N}{N_j} - \nu_1^2 = \left(\frac{D}{\underline{R}T} + 1\right) + \left(\frac{N}{N_1} + \frac{4N}{N_2}\right) - 1 = \frac{D}{\underline{R}T} + \left(\frac{N}{N_1} + \frac{4N}{N_2}\right) \tag{85}$$

$$C_1 = \frac{W_1}{\underline{R}T} - \nu_1 = -\left(\frac{D}{\underline{R}T} + 1\right) + 1 = \frac{-D}{\underline{R}T} \tag{86}$$

For the dissociation Einstein assumes a reaction of the first order and for the recombination one of second order. This gives in equation (68):

$$U_1 = \overrightarrow{k}_1 c_1 = \overleftarrow{k}_1 c_2^2$$

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[13] The type of molecule is denoted by the first index and the reaction by the second.

or

$$\varphi_{11} = \frac{\omega N}{\vec{k}_1 N_1} \quad \text{with} \quad \omega = 2\pi f \tag{87}$$

From equation (70) there is then obtained

$$\frac{\underline{p}}{\underline{r}} = \frac{p}{\rho}\, m e^{i\varphi} = \frac{p}{\rho}\left\{\kappa + \frac{-A_1{}^2}{B_{11} + i\varphi_{11} - A_1C_1}\right\} = \frac{p}{\rho}\left\{1 + \frac{(\kappa - 1)\left[B_{11} + i\varphi_{11} - A_1C_1\right] - A_1{}^2}{B_{11} + i\varphi_{11} - A_1C_1}\right\} \tag{88}$$

Since $(\kappa - 1)\ C_1 + A_1 = -1$, we have

$$\frac{\underline{p}}{\underline{r}} = \frac{p}{\rho}\left\{1 + \frac{(\kappa - 1)\left[\frac{D}{\underline{R}T} + \left(\frac{N}{N_1} + \frac{4N}{N_2}\right) + \frac{i\omega N}{\vec{k}_1 N_1}\right] + \left[(\kappa - 1)\frac{D}{\underline{R}T} - 1\right]}{\frac{D}{\underline{R}T} + \left(\frac{N}{N_1} + \frac{4N}{N_2}\right) + \frac{i\omega N}{\vec{k}_1 N_1} + \frac{D}{\underline{R}T}\left[(\kappa - 1)\frac{D}{\underline{R}T} - 1\right]}\right\} \tag{89}$$

or

$$\frac{\underline{p}}{\underline{r}} = \frac{p}{\rho}\left\{1 + \frac{(\kappa - 1)\left[\frac{2D}{\underline{R}T} - \left(\frac{1}{\kappa - 1}\right) + \left(\frac{N}{N_1} + \frac{4N}{N_2}\right) + \frac{i\omega N}{\vec{k}_1 N_1}\right]}{(\kappa - 1)\left[\frac{D^2}{\underline{R}^2T^2} + \left(\frac{1}{\kappa - 1}\right)\left(\frac{N}{N_1} + \frac{4N}{N_2}\right) + \left(\frac{1}{\kappa - 1}\right)\frac{i\omega N}{\vec{k}_1 N_1}\right]}\right\} \tag{90}$$

Taking into account the previously given relation $R/(\kappa - 1) = C_v/N$ there is obtained finally

$$\frac{\underline{p}}{\underline{r}} = \frac{p}{\rho}\left\{1 + \frac{\left(\frac{2D}{T} - \frac{C_v}{N}\right)\frac{N_1}{N} + \underline{R}\left(1 + \frac{4N_1}{N_2}\right) + \frac{i\omega}{\vec{k}_1}\underline{R}}{\frac{D^2}{\underline{R}T^2}\,\frac{N_1}{N} + \frac{C_v}{N}\left(1 + \frac{4N_1}{N_2}\right) + \frac{i\omega}{\vec{k}_1}\,\frac{C_v}{N}}\right\} \tag{91}$$

This equation is entirely identical with the expression (19) given in the Einstein paper (loc. cit.) if we note that the term in parenthesis $(1 + 4N_1/N_2)$ is there erroneously written as $(1 - 4N_1/N_2)$.

It may be remarked that the expression (91) even for the simple dissociation equation (81) is already quite complicated. In particular it is difficult to see how it can be generalized when there are several dissociation equilibria under consideration. By way of contrast the new expressions (29) and (70) of the present paper are of very symmetric form and such that the physical meaning is clear.

M. O. Kneser[14] considers a gas whose molecules possess a single internal energy term and which in the sound field is incompletely excited. In order to be able to treat this case with the formulas of the present paper we consider the gas as built up of two types of molecules X_1 and X_2: the former is assumed not to be excited in the energy term under consideration while the latter is assumed to possess the exciting energy ϵ per mol. The excitation may then be considered as a chemical reaction[15].

$$X_1 \longrightarrow X_2 \tag{92}$$

which occurs without change in the total molecule number with the heat of reaction

$$W_1 = -\epsilon \tag{93}$$

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[14] Kneser, M. O., Ann. Physik II, 761 (1931)

[15] As a single reaction it is denoted with the reaction index 1.

The stoichiometric coefficients are then

$$\nu_{11} = 1 \quad \nu_{21} = -1 \quad \nu_1 = \sum^{j} \nu_{j1} = 0 \tag{94}$$

In the computation of κ only that part $\underline{C}_a$ of the molar heat $\underline{C}_v$ may naturally be used which, independently of the sound frequency, is always fully excited (as for example translational and rotational energy) and corresponds to the so-called external degrees of freedom: ($\therefore$ the index a) Hence

$$\kappa = \frac{\underline{C}_a + \underline{R}}{\underline{C}_a} \tag{95}$$

The ratio of the internally excited to the unexcited particles is given by the Boltzmann law

$$\frac{N_2}{N_1} = e^{\frac{-\epsilon}{\underline{R}T}} \quad \text{and} \quad \frac{N}{N_1} = 1 + e^{\frac{-\epsilon}{\underline{R}T}}$$

thus

$$\frac{N}{N_2} = 1 + e^{\frac{\epsilon}{\underline{R}T}} \tag{96}$$

for complete equilibrium the part $\underline{C}_1$ of the molar heat $\underline{C}_v$ due to the vibrational internal energy term is

$$\underline{C}_1 = \underline{R}\,\frac{\left(\frac{\epsilon}{\underline{R}T}\right)^2 e^{\frac{\epsilon}{\underline{R}T}}}{\left(1 + e^{\frac{\epsilon}{\underline{R}T}}\right)^2} \tag{97}$$

C_1 corresponds to the heat capacity of a "Schottky hump"[16] of the excitation energy ϵ. We thus have

$$\frac{N}{N_1} + \frac{N}{N_2} = e^{\frac{-\epsilon}{RT}} + 2 + e^{\frac{\epsilon}{RT}} = \frac{\left(1 + e^{\frac{\epsilon}{RT}}\right)^2}{e^{\frac{\epsilon}{RT}}} = \frac{R}{C_1}\left(\frac{\epsilon}{RT}\right)^2 \qquad (98)$$

The constants (22) to (24) then become

$$A_1 = \kappa\nu_1 - (\kappa - 1)\frac{W_1}{RT} = \frac{R}{C_a}\left(\frac{\epsilon}{RT}\right) \qquad (99)$$

$$B_{11} = \frac{W_1}{RT}\nu_1 + \sum^{j} \nu_{j1}^2 \frac{N}{N_j} - \nu_1^2 = \frac{N}{N_1} + \frac{N}{N_2} = \frac{R}{C_1}\left(\frac{\epsilon}{RT}\right)^2 \qquad (100)$$

$$C_1 = \frac{W_1}{RT} - \nu_1 = \frac{-\epsilon}{RT} \qquad (101)$$

Kneser assumes both the excitation and "deexcitation" of the inner molecular term as a bimolecular reaction, i. e.

$$U_1 = \overrightarrow{k}\,\frac{N_1N}{V^2} = \overleftarrow{k}\,\frac{N_2N}{V^2} \qquad (102)$$

Introducing the mean time required to attain equilibrium as used by Kneser

$$\beta = \frac{V}{N(\overrightarrow{k} + \overleftarrow{k})}$$

and remembering that according to (96) and (102) $k/k = e^{\frac{-\epsilon}{RT}}$ one obtained

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[16] Eucken, Chem., Eng. III, 1, 104 (1937)

after brief computation for our expression (68) above

$$\varphi_{11} = 2\pi f\beta \frac{\left(1 + e^{\frac{\epsilon}{\underline{R}T}}\right)^{2}}{e^{\frac{\epsilon}{\underline{R}T}}} = 2\pi f\beta \frac{\underline{R}}{\underline{C}_1}\left(\frac{\epsilon}{\underline{R}T}\right)^{2} \tag{103}$$

Substituting the expressions (99) to (101) and (103) in equation (70) there is obtained

$$\frac{\underline{p}}{\underline{r}} = \frac{p}{\rho}\left\{me^{i\varphi}\right\} = \frac{p}{\rho}\left\{1 + \frac{\underline{R}(1 + i\ 2\pi f\beta)}{\underline{C}_a(1 + i\ 2\pi f\beta) + \underline{C}_1}\right\} \tag{104a)}$$

or using equations (78) to (80)

$$a \approx \sqrt{\frac{m\underline{R}T}{\overline{M}}}$$

$$\approx \sqrt{\frac{\underline{R}T}{\overline{M}}\left(1 + \frac{\underline{R}\left[\underline{C}_v + \underline{C}_a(2\pi f\beta)^{2}\right]}{\underline{C}_v^{2} + \underline{C}_a^{2}(2\pi f\beta)^{2}}\right)} \tag{104b}$$

$$\gamma \approx \frac{\pi f\varphi}{a}$$

$$\approx \frac{\underline{R}\ \underline{C}_1\ 2\pi^{2}f^{2}\beta}{a\left[\underline{C}_v(\underline{C}_v + \underline{R}) + \underline{C}_a(\underline{C}_a + \underline{R})(2\pi f\beta)^{2}\right]} \tag{104c}$$

$$\gamma l \approx \pi\varphi$$

$$\approx \frac{\underline{R}\underline{C}_1\ 2\pi^{2}f\beta}{\underline{C}_v(\underline{C}_v + \underline{R}) + \underline{C}_a(\underline{C}_a + \underline{R})(2\pi f\beta)^{2}} \tag{104d}$$

These equations are entirely identical with those obtained by Kneser. Equation (104d) represents as a function of the frequency f a bell-shaped curve whose maximum lies at

$$f_m = \frac{1}{2\pi\beta}\sqrt{\frac{\underline{C}_v(\underline{C}_v + \underline{R})}{\underline{C}_a(\underline{C}_a + \underline{R})}} \tag{104e}$$

and whose half value width in the case $\underline{C}_a \approx \underline{C}_v$ lies at about 3.8 octaves.

The example considered above of the incomplete molecular excitation in the sound field naturally represents a very simple case. Considerably more complicated cases have already been both experimentally and theoretically investigated.[17] Of interest is the more or less mutually independent excitation of the various natural vibrations in the same molecule. A theoretical contribution to this problem has recently been given by Kl. Schäfer.[18] It is not impossible that in this case, too, the formulas derived in the present paper can be successfully applied if it is desired to make no assumptions of any kind on the kinetic laws of the vibration excitation and yet derive definite numerical values for the reaction velocity. If, for example, each gas molecule possesses two different natural vibrations then, in a correspondingly chosen temperature range, the molecules could be divided into the following types:

1. molecules X_1 without any vibration excitation
2. molecules X_2 in which only the first natural vibration is excited
3. molecules X_3 in which only the second natural vibration is excited.

Among these three types of molecules there exist two equilibrium conditions so that in equation (70) we have 3-rowed determinants. This example will, however, not be further considered here since this would exceed the limits of the present paper. We shall discuss however a few properties of the overall reactions involved:

a. For describing the previously assigned changes in molar numbers δN_j the transformation frequency δZ_l of the l-th overall reaction depends on the choice of the other overall reactions although the individual overall reactions are thermodynamically independent of each other since they correspond to n independent equilibrium conditions.

b. In particular cases from the velocities obtained for the overall reactions there may be derived the elementary reactions that are of most interest.

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[17] See in particular the papers of the Eucken Institute especially in the Ztschr. physikal. Chem. B. since 1934.

[18] Schäfer, Kl., Ztsch. physikal Chem. B. 46, pp. 212-228, 1940.

2. Relations Between the Overall and Elementary Reactions

Among the three types of molecules X_1, X_2, and X_3 which in our case represent three different excitation stages or tautomeric forms of the same chemical substance we have the following essential possibilities

$$\text{Reaction 1} \quad X_1 \rightleftarrows X_2 \tag{105}$$

$$\text{Reaction 2} \quad X_1 \rightleftarrows X_3 \tag{106}$$

$$\text{Reaction 3} \quad X_2 \rightleftarrows X_3 \tag{107}$$

They can be looked upon as elementary reactions or as overall reactions. In the latter case only two of these three reaction equations can be considered as thermodynamically independent. The frequency with which, for given molecular changes δN_j, the l-th reaction proceeds from left to right is as before assumed to be δZ_l. In the case of equilibrium the velocities of the overall reactions will as before be denoted by U_l, the velocities of the elementary reactions by $\overrightarrow{u}_l$ and $\overleftarrow{u}_l$, depending on the direction. The questions as to whether in the equilibrium case $\overrightarrow{u}_l = \overleftarrow{u}_l$, i.e. whether the principle of microscopic reversibility holds, may be left open. In Table 1 are given three possibilities for the choice of the overall reactions (denoted by the thick lines in the diagrams) and the relations between the δN_j and the δz_l and between U_l and the various $\overrightarrow{u}_m$ and $\overleftarrow{u}_m$. For the δz_l and U_l the three possibilities of the choice of the overall reactions are distinguished by strokes above the symbols.

Inspection of Table 1 leads to the following conclusions: Although in the two cases I and II the same overall reaction occurs, namely, $X_1 \rightleftarrows X_2$, the frequencies δz_1 and $\delta \overline{z}_1$ for describing any molar number changes δN_j are in general different. For, on the one hand we have $\delta z_1 = \delta N_2$ and on the other $\delta \overline{z}_1 = -\delta N_1$, and δN_2 and $-\delta N_1$ need not be equal. Also the velocity frequencies U_1 and $\overline{U}_1$ corresponding to the overall reaction in the two cases I and II are not necessarily identical. For it is not possible to derive from Table I that $U_1 = \overline{U}_1$. There exist, however, between the various stroked U_l values certain relations which are given in the lower part of the table. They correspond except for the sign, which for the U_l is always positive from the definition, completely to the relations between the various stroked δz_l.

Of the six different stroked U_l values shown in the right part of Table 1 only 3 are mutually independent and these can be obtained from sound dispersion measurements. For this purpose it is only necessary to compare the experimentally obtained dispersion curve with the two theoretically obtained curves for the overall reactions of case I and case II respectively.

In the right part of Table 1 are found 6 equations with which for the equilibrium case the velocities $\overrightarrow{u}_l$ and $\overleftarrow{u}_l$ of the elemetary reactions are expressed in terms of the overall reaction velocities U_m. Since altogether only 6 elementary reaction velocities exist (reactions to left and right counted separately) it might be thought that they could be computed individually from the U_m values. In this way might perhaps be proved the principle of microscopic reversibility which in the case of equilibrium requires that the velocities of the elementary reactions to the right agree with the velocities of the elementary reactions to the left. This however is only a pure assumption which need not be satisfied for maintaining a state of equilibrium and which is obvious only for the over-all reactions in either direction.[19]

The six equations on the right of Table 1 for the $\overrightarrow{U}_l$ and $\overleftarrow{U}_l$ are not independent of one another. Writing them in the somewhat clearer form

$$\begin{array}{lllllll}
U_1 = \overrightarrow{u}_1 & & & & & & + \overleftarrow{u}_3 \\
U_1 = & & & \overrightarrow{u}_3 & + \overleftarrow{u}_1 & & \\
U_2 = & & \overrightarrow{u}_2 & + \overrightarrow{u}_3 & & & \\
U_2 = & & & & & \overleftarrow{u}_2 & + \overleftarrow{u}_3 \\
\bar{U}_1 = \overrightarrow{u}_1 & & + \overrightarrow{u}_2 & & & & \\
\bar{U}_1 = & & & & \overleftarrow{u}_1 & + \overleftarrow{u}_2 &
\end{array} \qquad (108)$$

---

[19] To assume the law of microscopic reversibility as a generally valid law of nature is equivalent to denying for the molecular aspect any type of check such as not only very frequently occurs in the microscopic aspect but is often found of very great use. I have in mind the "catch" type of control such as is used in rotating doors for regulating the traffic through them and which can also be observed in nature (for example for the artifically constructed cases of certain meat-eating plants). Naturally such a catch control in the molecular aspect can not be described by a fixed potential surface such as introduced for example by H̄. Eyring and M. Polanyi (Ztschr. physikal. chem. B. 12, 279 (1931) for the theoretical investigation of the activation heats.

The $\overrightarrow{u}_l$ and $\overleftarrow{u}_l$ are obtained as the quotient of two determinants which now both possess the value zero. The determinant in the denominator for example becomes

$$\left|\begin{array}{cccccc} 1 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 1 & 0 & 0 \\ 0 & 1 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 1 \\ 1 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 1 & 0 \end{array}\right| \begin{array}{c} + \\ - \\ + \\ - \\ - \\ + \end{array} \tag{109}$$

It remains unchanged if to the first row are added other rows multiplied by the signs given on the right. There is then obtained a new zero-rowed determinant, so that the latter vanishes. For the corresponding numerator determinants the proof is quite analogous.

If therefore, for the equilibrium case it is desired to compute the velocities $\overrightarrow{u}_l$ and $\overleftarrow{u}_l$ of the elementary reaction from the overall reaction velocities U_l, assumed known, further assumptions must be made. The principle of microscopic reversibility might for example be tentatively assumed as correct and there would then be obtained

$$\overrightarrow{u}_l = \overleftarrow{u}_l = u_l \tag{110}$$

and therefore from equation (108)

$$u_1 = \frac{1}{2}(U_1 - U_2 + \overline{U}_1) \tag{111}$$

$$u_2 = \frac{1}{2}(- U_1 + U_2 + \overline{U}_1) \tag{112}$$

$$u_3 = \frac{1}{2}(U_1 + U_2 - \overline{U}_1) \tag{113}$$

If in particular

$$U_1 = U_2 = \overline{U}_1 = U \tag{114}$$

there would thus be obtained on the assumption of the validity of the principle of microscopic reversibility

$$\overrightarrow{u}_1 = \overleftarrow{u}_1 = \overrightarrow{u}_2 = \overleftarrow{u}_2 = \overrightarrow{u}_3 = \overleftarrow{u}_3 = \frac{1}{2}U \tag{115}$$

For the case of complete checking of the reaction in one direction, on the contrary, there would be obtained, as can be easily seen from the schematic diagrams on the left of Table 1,

$$\left.\begin{aligned} &\overrightarrow{u}_1 = \overrightarrow{u}_3 = \overleftarrow{u}_2 = 0 \\ \text{and} \\ &\overleftarrow{u}_1 = \overleftarrow{u}_3 = \overrightarrow{u}_2 = U \end{aligned}\right\} \tag{116}$$

or

$$\overrightarrow{u}_1 = \overrightarrow{u}_3 = \overleftarrow{u}_2 = U \quad \text{and} \quad \overleftarrow{u}_1 = \overleftarrow{u}_3 = \overrightarrow{u}_2 = 0 \tag{117}$$

The question as to the manner in which the thermodynamic equilibrium between the three forms X_1, X_2, and X_3 is maintained, whether microscopically reversible or irreversible, remains entirely open and there exists as yet no experimental possibility of providing a reliable decision. Nevertheless in very many cases the principle of microscopic reversibility will have to be assumed although on the basis of molecular theory the checking by means of the potential barriers in the sense of Eyring-Polanyi could be considered. Under these conditions it is possible from sound dispersion measurements for the equilibrium case to determine not only the velocities U_l of the overall reactions but also the velocities of u_l of the elementary reactions. The given procedure, which was here carried out only for a special reaction kinetic system, can readily be generalized to other cases.

3. High-Temperature Systems (Dissociation of O_2 and CO_2)

We now come to the main consideration itself of the present paper, namely the kinetic investigation of very rapid homogeneous gas reactions in the high-temperature range where dissociation effects assume prime importance. The application of the formulas will be clarified with the aid of two examples, namely, the dissociation of pure O_2 and pure CO_2.

In the dissociation of pure O_2, which we shall consider at $T = 2600^{\circ}K$ and 1 atm, we are dealing with a single reaction which again we denote by the index 1. We have

$$O_2 \rightleftarrows 2\,O \tag{118}$$

$$W_1 = -\ 121.61 \text{ kcal} \tag{119}$$

$$\frac{p_O}{\sqrt{p_{O_2}}} = 0.0243 \text{ Atm}^{\frac{1}{2}} \tag{120}$$

$$\frac{W_1}{\underline{R}T} = -\ 23.56 \tag{121}$$

Type of Particle j	Index	p_j	$\frac{N}{N_j}$	ν_{j1}	$\underline{C}_{pj}$
O_2	1	0.9760	1.025	1	[20]9.340 to 9.022
O	2	0.0240	41.66	-2	4.965
		$p = 1.0000$		$\nu_1 = -1$	

$$\sum^{j} \frac{N_j}{N} \underline{C}_{pj} = 9.235 \text{ to } 8.925, \quad \kappa = 1.274 \text{ to } 1.286 \tag{122}$$

$$A_1 = \kappa\nu_1 - \left[\kappa - 1\right]\frac{W_1}{\underline{R}T} = \begin{cases} -\ 1.274 + 0.274\ (23.56) = 5.182 & \text{(123a)} \\ -\ 1.286 + 0.286\ (23.56) = 5.452 & \text{(123b)} \end{cases}$$

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[20] Both values are taken from Johnston and Walker. The higher value from the Jour. Amer. Chem. Soc. 57, 682 to 684 (1935), the lower value from Jour. Amer. Chem. Soc. 55, 172, 187 (1933). The computation is here carried out with the two values, which differ appreciably, in order to learn the effect of such uncertainty on m and κ - m. The higher $\underline{C}_p$ value is probably the more correct since for it the $^1\Delta_g$ level (7881.6 cm^{-1}) of the O_2 is taken into account.

$$B_{11} = \frac{W_1}{\underline{RT}}\nu_1 + \sum^{j} \nu_{j1}^2 \frac{N}{N_j} - \nu_1^2 = 23.56 + 1\ (1.025) + 4\ (41.66) - 1 = 190.23 \qquad (124)$$

$$C_1 = \frac{W_1}{\underline{RT}} - \nu_1 = - 23.56 + 1 = - 22.56 \qquad (125)$$

Substituting these numerical values in equation (29) there is obtained for the differential isentropic exponents

$$m = \kappa + \frac{\begin{vmatrix} 0 & A_1 \\ A_1 & B_{11} \end{vmatrix}}{\begin{vmatrix} 1 & A_1 \\ C_1 & B_{11} \end{vmatrix}} = \begin{cases} 1.274 - 0.0874 = 1.1866 & (126a) \\ 1.286 - 0.0949 = 1.1911 & (126b) \end{cases}$$

Although in the example under consideration only about 1.2 percent of the O_2 is dissociated the difference between the isentropic exponent m and the ratio of the specific heats κ is already quite considerable, namely, 0.091 ± 0.004, i.e. 7.1 percent of the κ value.

We shall now estimate in what frequency range the sound dispersion by the O_2 dissociation is to be expected and what values of the sound velocity and sound absorption come into question. The excitation of the vibration heats will first be assumed to follow completely the sound frequencies, i.e. we shall for the present dispense with the Kneser case of the sound dispersion.

In equation (70) we now require as a new constant φ_{11}, i.e. we must first estimate the reaction velocity U_1:

$3 \times 10^9 \approx$ number of the bimolecular collisions per second of an O atom at 273° K and 1 atm. with other particles

$3 \times 10^9 \left(\sqrt{273/2600}\right) = 1 \times 10^9 \approx$ number of bimolecular collisions per second of an O atom at 2600° K and 1 Atm. total pressure with other particles

$0.024 \times 10^9 \approx$ number of bimolecular collisions per second of an O atom with other O atoms at 2600° K and 1 Atm. total pressure.

$0.024 \times 10^9\left(10^{-13}/10^{-9}\right) = 2.4 \times 10^3 \approx$ number of collisions per second of an O atom at 2600° K and 1 atm. total pressure with other O atoms in the presence of a third particle of the collision complex of the two O atoms possesses a life of 10^{-13} seconds.

If each of the last-named termolecular collisions is suitable for a recombination of the O atoms there follows from equation (68):

$$\varphi_{11} = \frac{\left(2\pi f \cdot 2\right)}{2.4 \times 10^3 \times 0.024} = 0.218f \tag{127}$$

The 2 in the numerator compensates exactly the error arising in the denominator from the fact that in the summation over all successful collisions each collision, on account of the two O atoms that take part, was counted twice.

The order of magnitude of φ_{11} can be estimated, however, not only from the recombination of the O atoms but also from the dissociation of the O_2 molecule, though less accurately. Assuming a monomolecular reaction

$$\frac{U_1V}{N} = 0.976 \times 10^{13} \times e^{\frac{-122 \times 10^3}{RT}} \tag{128}$$

in which the factor 10^{13} is uncertain by two powers of ten but still possesses the correct order of magnitude, then we have for 2600° K:

$$\frac{U_1V}{N} = 0.976 \times 10^{13} \times 10^{-10.25} = 5.49 \times 10^2 \tag{129}$$

and therefore

$$\varphi_{11} = \frac{2\pi f}{5.49 \times 10^2} = 0.0115f \tag{130}$$

The agreement between the two entirely different estimates which lead to (127) and (130), respectively, is quite satisfactory and cannot be expected to be better. We continue the computation with the following numerical values: $\varphi_{11} = 0.2f$ and the following constants obtained from $\kappa = 1.274$:

$$A_1 = 5.182 \quad B_{11} = 190.23 \quad C_1 = -22.56 \tag{131}$$

Substituting in equation (70) there are obtained for the various frequencies f the numerical values given in Table 2 and figs. 1(a) to 1(c).

In figures 1(a) to 1(c) a logarithmic scale was chosen for the frequencies f along the axis of abscissas as is customary in representing sound dispersion measurements. The magnitude m, the sound velocity a, and the amplitude damping γ referred to unit length with increasing f pass through a point of inflection which lies at about 1450 cycles per second. The limiting values of m, as was to be expected, are, for very low frequencies, the differential isentropic exponent for complete equilibrium attainment, and, for very high frequencies, the ratio of the specific heats $\kappa = 1.2740$ at constant pressure and constant volume. The sound velocity a changes in the entire dispersion region by about 3.6 percent. The amplitude damping γ per centimeter amounts to about 2×10^{-3} cm^{-1} at the point of inflection so that the sound intensity decreases over a distance of 10 centimeters by $(1 - e^{-2\gamma} \times 10) \approx 2\gamma \times 10 = 0.04$ times the initial intensity, or a lowering by 4 percent.

The phase angle φ and the amplitude damping γl per wave length l with increasing frequency reach a maximum which similarly lies at about 1450 cycles per second, the numerical value of φ being very small since $\varphi = 0.0349$ corresponds to 2°. The previously given approximation equations (78) to (80) are thus entirely justified and the term in parenthesis proportional to φ^2 can even be neglected. The maximal γl values here computed on the basis of dissociation are about 10 times as large as the former γl values which, for moist O_2 at room temperature, were found in about the same frequency range and are conditioned by incomplete vibration excitation.[21]

As a second high-temperature example we consider the dissociation of pure CO_2 between $T = 2000$ and 3200° K at a total pressure $p = 1$ atm.

Here we must consider a total of 4 types of particles, namely, CO_2, CO, O_2, and O which we denote by the particle index 1 to 4 and which are obtained on the basis of two overall reactions. The corresponding stoichiometric coefficients ν_{jl} are given in table 3.

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[21] Kneser, H. O., Ztschr. techn. Physik 16, 216 (1935), fig. 5.

There will again first be computed the isentropic exponent m for complete attainment of equilibrium. The required numerical values are given in Table 4. Since according to the latter the partial pressure of the O atoms is still quite small, it is natural to use two types of computations for the isentropic exponent m, namely, the exact computation taking into account the two reactions 1 and 2 (see Table 3) and an approximation computation in which only reaction 1 is taken into account and reaction 2 neglected. The isentropic exponent obtained by the second method will be denoted by m'. We thus have:

$$m = \kappa + \frac{\begin{vmatrix} 0 & A_1 & A_2 \\ A_1 & B_{11} & B_{12} \\ A_2 & B_{21} & B_{22} \end{vmatrix}}{\begin{vmatrix} 1 & A_1 & A_2 \\ C_1 & B_{11} & B_{12} \\ C_2 & B_{21} & B_{22} \end{vmatrix}} \tag{132}$$

and

$$m' = \kappa + \frac{\begin{vmatrix} 0 & A_1 \\ A_1 & B_{11} \end{vmatrix}}{\begin{vmatrix} 1 & A_1 \\ C_1 & B_{11} \end{vmatrix}} \tag{133}$$

Substituting the numerical values of Table 4 there is obtained Table 5 and figure 2.

The ratio κ of the specific heats rises continuously in the temperature range 2000 to 3200° K because by the increasingly stronger dissociation the number of the 2- and 1-atom molecules increases at the cost of the 3-atom CO_2 molecules. $\kappa - m$ and $\kappa - m'$ are positive and increase with increasing temperature on account of the increasing dissociation. The isentropic exponents m and m' respectively run through a minimum because above 2600° K with increasing temperature κ increases more rapidly than $\kappa - m$ and $\kappa - m'$. The values m and m' obtained with and without account taken of the O_2 dissociation respectively differ only very little.

The fact that the approximate expression (133) yields practically the same numerical value as the exact expression (132) is due to the circumstance that B_{22} is considerably greater than the absolute values of the remaining terms of the two determinants. If the latter are developed in minors there is obtained

$$\left.\begin{aligned} \begin{vmatrix} 0 & A_1 & A_2 \\ A_1 & B_{11} & B_{12} \\ A_2 & B_{21} & B_{22} \end{vmatrix} &\approx B_{22} \begin{vmatrix} 0 & A_1 \\ A_1 & B_{11} \end{vmatrix} \\ \text{and} \qquad \begin{vmatrix} 1 & A_1 & A_2 \\ C_1 & B_{11} & B_{12} \\ C_2 & B_{21} & B_{22} \end{vmatrix} &\approx B_{22} \begin{vmatrix} 1 & A_1 \\ C_1 & B_{11} \end{vmatrix} \end{aligned}\right\} \tag{134}$$

from which $m \approx m'$. The expression

$$B_{22} = \frac{W_2}{\underline{R}T}\nu_2 + \sum^{j} \nu_{j2}^{\,2} \frac{N}{N_j} - \nu_2^{\,2}$$

is considerably greater than the other B_{lm} because, on account of the stoichiometric coefficients ν_{jl} (see Table 3), it contains a term N/N_j referring only to the O atoms and, since the latter is inversely proportional to the small partial pressure p_o of the O atoms, it is very large.

We shall now consider the sound dispersion which can be expected in pure CO_2 on the basis of the dissociation equations 1 and 2 (see Table 3) at 2600° K and 0.9994 atm total pressure. For this purpose we must first estimate the overall reaction velocities U_1 and U_2 for the equilibrium case which according to equation (68) also determine the values φ_{11} and φ_{22} entering equation (70).

We start with the reaction velocity U_2 since it is of small effect for the process of the sound dispersion and we can dispense with its consideration briefly. For if at complete attainment of equilibrium of reaction 1 the reaction 2 were no longer able to follow the increasing sound frequency f then according to Table 5 the m value of equation (70) would in order of magnitude increase only from $m = 1.1003$ to $m' = 1.1022$, that is very slightly compared to the stage $\kappa - m' = 0.0728$ which will be passed through if the reaction 1 does not occur together with 2. But even if the reactions 1 and 2 in the same frequency range can no longer follow the sound frequencies there is still no basis found for a larger effect of the reaction 2 on the dispersion process. We estimate as before the recombination of the O atoms in the termolecular collision:

$1 \times 10^9 \approx$ number of the bimolecular collisions per second of an O atom with other particles at 2600° K and 1 atm total pressure.

$0.00679 \times 10^9 = 6.79 \times 10^6 \approx$ number of bimolecular collisions per second with other particles of an O atom in dissociating CO_2 at 2600° K and 1 atm total pressure.

$6.79 \times 10^6 \times 10^{-13}/10^{-9} = 6.79 \times 10^2 \approx$ number of collisions per second of an O atom in dissociating CO_2 at 2600° K and 1 atm total pressure with other O atoms in the presence of a third particle.

If each of these termolecular collisions leads to recombination there is obtained

$$\varphi_{22} = \frac{2\pi f2}{6.79 \times 10^2 \times 0.00679} = 2.72f \tag{135}$$

To estimate the reaction velocity U_1 we similarly use the reverse reaction, i.e. the combustion of CO with O_2 at 2600° K in the presence of excess CO_2 and the O atom content of the equilibrium. As elementary reactions that determine the velocity we shall take the following into consideration:[22]

Elementary reaction I:

$$CO + O + M \longrightarrow CO_2 + M + \text{ca. } 125 \text{ kcal} \tag{136}$$

Elementary reaction II:

$$CO + O_2 \longrightarrow CO_2 + O + \text{ca. } 8 \text{ kcal} \tag{137}$$

For the reaction I we estimate:

$7 \times 10^9 \approx$ number of bimolecular collisions per second of a CO molecule at 273° K and 1 atm. total pressure with other particles.

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[22] Jost, W., Explosions- und Verbrennungsvorgänge in Gasen, Berlin 1939, p. 338.

$7 \times 10^9 \sqrt{273/2600} = 2.27 \times 10^9 \approx$ number of bimolecular collisions per second of a CO molecule at 2600° K and 1 atm. total pressure with other particles.

$2.27 \times 10^9 \times 0.00679 = 1.54 \times 10^7 \approx$ number of bimolecular collisions per second of a CO molecule at 2600° K and 1 atm. total pressure with other O atoms.

$1.54 \times 10^7 \times 10^{-13} \times 2.26 \times 10^9 = 3.5 \times 10^3 \approx$ number of collisions per second of a CO molecule at 2600° K and 1 atm. total pressure with O atoms in the presence of a third particle.

If the elementary reaction I, which is assumed to occur for each termolecular collision, determines in general the velocity for the overall reaction $2CO + O_2 \longrightarrow 2CO_2$ there would be obtained from equation (68)

$$\varphi_{11} = \frac{2\pi f \times 2}{3.5 \times 10^3 \times 0.1628} = 2.2 \times 10^{-2} f \qquad (138)$$

In the high-temperature range the elementary reaction II of equation (137) could also be an important factor. It undoubtedly possesses a considerable, though as yet unknown activation energy q_{II}. We shall estimate with various arbitrarily assumed q_{II} values and obtain:

$2.27 \times 10^9 \times 0.078 = 1.77 \times 10^8 \approx$ number of the bimolecular collisions per second of a CO molecule at 2600° K and 1 atm total pressure with O_2 molecules.

The conversion probability per second of a single CO molecule with an O_2 molecule under the same temperature and pressure conditions then becomes

$$1.77 \times 10^8 \times e^{\frac{-20000}{1.986 \times 2600}} = 3.69 \times 10^6 \quad \text{for} \quad q_{II} = 20 \text{ kcal}$$

$$1.77 \times 10^8 \times e^{\frac{-40000}{1.986 \times 2600}} = 7.69 \times 10^4 \quad \text{for} \quad q_{II} = 40 \text{ kcal}$$

$$1.77 \times 10^8 \times e^{\frac{-60000}{1.986 \times 2600}} = 1.604 \times 10^3 \quad \text{for} \quad q_{II} = 60 \text{ kcal}$$

If the elementary reaction II of equation (137) were alone to determine the velocity of the reaction $2CO + O_2 \longrightarrow 2CO_2$ there would be obtained

$$\varphi_{11} = \frac{2\pi f \times 2}{3.69 \times 10^6 \times 0.1628} = 2.09 \times 10^{-5} f \quad \text{for} \quad q_{II} = 20 \text{ kcal} \qquad (139)$$

$$\varphi_{11} = \frac{2\pi f \times 2}{7.69 \times 10^4 \times 0.1628} = 1.005 \times 10^{-3} f \quad \text{for} \quad q_{II} = 40 \text{ kcal} \qquad (140)$$

$$\varphi_{11} = \frac{2\pi f \times 2}{1.604 \times 10^3 \times 0.1628} = 4.82 \times 10^{-2} f \quad \text{for} \quad q_{II} = 60 \text{ kcal} \qquad (141)$$

These values of φ_{11} computed on the basis of reaction II extend over the range $2 \times 10^{-5} f$ to $5 \times 10^{-2} f$ which includes the value $\varphi_{11} = 2.2 \times 10^{-2} f$ obtained from equation (138). This is 22 times as great as the value of φ_{11} that is obtained from equation (140) for the reaction II with $\varphi_{11} = 40$ kcal. As long, therefore, as q_{II} is not considerably greater than 40 kcal, it must be possible on the basis of sound dispersion measurements to distinguish between the two reaction possibilities I and II and at the same time it should be possible from tests at various temperatures to determine q_{II}.[23] The relations are numerically even more favorable, i.e. q_{II} becomes also greater than 40 kcal, if we drop two of the restricting assumptions used thus far, namely, that the reaction I is successful for each three-particle

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[23] Case II, i.e. the reaction equation (137) is the more interesting as it takes place between two quite stable initial molecules and still leads to an active particle (O atom) so that chains can be initiated. The knowledge of the reactions between such stable initial molecules where high activation energies must always be expected is quite generally important for many starting processes (induction periods) such as for example occur in the prereactions in the knocking engines.

collision and that for the kinetic process of II only two quadratic energy terms are of importance.[24] If in the first case only the nth termolecular collision leads to a transformation and if, in the second case 6 quadratic energy terms were effective[25] there would be obtained in place of (138):

$$\varphi_{11} = n \times 2.2 \times 10^{-2} f \tag{142}$$

and in place of equation (140):

$$\varphi_{11} = \frac{1.005 \times 10^{-3} f}{\frac{1}{\Gamma 3}\left(\frac{40{,}000}{1.986 \times 2600}\right)^{2}} = \frac{1.005 \times 10^{-3} f}{30} \tag{143}$$

This means that the experimental differentiation between the reaction possibilities I and II would become still easier because the already large value (138) would become still larger and the small value (140) still smaller.

We shall now see in what frequency range the sound dispersion in pure CO_2 at 2600 °K and 1 atm. total pressure is to be expected and what numerical values are assumed by the sound velocity and sound absorption. We shall compute the dispersion curves from equation (70).

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[24] The probability that a system with s quadratic energy terms 5 possesses a total energy greater than q is given by

$$w_{s(q)} \approx e^{\frac{-q}{RT}} \times \frac{1}{\Gamma s/2} \left(\frac{q}{RT}\right)^{\frac{s}{2}-1}$$

so that for $s = 2$ there follows the expression used $w_{2(q)} \approx e^{\frac{-q}{RT}}$

See H. J. Schumacher, Chemische Gasreaktionen, p. 15, Leipzig 1938.

[25] 4 terms from the vibrations of the CO and O_2 terms from the relative motion of the colliding molecules; or 2 terms from the O_2 vibration and 4 terms from the relative motion: see J. J. Schumacher loc. cit. p. 20.

The required values of A_l, B_{lm}, and C_l are given in table 4. For φ_{11} are used the rounded numerical values of the expressions (135), (138), and (140), that is,

$$\begin{aligned} &\text{Case I:} \quad \varphi_{11} = .02f \qquad \varphi_{22} = 2f \\ &\text{Case II:} \quad \varphi_{11} = .001f \qquad \varphi_{22} = 2f \end{aligned} \tag{144}$$

The results of the computation are given in table 6 and figures 3a to 3c.

The m and a curves in figure 3a again show an S-shaped trend as was found to be the case in figure 1a for the O_2 dissociation. In figure 3a for the case II two points of inflection can clearly be seen: the first at about 500 cycles per second for the small stage of the O_2 dissociation ($O_2 \rightleftarrows 2O$) and a second one at 1.5×10^5 cycles per second for the large stage of the CO_2 dissociation $2CO_2 \rightleftarrows 2CO + O_2$.

The φ and γl curves possess in figure 3b marked maxima (compare also fig. 1b for the dissociation of pure O_2 at 2600° K and 1 atm.) which moreover in the two cases I and II are at the same height and possess approximately the γl value 0.1. The maximum γl values are thus evidently to a large extent independent of the assumed reaction velocity U_1 for the CO_2 dissociation.[26]

The equally large maximum values of γl (damping coefficient per wave length) bring about the result that the damping coefficient γ per cm in case II assumes on the average larger values than in case I. Moreover in the reaction-kinetically determined sound dispersion only the γl values run through a maximum with increasing frequency while the γ values approach a constant maximum value,[27] which lies higher the higher the frequencies in the sound dispersion range; γ_{max} is in case II, for example, 20 times as large as in case I; see figure 3c.

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[26] It may be noted that the maximum γl value in figure 1b likewise lies at about 0.1.

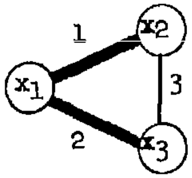
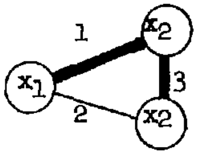
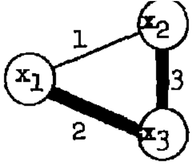
[27] The reaction-kinetically determined sound absorption corresponds in optics to a continuous absorption which sets in at a definite frequency range with constant intensity and which extends up to infinitely high frequencies. The case of light absorption in a finite frequency range restricted at each end, such as occurs, for example, in color filters, appears to have no counterpart in sound absorption.

In order to obtain a still clearer picture of the magnitude of the sound absorption determined by pure reaction kinetics there are shown in figure 3d the curves of $e^{-10\gamma}$ and $e^{-20\gamma}$. These give the transmitted fraction of the sound energy if the sound wave traverses a distance of 5 and 10 cm respectively. In case II for 10^7 cps only 2.7 or 0.074 percent of the initial sound intensity remains. Above 5.10^5 cps no sound measurement is any longer possible if the sound must traverse a path from 5 to 10 cm from the sound source over a medium uniformly heated to 2600° K. It is not possible however to dispense with such measurement if sound of definite and controllable frequency can be produced at 2600° K. As a result of this too high sound absorption the experimentally accessible sound dispersion range is as yet in many cases for high-temperature reactions limited toward the high frequencies. We shall return to this question later. But first there will be discussed other effects on the sound dispersion which for reaction-kinetical investigations can similarly restrict the useful frequency range for the evaluation of sound tests.

Translated by S. Reiss
National Advisory Committee
for Aeronautics

TABLE 1

TRANSFORMATIONS AND EQUILIBRIUM REACTION VELOCITIES BETWEEN THREE DIFFERENT EXCITATION STAGES OR TAUTOMERIC FORMS OF THE SAME CHEMICAL SUBSTANCE

Case	Scheme	Overall Reactions		δN_j as function of the individual δz_l	U_l as function of the $\overrightarrow{u_m}$ and $\overleftarrow{u_m}$
		Equation	Index		
I		$X_1 \rightleftarrows X_2$ $X_1 \rightleftarrows X_3$	1 2	$\delta N_1 = -\delta z_1 - \delta z_2$ $\delta N_2 = \delta z_1$ $\delta N_3 = \delta z_2$	$U_1 = \overrightarrow{u_1} + \overleftarrow{u_3} = \overleftarrow{u_1} + \overrightarrow{u_3}$ $U_2 = \overrightarrow{u_2} + \overrightarrow{u_3} = \overleftarrow{u_2} + \overleftarrow{u_3}$
II		$X_1 \rightleftarrows X_2$ $X_2 \rightleftarrows X_3$	1 3	$\delta N_1 = -\delta \bar{z}_1$ $\delta N_2 = \delta \bar{z}_1 - \delta \bar{z}_3$ $\delta N_3 = \delta \bar{z}_3$	$\bar{U}_1 = \overrightarrow{u_1} + \overrightarrow{u_2} = \overleftarrow{u_1} + \overleftarrow{u_2}$ $\bar{U}_3 = \overrightarrow{u_3} + \overrightarrow{u_2} = \overleftarrow{u_3} + \overleftarrow{u_2}$
III		$X_2 \rightleftarrows X_3$ $X_1 \rightleftarrows X_3$	3 2	$\delta N_1 = -\delta \bar{\bar{z}}_2$ $\delta N_2 = -\delta \bar{\bar{z}}_3$ $\delta N_3 = \delta \bar{\bar{z}}_2 + \delta \bar{\bar{z}}_3$	$U_3 = \overleftarrow{u_3} + \overrightarrow{u_1} = \overrightarrow{u_3} + \overleftarrow{u_1}$ $U_2 = \overleftarrow{u_2} + \overleftarrow{u_1} = \overrightarrow{u_2} + \overrightarrow{u_1}$

Conclusions:

$\delta z_1 = -\delta \bar{\bar{z}}_3$

$\delta z_2 = \delta \bar{z}_3$

$\delta \bar{z}_1 = \delta \bar{\bar{z}}_2$

$U_1 = \bar{\bar{U}}_3$

$U_2 = \bar{U}_3$

$\bar{U}_1 = \bar{\bar{U}}_2$

TABLE 2

ESTIMATED SOUND DISPERSION IN THE O_2 AT 2600 °K AND 1 ATM.

ON THE BASIS OF DISSOCIATION ALONE

f $[s^{-1}]$	m	φ	a $[cm\ s^{-1}]$	γ $[cm^{-1}]$	γl
10	1.1866	4.80×10^{-4}	9.006×10^{4}	1.675×10^{-7}	1.508×10^{-3}
1×10^{2}	1.1869	4.78×10^{-3}	9.007×10^{4}	1.665×10^{-5}	1.499×10^{-2}
5×10^{2}	1.1953	2.155×10^{-2}	9.040×10^{4}	3.746×10^{-4}	6.773×10^{-2}
1×10^{3}	1.2132	3.299×10^{-2}	9.107×10^{4}	1.138×10^{-3}	1.036×10^{-1}
2×10^{3}	1.2423	3.400×10^{-2}	9.217×10^{4}	2.319×10^{-3}	1.068×10^{-1}
1×10^{4}	1.2721	1.031×10^{-2}	9.325×10^{4}	3.474×10^{-3}	3.239×10^{-2}
1×10	1.2740	1.054×10^{-3}	9.332×10^{4}	3.550×10^{-3}	3.312×10^{-3}

Table 3

REACTION EQUATIONS AND STOICHIOMETRIC COEFFICIENTS FOR THE DISSOCIATION OF CO_2

		Type of Particle Particle Index	CO_2 1	CO 2	O_2 3	O 4	
Reaction 1	$2\ CO_2 \rightleftarrows 2\ CO + O_2$	$\nu_{j1} =$	2	−2	−1	0	$\nu_1 = -1$
Reaction 2	$O_2 \rightleftarrows 2\ O$	$\nu_{j2} =$	0	0	1	−2	$\nu_2 = -1$

TABLE 4

NUMERICAL VALUES FOR THE COMPUTATION OF THE DIFFERENTIAL ISENTROPIC EXPONENT m IN DISSOCIATING CO_2 (1 atm = 760 Hg)

T in °K	2000	2300	2600	2900	3200
$\dfrac{p_{CO}\sqrt{p_{O_2}}}{p_{CO_2}}$ in $\text{Atm}^{1/2}$. . . .	0.001337	0.01150	0.0605	0.2235	0.640
$\dfrac{p_O}{\sqrt{p_{O_2}}}$ in $\text{Atm}^{1/2}$	0.000708	0.00525	0.0243	0.0835	0.220
p_{CO_2} in Atm	0.9960	.9100	.7518	.5185	.2912
p_{CO} in Atm	.01528	.06045	.1628	.3106	.4443
p_{O_2} in Atm	.00760	.03000	.0780	.1393	.1760
p_O in Atm	.00006	.00091	.00679	.03116	.0923
$p = \sum^{j} p_j$ in Atm	1.01894	1.0014	.9994	.9996	1.0038
κ	1.1610	1.1635	1.1750	1.1982	1.2350
W_1 in kcal	-132.79	-131.96	-131.16	-130.31	-129.44
W_2 in kcal	-121.15	-121.41	-121.61	-121.78	-121.90
A_1	4.221	3.558	3.270	3.286	3.554
A_2	3.749	3.182	2.945	2.992	3.275
B_{11}	437.29	131.96	67.09	49.40	47.90
B_{12}	-101.62	-5.50	11.587	14.453	13.666
B_{21}	-104.55	-7.80	9.737	12.973	12.486
B_{22}	6.812×10^4	4463	624.16	155.73	67.39
C_1	-32.43	-27.88	-24.40	-21.63	-19.37
C_2	-29.50	-25.58	-22.55	-20.15	-18.19

TABLE 5

COMPARISON OF THE DIFFERENTIAL ISENTROPIC EXPONENTS m AND m' WITH THE VALUE FOR DISSOCIATING CO_2

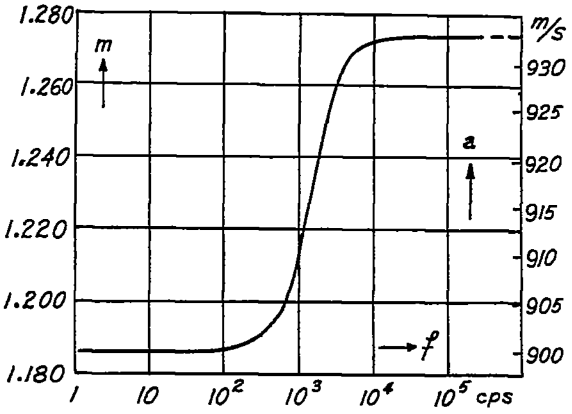
T in $^{\circ}$K	2000	2300	2600	2900	3200
κ	1.1610	1.1635	1.1750	1.1982	1.2350
$\kappa - m$	.0312	.0555	.0747	.0939	.1195
m	1.1298	1.1080	1.1003	1.1043	1.1155
$\kappa - m'$	.0310	.0548	.0728	.0896	.1082
m'	1.1300	1.1087	1.1022	1.1086	1.1268

TABLE 6

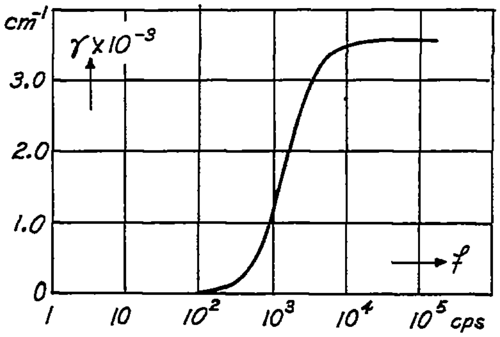
ESTIMATED SOUND DISPERSION IN CO_2 AT 2600 °K AND 1 ATM. ON THE BASIS OF DISSOCIATIONS

$$2CO_2 \rightleftarrows 2CO + O_2 \quad \text{and} \quad O_2 \rightleftarrows 2\,O$$

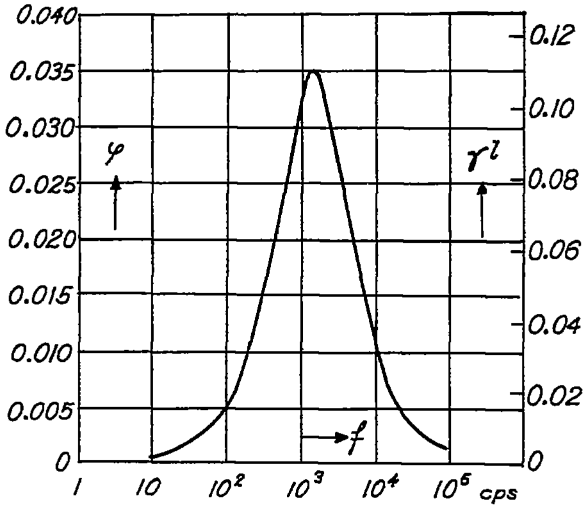
f $[s^{-1}]$	m	φ	a $[cm\ s^{-1}]$	γ $[cm^{-1}]$	γl	l [cm]	$e^{-10\gamma}$	$e^{-20\gamma}$
Case I								
1×10^2	1.1005	1.295×10^{-3}	7.682×10^4	5.296×10^{-6}	4.067×10^{-3}	768.2	1.0000	1.0000
1×10^3	1.1030	9.25×10^{-3}	7.695×10^4	3.779×10^{-4}	2.906×10^{-2}	76.95	.9962	.9924
2×10^3	1.1070	1.693×10^{-2}	7.705×10^4	1.381×10^{-3}	5.318×10^{-2}	38.51	.9862	.9726
3×10^3	1.1125	2.312×10^{-2}	7.722×10^4	2.822×10^{-3}	7.260×10^{-2}	25.75	.9721	.9450
5×10^3	1.1255	3.030×10^{-2}	7.770×10^4	6.122×10^{-3}	9.516×10^{-2}	15.54	.9407	.8849
7×10^3	1.1372	3.220×10^{-2}	7.814×10^4	9.065×10^{-3}	1.011×10^{-1}	11.16	.9134	.8343
1×10^4	1.1498	3.043×10^{-2}	7.853×10^4	1.217×10^{-2}	9.558×10^{-2}	7.853	.8854	.7839
2×10^4	1.1665	2.036×10^{-2}	7.912×10^4	1.617×10^{-2}	6.396×10^{-2}	3.956	.8507	.7237
1×10^5	1.1746	4.569×10^{-3}	7.937×10^4	1.808×10^{-2}	1.435×10^{-2}	.7937	.8346	.6966
1×10^6	1.1750	4.592×10^{-4}	7.940×10^4	1.817×10^{-2}	1.443×10^{-3}	.0794	.8339	.6954
1×10^7	1.1750	4.592×10^{-5}	7.940×10^4	1.817×10^{-2}	1.443×10^{-4}	.00794	.8339	.6954
Case II								
1×10^2	1.1005	4.925×10^{-4}	7.685×10^4	2.013×10^{-6}	1.547×10^{-3}	768.5	1.0000	1.0000
1×10^3	1.1019	8.96×10^{-4}	7.690×10^4	3.660×10^{-5}	2.814×10^{-3}	76.90	.9996	.9992
1×10^4	1.1024	4.53×10^{-3}	7.690×10^4	1.850×10^{-3}	1.423×10^{-2}	7.690	.9815	.9633
3×10^4	1.1051	1.296×10^{-2}	7.700×10^4	1.586×10^{-2}	4.074×10^{-2}	2.567	.8533	.7281
6×10^4	1.1128	2.295×10^{-2}	7.724×10^4	5.604×10^{-2}	7.210×10^{-2}	1.287	.5710	.3260
1×10^5	1.1257	3.011×10^{-2}	7.770×10^4	1.218×10^{-1}	9.46×10^{-2}	.777	.2958	.08750
2×10^5	1.1500	3.026×10^{-2}	7.860×10^4	2.419×10^{-1}	9.505×10^{-2}	.393	.08901	7.923×10^{-3}
4×10^5	1.1665	2.020×10^{-2}	7.912×10^4	3.208×10^{-1}	6.345×10^{-2}	.1978	.04044	1.635×10^{-3}
1×10^6	1.1735	8.935×10^{-3}	7.932×10^4	3.539×10^{-1}	2.808×10^{-2}	.0793	.02904	8.433×10^{-4}
1×10^7	1.1750	9.108×10^{-4}	7.938×10^4	3.605×10^{-1}	2.861×10^{-3}	.00794	.02719	7.393×10^{-4}



(a) Dependence of m and the sound velocity a on the frequency.



(b) Dependence of the damping constant γ referred to unit length (cm) for the sound amplitude.



(c) Dependence of the phase angle φ and of the damping constant γl referred to the wave length l on the frequency.

Figure 1.- Estimated sound dispersion in pure O_2 at 2600° K and 1 atmosphere total pressure on the basis of the dissociation $O_2 \rightleftarrows 2\ O$ alone.

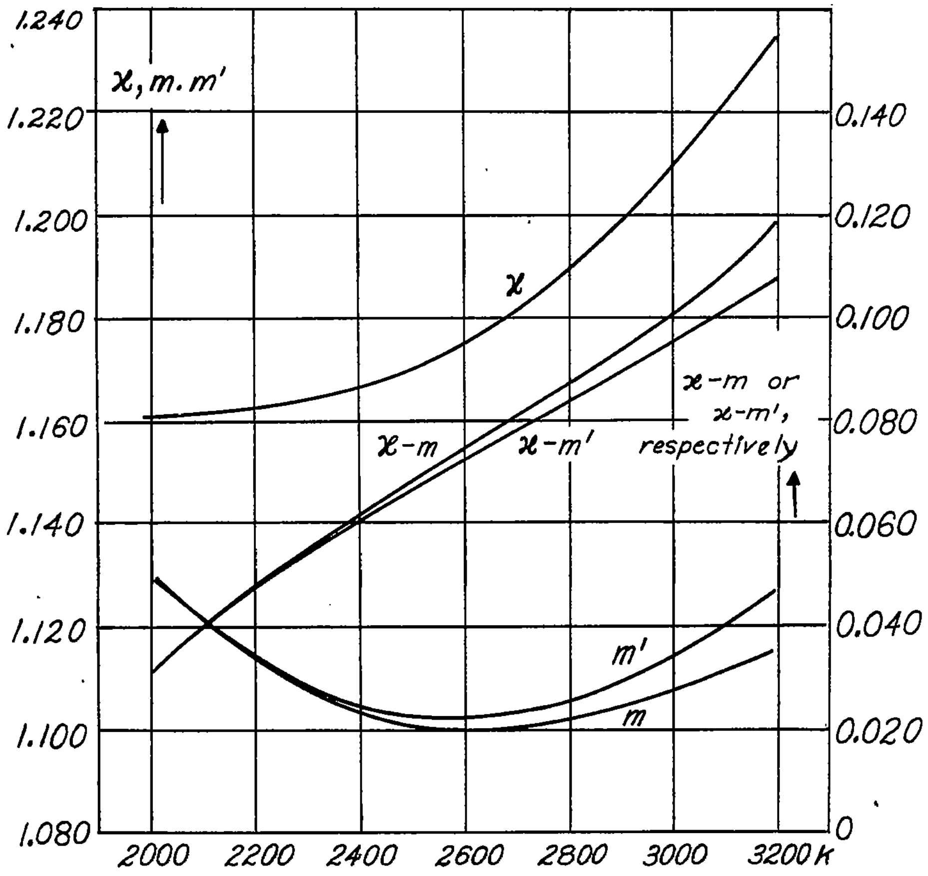
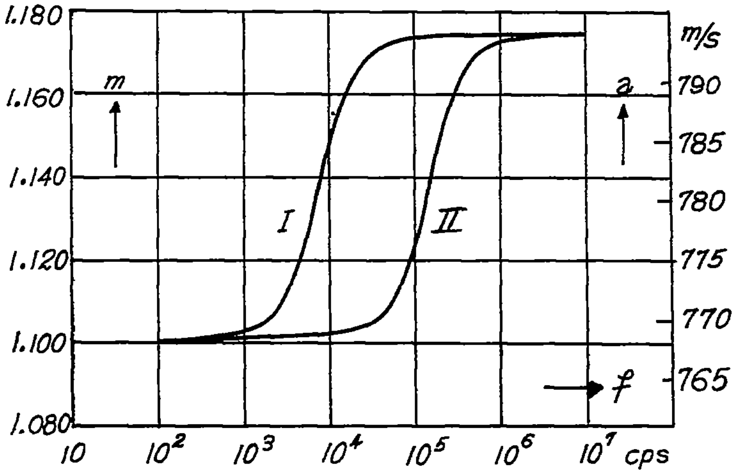
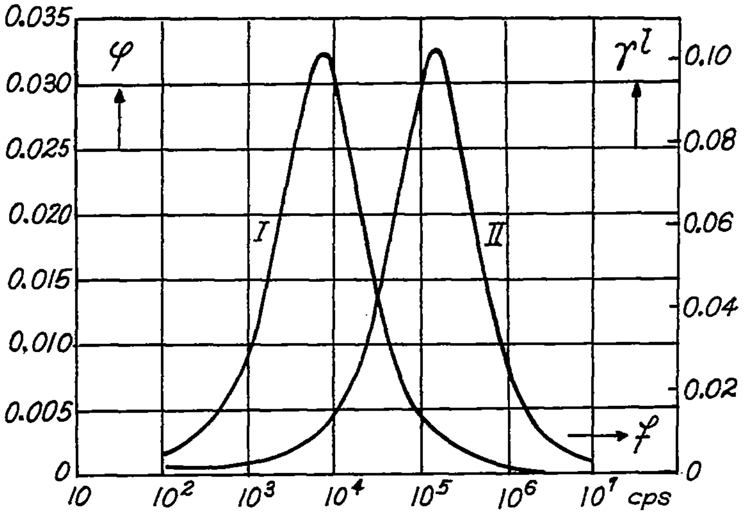


Figure 2.- Differential isentropic exponent in pure CO_2 for full equilibrium: $\kappa = \frac{C_p}{C_v}$ = ratio of molar heats, m = exponent in the isentropic curve pV^m = const. taking account of the two equilibria $2CO_2 \rightleftarrows 2CO + O_2$ and $O_2 \rightleftarrows 2\ O$. m' = isentropic exponent for the case of the first reaction alone.

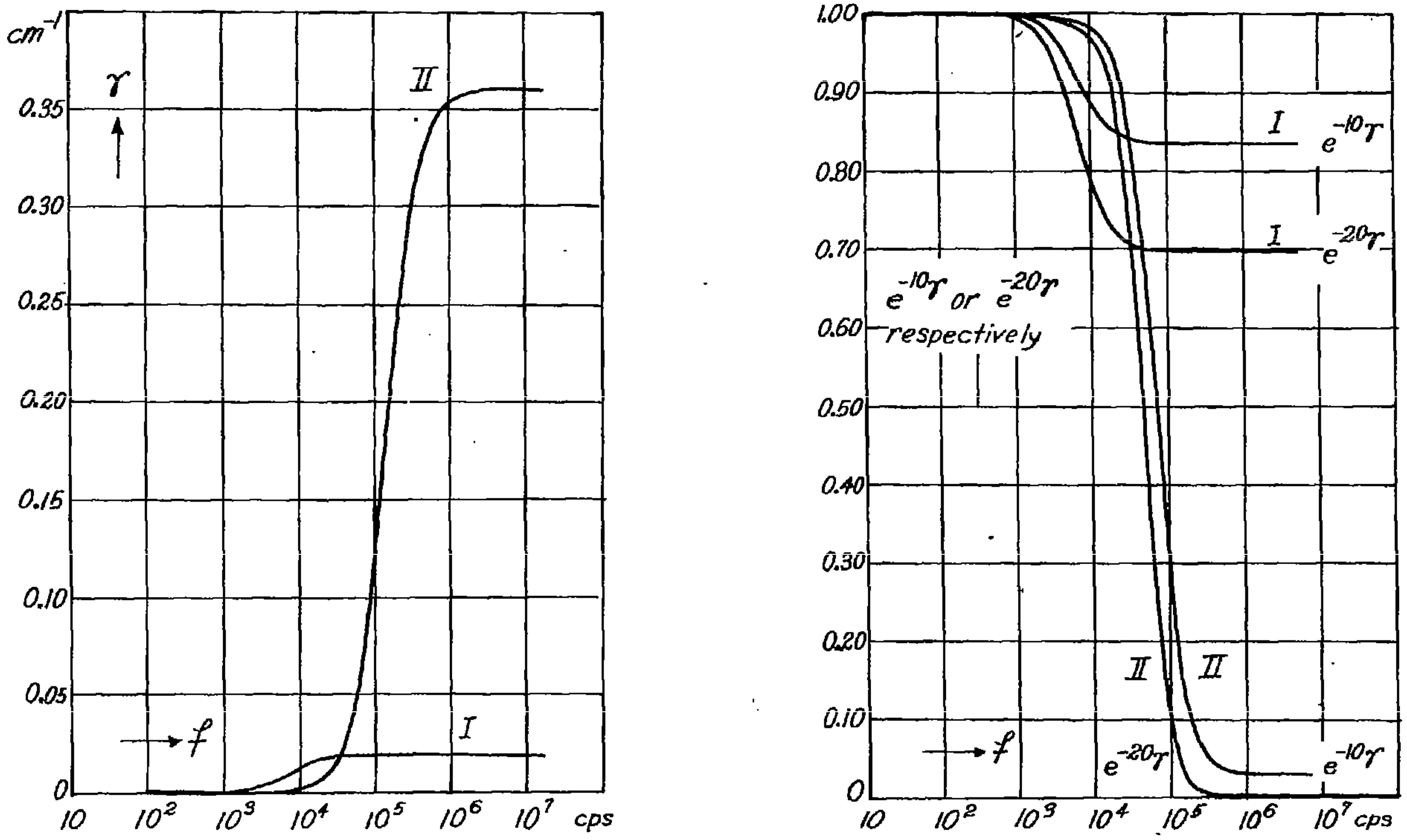


(a) Dependence of m and the sound velocity a on the frequency.



(b) Phase angle φ and damping constant γl referred to the wave length l as functions of the frequency.

Figure 3.- Estimated sound dispersion in CO_2 at 2600° K and 1 atmosphere total pressure on the basis of the dissociations $2CO_2 \rightleftarrows 2CO + O_2$ and $O_2 \rightleftarrows 2\ O$.



(c) Damping constant γ referred to unit length (cm).

(d) Fraction of sound intensity transmitted for a path of 5 and 10 cm length.

Figure 3.- Concluded.

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