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Adiabatic change of state in dissociating gases and the method of sound dispersion for the study of very rapid, homogeneous gas reactions (1).

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Rapid, homogeneous gas reactions such as we find in combustion present various special problems. Their solution implies on one hand the development of new methods of investigation and on the other the improvement of existing ones. Adiabatic changes of molecular state are used in certain methods. They can be large and measured in atmospheres, as earlier mentioned, or very small, of the order of 1 dyn/sq.cm., as in the case of sound waves.

The sound dispersion method for the study of very rapid, homogeneous gas reactions, discovered by W. Nernst (2) over 30 years ago, works as follows: the test gas, originally in a state of thermodynamic oquilibrium, is subjected to the rapid adiabatic pressure of a sound wave; then we observe which frequencies can be followed by the chemical reactions continuously developing to maintain the thermodynamic equilibrium. As soon as the limit is reached, both the sound velocity and the sound absorption vary with the frequency in a special way.

In the adiabatic change of molecular state of an ideal gas the pressure p and the volume V are connected by the equation:

 $pV^{m} = const.$ (1)

In non-dissociating gases the exponent \underline{m} is identical with the ratio $\underline{m} = C_D/C_V$ of the thermal capacities at constant pressure, or volume. In dissociating gases \underline{m} is smaller; in their adiabatic expansion cooling occurs, the dissociation retrocedes, the recombination heat is liberated, i.e. the gas has internal sources of heat and its change approaches the isotherm, for which the polytropic exponent \underline{m} is equal to 1 in the formula $\underline{pV^1} = const.$

First we consider the differential adiabatic changes & of a given gas volume V, in which n thermodynamically independent empirical molecular reaction equations can develop. The equilibrium states must be fully reached at all moments, which would correspond to sufficiently low sound frequencies. The following relations must obtain for such a change:

⁽¹⁾ This lecture is taken from the more detailed study in the Zs.f. Elektrochem. und angew. physikal. Chemie 48 (1942) 62 - 82, 116 - 131.

See the dissertation of F. Keutel, (Nernstschen Laboratorium) Berlin 1910.

Conservation of energy:

$$\delta H = \left(\frac{\partial H}{\partial T}\right)_{pN,1} \delta T + \left(\frac{\partial H}{\partial p}\right)_{TN,1} \delta p + \sum_{i=1}^{n} \left(\frac{\partial H}{\partial N_{i}}\right)_{pT} \delta N j \qquad (4)$$

1 equation
$$\left\{C_{p}\delta T - V_{\delta p} - \frac{m}{2} V_{m\delta} z_{m} = 0\right\}$$
 (5)

1th Reaction equation

$$|v_{1}||x_{1}||v_{2}||x_{2}||+...+|v_{5}||x_{5}||x_{5}||x_{6}||x_{6}||x_{6}||$$
 (6)

Mass action laws:

$$\sum_{j=1}^{n} v_{j} = lnK_{j} \qquad (7)$$

$$\sum_{i=1}^{n} v_{i} \frac{\delta^{p_{i}}}{2} = \delta^{1} n^{K} = \frac{W_{i}}{RT^{2}} \delta T \qquad (8)$$

The symbols are:

V - volume of the given gas mass.

T = absolute temperature

p = total pressure

R = gas constant per mol.

E = energy of the given gas mass.

H = enthalpy of same

Cp = thermal capacity of same at constant pressure.

Nj = number of type j mols contained in V.

p; = type j partial pressure

W/ = heat of reaction of the 1th empirical reaction (W, > 0 with exothermic course of reaction 6 from left to right)

K, = equilibrium constant of 1th empirical reaction

X; = chemical symbol of type j molecules

|vi/ = absolute value of stoichiometric type j concentration (first index) in the 1th reaction equation (6) (second index); if it goes from left to right, with Eucken's method of notation it is:

If we apply the ideal gas law pV = RT $\stackrel{1}{\sim}$ N₁ and replace in equations 5 and 8 the temperature variation δ T by the volume variation δ V and finally eliminate quantities δ N₁ or δ Z_m, we obtain the final equation for the differential adiabatic exponents of a dissociating gas mixture

with the abbreviations

$$\mathcal{H} = \frac{C_{\mathbf{p}}}{C_{\mathbf{v}}} \tag{10}$$

$$A_{\ell} = x v_{\ell} - (x - 1) \frac{W}{RT}$$
 (11)

$$\frac{1}{-B_{lm}} = \frac{W_{l}}{RT} v_{m} + \sum_{i=1}^{l} v_{i,l} v_{i,m} \frac{N}{N_{i}} v_{l} v_{m}$$

$$(12)$$

$$\overline{C_{i}} = \frac{W_{i}}{R T} V_{i}$$
(13)

The abbreviations A; B m, C; in the two determinants of equation 9 can be immediately expressed, once the equilibrium composition of the gas and the heat of reactions of the empirical molecular reactions are known. The first line of each determinant corresponds to the first law (equation 5), the n further lines cover the n thermodynamically independent reactions. If those are absent, the numerator determinant in equation 9 disappears, and m becomes = X, as is the case for a non-dissociating gas.

The following equations apply to the adiabatic changes in an even, infinitely wide sound wave.

Conservation of masses:
$$\frac{dN}{dt} = -\sum_{i,m}^{m} \frac{dz_{m}}{dt}$$
 (14)

$$\frac{dN}{dt} = \sum_{m}^{m} v_m \frac{dz_m}{dt} \qquad (15)$$

$$\frac{1}{V} \frac{dV}{dt} = \frac{3W}{2X}$$
 (16)

Conservation of energy:

$$\frac{dE}{dT} = -p \frac{dV}{dt} \tag{17}$$

$$C_{p} \frac{dT}{dt} - V \frac{dp}{dt} - \sum_{m}^{m} W_{m} \frac{dz_{m}}{dt} = 0$$
 (18)

Conservation of impulse:

$$\frac{dw}{dt} = -\frac{\partial p}{\partial x} \tag{19}$$

The new factors on the time coordinate t are the space coordinate x (direction of propagation of the sound wave), the linear flow velocity w and the density ? Periodic positive and negative variations of all factors we produced in the sound wave, i.e. we can consider the same as real parts of complex periodic functions:

$$p = p_0 + \delta p \qquad \delta p = Re \left\{ p_0 gx + ht \right\}$$

$$V = V_0 + \delta V \qquad \delta V = Re \left\{ v_0 gx + ht \right\}$$

$$\delta z_m = Re \left\{ z_m^{0} gx + ht \right\}$$

$$w = Re \left\{ w_0 gx + ht \right\}$$

Its argument

gx • ht
$$= 2\pi \operatorname{fi}\left\{\hat{t} - \frac{x}{a}\right\} - yx$$
 (21)

contains beside the time and space coordinates t and x also the factors:

f = sound frequency

a = sound velocity

y - damping constant of the sound amplitude per cm. of path.

From the frequency dependence of a and y, i.e.:

we want to ascertain whether the chemical reaction velocities can follow the sound frequency in question. We consider the 1th empirical molecular reaction and indicate by:

U its frequency from left to right per unit of time and volume at any moment;

its frequency from right to left per unit of time and volume at any moment;

Ut its frequency from to right and from right to left in the state of equilibrium (in this case the state in the medium at rest mean value of the states in the sound field) where U, = U, = U,

How often per unit of time in the given gas volume V the 1th reaction occurs from left to right is expressed by:

$$\frac{\mathrm{d}\mathbf{z}}{\mathrm{d}\mathbf{t}} = \mathbf{v} \left(\overrightarrow{\mathbf{U}}_{\mathbf{i}} - \overleftarrow{\mathbf{U}}_{\mathbf{i}} \right). \tag{24}$$

Its left hand side appeared before in the initial equations 14, 15 and 18; we want to refer its right hand side to the conversion frequency U in the state of equilibrium. We apply Taylor's laws:

$$\frac{\partial \vec{v}_{i}}{\partial t} = \frac{\partial i \vec{n} \vec{v}_{i}}{\partial T} \delta T + \sum_{i=0}^{N} \frac{\partial i \vec{n} \vec{v}_{i}}{\partial c_{i}} = \frac{\partial \vec{v}_{i}}{\partial c_{i}} \delta c_{i} =$$

$$\begin{cases} n \frac{\overline{U}_1}{U_1} = \frac{\partial \ln \overline{U}_2}{\partial T} \, \delta T + \sum_{i} \frac{\partial \ln \overline{U}_2}{\partial c_1} \, \delta c_1 = \\ \ln \left(1 + \frac{\overline{U}_1 - U_1}{U_2} \right) \approx \frac{\overline{U}_1 - U_2}{U_1} \tag{26}$$

In order that the mass action law be fulfilled in the point of equilibrium proper for reaction

$$\begin{vmatrix} v_{11} & x_{1} & v_{21} & x_{2} & \cdots & w_{51} & x_{5} & v_{61} & x_{6} & \cdots & w_{6} & \cdots & w_{61} & \cdots & w_{6$$

the reaction velocities \tilde{U}_{c} and \tilde{U}_{c} in its vicinity must depend on concentrations c_{1} as follows:

$$\frac{1}{V_{1}} - k_{1}c_{1} - V_{1}(|c_{2}| V_{2}| ... F(T, c_{j})) - (28)$$

$$\frac{1}{V_{1}} - k_{1}c_{5} - V_{5}(|c_{6}| V_{6}| ... F(T, c_{j})) - (29)$$

F(T, c;) can be any arbitrary function of T and c;. If we express the temperature function of the velocity constants k; and k; by:

$$\frac{\Im \ln k_1}{\partial T} = \frac{\vec{q}_1}{RT^2} \quad (30) \quad \text{and} \quad \frac{\partial \ln k_2}{\partial T} = \frac{\vec{q}_1}{RT^2} \quad (31)$$

where q and q are the activation heats of the 1th forward and reverse reaction; from 25 and 31 we have

$$\frac{\vec{v}_{i} - \vec{v}_{i}}{v_{i}} = \frac{\vec{q}_{i} - \vec{q}_{i}}{RT^{2}} \delta_{T} \cdot \sum_{i=1}^{J} v_{i}, \frac{\delta c_{i}}{c_{i}}$$
(32)

i.e. by means of 32 and 24 we can express $\frac{dz_m}{dt}$ in equations 14,15 and 18

by the forward or reverse reaction velocity U_m in the point of equilibrium and by the difference of activation heat \vec{q}_m , which

can again be expressed by the heat of reaction W_m . The originally arbitrary function $F(T,c_1)$ in (28) and (29) disappears, and our further result is thus independent of any special hypothesis on the kinetics of the reactions in question (1).

For a sound velocity a, for the amplitude damping constant y per unit of length and for the amplitude damping constant y per wave length / the final formulae for the evaluation of sound dispersion measurements are:

$$a = \sqrt{\frac{mRT}{M}} \cdot \frac{1}{\cos \varphi} = \sqrt{\frac{mRT}{M}} \cdot \left(1 + \frac{2}{8}\right)$$
 (33)

$$y = 277 \sqrt{\frac{M}{mRT}} \sin \frac{\varphi}{2} \approx 71 f \sqrt{\frac{M}{mRT}} \varphi \left(1 - \frac{\varphi^2}{24}\right)$$
 (34)

$$y = \frac{y \cdot a}{f} = 2 \eta \operatorname{tg} \frac{\varphi}{2} \approx \eta \varphi \left(1 \cdot \frac{\varphi^2}{12} \right)$$
 (35)

(M = mean gramolecular weight of gas). The real "adiabatic exponent" \underline{m} and the real "angle of phase" φ (2) result from:

with abbreviations:

$$A_1 = xv_1 - (x - 1) \frac{W_1}{RT}$$
 (37)

$$B_{lm} = \frac{W_{l}}{RT} v_{m} + \sum_{i} v_{i} (v_{jm} - v)v_{m} - v)v_{m}$$
 (38)

$$C_{l} = \frac{W_{l}}{RT} = V_{l}$$
 (39)

$$q_{11} = \frac{2 \pi f N}{U, V} \tag{40}$$

⁽¹⁾ In contrast to the hitherto existing evaluations of sound dispersion measurement in Sitzungsbericht.d. Akad.d. Wiss. zu Berlin 1920, 380 to 385; H.O. Kneser, Ann. d. Phys. 11 (1931) 761.

Which indicates by how much the pressure amplitude on advances the volume or the density amplitude & V or & in the sound wave.

The sound dispersion method works as follows: at constant temperature and pressure conditions the frequency function of the sound velocity a (or of the amplitude damping constant y) is first of all determined experimentally. Then corresponding curves are calculated theoretically with equations 33 to 40, assuming certain numerical values for the reaction velocity U; in 40. The theoretical curves are compared with the experimental ones. The most correct values of U; are given by that theoretical curve which coincides throughout with the experimental one. The method is univocal, provided only one dissociation equilibrium moves in the sound wave. In the case of several dissociation equilibria, the result must be reached with certain methods of successive approximation which we cannot liscuss here.

The sound dispersion method gives fundamentally only the forward and reverse velocities of the overall reactions in the equilibrium. The velocities of the elementary reactions, still more interesting for kinetics questions, must be derived secundarly.

In order to see the shape of the expected sound dispersion curve, two cases of high temperature dissociation are approximately estimated, i.e. that of oxygen and that of carbon dioxide. For details and especially as regards the chemical reaction velocities used see the complete report (1).

At 2.600 K and 1 atm. in the case of oxygen dissociation only one equilibrium must be considered

$$0_2 \rightleftharpoons 20$$
 (41)

Partial pressures obtained are $p_{02} = 0.976$ and $p_0 = 0.024$ atm. Sound dispersion curves are reproduced in Fig. la to 1c. The adiabatic exponent m, the sound velocity a and the amplitude damping constant y per unit of longth show a turning point in the critical frequency region, in which the reaction velocity no longer keeps pace with the sound frequency. Both the angle of phase Y and the amplitude damping constant y: referred to the wave length | reach a maximum there. The left hand ordinate in Fig. 1a gives the adiabatic exponent m, which in case of complete equilibrium is $m_{\min} = 1.187$. If the dissociation can no longer follow the sound frequency, exygen behaves as a non-dissociating gas, i.e. $m_{\max} = N = C_p/C_V = 1.274$. Although only 2.4% O atoms are present in the gas, at any complete equilibrium the difference is N - m = 0.087, amounting to about 7% of the N value. The angle of phase N between pressure and volume amplitude (fig. 1c) is always bery small and reaches its maximum 0.0350 at 2 radians in the dispersion region.

Two equilibria must be considered in the dissociation of carbon dioxide, i.e.:

The differences between the adiabatic exponent m and the mol heat ratio K are reproduced in Fig. 2 for 2,000 to 3,200 K. Here too the adiabatic exponents m are smaller than the K values. The m' values

⁽¹⁾ Zs. f. Elektrochem. u. angew. physokal. Chemio 48 (1942) 62 - 68, 116 - 131.

calculated neglecting the second dissociation equilibrium (43) differ only slightly from the correct m values, i.e. the oxygen dissociation plays a secondary part as compared with the CO₂ dissociation proper. This is also manifest in the sound dispersion curves of Fig. 3a to 3d. They apply to 2,600°K and 1 atm., and the partial pressures are $p_{\rm CO_2} = 0.7518$, $p_{\rm CO_3} = 0.1628$, $p_{\rm O_2} = 0.0780$ and $p_{\rm O_3} = 0.00679$ atm.

Two different reaction velocities U? were tentatively assumed for the first dissociation reaction (42). The corresponding curves are marked I and II. Only in curve II of Fig.3a does a weak point of inflexion appear at about 10 Hertz, corresponding to the oxygen dissociation (43). Otherwise the curve shapes are determined merely by CO2 dissociation (42). Remarkably the peaks of y curves in Fig. 3b have the same height. In Fig. 3c however the top limit values of the amplitude damping constants y referred to 1 cm. mount with the frequencies of the dispersion region proper, i.e. the higher the velocity of reaction (42). Fig. 3d shows the amount of sound energy passing through a 5 or 10 cm. CO2 layer at 2,600° K due to dissociation sound dispersion. It is clear that in curve II no measurement would be possible above 105 Hertz.

We have seen how the forward and roverse velocities of the reactions at the equilibrium point can be determined from sound dispersion measurements. The method is based on the assumption that the sound dispersion observed is only due to the dissociation reactions and not to any other interferences, such as: 1. sound dispersion due to imperfect adjustment of the vibrational degrees of freedom (1); 2. sound dispersion due to the irreversible processes of friction and heat conductivity (2).

The first seems unlikely, especially in high temperature tests, on three independent grounds:

- a) According to tests by Eucken and co-workers (3) the adjustment time clearly decreases as the temperature ascends, in
 the case of a maladjustment of the vibrational degree of
 freedom; this applies at least to the temperature range upto 400°C covered so far. A bold extrapolation to 2.600° K
 gives about 105 Hertz for the region of the vibration sound
 dispersion. The sound absorption there is however too high
 to allow measurements.
- b) According to Eucken the adjustment time of the vibrational degree of freedom can be considerably shortened, by adding to the gas in question elements which can produce quasicompounds with the molecules. Such elements are however automatically produced at high temperatures by the atoms; e.g. O atoms could produce:

$$0 + 0_2 \rightarrow 0 \cdot 0 = Quasi-0_3$$
 (44)

$$0 \cdot N_2 \rightarrow 0 \cdot N_2 = \text{Quasi-N}_20$$
 (45)

⁽¹⁾ H.O. Kneser, Ann. d. Phys. 11 (1931) 761.

⁽²⁾ G. Kirchhoff, Pogg. Ann. d. Phys. 134 (1868) 177 - 193.

⁽³⁾See various works in the Zs. f. physikal. Chemie B since 1934.

a reaction stage is 30 to 50 times the energy quantum required for the vibrational excitation (1); with the result that the first process will in all probability be slower than the second. The region of vibrational dispersion would thus correspond to higher frequencies than the region of dissociation dispersion.

The second possible interference due to friction and heat conductivity should be thoroughly discussed, but we cannot do it now. We want to investigate instead to what extent this type of sound dispersion can restrict the frequency range accessible to measurement.

On a real sound wave the transport of impulse (friction) and heat occurs mainly in two directions, i.e. along and across the sound propagation direction. The latter applies naturally only to laterally limited sound wave, which can no longer be strictly treated as a linear problem; but a real sound wave has always a lateral boundary, e.g. a pipe wall. The irreversible transport processes produce damping. We can divide this into longitudinal and transverse damping. Fig. 4, curves III and IV, show the frequency and the amplitude damping constant y obtained from Kirchhoff's law. Curves I and II serve as a comparison and represent the above estimated cases of CO2 dissociation dispersion at 2,600° K and 1 atm. It is easy to see that at high temperatures all damping constants together could not exceed the value y = 0.1. So far the sound of a given and adjustable frequency can only be produced outside the high temperature test chamber proper. The sound must therefore be transmitted by a pipe, which in order to conserve the temperature must not be too wide and not shorter than 10 cm. Then the proportion of the sound energy passing through must be:

$$\frac{J_2}{J_1} = e^{-/2y \cdot 10} > 0.13$$
 (47)

which again implies that y must be less than 0.1. According to Fig.4 with f = 105 Hertz for a pipe 6 mm. bere the transverse damping constant is $y_{TV} \approx 0.055$. If we add the longitudinal damping constant and the reaction kinetics damping, in case I of CO₂ dissociation we approach closely the just permissible total value y = 0.1; in case II of CO₂ dissociation this would be exceeded by far. The estimate can naturally be made otherwise, but the result is the same: the top limit of the frequency range accessible to experiments at high temperatures should be about 10^5 Hertz.

The bottom limit is determined by the wave length which is inversely proportional to the sound frequency; in fact any sound velocity measurement becomes a sort of resonance measurement, in which the dimensions of the apparatus must be in a certain proportion to the sound wavelength. However the apparatus cannot be enlarged ad lib. In the high temperature region at 10° Hertz the wavelength is about 80 cm. At this frequency, measurement is possible only if we use a method in which the dimensions of the resonance chamber are much smaller than the wavelength. It is therefore impossible to work with a stationary wave in a pipe closed at both ends, as so far customary in sound dispersion tests. Helmholtz's resonator seems to answer the purpose, though its suitability to sound dispersion measurements will have to be checked experimentally. Presumably Helmholtz's

⁽¹⁾ In contrast to this at room temperature where the first available sound dispersion for the dissociation of N204 takes place the ratio Dissociation energy: Vibrational energy is 14:2.

resonator will allow measurements down to a few hundred hertz.

Quite roughly, the equation: -

 $\beta = \frac{1}{20 \, \text{f}} \tag{48}$

connects the turning point frequency f' of the sound dispersion region and the adjustment time \$\beta\$ of the chemical reaction; the sound dispersion method could therefore presumably be applied in the high temperature region to study dissociation reactions of between 2.10-6 and 1.10-3 sec. These are reaction velocities such as occur in flame and detonation fronts.

Maturally it must be stressed that the experimental development of the sound dispersion method for the high temperature range
will still present many difficult problems. They must however be
approached as so far the only method that gives us reaction kinetics
data is the spectroscopic one, which is only applicable of the
molecules in question have a convenient absorption and emission
spectrum. Another reaction kinetics test method for high temperatures
would be very welcome, and the sound dispersion method seems to be
the most suitable.

Summary.

- 1. A general expression for the differential adiabatic exponent $\underline{m} = -\frac{V}{p} \left(\frac{\partial p}{\partial V} \right)$ in dissociating gases is obtained for any type and number of dissociation reactions.
- 2. Data on the kinetics of dissociation reactions can be obtained from sound dispersion measurements.
- 3. At high temperatures the experimentally accessible frequency range for the sound dispersion method might stretch from a few hundred to 105 Hertz, thus covering reactions of between 2.10.66 and 1.10.5 sec.
- Fig. 1 a to 1 c Estimated sound dispersion in pure 02 at 2,600° K and 1 atm. Total pressure based only on dissociation 02 20. Fig. 1 a: frequency in terms of adiabatic exponent m and sound velocity a. Fig. 1 b frequency function of amplitude damping constant y por cm. Fig. 1 c: frequency function of the angle of phase ** and of damping constant y! referred to wavelength **.
- Fig. 2 Differential adiabatic exponents in pure CO2 for complete equilibrium: x = Cp/Cy=ratio of mol heats. m = exponent in the adiabatic pVm = const. taking into account the two equilibria 2CO2 = 2CO + O2 as well as O2 = 2O; m' = adiabatic exponent considering only the first equilibrium.
 - Fig. 3a to 3d Estimated sound dispersion in CO₂ at 2.600° K and 1 atm. total pressure based on the dissociations 2CO₂ = 2CO₂ + O₂ and O₂ = 2O . Fig. 3a: frequency in terms of m and sound velocity a. Fig. 3b: the angle of phase f and the damping constant referred to the wavelength l. Fig. 3c: The damping constant y per cm. Fig. 3d: Fraction of sound intensity permeating a 5 or 10 cm. layer.

Fig. 4 - Amplitude damping constant y: I and II. Cases of CO2 dissociation (pure reaction kinetics sound dispersion)
III pure longitudinal damping. IV. pure transverse damping in the smooth pipe.