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H. A. BETHE

E. TELLER

NOTE

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DEVIATIONS FROM THERMAL EQUILIBRIUM IN SHOCK WAVES

By

H. A. BETHE

E. TELLER

Deviations from Thermal Equilibrium in Shock Waves

Report by H. A. Bethe, Cornell University, Ithaca, N. Y. in collaboration
with (sections 1 and 2)
E. Teller, George Washington University, Washington, D. C.

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DEVIATIONS FROM THERMAL EQUILIBRIUM IN SHOCK WAVES

SUMMARY

The various terms contributing to the energy content of a gas, viz. translation, rotation, vibration, electronic excitation and dissociation, are discussed (par. 1). Tables are given of the energy content and the specific heat of a simple harmonic oscillator (Table I), of the energy content and the dissociation of nitrogen, oxygen (Table II) and air (Table III). The molecular vibration becomes important for air at about 600°K, the dissociation at about 3000°K.

The theory of shock waves is generalized to the case when the specific heat changes with temperature (par. 3). General formulae are obtained for the velocity, (3.10), density (3.8a), pressure (3.8b), and temperature (3.9) on the high pressure side. It is shown that the asymptotic values of v, ρ, p and T on the high pressure side at sufficient distance from the front of the shock wave are uniquely determined by the values of these quantities on the low pressure side, and are independent of any intervening phenomena connected with the approach of statistical equilibrium between the various degrees of freedom of the molecule. This we consider the most important result of the present investigations.

A table is given (Table VIII) of the asymptotic values of v, ρ, p and T on the high pressure side as a function of the velocity v of the shock

wave. The four quantities are calculated (a) using the actual specific heat of air as a function of temperature, as given by Table III (quantities are subscript in Table VIII), and (b) using a constant specific heat equal to that at 300°K (subscript 2). Large differences are found for the temperature in the two calculations ($T_2 = 8000°$ when $T_3 = 5000°$) and for the density ($\rho_2 = 5.8$, $\rho_3 = 9.1$) but the pressure, which is the most important quantity for applications, is almost independent of the specific heat ($p_2 = 155$, $p_3 = 168$ atmospheres in the example quoted).

The sudden change of the temperature of a gas when passing through a shock wave destroys temporarily the statistical equilibrium between the various forms of energy of the gas molecules. The degrees of freedom of a molecule can conveniently be divided into two classes, the active ones and the inert ones (par. 2). The "active" degrees of freedom are translation and rotation; they come into thermal equilibrium after one or a few collisions (par. 2A). The most important "inert" degree of freedom is the vibration (par. 2B). Experiments on the absorption of sound show that between 20 and more than 500,000 collisions are necessary to establish thermal equilibrium between vibrations and the active degrees of freedom at room temperature (Table V). This result agrees with the expectation from the theory of Landau and Teller. This theory allows one to predict with moderate accuracy the temperature dependence of Z, the number of collisions necessary to de-excite the first vibrational quantum state, when a measurement of Z at one temperature is available (Table IV). Unfortunately no accurate measurements have been made for oxygen and none at all for nitrogen, which makes quantitative statements almost impossible. Therefore we have only listed (Table VI) the values of the mean free path for vibration, λ_v which follow from various assumption (par. 2D) about the efficiency of the collisions. The resulting values of λ_v for the cases which have practical importance for shock waves lie between 3 and 0.0016 millimeters, depending on the vibrating molecule (N_2 or O_2), the assumption made about the efficiency of various molecular collisions, and the humidity of the air.

The dissociation also requires a considerable time to come into equilibrium. The theory (par. 2C) is somewhat more definite in this case than for the vibrations because it depends on the Boltzmann factor rather than on assumptions about the kinetics of collisions. Very large values (from 1 millimeter to 1 meter) are obtained (par. 2D, Table VII) for the mean free path for dissociation, λ_d, in practical cases.

The theory of par. 2 is applied to shock wave in par. 4. It is shown that the shock wave has a sharp front on the low pressure side while on the high pressure side it extends over a distance of the order of the mean free path for vibration, λ_v, or for dissociation, λ_d. Immediately at the wave front, but on the high pressure side, the physical quantities P, ρ, T, v can be calculated assuming that only the active degrees of freedom exist (Table VIII, quantities with subscripts 2). Going away from the wave front into the high pressure region, the energy E_i of the inert degrees of freedom increases gradually and approaches the value corresponding to thermal equilibrium. In simple cases, E_i, p, ρ, T and v will follow an exponential law (cf. 4.10, 11). If the shock wave is violent enough so that dissociation occurs on the high pressure side, there is first a region of extension λ_v near the wave front in which vibrational equilibrium is established but in which the dissociation is hardly affected, and then a much more extended region (extension λ_d) in which dissociation takes place.

Two special cases of very soft shock waves are discussed in pars. 5 and 6, these discussions having mostly academic interest. In par. 5, we consider the case where the velocity of the shock wave v_1 is between the actual velocity of sound a_1 and the sound velocity obtained by considering only the active degrees of freedom, i.e.,

$$a_1 < v_1 < a_1 \left(1 + \frac{(c_v - c_{va})R}{2c_v \; c_{va}}\right) \qquad (A)$$

where c_v is the total specific heat at constant volume and c_{va} the specific heat due to the active degrees of freedom only. It is shown that in this narrow velocity interval the shock wave is diffuse on the low pressure as well as on the high pressure side. These diffuse shock waves go over automatically into shock waves with a sharp front when v_1 approaches the upper limit given in (A).

In par. 6, slightly faster shock waves are considered, viz. waves for which

$$a_1 \left(1 + \frac{(c_v - c_{va})R}{2c_v \; c_{va}}\right) < v_1 < a_1 \left(1 + \frac{R}{2c_v + R}\right) \qquad (B)$$

For such waves, the temperature on the high pressure side increases with increasing distance from the wave front while for waves of higher velocity v_1, the temperature has its maximum immediately at the wave front and decreases from there.

NOTATION

Throughout this Report, the following notations will be used:

ρ = density of gas

p = pressure (in atmospheres)

T = temperature in degrees Kelvin

E = energy content of one gram of gas

α = degree of dissociation,

$$1 + \alpha = p/(\rho RT)$$

β = $\frac{E}{p/\rho} + 1$

c_p = specific heat at constant pressure per gram

c_v = specific heat at constant volume per gram

γ = c_p/c_v

R = gas constant per gram

R_o = gas constant per mol

k = Boltzmann's constant (gas constant per molecule)

h = Planck's constant

v = velocity of the gas

m = ρ v = flow in grams per cm^2 per sec

V = $v + \frac{p}{m}$

c = velocity which the gas would have if streaming into vacuum

a = velocity of sound

λ_v = mean free path for vibrations

λ_d = mean free path for dissociation

ν = frequency of molecular vibrations

D = dissociation energy of molecules

SUBSCRIPTS

a	for active degrees of freedom
i	for inert degrees of freedom
v	for vibration
d	for dissociation
h	for an arbitrary point on the high pressure side of a shock wave
ℓ	for an arbitrary point on the low pressure side
1	for a point on the low pressure side where thermal equilibrium exists between all degrees of freedom of the molecules
2	for a point on the high pressure side immediately at the front of the shock wave
3	for a point on the high pressure side at sufficient distance from the wave front so that thermal equilibrium exists

Par. 1. The Energy Content of Gases

Perfect gases obey the equation of state

$$p/\rho = RT \tag{1.1}$$

where p, ρ, T are pressure, density and absolute temperature and where the gas constant R is a characteristic of the gas considered. If the gas dissociates, (1.1) ceases to be valid; in the particular case of a diatomic gas dissociating into atoms, we have instead:

$$p/\rho = RT(1 + \alpha) \tag{1.2}$$

where α is the degree of dissociation, i.e., the fraction of molecules dissociated. Generally, $p/\rho\ T$ is proportional to the number of separate particles (molecules or atoms) per gram of the substance.

The energy content of a gas consists of five main parts, viz:

(1) the kinetic energy of the translation of the molecules

(2) the energy of molecular rotation

(3) the energy of vibration

(4) the energy of electronic excitation of the molecule

(5) the energy of dissociation into atoms (or smaller groups of atoms).

We shall write the total energy content per gram in the form

$$E = (\beta - 1)\ (p/\rho) \tag{1.3}$$

The inclusion of the term -1 is convenient because the quantity occurring in the theory of shock waves is $E + p/\rho$, where p/ρ is connected with the work done by the pressure. Furthermore, we shall denote by β_t, β_r, β_v, β_e, β_d the energy of translation, rotation, vibration, excitation, and dissociation, each divided by p/ρ, so that

$$\beta = \beta_t + \beta_r + \beta_v + \beta_e + \beta_d + 1 \qquad (1.4)$$

The various contributions will now be discussed in order:

1. The translational energy is 3/2 p/ρ for any gas, independent of the number of atoms per molecule, the temperature, etc.

2. The rotational energy, for all gases except H_2, and at all temperatures at which the substance is gaseous, is given by the classical kinetic theory of gases without any important quantum correction. It is zero for atoms, 1 RT per gram for diatomic molecules and all polyatomic ones whose atoms lie on a straight line such as CO_2, and 3/2 RT for all other polyatomic molecules. At high temperatures, there is a correction because the molecules change their shape due to their vibrations. This correction, commonly called the interaction of vibrations and rotations, is usually not very great.

3. The vibrational energy can be approximated (at not too high temperatures) by resolving the vibration into normal modes and treating each mode as a harmonic oscillator.

The number of normal modes is 1 for a diatomic molecules, 3n-5 for a molecule containing n atoms on a straight line and 3n-6 for a molecule with n atoms not on a straight line. The energy contained in one mode is (per gram)

$$E_v = RT \frac{z}{e^z - 1} \qquad (1.5)$$

where

$$z = \frac{h\nu}{kT} , \qquad (1.5a)$$

ν is the frequency of the vibation, h Planck's and k Boltzmann's constant. If ν is given in wave numbers (cm^{-1}) and T in degrees Kelvin,

$$z = 1.438 \, \nu / T \qquad (1.5b)$$

The frequencies of the various normal modes of molecules can be obtained from band spectra. A good survey of data can be found in H. Sponer, Molekülspektren I (Springer 1935). The frequencies of simple light molecules are very high, e.g. for N_2 we have $\nu = 2345\ \text{cm}^{-1}$, for O_2, $1570\ \text{cm}^{-1}$. For more complicated, and especially for polyatomic molecules, the lowest frequencies are much smaller, the highest ones of the same order as for diatomic ones. E.g., CO_2 has four modes of vibration with frequencies $\nu = 667, 667, 1336$ and $2350\ \text{cm}^{-1}$.

For low temperatures (z large), the vibrational energy is negligible. E.g., for $z = 5$, it amounts only to 0.034 RT, i.e. 1 per cent of the value of $E + p/\rho$ for translation and rotation of a diatomic molecule. $z = 5$ corresponds to 680°K for N_2, 450° for O_2 but only 192° for the low frequency mode of CO_2. Thus the vibrations may be neglected at room temperature for N_2 and O_2 but not for CO_2.

At high temperatures (z small), the vibrational energy is RT per mode. This value is attained very slowly.

TABLE I

Energy Content of Harmonic Oscillator

$\frac{1}{z} = \frac{kT}{h\nu}$	$\frac{E_v}{RT}$	$\frac{c_v}{R}$	γ
0.05	$4.1 \cdot 10^{-8}$	$8.2 \cdot 10^{-7}$	1.400
0.1	$4.5 \cdot 10^{-4}$	$4.5 \cdot 10^{-3}$	1.399_5
0.15	0.0085	0.0566	1.391
0.2	0.0339	0.170_5	1.375
0.25	0.0747	0.304	1.357
0.3	0.123	0.426	1.342
0.4	0.223	0.609	1.321_5
0.5	0.313	0.723	1.310_5
0.6	0.389	0.800	1.303
0.8	0.502	0.880	1.296
1.0	0.582	0.921	1.292_5
1.5	0.704	0.963	1.289
2	0.771	0.979	1.287_5
large	$1-\frac{1}{2}z+\frac{1}{12}z^2$	$1-\frac{1}{12}z^2$	1.2857

In Table I, we give the vibrational energy of a harmonic oscillator as a function of the temperature. We also give the contribution of the vibration to the specific heat, viz.

$$c_{v,v} = \frac{DE_v}{dT} \tag{1.6}$$

which is seen to become appreciable at much smaller temperatures than E_v, and to approach its asymptotic value much faster. We have also included the ratio, γ of the specific heats at constant pressure and volume, for a diatomic gas with harmonic oscillation, viz.

$$\gamma = \frac{7/2\ R + c_{v,v}}{5/2\ R + c_{v,v}} \tag{1.6a}$$

At high temperatures, the vibrations can no longer be regarded as harmonic. The effect of the anharmonicity is to increase the energy content of the gas. E.g., for N_2 at 5000°K the harmonic oscillator model would give $\beta_v = 0.699$ while the correct value is 0.753, including the interaction of vibration and rotation, and a small contribution from excitation. The influence of the anharmonicity is greater for molecules which are easily dissociated.

4. The electronic excitation is usually rather unimportant compared with vibration and dissociation.

5. The dissociation becomes important at temperatures above 2-3000°K. If α is the degree of dissociation, p the total pressure, p_A and p_M the partial pressures of atoms and (diatomic) molecules, we have

$$\frac{p_A^2}{p_M} = \frac{4\alpha^2 p}{1-\alpha^2} = K = e^{\Delta F/R_o T} \tag{1.7*}$$

---

* p in (1.7) is considered a dimensionless quantity, viz. the ratio of the pressure to one atmosphere.

The first equality follows from $p_A = \frac{2\alpha}{1 + \alpha} p$, $p_M = \frac{1 - \alpha}{1 + \alpha} p$. K is the dissociation constant, R_o the gas constant per mole = 1.987 calories/degree, $\Delta F = F_M - F_A$ the difference of the free energies per mol of the molecular and the atomic gas, each taken at unit pressure. For some gases, like N_2 and O_2, tables of ΔF as a function of temperature have been published (cf. below). Where they are not published, ΔF can be calculated from the Stern-Tetrode formula, which reads for diatomic gases

$$K = \frac{(2\pi m_A kT)^{3/2}}{nh^3} \cdot \frac{g_A{}^2}{G_M} \quad e^{-\frac{D}{R_o T}} \tag{1.8}$$

where m_A is the mass of one atom, n the number of separate particles per cm^3 of the gas at unit pressure and temperature T, and D the dissociation energy in calories per mol. According to spectroscopic evidence (Sponer), D has the value 117,200 cal. for oxygen and 182,000 cal. for nitrogen, so that D/R_o = 59,000 and 91,600 degrees, respectively.

g_A and G_M are the statistical weights of the atom and the molecule. In general, g_A may be put equal to the combined weight of all states of the multiplet to which the ground state belongs, so that

$$g_A = (2L + 1)\ (2S + 1) \tag{1.9}$$

where L and S are orbital angular momentum and spin of the atomic ground state. N, having a ^4S ground state, has therefore $g_A = (1)(4) = 4$; oxygen, with a ^3P state, has a weight $g_A = (3)(3) = 9$. G_M consists of three factors referring to the electronic state (g_M) of the molecule, the vibration (g_v) and the rotation (g_r) respectively,

$$G_M = g_M\ g_v\ g_r \tag{1.10}$$

g_M can be calculated from spin S and orbital momentum Λ, viz.

$$\begin{aligned} g_M &= 2S + 1 && \text{for } \Sigma \text{ states } (\Lambda = 0) \\ &\quad 2(2S + 1) && \text{for all other states } (\Lambda \neq 0) \end{aligned} \tag{1.11}$$

The ground state of N_2 is a $^1\Sigma$ state ($g_M = 1$), that of O_2 a $^3\Sigma$ state ($g_M = 3$). g_r is always given with sufficient approximation by classical kinetic theory

$$g_r = \frac{kT}{hB_r} \tag{1.12}$$

where B_r is defined by the fact that the rotation levels of the molecule are $B_r j(j+1)$ if j is the rotational quantum number; $B_r = 1.44\ \text{cm}^{-1}$ for O_2 and $2.00\ \text{cm}^{-1}$ for N_2. If B_r is measured in cm^{-1} and T in degrees Kelvin, $g_r = T/1.438\ B_r$. The vibrational part, g_v, is given by

$$g_v = \frac{1}{1-e^{-z}} \tag{1.13}$$

with z defined as in (1.5a). Ordinarily, dissociation is only important at high temperatures; then g_v is sufficiently nearly

$$g_v = kT/h\nu \tag{1.13a}$$

If there are several modes of vibration, there is one factor of the type (1.13) for each mode.

When K has been calculated, and the total pressure p is known, α can be calculated immediately from (1.7), viz.

$$\alpha = \sqrt{\frac{K}{K + 4p}} \tag{1.14}$$

In the theory of shock waves, the density ρ on the high pressure side can be more readily estimated than the pressure (par. 3). Then, inserting (1.2) in (1.7), we have

$$4RT\, \rho\, \alpha^2 (1 + \alpha) = K(1 - \alpha^2) \tag{1.14a}$$

which gives

$$\alpha = - 1/2\, K' + \sqrt{K' + 1/4\, K'^2} \tag{1.15}$$

with

$$K' = \frac{K}{4RT\, \rho} \tag{1.15a}$$

If ρ_o is the density of the gas at temperature T_o and unit pressure, we have

$$K' = \frac{K}{4} \frac{T_o}{T} \frac{\rho_o}{\rho} \tag{1.15b}$$

The dissociation α depends strongly on the temperature (increasing with increasing T) and slightly on the pressure or density (decreasing with increasing p or ρ). The equation of state for a dissociated gas has already been given in (1.2). The energy content is given by

$$\beta = \frac{1 - \alpha}{1 + \alpha} \quad \beta_M + \frac{\alpha}{1 + \alpha} \quad \left(\frac{D}{R_oT} + 2\beta_A \right) \tag{1.16}$$

where β_M and β_A are the coefficients of energy content for the molecular and the atomic gas at the given temperature. Disregarding the term D/R_oT, (1.16) is simply the weighted average of B_M and B_A, the weights being given by the partial pressures. The dissociation itself contributes an energy αD per mol of the gas; to obtain β, the energy per mol must be divided by $Mp/\rho = (1 + \alpha)R_oT$ (M the molecular weight).

β_M can be calculated by adding the contributions 1 to 4 discussed above. β_A is essentially due to translational energy only, and has therefore the value 5/2. (The energy of electronic excitation of the atoms is seldom important below 5,000° and has therefore been neglected.)

At extremely high temperatures (above 5,000°) the ionization of atoms and molecules must be considered. This can be done using similar calculations as for dissociation.

Tables

Table II gives the energy constant β of nitrogen and oxygen at temperatures from 300 to 5000° Kelvin. The energy constant from 300° down to the liquefaction temperature remains almost unchanged. The data for nitrogen were taken from W. F. Giauque and J. O. Clayton, Journ. Am. Chem. Soc. 55, 4875 (1933), those for oxygen from H. J. Johnston and M. K. Walker, ibid. 55, 172 (1933). Both sets of data were calculated by the respective authors taking into account all corrections such as anharmonicity of the vibrations, interaction between rotation and vibration, and electronic excitation. The figures given in our table for nitrogen are less accurate because Giauque and Clayton give only the free energy from which the energy content had to be obtained by numerical differentiation, involving considerable inaccuracy. A graphical method was used to smooth out the results of the numerical differentiation. The energy content of O_2 could be read directly from the tables of Johnston and Walker as the difference between T times the entropy, and the free energy.

The dissociation was calculated for oxygen and nitrogen in air of a density equal to 8 times the density at 300°K and one atmosphere pressure. These conditions were chosen because in a shock wave in which the temperature is raised to 3000-5000°, the density is increased about 8 fold (cf. 3, Table VIII). Obviously, the figures for oxygen would also be valid for pure oxygen of a density of $(8)(0.210) = 1.680$ times that at 300° and one atmosphere, and the dissociation of nitrogen would be the same for pure nitrogen of a density of $(8)(0.780_5) = 6.244$ times the density of nitrogen at 300°K and one atmosphere.

Table II. Energy Content and Dissociation of Nitrogen and Oxygen

	Nitrogen				Oxygen			
T	β_M	K	α	β	β_M	K	α	β
300	3.493			3.493	3.493			3.493
400	3.499			3.499	3.520			3.520
500	3.508			3.508	3.548			3.548
600	3.521			3.521	3.590			3.590
700	3.541			3.541	3.636			3.636
800	3.564			3.564	3.684			3.684
900	3.594			3.594	3.731			3.731
1000	3.625			3.625	3.774			3.774
1250	3.702			3.702	3.871			3.871
1500	3.780			3.780	3.950			3.950
1750	3.845			3.845	4.015			4.015
2000	3.900	$4.0\cdot10^{-14}$	$1.55\cdot10^{-8}$	3.900	4.068	$5.15\cdot10^{-7}$	$1.07\cdot10^{-4}$	4.071
2500	3.992	$4.9\cdot10^{-10}$	$1.53\cdot10^{-6}$	3.992	4.157	$2.36\cdot10^{-4}$	$2.05\cdot10^{-3}$	4.199
3000	4.062	$2.61\cdot10^{-7}$	$3.23\cdot10^{-5}$	4.063	4.223	0.0142	0.0144	4.454
3500	4.127	$2.28\cdot10^{-5}$	$2.86\cdot10^{-4}$	4.134	4.278	0.268	0.0568	4.982
4000	4.177	$6.95\cdot10^{-4}$	$1.44\cdot10^{-3}$	4.205	4.327	2.45	0.152_3	5.79
4500	4.218	$9.85\cdot10^{-3}$	$5.12\cdot10^{-3}$	4.304	4.374	13.8	0.308	6.58
5000	4.253	$8.22\cdot10^{-2}$	$1.39\cdot10^{-2}$	4.457	4.412	55.4	0.500	7.07

It is seen that for oxygen the increase of the energy content, both due to vibrations and to dissociation, begins at much lower temperatures than for nitrogen. At 5000°, the values of β differ by more than 50 per cent. This is due mainly to the smaller dissociation energy and vibrational frequency of O_2, and to a small extent also to the smaller concentration of O_2 in air (cf. 1.15a).

Table III gives the necessary data for air. We have assumed a composition of

78.05 per cent	Nitrogen
21.00 per cent	Oxygen
0.92 per cent	Rare gases
0.03 per cent	CO_2

all percentages being by volume, i.e. by number of molecules. The energy content of the rare gases is $\beta = 5/2$ because they are monatomic. The β of CO_2 was only guessed because of its small concentration.

From the β's and α's of the constituent gases, the dissociation and the energy content of a mixture are calculated as follows:

$$\alpha = \sum_k c_k \alpha_k \tag{1.17}$$

$$\beta = \frac{\sum_k c_k \beta_k (1 + \alpha_k)}{1 + \alpha} \tag{1.18}$$

where c_k is the concentration (by volume) of the $k^{\underline{th}}$ component of the mixture ($\sum_k c_k = 1$), α_k and β_k its degree of dissociation and energy constant, respectively. α is mainly important for the calculation of p/ρ, Eq (1.2).

Specific Heat

The specific heat can be obtained by differentiating the energy content. As long as there is no dissociation, the specific heat per gram at constant pressure is

$$c_p = \frac{d}{dT}(RT\beta) = R(\beta + T\frac{d\beta}{dT}) \tag{1.19}$$

The velocity of sound, again in the absence of dissociation, is given by

$$a^2 = \gamma RT \tag{1.20}$$

where is the ratio of the specific heats at constant pressure and constant volume, viz.

$$\gamma = \frac{c_p}{c_v} = \frac{c_p}{c_p - R} \tag{1.21}$$

If β is independent of temperature, we may write from (1.19) and (1.21):

$$\beta = \frac{c_p}{R} = \frac{\gamma}{\gamma - 1} \tag{1.22}$$

as is commonly done in the theory of shock waves and other phenomena involving gases in rapid motion. While this is approximately justified for low temperatures, it is certainly not for air above 600°K.

We have not included the specific heat in our Tables II and III because another numerical differentiation would have been necessary which would have made the results very inaccurate. Moreover, we believed that there was at the moment no pressing need for a table of the specific heat and of the velocity of sound at very high temperatures but that the interest was centered around the shock waves.

If there is dissociation, (1.19) is no longer correct because the energy is RT $\beta(1 + \alpha)$ and α as well as β changes with temperature. Moreover, the derivative with respect to T must now be calculated at constant pressure. Furthermore, the difference between c_p and c_v is no longer R so that (1.21) is no longer valid.

Table III. Energy Content and Dissociation of Air

T	$c_k \beta_k (1+\alpha_k)$				$\beta(1+\alpha)$	α	β
	N	O	Rare gases	CO_2			
300	2.726	0.733	0.023	0.001	3.483		3.483
400	2.731	0.739	"	"	3.494		3.494
500	2.738	0.745	"	"	3.507		3.507
600	2.748_5	0.754	"	"	3.527		3.527
700	2.764	0.764	"	0.001_5	3.552		3.552
800	2.781_5	0.774	"	"	3.580		3.580
900	2.805	0.783_5	"	"	3.613		3.613
1000	2.829_5	0.792_5	"	"	3.647		3.647
1250	2.889_5	0.813	"	0.002	3.727		3.727
1500	2.950_5	0.829_5	"	"	3.805		3.805
1750	3.001	0.843	"	"	3.869		3.869
2000	3.044	0.855	"	"	3.924	0.0000	3.924
2500	3.115	0.883_5	"	0.002_5	4.024	0.0004	4.023
3000	3.171	0.949	"	"	4.145	0.0030	4.133
3500	3.227_5	1.106	"	"	4.359	0.0121	4.307
4000	3.287	1.400	"	0.003	4.713	0.0331	4.562
4500	3.376_5	1.808	"	0.003_5	5.211	0.0687	4.875
5000	3.527	2.226	"	0.004	5.780	0.1058	5.227

Finally, (1.20) ceases to be correct and is replaced by

$$a^2 = \frac{c_p}{c_v} \left(1 + \alpha + \left[\frac{\partial \alpha}{\partial \log \rho}\right]_T RT\right) \tag{1.22}$$

2. The Approach of Equilibrium between Various Degrees of Freedom of the Molecules.

Suppose the energy content of a mass of gas is suddenly changed, as it is when the gas passes through a shock wave. Then it will take some time until the various degrees of freedom adapt themselves to the new conditions, and this "time" of relaxation" will be different for the different degrees of freedom.

A. Translation and Rotation.

The equilibrium will be attained most rapidly by the translation. For this degree of freedom, one collision is in general sufficient to come close to equilibrium. In order to have conditions similar to those in a shock wave we may consider a gas of a certain temperature T_2, into which streams a more dilute gas of a lower temperature T_1. Then the molecules of the cooler gas will (on the average) become accelerated as soon as they make their first collision with those of the hotter gas. The average kinetic energy of a molecule of a cool gas will increase from $3/2\ kT_1$ in one collision to something of the order $(3/2\ k)1/2(T_1+T_2)$.

A shock wave can obviously never be quite discontinuous but the transition from temperature T_1 to T_2 takes place over a distance of at least one gas-kinetic mean free path λ_t (t for translation). For ordinary gases at room temperature and atmospheric pressure, λ_t is of the order of 10^{-5} cm; it is in first approximation independent of the temperature and inversely proportional to the density; therefore, even a very violent shock wave in which the density increases by a factor 6 to 10 (cf.par. 3 Table VIII), must have an extension of at least about 10^{-6} cm. The classical theory of the physical structure of shock waves as given by Becker (Zeits. f. Phys. 8, 321, 1922) gives extremely small extensions which become of the order of 10^{-7} cm for very violent waves. The theory of Becker which takes into account the heat conduction but neglects molecular effects can therefore not be correct, at least not for violent shock waves. Becker, himself, pointed out that the problem requires a treatment based on the kinetic theory of gases. In practice a spatial extension of the shock wave of the order of one mean free path is, of course, of no importance at all, even at rather low initial pressures.

The molecular rotation may approach equilibrium as rapidly as the translation. This would be expected for strongly elongated molecules such as CO_2. If the effective boundary of the molecule is nearly spherical (e.g. N_2 or S_2) the excitation of molecular rotations may be estimated to take roughly 10 to 100 collisions. To show that the rotation approaches equilibrium so quickly, we use the results of Landau and Teller, Physik. Zeits. d. Sowjetunion 10, 34(1936). These authors have found that the effectiveness of collisions on a certain degree of freedom is determined by the ratio

$$\chi = \tau_c/\tau_o \tag{2.1}$$

where τ_c is the effective duration of the collision and τ_o the natural period of the degree of freedom concerned. If χ is of order unity or smaller, one or a few collisions will be sufficient to establish equilibrium whereas a large number of collisions is required if $\chi \gg 1$ (cf. 2.5).

τ_c in (2.1) may generally be written

$$\tau_c = s/v \tag{2.2}$$

where v is the relative velocity of the two colliding molecules and s the range of the intermolecular forces, i.e. the distance over which the molecules interact strongly. We may expect s to be of the order of one half to one Bohr radius, i.e. 2.5 to $5 \cdot 10^{-9}$ cm, a range of values which seems confirmed by some experimental results on the approach of vibrational equilibrium (cf. Table IV). In the case of rotation τ_o may be taken as the time required for one revolution, or rather this time divided by 2π (cf. 2.4) so that $\tau_o = r/v_r$ where r is the radius of the molecule (distance of an atom from the center of gravity) and v_r is the velocity of the atoms in their revolution around the center of gravity. Now v_r is of the same order as v, the velocity of molecular translation (equipartition of energy!) and r is of the same order as s. Therefore χ is of order unity for rotation, and equilibrium between rotations and translation will be attained in a few collisions.

We shall find in the following that all other degrees of freedom behave quite differently in that many collisions are necessary to establish equilibrium. Therefore it will be convenient to group together translation and rotation on one side, and all other degrees of freedom on the other. The latter we shall call the "inert" degrees of freedom while translation and rotation will be denoted as the "active" degrees of freedom. For all practical purposes we may say that the energy content of the active degrees of freedom can change almost discontinuously, because a distance of a few mean free paths may be considered negligible. We can then define the temperature of a moving gas at each point by the energy content of the active degrees of freedom, which is

$$E_a + p/\rho = \beta_a \, p/\rho = \beta_a RT \tag{2.3}$$

(the last relation being only valid if there is no dissociation). In (2.3) β_a is independent of the temperature and equal to 5/2 for monatomic, 7/2 for diatomic gases (cf. par. 1). The energy content of the <u>inert</u> degrees of freedom, E_i, on the other hand, cannot change abruptly and is therefore not always in equilibrium with that of the active ones; in other words, E_i is not necessarily related to the local temperature T in the way discussed in par. 1.

B. Vibrations

Theory

The most important inert degree of freedom are the vibrations. For these, we set in (2.1)

$$\tau_0 = 1/2 \pi \nu \tag{2.4}$$

where ν is the natural frequency of the molecular vibration. (In all formulae like (2.1) $2\pi\nu$ rather than ν should be used as representing the frequency because the frequency is generally introduced into physical formulae by taking the time derivative of experssions like $\sin 2\pi\nu t$. If we took ν instead of $2\pi\nu$ in (2.4), the only change would be that the values of s deduced from experimental data would be multiplied by 2π). Since the frequencies of molecular vibrations are rather high, it is plausible that χ is rather large; this will be shown by direct calculation and by discussion of experimental results below. For the case $\chi \gg 1$, Landau and Teller give the formula

$$p_{10} \doteq Ce^{-\chi} \tag{2.5}$$

Here p_{10} is the probability that a molecule in the first excited state of vibration is de-excited by a collision with another molecule. C is a geometrical factor which gives the probability that the collision of the two molecules will take place in a direction suitable for excitation or de-excitation of the vibration. There are no experimental data sufficiently accurate to deduce C, so that qualitative arguments must be used for its determination. Obviously, C must be less than unity, and probably it will lie between 1/3 and 1/30 in most cases, its value being higher for diatomic and lower for polyatomic molecules because it is less likely that a complicated molecule is hit at the right place to induce a given mode of vibration. In our computations below, we shall use arbitrarily $C \approx 1/10$.

Presumably, a better approximation could be obtained by introducing in (2.5) another factor, viz. a certain power of χ. Arguments can be given for a factor χ^{-2}. However, these arguments are too uncertain to justify at present the inclusion of such fine points.

The most important factor in (2.3) is the exponential $e^{-\chi}$ where (cf. 2.1, 2.2, 2.4)

$$\chi = 2\pi\nu\, s/v \tag{2.6}$$

Let us investigate χ for the case when the kinetic energy of the relative motion of the colliding molecules is just kT, i.e.

$$1/2\ Mv^2 = kT \tag{2.7}$$

where M is the reduced mass of the two molecules; if they are equal, M is one half the mass of one molecule. The value of χ for the velocity determined by (2.7) is

$$\chi_1 = 2\pi\nu s \sqrt{M/2kT} \tag{2.8}$$

This can be re-written as follows:

$$\chi_1 = \sqrt{h\ /2kT}\ .\ s\sqrt{\frac{4\pi^2\ M\nu}{h}} \tag{2.9}$$

For the collision of two equal diatomic molecules, each consisting of two equal atoms, M is the mass of one atom; then the reciprocal of the last factor is (2.9) viz.

$$b = \sqrt{h/4\pi^2 M\nu} \tag{2.10}$$

represents the amplitude of the molecular vibration in the lowest quantum state. Generally, the b defined in (2.10) has the value

$$b = \frac{8.2.10^{-8}}{\sqrt{\mu\nu}} \quad \text{cm} \tag{2.10a}$$

where μ is the molecular weight of the molecule (assuming collision between equal molecules) and ν the vibrational frequency in cm^{-1}. For N_2, $\nu = 2345$ and $\mu = 28$ so that $b = 3.1.10^{-10}$cm. Thus we see that b is very small compared with the range s of the forces. The factor $\sqrt{h\nu/2kT}$ is (2.9) is also in general greater than unity, so that χ_1 is indeed very large compared with unity as we expected above. Therefore (cf. 2.5) the probability of transfer of energy between vibration and translation is very small; the vibration is an inert degree of freedom. It is seen from the derivation that the reason for this result is not so much that the energy of one vibrational quantum $h\nu$ is large compared with the average energy of translation, kT, but rather that the amplitude of the vibrations, b, is very small compared with the range s of the intermolecular forces. This in turn is due to the large elastic forces which govern the elastic vibrations.

The quantity χ (2.6) will be reduced, and therefore the probability of energy transfer p_{10} (2.5) considerably increased, if we take higher velocities v. Therefore a given molecule will lose and gain vibrational energy mostly at the times when its kinetic energy of translation is high compared with kT, i.e. when it is in the tail of the Maxwell distribution. If we average over all the molecules in the gas, the probability of energy transfer per collision becomes

$$P_{10} = 2/\sqrt{\pi} \int e^{-x} \sqrt{x}\, dx\, C e^{-\chi} \qquad (2.12)$$

where

$$x = \frac{M\ v^2}{2kT} \qquad (212a)$$

(2.12) represents the probability (2.5), averaged over the Maxwell distribution of the relative velocities of the two colliding molecules.* With (2.6) for χ, the integration of (2.12) can be carried out by the saddle point methods, the integrand having a steep maximum near

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* It might be preferable to take into account the different collision probability of fast and slow molecules, i.e. to replace (2.12) by

$$P_{10} = \int e^{-x}\, x\, dx\, C\, e^{-\chi} \qquad (a)$$

which would give instead of (2.13)

$$P_{10} = 2/9\ \sqrt{\pi}\ \sigma^{3/2}\, e^{-\sigma} \qquad (b)$$

The temperature dependence of P_{10} would not be changed very much by this correction because the difference between (b) and (2.13) would be largely compensated by a different value of s deduced from the experiments.

$$x_o = 1/2\ (2\pi s \nu)^{2/3}\ (M/kT)^{1/3} \qquad (2.12b)$$

The integration gives

$$p_{10} = C'\, \sigma\, e^{-\sigma} \qquad (2.13)$$

where

$$\sigma = 3x_o = 3/2\ (S/b)^{2/3}\ (h\nu/kT)^{1/3} \qquad (2.14)$$

$$C' = \frac{4}{(3)}\ 3/2\ C \qquad (2.14a)$$

(b as defined in (2.10, 2.10a), s the range of the molecular forces, ν the frequency of vibration). (Eqs. (2.13, 14) are similar to the equations determining the rate of nuclear reactions in stars).

Numerically, (2.14) may be written

$$\sigma = 0.090\ (\nu s)^{2/3}\ (\mu/T)^{1/3} \qquad (2.15)$$

where ν is measured in cm^{-1}, s in units of 10^{-9} cm, T in degrees Kelvin, and μ is the molecular weight per molecule (or twice the reduced molecular weight, $2\mu_A\mu_B/(\mu_A + \mu_B)$, if two unequal molecules collide).

We shall now try to get a more quantitative estimate of s. Experiments are available (cf. below), among other gases, for pure CO_2, and for the action of N_2 on the vibrations of O_2. For CO_2, Fricke (Journ. of the Acoust. Soc. of Am. 12, 245(1940)) finds that Z = 86,000 collisions are necessary for de-excitation of the first excited vibrational state, so that

$$P_{10} = \frac{1}{Z} = \frac{1}{86,000} = 1.15 \cdot 10^{-5}$$

Taking C' = 1/10, (2.13) gives $\sigma = 11.5$. Using this number in (2.15) with $\nu = 667\ cm^{-1}$, we find,

$$s = 5.6 \cdot 10^{-9}\ \text{cm.} \quad (CO_2) \qquad (2.16a)$$

For the de-excitation of the vibrations of O_2 by collisions with N_2, Kneser and Knudsen find $P_{10} = 10^{-5}$. Inserting this figure in (2.13, 15) and taking $\nu = 1570$ cm^{-1}, we obtain

$$S = 3 \cdot 10^{-9} \text{ cm } (O_2/N_2) \ . \qquad (2.16b)$$

Both the results (2.16a) and (2.16b) are of the order of the Bohr radius as we assumed above. Differences between the values of s for different molecules are, of course, to be expected. We can therefore not predict the value of s for a pair of molecules for which it has not been measured experimentally. This is very unfortunate because P_{10}, or

$$Z = 1/P_{10} \ , \qquad (2.17)$$

is very sensitive to s. This can be seen directly from (2.13, 14) or from Table IV in which we have calculated Z from (2.13, 14) for O_2 and N_2, in each case for two different values of s. A more detailed discussion of Table IV will be given in par. 2D.

Influence of foreign gases, experimental difficulties.

Collisions between two different molecules are often more effective in transferring energy to and from the vibrations than collisions between like molecules. This is the case especially (1) if the two colliding molecules have a chemical affinity and (2) if one molecule is very light so that its velocity is great. In case (2) which is realized for H_2, He, etc., μ in (2.15) is very small. In case (1) the interaction between the two molecules is much more intense than usually which may perhaps result in more sudden changes of interaction and correspondingly shorter effective range, or even in a complete failure of the Landau-Teller theory when the two molecules penetrate so deeply into each other that they can be said to form a temporary compound. In the latter case, the temperature dependence may be quite different from that indicated in (2.13).

Table IV. Theoretical Temperature Dependence of the Number of Collision Necessary for De-excitation of the First Vibrational State.

Vibrating Molecule	s	Temperature °K)	300	500	700	1000	1500	2000	3000	5000
CO_2	$5.6 \cdot 10^{-9}$	σ	11.20	9.45	8.45	7.50	6.55	5.95	5.20	4.38
		Z	65,000	13,500	3500	2400	1080	650	340	180
O_2	$4 \cdot 10^{-9}$		14.32	12.08	10.80	9.58	8.37	7.60	6.56	5.60
		Z	$1.1 \cdot 10^6$	$1.4_5 \cdot 10^5$	46,000	15,000	5100	2600	1150	380
	$3 \cdot 10^{-9}$	σ	11.82	9.97	8.91	7.91	6.91	6.28	5.49	4.62
		Z	$1.1 \cdot 10^5$	21,500	8400	3400	1450	850	440	220
N_2	$3 \cdot 10^{-9}$	σ	14.78	12.48	11.14	9.89	8.64	7.85	6.75	5.77
		Z	$1.7 \cdot 10^6$	$2.0 \cdot 10^5$	62,000	20,000	6600	3200	1400	570
	$2.5 \cdot 10^{-9}$	σ	13.08	11.05	9.88	8.77	7.66	6.96	6.08	5.11
		Z	$3.7 \cdot 10^5$	57,000	19,500	7500	2700	1500	720	320
Collisions with H_2O										
O_2	$0.93 \cdot 10^{-9}$	Z	400	210	140	100	75	60	50	40
N_2	"	Z	1300	650	320	200	130	100	75	50

As will be seen from Table V, the foreign gases investigated are 3 to 4000 times more effective in de-exciting the vibration of O_2 than O_2 itself, the effect being greatest for complicated molecules such as C_2H_2OH which has a chemical affinity to O_2, and for water, which can probably form a temporary compound with O_2. The effect of N_2 on O_2 is almost as small as that of O_2 itself because there is not much chemical interaction; the collisions between O_2 and N_2 will be discussed in more detail in par. 2D.

The large effect of water vapor on the variation of oxygen makes it extremely difficult to measure the small effect of collisions between O_2 molecules themselves. Only a lower limit for Z was therefore obtained in the experiments on "pure" O_2, viz. 500,000.

For the problem of shock waves we must conclude that the establishing of vibrational equilibrium will depend sensitively on the humidity of the air. On hot humid days, the water vapor content of the air may easily reach 3 per cent (23 mm vapor pressure) so that only 400/0.03 = 13,000 collisions would be necessary to establish vibrational equilibrium for the oxygen. On the other hand, for completely dry air the necessary number of collisions is about 10^5 because then only the collisions with nitrogen will be important. A more accurate discussion of the humidity effect will be given in Table VI.

Excitation and De-excitation. Instead of the probability P_{10} of de-excitation per collision, it is convenient to introduce the probability k_{10} of de-excitation per second which is given by

$$K_{10} = P_{10} \cdot N = N/Z \tag{2.18}$$

where

$$N = \mathcal{N} \gamma \bar{v} \tag{2.18a}$$

is the number of collisions per second, $\mathcal{N}$ the number of molecules per cm^3, γ the gas-kinetic collision cross section and $\bar{v}$ the average relative velocity of two colliding molecules, viz. $\sqrt{\frac{\delta}{\pi}\frac{kT}{M}}$. The quantity k_{10} has two advantages compared with P_{10}, viz. (1) that it is more directly related to the extension of the shock wave and (2) that it is directly connected with observational data (cf. 2.22, 26) whereas the connection of P with these data involves the somewhat uncertain cross section q.

The probability of excitation, k_{01}, is connected with the probability of de-excitation, k_{10}, by the statistical principle of detailed balancing according to which

$$k_{01} = k_{10}\, e^{-\frac{h\nu}{kT}} \tag{2.19}$$

The time rate of change of the number y_o of molecules without vibration is then

$$\frac{dy_o}{dt} = k_{10}\, y_1 - k_{01}\, y_o \tag{2.19a}$$

where y_1 is the number of molecules in the first excited vibrational state. Similar equations hold for the other y_n where, according to quantum theory, $k_{n,\, n-1} = nk_{10}$ and $k_{n-1,\, n} = k_{n,n-1}\, e^{-h\nu/kT}$. By adding the equations for the various y_n, an equation for the total energy of vibration,

$$E_v = h\nu \sum_{n=o}^{\infty} n v_n \tag{2.19b}$$

can be obtained, namely

$$\frac{dE_v}{dt} = k_{10}\,(1 - e^{-n\nu/kT})\,(E'_v - E_v) \tag{2.20}$$

Here E'_v is the vibrational energy in thermal equilibrium, viz.

$$E'_v = \frac{h\nu}{e^{h\nu/kT}-1} \tag{2.20a}$$

Eq. (2.20) is valid no matter how large the deviation from thermal equilibrium. The factor 1 - e - h   /kT takes account of the fact that there occur transitions away from equilibrium as well as towards equilibrium. The solution of (2.20) is

$$E'_v - E_v = Ae^{-\omega_o t} \tag{2.21}$$

where ω_o is the reciprocal of the time of relaxation and is given by (cf. 2.20).

$$\omega_o = k^*_{10} \left(1 - e^{-h\nu/kT} \right) \tag{2.22}$$

It has been assumed in (2.21) that T remains constant. This not strictly correct in shock waves (cf. par. 3,4) where ω_o, being a function of T, will change with time so that the integral of (2.20) cannot be given in closed form.

In shock waves, we are interested in the *spatial* variation of E_v. If the gas flows with a velocity v, we may write

$$\frac{dE_v}{dx} = \frac{1}{v}\frac{dE_v}{dt} = \frac{E_v' - E_v}{\lambda_v} \tag{2.23}$$

where

$$\lambda_v = v/\omega_o \tag{2.24}$$

defines the *mean free path for vibration*.

Evaluation of Experiments . The experimental determination of ω_o is based upon the absorption and dispersion of sound in gases. The theory of this phenomenon has been given by H. O. Kneser, Ann. d. Phys. 16, 337 (1933) and Journ. Acoust. Soc. Amer. 5, 122 (1933), and others. The absorption coefficient μ *per wave length* depends on the circular frequency ω of the sound wave approximately* as

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* In order to obtain (2.25), $c_p - c_{pa}$ must be assumed to be small in comparison with c_p. Since μ is the absorption coefficient per wave length, the absorption coefficient per centimeter will behave as $\frac{\omega^2}{\omega_{max}^2 + \omega^2}$ and will therefore obtain its maximum value for $\omega = \infty$.

$$\mu \approx \frac{\omega}{\omega_{max}{}^2 + \omega^2} \qquad (2.25)$$

where ω_{max} is the frequency of maximum absorption per wave length. ω_{max} can be determined experimentally, and ω_0 may be deduced from it using the relation

$$\frac{\omega_0}{\omega_{max}} = \frac{c_{pa}\,(c_{pa} - R)}{c_p\,\,(c_p - R)}\,. \qquad (2.26)$$

Here c_p is the ordinary specific heat at constant pressure and c_{pa} the specific heat counting the "active" degrees of freedom only. In contrast to (2.25), (2.26) is exact.

Experimental Results. Experiments were made by H. O. Kneser and V. O. Knudsen, Ann. d. Physik 21, 682 (1935) on the vibrations of O_2, by Fricke and by Knudsen and Fricke, Journ. Acoust. Soc. Amer. 12, 245 and 255 (1940) on CO_2 and a few other gases, and by Küchler, Zeits. f. phys. Chemie B 41, 199 (1938), on the temperature dependence of the time of relaxation. The latter experiments were probably carried out with somewhat impure gases because Küchler finds for CO_2 at room temperature Z = 50,000 whereas Fricke gives 86,000 (impurities reduce Z, cf. above and Table V), and a similar decrepancy exists for N_2O (7,500 vs. 11,800). The experiments of Kneser and Knudsen were the first systematic ones carried out and were therefore less accurate than the later work of Knudsen and Fricke, but the results of Kneser and Knudsen are most important for us because they were done with oxygen. For N_2 there are no experiments but only an estimate by P. S. H. Henry, Nature 129, 200 (1932) based on the failure to detect the influence of the vibrational specific heat on the velocity of sound in certain experiments. Henry estimates $\omega_0 \approx 10^4$ sec^{-1}, i.e. $Z \approx 10^6$ for N^2 which seems not implausible.

Table V gives some of the experimental results. They bear out the features discussed above and expected theoretically, viz.

Table V. Experimental Results on the Excitation of Molecular Vibrations. Number of Collisions Required for De-excitation, Z, and Reciprocal Time of Relaxation, ω_o (in sec^{-1}), for Various Molecules Colliding with other Molecules.

Collision with		O_2	N_2	H_2	CO_2	H_2O	H_2S	CH_3OH	C_2H_5OH
Vibration of O_2	Z	$> 500,000$	100,000	20,000	25,000	400	4,200	---	120
(Knudsen and Kneser)	ω_o	$< 8 \cdot 10^3$	$5 \cdot 10^4$	$5 \cdot 10^5$	$1.7 \cdot 10^5$	$1.1 \cdot 10^7$	$1.3 \cdot 10^6$	---	$6 \cdot 10^7$
Vibration of CO_2	Z	----	-----	215	86,000	17	1,200	36	------
(Kneser and Fricke)	ω_o	----	-----	$8.0 \cdot 10^7$	$9.8 \cdot 10^4$	$1.02 \cdot 10^9$	$1.14 \cdot 10^7$	$3.1 \cdot 10^8$	------

The same quantities for some pure gases (Fricke)

Gas	O_2	CO_2	N_2O	COS	CS_2	SO_2
Z	$> 500,000$	86,000	11,800	9,600	8,700	1,900
$_o$(in 10^5 sec^{-1})	< 0.08	0.98	6.9	11.5	14.3	55

Z for CO_2 at various temperatures (Küchler)

T(degrees Kelvin)	293	373	473	573	673
Z	50,000	31,000	19,000	12,000	9,000

Ratio of $Z_{293°}/Z_{673°}$ for various gases (Küchler)

Colliding gases	CO_2 - CO_2	N_2O - N_2O	CO_2 - H_2	CO_2 - H_2O
$Z_{293°}$	50,000	7,500	300	105
Z_{293}/Z_{673}	5.6	3.6	1.0	0.4

1. All the pure gases investigated have rather high Z (small ω_0, long relaxation times), the smallest being SO_2 with $Z \approx 2,000$, the largest O_2 with $Z > 500,000$. The large value for O_2 is probably due mostly to its high vibration frequency. The decrease of Z from CO_2 to COS to CS_2 is also in the direction of decreasing ν; on the other hand, the small value for SO_2 is presumably due to the greater chemical activity of that molecule.

2. The impurities investigated gave smaller Z than pure gases. It cannot be decided at present whether this is due to the selection of gases used in the experiments, or to a general rule. Among diatomic molecules, H_2 is most effective in de-exciting O_2 and CO_2; this is to be expected theoretically from its small mass (large velocity). Triatomic gases are on the whole more effective than diatomic ones; this may be due to the fact that there will always be some "corner" of a triatomic molecule which has a chemical affinity or at least a strong interaction with a given molecule. Among the triatomic gases, there is again a decrease of Z with increasing chemical activity (CO_2 to H_2S and H_2O). Polyatomic molecules are even more effective than triatomic ones, for the same reason.

By collisions with the same molecule, the vibrations of CO_2 are in general more affected than those of O_2, because of the smaller frequency of vibration.

3. The temperature dependence of Z for CO_2 is about as expected (cf. Table IV). Generally, the decrease of Z with increasing temperature is most pronounced if Z is large, in agreement with theoretical expectation. Whether the increase of Z with the temperature as found by Küchler for collisions between CO_2 and H_2O, is real cannot be decided at present; however, Z is very small in this instance so that the Landau-Teller theory can probably not be applied.

Several Degrees of Freedom. At first sight, it might be expected that each mode of vibration has its own relaxation time, this time being greater for the modes with higher frequency. Experiments show, however, that this is not the case because all the experimental curves show only <u>one</u> absorption maximum with the absorption coefficient falling off on both sides according to (2.25). This behavior can easily be understood if we remember that the resolution of the vibration into normal modes is only an approximation which is correct only for exactly harmonic forces. The anharmonicity will mix the various normal modes in each vibrational quantum state. An extreme case of mixing is known in CO_2 where the second excited state (vibrational quantum number* $n_1 = 2$) of the first mode of vibration ($\nu_1 = 667_{cm}{}^{-1}$) is degenerate with the first quantum state of the second mode ($\nu_2 = 1336\ cm^{-1}$) ($n_2 = 1$) (cf., e.g., Sponer, loc. cit.). The anharmonicity causes an "interaction" of the two resonating quantum states with the result that a splitting occurs into two states of considerably different frequency (1286 and 1388 cm^{-1}). The form of vibration in each of these states is a combination of modes 1 and 2 with about equal amplitudes.

In other molecules, the mixing of different modes is usually less strong but it must always exist to some extent. Let us assume, e.g., that there is a mode of vibration with a high frequency ν_2 which is between 3 and 4 times the frequency ν_1 of another mode. Then the first excited state of mode 2 ($n_2 = 1$) will contain some admixture of the fourth state of mode 1 ($n_1 = 4$). In this case, the excitation of the state $n_2 = 1$ will not take place by direct transfer of energy from the translation, but the translation will excite in successive collisions the states $n_1 = 1$, 2 and 3, and finally, in a fourth collision, the state $n_2 = 1$. This mechanism avoids large energy transfers in one collision which are very improbable according to the Landau-Teller theory (cf. 2.15). The transition from $n_1 = 3$ to $n_2 = 1$ is somewhat less probable than a collision in which n_1 is raised by one unit because the mixing between $n_2 = 1$ and $n_1 = 4$ is assumed small; on the other hand, it is more probable because the energy difference between $n_2 = 1$

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* In order to avoid confusion with the velocity v, we denote the vibrational quantum number by n rather than the customary v.

and $n_1 = 3$ is smaller than ν_1. The Z for the transition $n_1 = 3$ to $n_2 = 1$ is therefore probably of the same order or smaller than for the excitation of the first mode, and it can therefore be understood that only the successive excitation of quantum states of the lowest mode of vibration gives rise to an observable absorption of sound.

C. Dissociation

The dissociation differs from other degrees of freedom in that it becomes appreciable at temperatures at which kT is still very small compared with the dissociation energy D per molecule. We have mentioned in par 1 that $\frac{D}{kT} = \frac{59,000}{T}$ for oxygen and 91,600/T for nitrogen. On the other hand, we have shown in Table II that the degree of dissociation is as much as 1.4 per cent for O_2 at 3000° K and for N_2 at 5000° K. At these temperatures, D/kT is about 20 in both cases, and the Boltzmann factor $e^{-\frac{D}{kT}} \approx e^{-20} \approx 10^{-9}$. The fact that an appreciable dissociation is possible for such a small Boltzmann factor is due to the large a priori probability of the dissociated states.

In order to produce dissociation, two molecules must collide which have a relative kinetic energy at least equal to D. Such molecules are very rare because of the small Boltzmann factor $e^{-\frac{D}{kT}}$. Dissociation will therefore take a considerable time at 3000-5000° K even if every collision between molecules of sufficient energy is effective.

The same conclusion can be reached by considering the inverse process, viz. recombination. In order that two atoms recombine into a molecule, there must be a triple collision between the two atoms and another molecule which takes up the excess energy and momentum. Triple collisions, however, are rare events especially if two of the colliding particles must be atoms which are relatively rare as long as the degree of dissociation remains low.

We must now examine the efficiency of collisions between two molecules of sufficient relative velocity in causing dissociation of one of the molecules.

If two molecules have relative kinetic energy equal to D, i.e. several electron volts, they will penetrate very deeply into each other. In this case, we can no longer distinguish between fast motions (of the electrons) and slow motions (of the molecules as a whole), and we can therefore no longer conclude that the transfer of energy from the slow molecular translation to the fast electronic motion is improbable. It is very difficult to make any quantitative estimates but we believe that the efficiency of collisions between molecules of energy greater than D will not be reduced by a factor of the type of (2.5) but will be determined mainly by a geometrical factor which may perhaps be somewhat smaller than for the excitation of vibrations. In numerical calculations, we shall assume an efficiency $C_d = 1/100$ which may be wrong by a factor of 10 or more either way.

The probability that the relative kinetic energy of a pair of molecules is between kTx and kT (x + dx), is given by the Maxwell distribution

$$\frac{2}{\sqrt{\pi}} \sqrt{x} \quad dx \; e^{-x}$$

The velocity of the molecules in question is $\frac{\sqrt{\pi}}{2} \sqrt{x}$ times the average relative velocity $\bar{v}$ of two molecules. Therefore, the fraction of all molecular collisions for which the relative kinetic energy of the colliding molecules lies in the interval mentioned, is approximately

$$f(x)dx = e^{-x} \, x \, dx \qquad (2.27)$$

The fraction of collisions for which

$$x > x_o \equiv \frac{D}{kT} \qquad (2.27a)$$

is then

$$F\,(x_o) = \int_{x_o}^{\infty} f(x)dx = e^{-x_o}\,(x_o + 1) \approx x_o e^{-x_o} = \frac{D}{kT}\; e^{-D/kT} \qquad (2.27b)$$

Therefore, the number of ordinary molecular collisions required per dissociation, is

$$Z_d = \frac{1}{C_d\,F(x_o)} = \frac{1}{C_d}\,\frac{e^{x_o}}{x_o} \tag{2.28}$$

where C_d is the efficiency of the collisions between molecules of sufficient energy in producing dissociation. The reciprocal relaxation time for dissociation is

$$\omega_d \approx \frac{N}{Z_d}\,d \tag{2.29}$$

where N is the number of collisions per second (cf. 2.18, 2.18a). The mean free path for dissociation is (cf. 2.24).

$$\lambda_d = y/\omega_d \tag{2.29a}$$

Because of the large factor e^{x_o}, the number of collisions required for dissociation is very large at temperatures of 3000-5000° K at which the dissociation of air becomes important (Tables II and III). In Table VII (cf. p. 52a) we give the values of Z_d, ω_d, and λ_d for oxygen and nitrogen; it is seen that Z_d lies between 10^6 and 10^{12} and is thus much higher than for the vibration. It is obvious that impurities cannot greatly affect Z_d because the decisive factor is the Boltzmann factor rather than the efficiency of the collisions.

D. Conclusions on the Excitation of Air.

Vibrations

Neither the theory nor the available experimental results are sufficiently accurate to permit any quantitative predictions on the mean free path for the vibrations of the most important gases, O_2 and N_2. It is certain that these mean free paths are rather long, and under certain circumstances they may become comparable with the dimensions of a projectile.

Experimental information is available (Table V) only on the effect of N_2 and of water vapor on the vibration of O_2; in addition an upper limit is known for the effect of O_2 on the O_2 vibration. The effect of N_2 on O_2 is described by an effective range $s = 3\cdot10^{-9}$cm as computed in (2.18a). In Table IV, we have calculated Z as a function of temperature with this value of s. These calculated values should represent the temperature dependence of the effect of N_2 on the vibrations of O_2 fairly accurately, i.e., within a factor of perhaps 3.

For the collisions between two O_2 molecules, the experiments give $Z \gtrsim 500{,}000$ at room temperature. Assuming $Z = 10^6$, we obtain $s = 4\cdot10^{-9}$ cm from (2.13, 15). The values of Z for O_2 at various temperatures with $s = 4\cdot10^{-9}$ are also given in Table IV; the actual Z for O_2 - O_2 collisions may be smaller than the values given in the table by about a factor of 2, but greater by any amount. In any case, in air the vibrations of O_2 will be excited much more easily by collisions with N_2 than by collisions with other O_2 molecules, both because of the greater abundance of N_2 and of the smaller Z.

In Table VI we give the estimated times and distances required to establish equilibrium of the molecular vibrations in air. In particular, Table VI A gives the reciprocal time of relaxation, ω_0, as a function of temperature for various assumptions. ω_0 has been calculated from (2.18, 18a and 22), considering q as independent of the temperature. The values of q were obtained by comparing the values of Z and ω_0 given by Kneser and Kunze for room temperature; these q's seem somewhat low but the errors are not important compared with the uncertainties in the theory. The density of the air was assumed to be $1.18\cdot10^{-3}$, corresponding to atmospheric pressure at 300°K. In the first row of Table VI A, ω_0 is given for the vibrations of O_2, taking into account only the collisions with N_2 molecules. The neglected collisions with O_2 can increase ω_0 by 10 per cent at most.

Collisions with water molecules are very effective in exciting the vibrations of O_2 (Table V). Four hundred collisions with H_2O are sufficient for deexcitation of O_2 at room temperature; therefore, as little as one per cent of water vapor will be three times as effective as all the nitrogen in the air. In the second row of Table VI A we have listed the value of ω_o for collisions of O_2 molecules with H_2O, assuming a concentration of 1 per cent water vapor by volume. On hot humid days, the water concentration may be easily 3 per cent. It is seen that, at 1 per cent, the collisions with H_2O are more effective than those with N_2 at 500° K, but less effective at 700° and higher temperatures. This behavior is due to the fact that ω_o rises very rapidly with temperature for collisions with N_2, but rather slowly for collisions with H_2O. (Table IV)

While the information obtainable on O_2 is fairly satisfactory, very little can be said about the excitation of the vibrations of N_2. It is reasonable to expect that the effect of O_2 on the N_2 vibrations can be described by the same effective range, $s = 3 \cdot 10^{-9}$ cm, as the effect of N_2 on O_2, although this is by no means certain. In Table IV we have given the corresponding Z for N_2; it is much higher than the Z for O_2 with the same S because the vibration frequency of N_2 is about 50 per cent higher than for O_2. The third row of Table VI gives ω_o for the excitation of the vibration of N_2 in air, assuming that only collisions w with O_2 are effective. These values for ω_o can therefore be regarded as lower limits.

No experimental results are available concerning the effect of collision with the N_2 molecules on the vibration of N_2. To obtain any theoretical estimate, we must find an interpretation of the difference between the effective range s for $O_2 - O_2$ and $O_2 - N_2$ collisions, viz. $s \approx 4 \cdot 10^{-9}$ and $s = 3 \cdot 10^{-9}$ cm, respectively. There are two possible interpretations: The first alternative is to assume that generally collisions between different molecules are more effective than between equal ones. Such a tendency seems to exist in the experimental result (Table V) but there appears to be no theoretical justification. Moreover, it is to be remembered that the experiments were mostly done with polyatomic molecules, for which there are other reasons for a stronger interaction (cf. point 2 in the section on Experimental Results of par. 28). Thus we do not get an explanation for the effectiveness of the collisions between O_2 and N_2, and we are led to the second alternative. This is based on the fact that N_2 is a more compact molecule than O_2, having a greater binding energy and smaller distance between the atoms. From this difference in structure we may expect a shorter range of the forces for N_2 which would explain the smaller value of s for O_2 - N_2 collisions as compared with O_2 - O_2.

If this second alternative is accepted, we should expect an even smaller s for the interaction between two N_2 molecules than for the N_2 - O_2 interaction. We have therefore included in Table IV the values of Z for N_2 obtained with $s = 2.5 \cdot 10^{-9}$ cm. These values are, of course, considerably smaller than for N_2 and $s = 3 \cdot 10^{-9}$ cm, and not much larger than for O_2 and $s = 3 \cdot 10^{-9}$ cm. In the fifth row of Table VI A we have given ω_o for N_2 in air, assuming $s = 2.5 \cdot 10^{-9}$ cm for the interaction N_2 - N_2; the values thus obtained are only slightly less than those for O_2 (first row).

On the other hand, if the first alternative explanation above is assumed, the interaction between two N_2 molecules would have a large s, just as the interaction between two O_2 molecules. In this case, the N_2 - N_2 collisions would not contribute appreciably to the excitation of N_2 vibrations, and ω_o for N_2 would be given by the third line in Table VI A in which the N_2 - O_2 collisions alone are taken into account.

Finally, as a compromise, we have also given the results when $s = 3 \cdot 10^{-9}$ cm is assumed to be valid for collisions between two N_2 molecules as well as between N_2 and O_2 (fourth row of Table VI A).

The effect of water vapor on N_2 is also unknown. H_2O is extremely effective in exciting the vibrations of O_2 and CO_2 (cf. Table V) as well as of N_2O, CS_2 and COS (Knudsen and Fricke, loc. cit.). By pure analogy we might therefore conclude that it would also be effective on N_2, and we have therefore included in Table IV a calculation of Z for collisions between N_2 and H_2O, assuming the same s as for collisions between O_2 and H_2O but taking into account the higher ν of N_2. However, it must be remembered that O_2 has a chemical affinity to H_2O while N_2 has very little; therefore, collisions with water may be much less effective on N_2 (Z higher) than is indicated by the last line of Table IV.

In Table VI A, last row, we have computed ω_o for collisions between N_2 and H_2O, assuming 1 per cent water vapor in air of density $1.18 \cdot 10^{-3}$, and assuming the Z as given in Table IV. Presumably, these values of ω_o are on the high side. Whether or not the humidity has an appreciable influence on the vibrations of N_2, depends not only on the temperature and on the correctness of our assumption about the interaction between N_2 and H_2O, but also on the assumed interaction between N_2 and N_2. If the latter is strong ($s = 2.5 \cdot 10^{-9}$), the humidity is rather unimportant even at low T; if it is weak (collisions with O_2 only), the humidity is the decisive factor. This again indicates the extreme uncertainty of the data on the excitation of the vibration of N_2.

In Table VI B, we have calculated the mean free path for vibration, λ_v, the high pressure side of a shock wave produced in "standard air", i.e., when the temperature and pressure on the low pressure side are 300° and 1 atmosphere respectively. λ_v is given in Table VI as a function of the temperature T_3 which is obtained on the high pressure side at large distance from the front of the shock wave (par. 3); T_3 again is a known function of the velocity v_1 of the shock wave (Table VIII). Velocity and density on the high pressure side were also taken from Table VIII (par. 3), the asymptotic values v_3, ρ_3 being used. The so defined λ_v is related to the ω_o given in Table VI A by

$$\lambda_v = \frac{v_3}{\omega_o} \frac{\rho_1}{\rho_3} \tag{2.30}$$

Table VI. Relaxation Time and Mean Free Path of Vibration for O_2 and N_2 in Air.

Vibration of	Collisions with	Abundance %	(10^{-9}cm)	Temperature 300	500	700	1000	1500	2000	3000	5000
				A. Reciprocal Relaxation Time ω_o (in 10^5 sec^{-1})							
O_2	N_2	78	3	0.35	2.3	7	19	50	80	140	260
	H_2O	1	0.93	1.1	2.8	5	7.5	11	13	14	17
N_2	O_2	21	3	0.006	0.07	0.26	0.9	5.2	7	16	37
	N_2	78	3	0.024	0.25	0.95	3.5	12	26	60	140
	N_2	.78	2.5	0.10	0.9	3.0	9	30	55	115	240
	H_2O	1	0.93	0.35	0.9	2.2	4	7	10	13	18

B. Mean Free Path of Vibration λ_v (in millimeters)

		300	500	700	1000	1500	2000	3000	5000
$v_3 \cdot \rho_1/\rho_2$(meters/sec)		350	98	71	61	56	56	58	48
Vibration of	Collisions with								
O_2	N_2 only	10	0.4_3	0.10	0.032	0.011	0.007	0.004	0.0018
	N_2 and H_2O(1%)	2.4	0.19	0.06	0.023	0.009	0.006	0.003_7	0.0017
N_2	O_2 only	550	14	2.7	0.7	0.18	0.08	0.03_6	0.013
	O_2 and N_2($s=3\cdot10^{-9}$cm)	110	3.0	0.6	0.14	0.03_7	0.017	0.007_5	0.0027
	O_2 and N_2($s=2.5\cdot10^{-9}$cm)	33	1.0	0.22	0.06	0.017	0.009	0.004_5	0.0017
	O_2 and 1% H_2O	10	1.0	0.20	0.12	0.05_5	0.033	0.020	0.009
	O_2,N_2($s=3\cdot10^{-9}$)and H_2O	9.5	0.8	0.21	0.07	0.025	0.013	0.006_5	0.0025
	O_2,N_2($s=2.5\cdot10^{-9}$)and H_2O	8	0.5	0.13	0.04	0.014	0.008	0.004	0.0016

The quantity $v_3 \cdot \rho_1/\rho_3$ is given in the first row of the Table VI B, in meters per second. Then λ_v is given for various assumptions.

The value of λ_v for O_2 in dry air decreases from 10 millimeters at 300° to 1/150 millimeter at 2000° and 1/500 at 5000°. If the initial pressure is low--let us say, 1/100 atmosphere--λ_v is proportionally greater (100 times) and may therefore easily reach considerable values. In wet air containing 1 per cent of water vapor by volume, λ_v for O_2 is reduced to 2 mm at 300° but is almost the same as for dry air when $T \gtrsim 1500^\circ K$.

For the vibrations of nitrogen, the value of λ_v is extremely uncertain. If the collisions with N_2 are unimportant (cf. above) and if the air is dry, only collisions with O_2 need to be considered; then λ_v is as large as half a meter at $300^\circ K$. Since the vibrational energy of N_2 becomes important only for $T > 600^\circ$ (Table II), λ_v is important only at higher temepratures; but even at $T = 700^\circ$ we obtain $\lambda_v \approx 3$ mm if only collisions with O_2 are effective. On the other hand, if collisions with N_2 are very effective ($s = 2.5 \cdot 10^{-9}$ cm), λ_v is reduced by about a factor of 12 at 700°, and a factor of 8 at 5000°. If collisions with H_2O are as effective as assumed in Table IV and VI A, a water vapor content of 1 per cent reduces λ_v by factors varying from 9 to 1.05 when only temperatures $\gtrsim 700^\circ$ are considered.

Apart from the uncertainties in the assumptions, there is also an uncertainty in the Landau-Teller theory itself which makes the temperature dependence of λ_v uncertain by a factor of about 3 even if ω_o at room temperature is accurately known.

The unsatisfactory state of our knowledge about the mean free path for molecular vibrations in air could be improved by experiments on the dispersion and absorption of sound in mixtures of O_2 and N_2 of varying composition and free from impurities. Such experiments should be done at $T \approx 700^\circ$ K or higher in order to ensure sufficient excitation of the molecular vibrations of N_2. With such experiments available, the dependence of λ_v on the temperature at higher temperatures could probably be calculated from the Landau-Teller theory with fair accuracy. The influence of humidity should also be investigated experimentally.

Nitrogen and oxygen are probably almost unique in their large values of Z, and therefore of λ_v. Other molecules have much lower frequencies or much greater chemical activity (cf. above). Therefore for most other gases, and especially for complicated polyatomic ones (explosives!), λ_v will in general be too small to be of any practical importance.

Dissociation. In Table VII, we give the number of molecular collisions Z_d required for one dissociation process, the reciprocal time of relaxation ω_d, and the mean free path λ_d for dissociation. These quantities were calculated from Eqns. (2.28, 29 and 29a). The constants N and v were assumed as in Table VI, namely $N = 5 \cdot 10^9$ sec^{-1} at 300° K. and one atmosphere, and proportional to $\rho\sqrt{T}$ otherwise; v equal to the velocity v_3 of air on the high pressure side of a shock wave produced in "standard air"; α was taken from Table II, C_d was arbitrarily put equal to 1/100. Z_d is, of course, independent of the pressure; ω_d is calculated for a density* of $1.18 \cdot 10^{-3}$ as in Table VI, and λ_d for the actual conditions on the high pressure side of a shock wave. It can be seen that the mean free paths obtained are very long indeed, decreasing for O_2 from a little under one meter at 2500° to a little over one millimeter at 5000°. Therefore we should expect large effects from lack of dissociation equilibrium in shock waves which are sufficiently violent to produce dissociation. We must emphasize again the great uncertainty of the figures in Table VII which is caused by the lack of knowledge of C_d. Here again experiments would be desirable but they seem considerably more difficult than in the case of vibrations. Possibly studies of the dissociation equilibrium of other gases (e.g., N_2O_4) would help.

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* This is not quite consistent since α, which occurs in (2.29), was calculated for an 8 times larger density, but $\rho = 1.18 \cdot 10^{-3}$ was chosen for comparison with the ω_o in Table VI.

Table VII. Relaxation Time and Mean Free Path for the Dissociation of Air

		T = 2500	3000	3500	4000	4500	5000
α	O_2	0.00205	0.0144	0.0568	0.152	0.308	0.500
	N_2	----	----	0.0003	0.0014	0.0051	0.0139
λ_o	O_2	23.60	19.67	16.86	14.76	13.12	11.81
	N_2	-----	----	26.17	22.90	20.36	18.32
Z_d	O_2	$7.5 \cdot 10^{10}$	$1.85 \cdot 10^{9}$	$1.27 \cdot 10^{8}$	$1.76 \cdot 10^{7}$	$3.8 \cdot 10^{6}$	$1.16 \cdot 10^{6}$
	N_2			$9.2 \cdot 10^{11}$	$4.0 \cdot 10^{10}$	$3.5 \cdot 10^{9}$	$5.1 \cdot 10^{8}$
ω_d	O_2	85	600	2400	6800	16,600	35,200
(sec^{-1})	N_2			65	320	1080	2900
$v_3 \cdot \rho_1/\rho_3$		57	58	57	55	52	48
λ_d	O_2	670	98	24	8.1	3.1	1.4
(mm.)	N_2			880	170	48	16

Par. 3. Theory of Shock Waves in the Case of Variable Specific Heat.

Notation:

We shall denote by letters without subscripts the physical quantities at any point in the shock wave, by letters with the subscript 1 the quantities on the low pressure side of the wave, by the subscript 2 those on the high pressure side immediately at the front on the wave, and by the subscript 3 those on the high pressure side at large distance from the wave front, i.e., where equilibrium has been established for vibrations and dissociation. We shall also use h and l for arbitrary points on the high and low pressure side, respectively. We consider the one-dimensional case throughout. For further notations, see the end of the introduction.

Fundamental Equations:

1. Equation of continuity

$$\rho v = \text{constant} = m \tag{3.1}$$

2. Conservation of momentum: The gain of momentum of the mass m of gas, $m\delta v$, is equal to the decrease in pressure, $-\delta p$. Therefore*

$$p + mv = \text{constant} = mV \tag{3.2}$$

(definition of V)

3. Conservation of energy

$$E + \frac{p}{\rho} + \frac{1}{2} v^2 + \text{constant} = \frac{1}{2} c^2 \tag{3.3}$$

When the gas flows adiabatically into vacuum, η/ρ and therefore also E go to zero so that v approaches c. Introducing β defined in (1.3), (3.3) becomes

$$\beta \frac{p}{\rho} + \frac{1}{2} v^2 = \frac{1}{2} c^2 \tag{3.3a}$$

has been extensively discussed in par. 1 and 2. It has been shown in par. 2 that β depends on the existence or non-existence of equilibrium between the various degrees

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* It is interesting that in our case $p + \rho v^2$ is constant while in the imcompressible fluid it is $p + (1/2)\ v^2$. In both conservation laws, the elementary law is $dp + \rho v dv = 0$, but for the integration we must assume ρ = constant in the incompressible fluid, ρv = constant in our case.

of freedom of the molecules. If there is equilibrium, β is a function of the temperature (or p/ρ) alone; tables of β for this case are given in par. 1 for nitrogen, oxygen and air (Tables II and III). Equilibrium will exist everywhere on the low pressure side of the shock wave ($\beta = \beta_1$) and asymptotically at large distance from the wave front on the high pressure side ($\beta = \beta_3$). The value of β on the high pressure side immediately <u>at the wave front</u> (β_2) can be calculated easily from the fact that the energy content of the inert degrees of freedom (vibration, excitation and dissociation) is the same as on the low pressure side (cf. beginning of par. 4). In the particular case when the temperature on the low pressure side is low enough so that there is no appreciable energy in the inert degrees of freedom (fulfilled for air below 400° K), we have simply $\beta_2 = \beta_1$ (= 7/2 for diatomic gases). In the intermediate region on the high pressure side, β must be considered as varying from β_2 to β_3 in a way which will be discussed in par. 4. For the moment, we shall consider β as given and determine the other physical quantities from it.

The three constants m, V, and c defined in (3.1, 2, 3) are given by the pressure, density, and velocity of the incoming gas on the low pressure side:

$$V = \frac{p_1}{\rho_1 v_1} + v_1 \tag{3.4a}$$

$$c^2 = v_1^2 + 2\rho_1 \frac{p_1}{\rho_1} \tag{3.4b}$$

It is often convenient to introduce the velocity of sound by putting

$$p/\rho = a^2/\gamma \tag{3.5}$$

(Valid only in the absence of dissociation)

In most practical applications, the temperature on the low pressure side is sufficiently low so that $d\beta/dT = 0$ and (cf. 1.19, 1.21)

$$\gamma = \frac{\beta}{\beta - 1} \tag{3.6}$$

If this is true, we may rewrite (3.4):

$$V = v_1 + \frac{\beta_1 - 1}{\beta_1} \frac{a_1^2}{v_1} \tag{3.7a}$$

$$c^2 = v_1^2 + 2(\beta_1 - 1)\, a_1^2 \tag{3.7b}$$

Solution of Fundamental Equations:

(3.1) and (3.2) may be used to eliminate p and ρ , viz.

$$\rho = m/v \tag{3.8a}$$

$$p = m(V - v) \tag{3.8b}$$

$$\frac{p}{\rho} = (V - v)\, v \tag{3.9}$$

These equations are important to calculate ρ, p, and T once v has been determined. Inserting now (3.9) into (3.3a), we find:

$$\beta\,(V - v)v + \frac{1}{2} v^2 = \frac{1}{2} c^2 \tag{3.9a}$$

and therefore

$$v = \frac{\beta V \pm \sqrt{\beta^2 V^2 - (2\beta - 1)c^2}}{2\beta - 1} \tag{3.10}$$

If V and c are given, there are, for any value of β, two solutions for v. In general, these two solutions are real (for exception, cf. par. 5, p. 71); <u>if</u> real, they are both positive. It can easily be shown that the larger value of v [plus sign in (3.10)] in general is greater than the corresponding velocity of sound, the smaller v smaller than the corresponding a.

To show this, we calculate from (3.9)

$$\frac{p}{\rho} = \frac{v}{2\beta - 1} \left[(\beta - 1)V \mp \sqrt{\beta^2 V^2 - (2\beta - 1)c^2} \right] \tag{3.11}$$

where the upper and lower sign correspond to the upper and lower sign in (3.10). Now if we assume that β does not depend much on the temperature, we may use (3.5, 6) and have

$$a^2 = \gamma\frac{p}{\rho} = \frac{v}{2\beta - 1}\left[\beta v \mp \frac{\beta}{\beta - 1}\sqrt{\beta^2 v^2 - (2\beta - 1)c^2}\right] \qquad (3.12)$$

This gives

$$v - \frac{a^2}{v} = \mp\frac{1}{\beta - 1}\sqrt{\beta^2 v^2 - (2\beta - 1)c^2} \qquad (3.12a)$$

i.e. $v > a$ for the upper, $v < a$ for the lower sign.

In reality, β does depend on T and therefore (3.6) is not correct but should be replaced by (cf. 1.19)

$$\gamma = \frac{\beta + d\beta/d\log T}{\beta - 1 + d\beta/d\log T} \qquad (3.13)$$

(assuming no dissociation).

In all practical cases β increases with temperature so that γ (and therefore a^2) is slightly less than it would be if (3.6) were valid. Therefore it remains true that for the upper sign in (3.10 - 12) v is greater than a, but for the lower sign v is not necessarily less than a. However, the difference between (3.6) and (3.13) is only very slight; therefore the exceptional case that the smaller v is greater than the corresponding a will be of minor importance. A more detailed discussion will be given in par. 5, p. 80, 81.

Discussion:

On the low pressure side of the shock wave, the velocity will be given by (3.10) with the plus sign (in the following denoted by the subscript ℓ, for low), on the high pressure side by the solution with the minus sign (subscript h for high). We have pointed out above that β will have the equilibrium values,

β_1 and β_3, both on the low pressure side and on the high pressure side at large distance from the wave front. The equilibrium value of β is a unique function of the temperature so that β_1 and β_3 are completely determined by T_1 and T_3. Let us denote by T_e (β) the temperature which belongs to a given β in thermal equilibrium ; it is the function tabulated in Tables II and III and it increases monotonically with β. On the other hand, the theory of shock waves (Eq. 3.10) gives v_3 uniquely in terms of β_3 since V and c are given by the initial conditions (cf. 3.4a, b) and the sign of the square root is also determined (negative). From v_3 in turn T_3 is determined through (3.9)* so that T is, by the shock wave theory, a given function of β which we shall denote by $T_s(\beta)$. The temperature T_3, and the energy content β_3, are determined by solving the equation

$$T_s(\beta) = T_e(\beta) \qquad (3.14)$$

It can easily be shown that this equation has only one solution for which the velocity v is smaller than the corresponding velocity of sound, i.e., only one "high pressure" solution. In most cases, this follows from the fact that $T_s(\beta)$ decreases with increasing β over almost the whole range of β (cf. 3.16c and especially par. 6) whereas $T_e(\beta)$ increases monotonically. In the small range of β in which $T_s(\beta)$ increases (cf. par. 6), this increase is slower than that of T_e; in fact, the condition $v < a$ is equivalent with $\frac{dT_s}{d\beta} < \frac{dT_e}{d\beta}$.

We may conclude, then, that β_3, T_3 and of course also the other physical quantities (p_3, ρ_3, v_3) are uniquely determined by the initial conditions p_1, ρ_1, v_1. In other words, all the physical quantities (v, p, ρ, T, etc.) on the high pressure side at sufficient distance from the shock wave are independent of all intervening processes connected with the establishment of equilibrium between

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* If there is dissociation, (1.2) must be used together with (3.9).

"inert" and "active" degrees of freedom. Therefore, if the dimensions of the obstacle causing the shock wave are large compared with the mean free path for vibration, etc. (par. 2), the pressure, resistance, etc. will be the same as if all degrees of freedom were in equilibrium all the time.

We could rewrite Eq.(3.10) inserting the values (3.4a, b) or (3.7a, b) for V and c. This would in general lead to complicated expressions if $\beta \neq \beta_1$. However, simple results are obtained in the two cases (a) $\beta = \beta_1$ and (b) $v_1 \gg a_1$.

a) For $\beta = \beta_1$ and $(d\beta/d \log T)_1 = 0$ our theory reduces to the usual theory of shock waves, and (3.10) becomes (use 3.7a, b!)

$$v = \frac{v_1 + (\beta - 1)\dfrac{a_1^2}{v_1} \pm (\beta - 1)\left(v_1 - \dfrac{a_1^2}{v_1}\right)}{2\beta - 1}$$

which gives

$$v_\ell = v_1$$

$$v_h = \frac{1}{2\beta - 1}\left[v_1 + 2(\beta - 1)\frac{a_1^2}{v_1}\right] \qquad (3.15)$$

(3.15) is the fundamental equation of the usual theory in an especially convenient form.

b) Simple expressions can also be obtained if $v_1 \gg a_1$ no matter whether $\beta = \beta_1$ or not. In this case (cf. 3.4a, b) we have $V \simeq c \simeq v_1$ and (3.10) gives

$$v_h = \frac{v_1}{2\beta - 1} \qquad (3.16)$$

From (3.8, 9) we find then

$$\rho_h = \rho_1 (2\beta - 1) \qquad (3.16a)$$

$$p_h = \rho_1 v_1^2 \, \frac{2(\beta - 1)}{2\beta - 1} \qquad (3.16b)$$

$$(RT_h=) \quad \frac{p_h}{\rho_h} = v_1^2 \; \frac{2(\beta - 1)}{(2\beta - 1)^2} \qquad (3.16c)*$$

The relative error of these formulae is about $2\beta_1 a_1^2/v_1^2$ (for p_h only a_1^2/v_1^2). In the approximation used here, the quantities on the high pressure side are independent of β_1 and depend only on the local value of β on the high pressure side. It is seen that the value of ρ_h increases linearly with β; in the special case $\beta = 7/2$ (diatomic gases with translation and rotation only), (3.16a) gives the well-known result that the density in a shock wave can only increase six-fold. Since β increases considerably at high temperatures, the actual increase of ρ can be much greater than six-fold. p_h depends only slightly on β (for large β) because, in our limit $v_1 \gg a_1$, we have $v_h \ll V$ and therefore p_h is approximately mV (cf. 3.8b) which is a constant.

Finally, T_h decreases** strongly with increasing β because the total energy $E + \frac{p}{\rho} = RT$ is almost independent of β when $v_h \ll c$. (cf. 3.3) (Only a very small amount of kinetic energy is left!). As an example, we compare the asymptotic values of the physical quantities for air at ordinary temperatures ($\beta = 7/2$) and for hot air with the vibrations fully excited but no dissociation ($\beta = 9/2$).

	$\beta = 7/2$	$\beta = 9/2$
v_h/v_1	1/6	1/8
ρ_h/ρ_1	6	8
$p_h/\rho_1 v_1^2$	5/6 = 0.833	7/8 = 0.875
RT_h/v_1^2	5/36 = 0.139	7/64 = 0.109

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* In case of dissociation, (3.16c) holds for $RT_h\,(1 + \alpha_h)$ rather than for RT_h.

** This statement holds also in case of dissociation because T is a monotonic function of p/ρ.

Table:

Table VIII gives the physical characteristics on the high pressure side of a shock wave produced in air of 300° Kelvin (27° Centigrade) by incident streams of various velocities. For the construction of such a table, it is convenient to consider the temperatures T_1 and T_3 as given and to calculate v_1 and v_3, rather than to start from T_1 and v_1 and calculate T_3, v_3 from them. β_3 is a tabulated function of T_3 (cf. Table III). Eqs (3.3) and (3.9) may be rewritten

$$\frac{p_3}{\rho_3} \cdot \frac{1}{v_3} + v_3 = \frac{p_1}{\rho_1} \cdot \frac{1}{v_1} + v_1 \tag{3.17a}$$

$$2\beta_3 \frac{p_3}{3} + v_3^{\,2} = 2\beta_1 \frac{p_1}{\rho_1} + v_1^{\,2} \tag{3.17b}$$

Solving for v_1, v_3 we obtain

$$\frac{v_1}{v_3} = b + \sqrt{b^2 + \frac{p_1/\rho_1}{p_3/\rho_3}} \tag{3.18}$$

and

$$\frac{v_3^{\,2}}{p_3/\rho_3} = \frac{2b + 1 - p_1\rho_3/p_3\rho_1}{(v_1/v_3)^2 - 1} \tag{3.18a}$$

where

$$b = \beta_3 - \frac{1}{2} - \frac{p_1/\rho_1}{p_3/\rho_3} \left(\beta_1 - \frac{1}{2}\right) \tag{3.18b}$$

These formulae are suitable for comption.

Table VIII gives the important physical quantities as functions of v_1/a_1, the ratio of the velocity of the incoming stream to the corresponding velocity of sound, for values of v_1/a_1 from 1.5 to 11.6. Velocity, density, temperature and pressure on the high pressure side are given both at large distance from the wave front (subscript 3) and immediately at the wave front (subscript 2). The latter

Table VIII. Characteristics of Shock Waves in Air

v_1/a_1	v_3/a_1	v_2/a_1	$_3/\ _1$	$_2/\ _1$	T_3	T_2	p_3/p_1	p_2/p_1
1.523	0.798	0.800	1.907	1.904	400	400	2.543	2.538
1.984	0.746	0.749_5	2.659	2.647	500	501	4.432	4.42_5
2.377	0.737	0.747	3.225	3.189	600	604	6.450	6.41_5
2.725	0.744	0.759	3.663	3.591	700	709	8.547	8.49
3.041	0.757_5	0.779	4.015	3.904	800	816	10.707	10.62
3.331	0.772_5	0.803_5	4.314	4.146	900	925	12.94	12.77
3.611	0.795_5	0.831	4.540	4.346	1000	1036	15.23	15.01
4.235	0.835_5	0.900	5.069	4.706	1250	1320	21.12	20.72
4.797	0.880	0.970	5.454	4.945	1500	1616	27.27	26.66
5.307	0.923_5	1.041	5.746	5.098	1750	1925	33.52	32.7
5.778	0.966_5	1.103_5	5.978	5.236	2000	2222	39.85	38.7_5
6.643	1.045	1.228_5	6.359	5.409	2500	2848	53.01	51.4
7.453	1.115	1.350	6.685	5.521	3000	3510	67.05	64.6
8.315	1.167_5	1.481	7.122	5.615	3500	4300	84.09	80.5
9.297	1.208	1.633_5	7.697	5.691	4000	5300	106.02	100.6
10.410	1.241_5	1.809	8.385	5.754	4500	6570	134.40	126.2
11.595	1.269	1.997	9.136	5.804	5000	8030	168.38	155.6

quantities were calculated assuming that the inert degrees of freedom retain the same energy as on the low pressure side. Since this energy is practically zero, we can put $\beta_2 = \beta_1 = 3.483$ (cf. Table III), and can therefore calculate v_2 from (3.15) (and the remaining quantities from (3.8, 9)).

Comparing the quantities with subscripts 2 and 3, we find approximate agreement up to about $v_1/a_1 = 3$. At higher v_1/a_1, we find that ρ_3 is considerably greater than ρ_2 (cf. 3.16a) and, correspondingly (because of the continuity equation) $v_3 < v_2$. Thus the shock wave consists of a discontinuous compression followed by a gradual further compression which extends over a distance determined by the considerations of par. 2 and 4. Along with the strong increase of the density there is a small increase of the pressure from p_2 to p_3 (last two columns, cf. also 3.16b), but even if the discontinuous change of the pressure is by as much as a factor of 100, the following continuous one is only 5.4 per cent. Therefore, as far as the pressure is concerned, the change of β with temperature is rather unimportant. The temperature increases discontinuously at the wave front from $T_1 = 300°$ to T_2 and then decreases* gradually to T_3, due to a transfer of energy from the "active" degrees of freedom by whose excitation the temperature is defined, to the "inert" degrees. The temperature decrease is greatest for the highest v_1/a_1 where it is from over 8000 to 5000 degrees.

Of some interest are perhaps the columns v_2/a_1 and v_3/a_1. It is seen that for relatively small v_1, the velocities v_2 and v_3 are smaller than the velocity of sound on the low pressure side, a_1, and that they decrease with increasing v_1. Then a minimum is reached and at still larger values of v_1, the high pressure velocities v_2 and v_3 become greater than a_1. For v_2, the existence of a minimum can be seen directly from (3.15); the minimum is obtained for

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* For very "soft" shock waves (v_1 only slightly greater than a_1) there can be a slight increase from T_2 to T_3, cf. par. 6.

$$\frac{v_1}{a_1} = \sqrt{2(\beta_1 - 1)} = 2.23 \qquad (\text{for } \beta = 3.483) \tag{3.19}$$

and has the value

$$\frac{v_{2\,\min}}{a_1} = \frac{2\sqrt{2(\beta_1 - 1)}}{2\beta_1 - 1} = 0.747 \quad (\text{for } \beta = 3.483) \tag{3.19a}$$

For very high v_1 we obtain

$$v_2 = \frac{v_1}{2\beta_1 - 1} \tag{3.19b}$$

$$v_3 = \frac{v_1}{2\beta_3 - 1} \tag{3.19c}$$

Par. 4. The Approach of Equilibrium.

We may assume that the energy of the inert degrees of freedom (vibration, etc.) does not change discontinuously at the front of the shock wave while that of the active degrees of freedom does. It will therefore be convenient to split the total energy E into the part due to translation and rotation, E_a (a = active) and the part due to vibrations, electronic excitation and dissociation, E_i (i = inert). We put

$$E_a + \frac{p}{\rho} = \beta_a \frac{p}{\rho} \tag{4.1}$$

where β_a is practically constant and equal to 7/2 for diatomic gases (5/2 for monatomic ones). Further, we must have

$$E_{i1} = E_{i2} \tag{4.2}$$

i.e., the energy of the inert degrees of freedom is the same on both sides of the shock wave front. Then (3.3a) becomes:

$$\beta_a \frac{p}{\rho} + E_i + \frac{1}{2} v^2 = \frac{1}{2} c^2 \tag{4.3}$$

Instead of (3.9a) we have

$$\beta_a(V - v)v + \frac{1}{2} v^2 = \frac{1}{2} c^2 - E_i \tag{4.4}$$

and instead of (3.10):

$$v = \frac{\beta_a V \pm \sqrt{\beta_a{}^2 V^2 - (2\beta_a - 1)\,(c^2 - 2E_i)}}{2\beta_a - 1} \tag{4.5}$$

Equation (3.4a) is unchanged:

$$V = \frac{p_1}{\rho_1 v_1} + v_1 \tag{4.6a}$$

while (3.6b) is replaced by

$$c^2 = v_1{}^2 + 2\beta_a RT_1 + 2E_{i1} \tag{4.6b}$$

It can be seen easily that the physical quantities p_2, ρ_2, v_2, T_2 on the high pressure side immediately at the front of the shock wave are exactly as if the molecular vibration were absent entirely. We may use Eq. (3.15) with β_a instead of β to calculate v_2, and then obtain the other quantities from (3.8, 9). This has actually been done in Table VIII.

Farther in the high pressure region, the inert degrees of freedom will gradually come into equilibrium. If we have only one such degree, e.g., the vibration (subscript v), we may write (par. 2)

$$\frac{dE_v}{dx} = \frac{E_v'(T) - E_v}{\lambda_v(T,\rho)} \tag{4.7}$$

where T is the local temperature (defined as $p/\rho R$), $E_v'(T) = \beta_v(T)p/\rho$ the equilibrium value of the vibrational energy corresponding to T, E_v the actual local value of the vibrational energy, x the coordinate perpendicular to the wave front counted from the low pressure to the high pressure side, and λ_v the mean free path for vibrations (par. 2) which will depend on the local density and temperature. Similar equations, but with a different λ, will hold for dissociation and excitation.

To integrate (4.7), it is more convenient to calculate x as a function of the physical variables than to do the reverse. The integration must in general be done numerically because λ_v and $E_v{}'$ are given only by numerical tables (Tables II to VII) and depend in a complicated way on the variable T. A dependence of $E_v{}'$ and λ_v on the density does not present any additional difficulty because ρ is, by (3.8a) and (3.9), a unique function of $p/\rho = RT$. Assuming again that vibration is the only inert degree of freedom* (true for air below 2500° K), E_v can be calculated in terms of T from (4.3), eliminating v by use of (3.8b):

$$E_v = \frac{1}{2} c^2 - \frac{1}{4} v^2 - (\beta_a - \frac{1}{2})Rt + \frac{1}{4}v \sqrt{v^2 - 4RT} \qquad (4.8)$$

This is a fairly complicated dependence. It seems hardly worth while to carry out numerical integrations of (4.7), (4.8) for special cases.

However, it is easy to estimate the distance required to establish equilibrium. It must be of the order of λ_v, more precisely of the largest value of λ_v occurring, i.e., the one corresponding to the lowest temperature (par. 2) existing on the high pressure side of the shock wave. Ordinarily (i.e., with the exception of the case discussed in par. 6), this lowest temperature is reached

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* If there are several inert degrees of freedom (vibration, excitation, dissociation, possibly of several gases), there is one equation of the type (4.7) for each of them. The unknowns are the energies $E_i^{(1)}$, $E_i^{(2)}$, etc., in the various inert degrees of freedom, and T, the temperature as defined by the energy in the active degrees of freedom. From the temperature, v, ρ, and p can be determined, and also the equilibrium values of the E_i's, viz. $E_i^{(1)}{}'$, $E_i^{(2)}{}'$, etc., and $\lambda^{(1)}$, $\lambda^{(2)}$, etc. The number of differential equations (4.7) is obviously one less than the number of unknowns. The system is completed by Eq (4.8), with E_v replaced by $E_i = E_i^{(1)} + E_i^{(2)} + \ldots.$

in the equilibrium state (highest β, cf. 3.16c). Therefore it is only necessary to read from Tables VI, VIII the λ for the temperature T_3 and pressure p_3.

The integration is simple if T_2, ρ_2 are sufficiently close to the values T_3, ρ_3. Then we may consider λ as constant and T [according to (4.8)] and therefore E_v' (according to par. 1) as depending linearly on E_v, viz.

$$\frac{dE_v'}{dE_v} = -\mu = \text{constant} \tag{4.9}$$

μ is positive because T, and therefore E_v', decreases with increasing E_v (cf. 4.8). Using (4.9), (4.7) integrates immediately to

$$E_v'(T) - E_v = \left[E_v'(T_2) - E_{v1}\right] e^{-x(1+\mu)/\lambda(T_3)} \tag{4.10}$$

[remembering (4.2)!] . Thus the deviation from equilibrium decreases exponentially as we go away from the wave front. Since all physical quantities are expected to change very little ($T_2 \approx T_3$, etc.), T, ρ, p, v, etc. are sufficiently nearly linear functions of $E_v' - E_v$, so that

$$T(X) - T_3 = (T_2 - T_3)\, e^{-x(1+\mu)/\lambda} \tag{4.11}$$

and similarly for the remaining quantities.

It need hardly be pointed out that the gradual change of the physical quantities occurs only on the high pressure side because the gas streams from the low pressure to the high pressure side if we consider the wave front as fixed. Increasing x means therefore a later time. On the low pressure side, the wave front is sharp (except in the case of par. 5) because any molecules which may cross the wave front against the stream, i.e., from high pressure to low pressure side, will soon revert to the high pressure side because of collisions. There will therefore be no perturbation of the state on the low pressure side outside of a distance of a few times the ordinary mean free path from the wave front.

The stability of the shock wave against diffusion is insured by the fact that the gas velocity relative to the shock wave is greater than the velocity of sound on the low pressure side, less on the high pressure side. If there should at any time be a splitting of the shock wave into two parts (due to a small obstacle or so), these two parts will soon reunite: suppose a small disturbance runs before the main shock wave; then its velocity will be the velocity of sound, a_1, and it will be overtaken by the shock wave of velocity v_1. If the small disturbance runs behind, its velocity (relative to the gas) will be a_3 and it will therefore catch up with the main shock wave which moves only with the velocity v_3 relative to the high pressure gas.

Par. 5. Diffuse Shock Waves.

In this and the following section, we shall discuss some peculiar phenomena which occur only for very "soft" shock waves, i.e., when the velocity v_1 of the shock wave is only slightly greater than the velocity of sound, a_1. These two sections are in no way important for the general problem of shock waves in a medium of variable specific heat which has been solved in par. 3 and 4. Especially for a substance like air, whose inert degrees of freedom are very little excited at room temperature, the effects discussed in par. 5 and 6 have no practical significance but only academic interest. In the two sections, we solve some mathematical difficulties which might occur if the formulae of par. 3 and 4 were applied indiscriminately, and complete some proofs which were left incomplete in par. 3 and 4. The most important of these is the proof (end of par. 5) that for any initial conditions p_1, ρ_1, T_1, v_1 there is always exactly one solution of the shock wave equations in thermal equilibrium for which v is less than the velocity of sound a (high pressure solution) and one for which $v > a$, the latter being identical with the initial conditions.

In particular, in par. 5 we shall discuss the case when the velocity v_1 of the shock wave is less than that velocity of sound, a_{a1}, which is obtained when only the specific heat of the active degrees of freedom is considered. Such shock waves are possible because the "active velocity of sound", a_{a1}, is greater than the ordinary velocity of sound; we have

$$a_{a1}^2 = \frac{p_1}{\rho_1}\left(1 + \frac{R}{c_{va1}}\right) \tag{5.1}$$

$$a_1^2 = \frac{p_1}{\rho_1}\left(1 + \frac{R}{c_{v1}}\right) \tag{5.1a}$$

where c_{v1} is the total specific heat at constant volume on the low pressure side of the shock wave while c_{va1} is the specific heat of the active degrees of freedom alone. Since $c_v > c_{va}$, we have $a_{a1} > a_1$, and therefore there are values of v_1 such that

$$a_1 < v_1 < a_{a1} \tag{5.2}$$

These values of v_1 shall be the subject of the investigations of this section.

The difficulty is the following: according to the general theory, a shock wave must exist if $v_1 > a_1$. On the other hand, the front of the shock wave behaves as if only the active degrees of freedom existed (par. 4), therefore the wave front cannot exist if $v_1 < a_{a1}$. Mathematically, this difficulty appears in the form that the square root in (4.5) becomes imaginary if the constants c, V and E_{i1} are inserted which correspond to the initial conditions.

Practically, the region determined by (5.2) is very narrow. If c_{v1} and c_{va1} are not too different, we have

$$\frac{a_{a1}}{a_1} = 1 + \frac{R\,(c_{v1} - c_{va1})}{2c_{va1}\,(c_{v1} + R)} \tag{5.3}$$

Taking $c_{val} = \frac{5}{2} R$ (diatomic molecule) and even assuming c_{vl} to be as large as 3R, this gives only 1.025. For air at 300°K, $c_{vl} - c_{val}$, i.e., the specific heat of the vibration, is about 0.007R; then $a_{al}/a_1 = 1.0004$ so that the interval (5.2) is exceedingly narrow.

The solution of the difficulty which we found above for the velocity interval (5.2) is as follows: there exists a shock wave which is propagated without change of shape, but in which the velocity goes continuously through the velocity of sound. The extension of this shock wave in space is again of the order of the mean free path for vibration, λ_v (cf. par. 4); and the variation of the physical quantities with x is again determined by (4.7) in conjunction with (4.5), (3.8), (3.9). However, instead of having a continuous variation only on the high pressure side (lower sign in (4.5)), we now have it also on the low pressure side. Coming from the latter, we have a gradual increase of temperature, density and pressure together with a gradual increase of the vibrational energy E_v. The connection between v and E_v is given by the positive sign in (4.5). The change of the temperature is such that the vibrational energy falls more and more short of its equilibrium value, or mathematically, the difference $E_v'(T) - E_v$ (or $\beta' - \beta$) increases (cf. 5.21). Thereby the square root in (4.5) is reduced until it vanishes. From then on, the negative sign must be taken with the square root; there is a further gradual increase of T, ρ and p but now the vibrational energy "catches up" again with its equilibrium value $E_v'(T)$ which it reaches at large distance from the shock wave.

For the quantitative treatment, we introduce that value β_o of β at which the square root in (3.10) vanishes when V and c are kept constant. β_o is thus a function of the initial conditions of the shock wave. The temperature, pressure, etc., which are obtained by setting $\beta = \beta_o$ in (3.10), will be denoted by T_o, p_o, etc.

Obviously, β_o is defined by

$$\beta_o{}^2 V^2 = (2\beta_o - 1)\, c^2 \tag{5.4}$$

which has the solution*

$$\beta_o = \frac{c}{V^2}\left(c + \sqrt{c^2 - V^2}\right) \tag{5.4a}$$

β_o is thus uniquely determined by the initial conditions v_1, p_1, ρ_1 and β_1 (cf. 3.4a, b).

The square root in (3.10), divided by V, may now be written

$$\sqrt{\beta^2 - \frac{\beta_o^2}{2\beta_o - 1}(2\beta - 1)} = \sqrt{(\beta - \beta_o)\cdot\left(\beta - \frac{\beta_o}{2\beta_o - 1}\right)} \tag{5.5}$$

Neglecting all higher terms in $\beta - \beta_o$, this gives

$$\sqrt{\beta - \beta_o}\cdot\sqrt{\frac{\beta_o(\beta_o - 1)}{\beta_o - \frac{1}{2}}} \tag{5.5a}$$

Inserting this into (3.10) and neglecting again all higher powers of $\;-\;_o$ than the square root (for more accurate formula, see (6.9a)), we get

$$\frac{v}{V} = \frac{1}{2\beta_o - 1}\left[\beta_o \pm \sqrt{\beta - \beta_o}\sqrt{\frac{\beta_o(\beta_o - 1)}{\beta_o - \frac{1}{2}}}\right] \tag{5.6}$$

Denoting the velocity for $\beta = \beta_o$ by v_o, this gives

$$\frac{v}{v_o} = 1 \pm \sqrt{\frac{\beta_o - 1}{\beta_o(\beta_o - \frac{1}{2}}}\cdot\sqrt{\beta - \beta_o} \tag{5.6a}$$

Similarly, we get from (3.11) for the temperature (assuming no dissociation):

$$\frac{T}{T_o} = 1 \mp \sqrt{\frac{\beta - \beta_o}{\beta_o(\beta_o - \frac{1}{2})(\beta_o - 1)}} \tag{5.7}$$

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* The negative sign before $\sqrt{c^2 - v^2}$ would lead to a value of β_o smaller than unity which cannot be attained by the physical quantity β ($\beta = 5/2$, cf. par. 1).

where T_o is the temperature corresponding to β_o, which is given by (cf. 3.9, 5.6)

$$RT_o = \frac{\beta_o - 1}{\beta_o} v_o^2 \tag{5.7a}$$

Introducing the abbreviation

$$y = \frac{T}{T_o} - 1 \tag{5.7b}$$

we have from (5.7)

$$\beta - \beta_o = \beta_o(\beta_o - \tfrac{1}{2})(\beta_o - 1) y^2 \tag{5.8}$$

and from (5.6a)

$$\frac{v}{v_o} - 1 = -(\beta_o - 1) y \tag{5.8a}$$

We consider three velocities of sound, viz.

(1) the velocity of sound with the active degrees of freedom alone.

$$a_a = \sqrt{\gamma_a RT} = \sqrt{\frac{\beta_a}{\beta_a - 1} RT} \tag{5.9}$$

(2) the true velocity of sound

$$a = \sqrt{\gamma RT} \tag{5.9a}$$

where (cf. 1.19)

$$\gamma = \frac{\beta + d\beta/d \log T}{\beta - 1 + d\beta/d \log T} \tag{5.10}$$

If β changes not too rapidly with T, this may be written:

$$\gamma = \frac{\beta}{\beta - 1} - \frac{d\beta/d \log T}{(\beta - 1)^2} \tag{5.10a}$$

(3) the expression

$$a' = \sqrt{\frac{\beta}{\beta - 1} RT} \tag{5.11}$$

which would result if $d\beta/d \log T$ were neglected in (5.10a). Ordinarily, the three velocities of sound are quite close to each other so that we may write, neglecting higher powers of $d\beta/d \log T$ and of $\beta - \beta_a$:

$$\frac{a_a}{a'} = 1 + \frac{\beta - \beta_a}{2\beta(\beta - 1)} \tag{5.12a}$$

$$\frac{a}{a'} = 1 - \frac{d\beta/d \log T}{2\beta(\beta - 1)} \tag{5.12b}$$

From (5.7a) and (5.11) we see that

$$v_o = a_o' \tag{5.13}$$

Since a' varies as $\sqrt{T}$, we have therefore from (5.8a)

$$\frac{v}{a'} - 1 = - (\beta_o - \frac{1}{2} y) \tag{5.14}$$

Therefore the value of y at which v is equal to the actual velocity of sound, is (cf. 5.12b)

$$y_m = \frac{d\beta/d \log T}{2\beta_o(\beta_o - \frac{1}{2})(\beta_o - 1)} \equiv B \tag{5.15}$$

The value of y at which v is equal to a_a, is (cf. 5.12a)

$$y_a = - \frac{\beta_o - \beta_a}{2\beta_o(\beta_o - \frac{1}{2})(\beta_o - 1)} \equiv -A \tag{5.16}$$

For $y_1 < y_a$, there will be an ordinary shock wave with wave front. Only for $y_a < y_1 < y_m$ there will be a diffuse shock wave (y_1 = initial value of y on low pressure side). From (5.14) and (5.15), we have *

$$\frac{v}{a} - 1 = (\beta_o - \frac{1}{2})\ (B - y) \tag{5.16a}$$

It is convenient to introduce the abbreviation

$$z = \frac{v_1 - a_1}{a_{a1} - a_1} = \frac{B - y_1}{B + A} \tag{5.17}$$

Diffuse shock waves will be obtained for z between 0 and 1.

Since the <u>local</u> value of β is given by (5.8) for all y, we may write

$$\beta - \beta_1 = \beta_o(\beta_o - \frac{1}{2})\ (\beta_o - 1)\ (y^2 - y_1{}^2) \tag{5.18}$$

On the other hand, the <u>equilibrium</u> value of β which we denote by β', as in (4.7), may be regarded as a linear function of y in the small temperature interval considered, and since $\beta_1' = \beta_1$, we have:

$$\beta' - \beta_1 = d\beta/d \log T \cdot (y - y_1) \tag{5.19}$$

Asymptotically on the high pressure side we must have equilibrium again so that $\beta_3' = \beta_3$. Comparing (5.18) and (5.19), we find

$$\beta_o(\beta_o - \frac{1}{2})\ (\beta_o - 1)\ (y_3{}^2 - y_1{}^2) = (d\beta/d \log T)\ (y_3 - y_1) \tag{5.19a}$$

Therefore (cf. 5.15)

$$y_3 = 2B - y_1 \tag{5.20}$$

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* Eq.(5.16a) contains the solution of the problem discussed after Eq (3.13). The vanishing of the square root (β_o, T_o, v_o) actually does not represent the point where v = a, but this point lies at slightly higher temperature and lower velocity (i.e. in the region described by the lower sign of the square root in (3.10)).

This means that the temperature at which v is equal to the velocity of sound (cf. 5.15) is the average of the initial and final temperature. For the final temperature, we have always $v < a$ as we might expect.

We can now discuss the actual equation (4.7) describing the change of the physical quantities in the shock wave. Eq (4.7) may be re-written

$$\frac{d}{dx}\left[T(\beta - \beta_a)\right] = \frac{1}{\lambda}(\beta' - \beta)T \tag{5.21}$$

Using (5.8), (5.18), (5.19) and neglecting higher powers of $\beta - \beta_o$, this gives

$$(\beta_o - \beta_a)\frac{dy}{dx} + \beta_o(\beta_o - \tfrac{1}{2})(\beta_o - 1)\,2y\,\frac{dy}{dx}$$

$$= \frac{1}{\lambda}\,\frac{d\beta}{d\log T}(y - y_1) - \beta_o(\beta_o - \tfrac{1}{2})(\beta_o - 1)(y^2 - y_1^2) \tag{5.21a}$$

With (5.15, 16, 20) this becomes

$$\frac{(A + y)\,dy}{(y - y_1)(y_3 - y)} = \frac{dx}{2\lambda} \tag{5.22}$$

Elementary integration gives

$$\frac{A + y_1}{y_3 - y_1}\log(y - y_1) - \frac{A + y_3}{y_3 - y_1}\log(y_3 - y) = \frac{x}{2\lambda} \tag{5.22a}$$

Using again (5.20) and (5.17), this may be written

$$(1 - z)\log(y - y_1) - (1 + z)\log(y_3 - y) = \frac{xz}{\lambda} \tag{5.23}$$

The temperature approaches T_1 asymptotically for large negative x, T_3 for large positive x. The approach in each case is exponential, viz.

$$T - T_1 \quad \exp\left(\frac{xz}{(1 - z)}\right) \text{ for } x \to -\infty \tag{5.24a}$$

$$T_3 - T \exp\left(-\frac{xz}{(1 + z)}\right) \quad \text{for } x \to +\infty \tag{5.24b}$$

Thus, for $z \neq 0$, the approach of the asymptotic value is more rapid on the low temperature side (T_1) than on the high temperature one (T_3). In the limit $z \rightarrow 1$, i.e. when v approaches the "active" velocity of sound, a_{a1}, the diffuse shock wave automatically goes over into a wave with a discontinuous front as we might expect.

In the other limiting case $z \rightarrow 0$, i.e., $v_1 \rightarrow a_1$, the shock wave becomes symmetrical and more extended; (5.23) is then equivalent to

$$T = \frac{1}{2}(T_1 + T_3) + \frac{1}{2}(T_3 - T_1)\frac{e^{xz/\lambda} - 1}{e^{xz/\lambda} + 1} \tag{5.25}$$

i.e., the extension of the shock wave is of the order λ/z.

The formulae of this section can also be applied to the approach of rotational equilibrium if v_1 is smaller than the velocity of sound, a_{t1}, which would be obtained if the translation alone is considered in the specific heat. In this case, (5.23) gives the distribution of temperature (defined by the translational energy) where λ is the mean free path for rotation which, of course, is very small (par. 2A).

Aside from giving the solution for shock wave velocities between a_1, and a_{a1}, this section completes two proofs which were left incomplete in par. 3:

1. <u>On the high pressure side of a shock wave, the gas velocity v_3 is always smaller than the velocity of sound a_3.</u> To show this, we calculate, instead of (3.12), the value of a^2/v with the correct value (3.13) of γ. If we use (5.10a) (in which higher powers of $d\beta/d \log T$ have been neglected), we obtain for the lower sign

$$\frac{a^2}{v} = \frac{1}{2\beta - 1}\left[\beta v - \frac{d\beta/d\log T}{\beta - 1} v + \frac{\beta}{\beta - 1}\sqrt{\beta^2 v^2 - (2\beta - 1)c^2}\right] \tag{5.26}$$

Subtracting this from (3.10) (again with the lower sign), we find

$$v - \frac{a^2}{v} = \frac{v}{\beta - 1}\left[\frac{d\beta/d\log T}{2\beta - 1} - \sqrt{\beta^2 - (2\beta - 1)\frac{c^2}{v^2}}\right] \tag{5.27}$$

In order that this be negative (i.e. $v_3 < a_3$), we must have (cf. 5.5a, 5.4)

$$\beta - \beta_o > \frac{(d\beta/d \log T)^2}{4\beta_o(\beta_o - \frac{1}{2})\ (\beta_o - 1)} \qquad (5.28)$$

The value of $\beta - \beta_o$ on the right hand side is sufficiently small so that (5.6a), (5.7) and all subsequent formulae are valid (cf. 6.18). If $\beta - \beta_o$ is equal to the right hand side of (5.28), it follows from (5.7), (5.15) that y is just equal to B.

This result coincides with (5.15) where we have shown that v is just equal to the velocity of sound <u>a</u> for $y = B$. Thus, as we have already pointed out, there is a certain interval, viz. $0 < y < B$, in which the lower sign in (3.10), etc., corresponds to $v > a$. In this interval, the lower sign solution corresponds to the <u>low</u> pressure side rather than the high pressure side of the shock wave, the velocity v_1 being between a_1 and a_1' (cf. 5.11). For any v_1, y_1 in this interval, the high pressure solution v_3, y_3 can be found immediately from (5.20), and for this high pressure solution we have (cf. 5.20, $y_1 < B$!) $y_3 > B$ and therefore $v_3 < a_3$. This proves the underscored statement above.

2. In par. 3 we have shown that there is, for any initial conditions, <u>one and only one solution of the shock wave equations</u> (3.10), (3.11) provided

$$\frac{dT_e}{d\beta} > \frac{dT_s}{d\beta} \qquad (5.29)$$

on the high pressure side. Here T_s is the temperature which belongs to a certain β according to the shock wave theory, T_e that which corresponds to the same β in thermal equilibrium. In the notation of the present section, (5.29) is equivalent to

$$\frac{d\beta'}{dT} < \frac{d\beta}{dT} \qquad (5.30)$$

Comparing (5.18) with (5.19), it can easily be seen that (5.30) is fulfilled when $y > B$, i.e. always on the high pressure side of a shock wave, q.e.d.

Par. 6. The Temperature on the High Pressure Side.

In par. 5 we have found that the temperature increases continuously from the low pressure to the high pressure side if v_1 is only slightly greater than a_1, and this remains true if v_1 becomes equal to a_{a1} so that sharp shock wave front is formed. In the case $v_1 = a_{a1}$, we have $T_2 = T_1$, and a gradual increase from T_2 to T_3 on the high pressure side of the wave front. On the other hand, for violent shock waves ($v_1 >> a_1$), we have proved in (3.16c) that the temperature decreases from the wave front into the high pressure region as the inert degrees of freedom become excited. In this section we want to investigate where the limit between these two types of behavior is to be expected.

For this purpose we have to examine the dependence of T on β on the high pressure side. We know that β increases from the wave front into the high pressure region; therefore $dT/d\beta$ will be the quantity determining whether T increases or decreases. This derivative must, of course, be taken with the initial conditions (i.e. V and c) kept fixed. The value of β at which $dT/d\beta$ is to be calculated, must be chosen in the range of values occurring on the high pressure side. The lowest value of β in that region, β_2, can be calculated from (4.2) and is given by

$$\beta_2 - \beta_a = \frac{T_1}{T_2}(\beta_1 - \beta_a) \qquad (6.1)$$

The highest value, β_3, is in sufficient approximation

$$\beta_3 = \beta_1 + \frac{d\beta}{d \log T} \frac{T_3 - T_1}{T_1} \qquad (6.2)$$

(6.2) is justified because, in the whole region in which $dT/d\beta > 0$, the temperature change $T_3 - T_1$ is small compared with T_1 itself. (cf. 6.11a, b). Therefore we can also rewrite (6.1):

$$\beta_2 = \beta_1 - (\beta_1 - \beta_a)\ \frac{T_2 - T_1}{T_1} \qquad (6.1a)$$

Both (6.2) and (6.1a) are rather close to β_1 because $\beta_1 - \beta_a$ and $d\beta/d \log T$ are small in practical cases; therefore it will be sufficient to calculate $dT/d\beta$ for $\beta = \beta_1$ on the high pressure side.

More convenient that the explicit calculation of the derivative $dT/d\beta$ will be an investigation of the behavior of T itself as a function of for given initial conditions V, c. It will turn out that for given V and c, the temperature T_h increases with β for values of β close to β_o as defined in (5.4), reaches a maximum for $\beta_m \approx \beta_o + \frac{1}{4(\beta_o - \frac{1}{2})}$ (cf. 6.8) and then decreases for larger β. If, then, β_1 lies between β_o and β_m, the temperature will increase from T_2 to T_3; if β_1 is greater than β_m, the temperature will decrease on the high pressure side. β_m is uniquely determined by V and c, therefore the condition $\beta_1 < \beta_m$ is equivalent to a condition for v_1/a_1 which will be given in (6.14c).

For the calculation, we insert v from (3.10) into (3.11) and obtain

$$\frac{p}{\rho} = \frac{1}{(2\beta - 1)^2}\left[(2\beta - 1)c^2 - \beta V^2 \mp V\sqrt{\beta^2 V^2 - (2\beta - 1)c^2}\right] \qquad (6.3)$$

Here we express c^2 in terms of β_o by (5.4), and introduce instead of β and β_o

$$b = \beta - \tfrac{1}{2} \qquad b_o = \beta_o - \tfrac{1}{2} \qquad (6.4)$$

Then we obtain

$$\frac{4p}{\rho V^2} = \frac{1}{b}\left[b_o + \frac{1}{4b_o} - \frac{1}{2b} \mp \frac{1}{b}\sqrt{(b - b_o)\left(b - \frac{1}{4b_o}\right)}\right] \qquad (6.5)$$

As usual, the lower sign is for the high pressure side of the shock wave. Putting $p/\rho = RT$, and neglecting all powers of $b - b_o$ higher than the square root, we obtain (5.7).

For our present purpose, we whall carry powers of $b - b_o$ up to the 3/2th, but we shall simplify the calculation by neglecting $1/4b_o$ compared with b_o. Since the interesting values of b_o are at least 3, we have $1/4b^2 \leq 1/36$.

Then (6.5) simplifies for the high pressure side to

$$\frac{4p}{\rho V^2} = \frac{b_o}{b} + \frac{\sqrt{b - b_o}}{b^{3/2}} \tag{6.6}$$

(high pressure side). The maximum of the right hand side is obtained for

$$\frac{1}{\sqrt{b - b_o}} \left(1 - \frac{3(b - b_o)}{b}\right) = 2 \frac{b_o}{b} \tag{6.6a}$$

In sufficient approximation, this equation is solved by

$$b - b_o = \frac{1}{4b_o + \frac{2}{b_o}} \tag{6.6b}$$

If the small terms of order $1/b_o^2$ in (6.5) are taken into account, (6.6b) is replaced by

$$b - b_o = \beta - \beta_o = \frac{1}{4b_o - \frac{1}{b_o}} = \frac{\beta_o - \frac{1}{2}}{4\beta_o(\beta_o - 1)} \tag{6.7}$$

For $b_o = 3$, this gives $b - b_o = \frac{3}{35} = 0.086$. <u>The maximum temperature is thus obtained at a value of β which is only slightly greater than β_o</u>. For larger β, the factor $1/b$ in (6.5) has a stronger influence than the increase of the square root, so the temperature (6.5) decreases again.

Thus we find that the temperature can <u>increase</u> on the high pressure side only if

$$\beta_1 < \beta_m = \beta_o + \frac{\beta_o - \frac{1}{2}}{\beta_o(\beta_o - 1)} \tag{6.8}$$

Since β_o is determined by V and c (cf. 5.4), (6.8) is equivalent to a condition for v_1/a_1. To derive this condition, we determine the dependence of v on β for fixed V and c. We have (cf. 3.10)

$$\frac{v}{V} = \frac{1}{2\beta - 1} \left[\beta \pm \sqrt{\beta^2 - \frac{2\beta - 1}{2\beta_o - 1} \beta_o^2} \right] \quad (6.9)$$

Introducing b, this gives

$$\frac{2v}{V} = 1 + \frac{1}{2b} \pm \frac{1}{b} \sqrt{(b - \frac{1}{4b_o})(b - b_o)} \quad (6.9a)$$

For the negative sign (high pressure side), (6.9a) gives a monotonic decrease of v with increasing b. Inserting in (6.9a) the value β_m (cf. 6.8) for $\beta = b + \frac{1}{2}$, we find on the high pressure side

$$v_{mh} = \frac{1}{2} V \quad (6.10a)$$

on the low pressure side

$$v_{m_1} = \frac{1}{2} V \left(1 + \frac{1}{\beta - \frac{1}{2}}\right) \quad (6.10b)$$

Similarly, inserting β_m into the expression (6.5) for the temperature, we obtain on the high pressure side

$$RT_{mh} = \left[\frac{p}{\rho}\right]_{mh} = \frac{1}{4} V^2 \quad (6.11a)$$

on the low pressure side

$$RT_{m_1} = \left[\frac{p}{\rho}\right]_{m_1} = \frac{1}{4} V^2 \left(1 - \frac{1}{b^2}\right) \approx \frac{1}{4} V^2 \left(1 - \frac{1}{\beta^2}\right) \quad (6.11b$$

Thus, at the value $\beta = \beta_m$ at which T_h reaches its maximum for given V and c, we have the simple relation (cf. 6.10a, 11a)

$$v_{mh} = \sqrt{RT_{mh}} = \frac{1}{2} V \qquad (6.12)$$

and from (3.8b)

$$p_{mh} = \frac{1}{2} mV = \frac{1}{2} p_{max} \qquad (6.12a)$$

where p_{max} is the pressure corresponding to v = 0.

The velocity of sound a' as defined in (5.11) is then for $\beta = \beta_m$ (cf. 6.11a, b)

$$a'_{mh} = \frac{1}{2} V \sqrt{\frac{\beta}{\beta - 1}} \qquad (6.13a)$$

$$a'_{m_1} = \frac{1}{2} V \sqrt{\frac{\beta + 1}{\beta}} \qquad (6.13b)$$

It can easily be seen (cf. 5.12b) that in all practical cases $a'_m - a_m$ is small compared with $v_m - a'_m$ on both sides of the shock wave. Therefore we can identify (6.13a , b) with the actual velocity of sound a and obtain:

$$\frac{v_{mh}}{a_{mh}} = \sqrt{\frac{\beta - 1}{\beta}} \approx 1 - \frac{1}{2\beta} - \frac{1}{8\beta^2} + \dots \qquad (6.14a)$$

$$\frac{v_{m_1}}{a_{m_1}} = 1 + \frac{1}{2\beta} + \frac{3}{8\beta^2} + \dots \qquad (6.14b)$$

Therefore we find that the temperature will increase on the high pressure side if

$$\frac{v_1}{a_1} < \frac{v_{m_1}}{a_{m_1}} = 1 + \frac{1}{2\beta} + \frac{3}{8\beta^2} + \dots \qquad (6.14c)$$

For $\beta = 7/2$, the right hand side is 1.173. This shows that a temperature increase from T_2 to T_3 is restricted to very soft shock waves.

The temperature change $T_3 - T_2$ itself can be calculated from (6.2), (6.1a):

$$T_3 - T_2 = \frac{dT_s}{d\beta} \cdot (\beta_3 - \beta_2) = \frac{dT_s}{d\beta} \cdot \frac{T_3 - T_1}{T_1} \cdot \left[\frac{d\beta}{d \log T_e} + \beta_1 - \beta_a\right] \tag{6.15}$$

Here we have denoted, as in par. 3, by T_s the temperature corresponding to a given β according to the shock wave theory, and by T_e that corresponding to the same β in thermal equilibrium. $T_2 - T_1$ in (6.1a) has been replaced by $T_3 - T_1$ because it will be shown (cf. 6.17) that $T_3 - T_2$ is small of a higher order. From (6.6) we have in sufficient approximation

$$\frac{d \log T_s}{d\beta} = \frac{1}{b_o^{\frac{3}{2}}} \left[\frac{1}{2\sqrt{b_1 - b_o}} - \sqrt{b_o}\right] \tag{6.16}$$

Likewise from (6.6), we can calculate the difference between the high pressure and the low pressure value of T for the same value of β, viz. β_1; this is

$$\frac{T_3 - T_1}{T_1} = 2\,\frac{b_1 - b_o}{b_o^{\frac{3}{2}}} \tag{6.16a}$$

Inserting in (6.16), (6.16a) into (6.15) and using the abbreviations A and B (cf. 5.15, 16) we obtain

$$\frac{T_3 - T_2}{T_3} = 2(A + B) \left[1 - \sqrt{4b_o(b_1 - b_o)}\right] \tag{6.17}$$

which may also be written (cf. 1.19)

$$\frac{T_3 - T_2}{T_3} = \frac{c_{i1}}{R(\beta_1 - \frac{1}{2})^3} \left[1 - \sqrt{4(\beta_1 - \tfrac{1}{2})\,(\beta_1 - \beta_o)}\right] \qquad (6.17a)$$

where c_i is the specific heat of the inert degrees of freedom. From (6.17) it follows that the temperature change $T_3 - T_2$ is greatest when $\beta_1 = \beta_o$, i.e., for the softest shock waves; of course, this holds only when an actual wave front exists (i.e., for $v_1 > a_{a1}$) because otherwise T_2 cannot be defined. For "harder" shock waves, i.e., greater v_1/a_1 and $\beta_1 - \beta_o$, the square bracket decreases and reaches zero for $\beta_1 = \beta_m$ (cf. 6.8) as must be expected. For air of initial temperature $T_1 = 300°$, we have $c_{i1} = 0.007R$; then from (6.17a) the maximum possible value of $T_3 - T_2$ is $0.00025\ T_3 = 0.08°$. The temperature increase $T_3 - T_2$, if it occurs at all, is therefore extremely small in air at normal temperature. The temperature difference $T_{mh} - T_m$, on the other hand, is appreciable, viz. (cf. 6.11) $1/9\ T_1 = 33°$).

Finally, the developments of this section can be used to justify those of par. 5. In that section, we have neglected in (6.5) and similar equations all powers of $b - b_o$ higher than the square root. This is justified as long as $\beta - \beta_o$ is small compared with $\beta_m - \beta_o$ as given by (6.8). Now the largest value of $\beta - \beta_o$ which we have used in par. 5 is obtained for $y = 2B + A$ (cf. 5.15, 16). Using (5.8), (6.8) and neglecting quantities of relative order $1/\beta^2$ we have.

$$\sqrt{\frac{(\beta - \beta_o)_{max}}{\beta_m - \beta_o}} = 2b_o^2(2B + A) = \frac{2d\beta/d\log T + \beta - \beta_a}{\beta_o - \frac{1}{2}} \qquad (6.18)$$

For air at 300°, this is about 0.005.