The energy exchanges between molecules. By P. S. H. HENRY, Ph.D., Trinity College, 1851 Senior Student. (The Colloid Science Laboratory, Cambridge.)

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The marked disagreement between the specific heats at high temperatures of the diatomic gases as found by sound velocity measurements, and those calculated from theoretical considerations, has for long been a source of perplexity to statistical mechanists; a perplexity all the greater in view of the simple nature of the theoretical calculations which appeared to form as direct a test of Boltzmann's hypothesis and the theory of band spectra as was possible to large scale measurements. One way out of the difficulty is to attribute the differences to the experimental difficulties inherent in the sound velocity method of measurement at high temperatures(1), but it cannot be denied that there is a certain measure of agreement between the separate velocity determinations. It consequently becomes necessary to examine the theory.

The only apparent assumptions made in the derivation of the Planck formula for the vibrational specific heat are:

(1) that we are dealing with a state of equilibrium;

(2) that the distribution of energy in this state is that given by Boltzmann's hypothesis;

(3) that the vibrational energy levels and statistical weights have been correctly determined by the spectroscopists.

The spectra of the simple diatomic gases are now so well known that there is little possibility of error in the third assumption. Boltzmann's hypothesis, too, while not yet proved with complete logic from first principles, agrees so well with experiment in other branches of science that it can almost be regarded as an experimental fact. There remains, then, the assumption that the gas is always in a steady state when the sound is passing through it, and this would seem to be easiest of the three to attack.

In two recent papers(2) Kneser has shown, by means of sound velocity experiments over a wide range of frequencies in carbon dioxide, that there is a lag in the transfer of energy between the transverse vibrations of the CO_2 molecule and the other degrees of freedom much greater than that which would be expected from classical mechanics. In fact he found that the "mean life of a quantum" of the vibration concerned, which can also be regarded as the period of relaxation for the vibrational energy, was of the order

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of 10^{-5} of a second at room temperature in place of the usually assumed period of the order of 10^{-10} of a second. He obtained an expression for the sound velocity which, when expressed in terms of the specific heat, becomes

$$C_{\text{app}} = \frac{C_v^2 + 4\pi^2 n^2 \beta^2 C_a^2}{C_v + 4\pi^2 n^2 \beta^2 C_a} = \frac{C_v^2 + \alpha^2 C_a^2}{C_v + \alpha^2 C_a},$$

where C_v is the true specific heat at constant volume, C_a is that part of the specific heat which is contributed by the translations and rotations (i.e. $\frac{5}{2}R$ for a diatomic gas), n is the frequency of the sound, β is the period of relaxation of the vibrational energy, and $\alpha = 2\pi n\beta$.

Now if one admits a period of relaxation of the order of 10^{-5} seconds for CO_2, why should one not suppose that the vibrations of oxygen and nitrogen might have a relaxation period of the order of 10^{-4} of a second? Unless we are to disregard the sound velocity results in toto, we must make some fundamental alteration to the theory, and this seems to be the easiest to make. The results of Shilling and Partington can be accounted for if we assume the following periods of relaxation:

Temperature	Relaxation Period in Secs.		Transparency Coefficient	
	Oxygen	Nitrogen	Oxygen	Nitrogen
0° C.	—	—	370	8600
300° C.	$1{\cdot}0\times10^{-4}$	—	19·5	58
600° C.	1·2	$0{\cdot}88\times10^{-4}$	11·1	20
900° C.	1·1	0·92	9·4	12·5
1200° C.	1·0	—	7·9	10·3

At room temperatures the vibration comes in so little that the expected effect is smaller than the probable errors of the sound velocity determinations, and I have not included values for the relaxation period for these temperatures. The figures in the last two columns are explained below.

In confirmation of this theory it may be noted here that the experimental results available for oxygen above room temperatures lie in the order of the quickness with which the gas was heated. Thus the sound velocity determinations(3), using a frequency of about 3000 vibrations per second, gave the lowest results, the adiabatic expansion experiments of Eucken and Lüde(4) gave somewhat higher results, while the author's experiments(5), in which the heating took place in about a quarter of a second, gave much higher results, which were, in fact, a little higher than the theoretical.

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It may be pointed out that similar theories have been propounded before, by O. K. Rice(6) in connection with unimolecular reactions, and by N. Semenoff and A. Schechter(7) in connection with the dissociation of hydrogen molecules by ions.

There are various ways in which the problem might be attacked experimentally. The most obvious is the determination of the sound velocity over a wide range of frequencies in oxygen and nitrogen at temperatures considerably above that of the atmosphere. The various experiments which have been carried out at room temperatures in air are of little use for this purpose, since the predicted effect is too small at these temperatures to be verified or disproved with certainty and those experiments which have been done at higher temperatures used only one frequency.

Another method would be to investigate the absorption of the sound energy by the gases at elevated temperatures. At those frequencies at which the velocity changes, there should be considerable absorption owing to the irreversible heat transfer. The gas should, in fact, show a diffuse absorption band for each mode of vibration of the molecule, the frequencies of the maxima depending upon the relaxation period for the vibration in question. Thus, as Kneser remarks, Pierce(8) found that CO_2 was nearly opaque to sound at just that frequency where Kneser found that the velocity changed most rapidly.

Calculations of the effect of such a lag in the energy transfer have been made by K. F. Herzfeld and F. O. Rice(9), and more elaborate ones by D. G. Bourgin(10). The case which we are considering, however, is not so complicated as theirs, and it may be worth while to give a simpler derivation of the effect, especially as the former authors assumed that the relaxation period was small compared with the period of a sound vibration.

Let C_v, C_a and C_x be the total specific heat per gm. mol., the specific heat of the translation and rotations, and that of the vibrations respectively, so that

$$C_v = C_a + C_x. \tag{1}$$

Let E_x be the actual energy per gm. mol. of the vibrations at any instant, and E_T the energy which the vibrations would have at equilibrium at the temperature T.

We shall suppose that

$$\frac{dE_x}{dt} = \frac{1}{\beta}(E_T - E_x), \tag{2}$$

so that we may call β the period of relaxation of the vibrational energy. This equation will be obeyed with sufficient exactness where there is only one vibrational level above the ground level appreciably in evidence; for small deviations from the equilibrium

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state such as occur in sound waves of average intensity it is likely enough to hold in any case. Where there is only one excited state concerned, β is equal to the "mean life of a quantum" of Kneser.

Now suppose that the gas is subject to small sinusoidal adiabatic variations of temperature of frequency $\frac{\omega}{2\pi}$. We can write

$$T = T_0 + T_1 e^{i\omega t},$$
$$E_T = E_0 + C_x T_1 e^{i\omega t}.$$

Substituting this in (2) and solving, we get

$$E_x = E_0 + \frac{C_x T_1}{1 + i\omega\beta} e^{i\omega t}. \tag{3}$$

We can thus regard the gas as having a complex specific heat given by

$$C_v' = C_a + \frac{C_x}{1 + i\omega\beta}. \tag{4}$$

In the usual way it can now be shown that the adiabatic elasticity of the gas is given by $H = p\gamma'$, where $\gamma' = 1 + R/C_v'$.

Substituting this in the equation of motion for plane waves,

$$\rho \frac{\partial^2 \xi}{\partial t^2} = H \frac{\partial^2 \xi}{\partial x^2},$$

and trying the solution $\xi = \Xi e^{i\omega t + (l+im)x}$, we get

$$-\rho\omega^2 = \gamma' p (l + im)^2.$$

If in this we write $\gamma' = \gamma_1 + i\gamma_2$, equate real and imaginary parts, and put $\mu = l/m$, we get

$$\left.\begin{aligned} \mu^2 + \frac{2\gamma_1}{\gamma_2}\mu - 1 &= 0, \\ \mu^2 - \frac{2\gamma_2}{\gamma_1}\mu - 1 &= -\frac{\rho}{p}\frac{\omega^2}{\gamma_1 m^2} = -\frac{\gamma_{\text{app}}}{\gamma}, \end{aligned}\right\} \tag{5}$$

where γ_{app} is the value for γ which would be deduced from the velocity measurements if the lag effect was ignored.

From these we get

$$\left.\begin{aligned} \mu &= -\frac{\gamma_1}{\gamma_2} + \sqrt{\frac{\gamma_1^2}{\gamma_2^2} + 1}, \\ \gamma_{\text{app}} &= 2\gamma_1 \left(\frac{\gamma_1}{\gamma_2} + \frac{\gamma_2}{\gamma_1}\right)\mu. \end{aligned}\right\} \tag{6}$$

If μ is small, as it must be if the velocity can be measured with any accuracy, these become

$$\left.\begin{aligned} \mu &= \gamma_2/2\gamma_1, \\ \gamma_{\text{app}} &= \gamma_1, \end{aligned}\right\} \tag{7}$$

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and from these we get, using equation (4) and the relation

$$\gamma' = 1 + R/C_v',$$

$$\text{apparent specific heat} = \frac{C_v^2 + \omega^2\beta^2 C_a^2}{C_v + \omega^2\beta^2 C_a}, \tag{8}$$

this expression being identical with that given on page 250, since $\omega = 2\pi n$, and equivalent to that given for the sound velocity by Kneser.

The absorption of the sound is most simply expressed in terms of the number of wave-lengths which the sound travels before its amplitude is diminished to $1/e$ times its initial value. It will be seen that this number is

$$N = \frac{1}{2\pi\mu} = \frac{C_v(C_v + R) + \alpha^2 C_a(C_a + R)}{\alpha\pi R(C_v - C_a)}, \tag{9}$$

where α, as before, is equal to $\omega\beta$ or $2\pi n\beta$.

The frequency at which the absorption, reckoned in this way, is a maximum is given by

$$n = \frac{1}{2\pi\beta}\sqrt{\frac{C_a(C_a + R)}{C_v(C_v + R)}}; \tag{10}$$

and the value of N at this frequency is

$$N_m = \frac{2\sqrt{C_v C_a(C_v + R)(C_a + R)}}{\pi R(C_v - C_a)}. \tag{11}$$

It will be seen that this latter is independent of the relaxation period, depending only on the relative values of the vibrational and other specific heats. This is only true for the transparency as defined above, for the ordinary absorption coefficient ($-2l$) has no maximum at a finite frequency, but tends to an upper limit as the frequency tends towards infinity. Values of N_m calculated for oxygen and nitrogen are given in the table on page 250. The frequency at which the gases should show the maximum absorption is about 1400 vibrations per second in each case. It will be seen that the absorption is negligible at room temperatures, but should become easily measurable at somewhat higher temperatures. The only absorption experiments which have been done, so far as the author is aware, are those at room temperatures(11). The calculated energy absorption coefficient for air arising from the effect under discussion is of the order of 2×10^{-4} per cm., while that arising from viscosity and heat conduction at the high frequencies used in the experiments is of the order of 10^{-1} or 10^{-2}, so that these experiments do not help us. It may be noted here that when Herzfeld and Rice deduced from these experiments a relaxation

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period of about 10^{-8} seconds, they were referring mainly to the rotational energy.

A more direct method of investigating the matter would be to photograph the ultra-violet absorption spectrum of oxygen as it is escaping from a cylinder at a high pressure (and possibly also high temperature). The gas would be subject to a sudden cooling on account of the expansion, and it might be possible to observe bands corresponding to transitions from the first excited vibrational state when the distribution of intensity in a given band shows that the rotations correspond to a temperature so low that there would normally be hardly any of the molecules in the excited vibrational state. The molecules would, in fact, have two temperatures, the rotational and the vibrational. An attempt to carry out this experiment will shortly be made in this laboratory, and more will be said about it later.

It is interesting to speculate about the manner of the energy exchanges if this theory be true. The slight decrease of the relaxation period of oxygen as the temperature rises would seem to indicate that vibrational energy can only be turned into translational energy in a collision of considerable relative kinetic energy, for the total number of collisions per molecule in a gas at constant pressure varies inversely as the square root of the temperature, and only the high-energy collisions increase in number as the temperature rises. This would mean, according to the principle of detailed balancing, that a vibration can only be started in a collision where the relative kinetic energy is considerably in excess of that required. The data are not sufficiently certain yet, however, for such considerations to have much weight.

In a recent paper Zener(12) has made tentative calculations of the probability that energy of vibration will be transferred from one molecule to another during a collision, using partly wave-mechanical principles and partly classical conceptions. Such a transfer would not, of course, affect the total vibrational energy of the gas, and what we are concerned with is transformation of vibrational energy into other forms. Such a transformation would have a smaller probability than the transfer which Zener considered; and it is interesting to note that he gave for the probability of transfer during a head-on collision between two diatomic molecules at 0° C., where one of them possessed one vibrational quantum, the value of 2×10^{-5}. The probability of transformation of the vibrational energy in a given collision between oxygen molecules at 600° C. calculated from the relaxation period given above is about $0{\cdot}5 \times 10^{-5}$.

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