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A collage featuring a Physics Today journal cover and a comment on an article. The journal cover, dated July 2012, page 10, has the title 'Measured energy in Japan quake' by David von Seggern. A large red arrow points from the journal cover to a comment box. The comment, dated 14 July 2012, discusses the article's claim that the 1964 Chilean earthquake released 50-megaton energy, comparing it to the 100-megaton explosion of Nagasaki and the 15-megaton atomic bomb of Hiroshima. The comment concludes that the article's calculations are flawed and that the energy released was likely much smaller.

## The Thermal Conductivity of Polyatomic Gases

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(Received December 12, 1934)

Reasons are given for supposing that the thermal conductivity of polyatomic gases should not be independent of pressure. A calculation is made for carbon dioxide, and the results suggest that a portion of the specific heat at 0°C has a relaxation constant considerably less than  $10^8$  if the discrepancy between experimental and theoretical values of thermal conductivity is due to restrictions on the energy exchange between molecules. When such effects are present, determinations using parallel plates give a more reliable result than those using a vertical wire.

KNOWLEDGE of the mechanism of heat transport in gases is important both in the kinetic theory, and in many chemical reactions involving activated molecules. The object of the present communication is to discuss the transport of vibrational heat in gases, and to point out that the thermal conductivity of polyatomic gases may vary with pressure. This is because of the fact that at higher pressures any departure from the Maxwell Boltzmann distribution of energies is more rapidly readjusted. A calculation is given for the heat transport between two parallel plates, and when certain simplifying assumptions are made, it is shown that the thermal conductivity  $K$  at any pressure is related to the maximum value  $K_{\max}$  with full participation of the vibrational energy, by an equation of the form  $K(1+F) = K_{\max}$ . The factor  $F$  depends on the pressure and dimensions of the apparatus, and has been evaluated in a typical case for  $\text{CO}_2$ . The bearing of this calculation on previously obtained experimental data for the thermal conductivity of polyatomic gases is discussed, and it is pointed out that empirical pressure corrections may be misleading. A correlation of the relaxation time for redistribution of vibrational energy in  $\text{CO}_2$ , as calculated from the dispersion of sound at high frequencies, with that calculated from thermal conductivity, is shown to be reasonable, though a quantitative check is hampered by lack of suitable experimental data.

Two methods are available for determining how far vibrational energy of the molecules of a gas takes part in heat transport. According to views developed by Eucken<sup>1</sup> if  $K$  is the thermal conductivity of a gas,  $C$  the specific heat at constant volume, and  $\eta$  the viscosity, the factor  $f$

in the equation  $K = f\eta C$  may be calculated. The translational energy is assumed to be transported according to the Chapman-Enskog formula  $K_{\text{trans}} = 2.5\eta C_{\text{trans}}$ , and if both rotational and vibrational transport are independent of translational,

$$K = (K_{\text{trans}} + K_{\text{rot}} + K_{\text{vib}}) \\ = \eta(2.5C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}}).$$

$$\text{If } \gamma = C_p/C, \quad C = R/(\gamma - 1),$$

and

$$f_{\text{(Eucken)}} = (2.5C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}}) / \\ (C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}})$$

$$\text{i.e., } f_{\text{(Eucken)}} = 1 + 1.5C_{\text{trans}}(\gamma - 1)/R = \frac{1}{4}(9\gamma - 5).$$

If vibration takes no part in heat transport but is operative in experiments determining  $C$  and  $\gamma$ ,

$$f_{\text{(no vib)}} = (2.5C_{\text{trans}} + C_{\text{rot}}) / \\ (C_{\text{trans}} + C_{\text{rot}} + C_{\text{vib}}) = (21/4)(\gamma - 1)$$

for polyatomic and  $(19/4)(\gamma - 1)$  for linear molecules.

A test of this calculation requires a precise knowledge of thermal conductivity, viscosity and specific heats, all at the same temperature and pressure. Such a calculation is possible for  $\text{CO}_2$ .<sup>2</sup> For other gases included in Table I less

TABLE I.

Gas	$\text{CO}_2$	$\text{N}_2\text{O}$	$\text{CO}$	$\text{CH}_4$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_2$	$\text{C}_2\text{H}_6$	$\text{H}_2\text{S}$	$\text{NH}_3$
$f_{\text{(Eucken)}}$	1.72	1.73	1.91	1.68	1.57	1.59	1.50	1.72	1.70
$K/\eta C$	1.64	1.71	1.92	1.69	1.43	1.42	1.54	(1.37)	(1.38)
$f_{\text{(no vib)}}$	1.52	1.55	1.92	1.60	1.34	1.37	1.16	1.68	1.63

<sup>1</sup> Eucken, *Physik. Zeits.* **14**, 324 (1913).

<sup>2</sup> Kannuluik and Martin, *Proc. Roy. Soc.* **A142**, 362 (1933).

reliable data are available.<sup>3</sup> Except in the last two cases, where there may be serious error in the data, the value of  $f$  calculated from  $K/\eta C$  lies between the two theoretical limits. For  $(C_2H_6)_2O$  and gases with smaller  $\gamma$  the effect is still more marked but the data less reliable. Eucken has suggested that the value of  $f$  is due to the fact that vibrational and in some cases even rotational energy is not taking full part in heat transport, owing to incomplete temperature equilibrium. A second method is now available to test this, since experiments on the velocity of sound in such gases as  $CO_2$  show that at ordinary temperatures and pressures dispersion sets in in the neighborhood of  $10^8$  cycles/sec. One explanation is that at still higher frequencies the vibrational energies are no longer able to follow the adiabatic temperature changes in a sound wave.

During the interval of  $10^{-8}$  sec., the average distance diffused by a molecule may be calculated from the formula  $\bar{x}^2 = 2Dt$ . For  $CO_2$  at  $0^\circ C$  and 20 cm of mercury,  $D = 0.4$  and  $x = 3 \times 10^{-3}$  cm, i.e., some 100 mean free paths. In such a case it is clear that in the parallel plate method for determining the thermal conductivity of a gas, we cannot assume complete equilibrium for the vibrational energy in various layers. In order to clear up certain difficulties in interpreting experiments on the dispersion of sound<sup>4</sup> and on thermal conductivity<sup>5</sup> it is important to correlate the two phenomena as far as possible.

Consider an experiment where the heat transport in a gas between two parallel plates is measured. If  $Q$  is the heat transport/unit area, and the plates are a distance  $z_0$  apart, and are maintained at temperatures  $T_{P_1}$  and  $T_{P_2}$ , the experimentally determined thermal conductivity is obtained from the equation  $Q = K\Delta T_P/z_0$  where  $\Delta T_P = T_{P_1} - T_{P_2}$ , and  $K$  is the mean value of the thermal conductivity over small ranges of temperature. This value of  $K$  may differ from that calculated from the kinetic theory of gases for one of two reasons:

(1) The average temperature  $T_V$  characterizing the distribution of vibrational energies in any layer will differ from the temperature  $T$

characterizing the distribution of rotational and translational energies by an amount  $L = T - T_V$  (see below).

(2) Because of temperature jumps at the surface, the difference  $\Delta T = T_1 - T_2$  and still more so  $\Delta T_V = T_{V_1} - T_{V_2}$ , may be appreciably less than the measured difference  $\Delta T_P = T_{P_1} - T_{P_2}$ .

At sufficiently high pressures the problem is best considered as a case of diffusion in the steady state. If the molecules are distributed  $N_1, N_0$ /unit volume, in classes characterized by vibrational energies  $E_1, E_0$  (in many cases it is sufficient to consider only two levels), then in the steady state the rate of increase of  $N_1$ /unit volume by diffusion is

$$D(\partial^2 N_1/\partial z^2) = (\partial N_1/\partial t)_{diff} \quad (a)$$

and must be balanced by the net rate of removal within the layer by collisions, i.e.,

$$(\partial N_1/\partial t)_{diff} + (\partial N_1/\partial t)_{coll} = 0,$$

where  $(\partial N_1/\partial t)_{coll}$  is a function of the composition of the layer. For the rotational and translational degrees of freedom,  $(\partial N_r/\partial t)_{coll}$  is usually assumed to be negligible, because of the displacement from a Maxwell Boltzmann distribution being so small, the use of a temperature parameter  $T$  to characterize this distribution is thus allowable. With respect to these degrees of freedom we then have for each class 1, 2, etc.

$$D(d^2 N_r/dz^2) = 0 \text{ and } dN_r/dz = \text{const} = k_{N_r} \quad (a_1)$$

Since the net number of molecules crossing any layer in unit time is  $D(dN_r/dz)$  the heat transfer

$$Q = \Sigma DE_r(dN_r/dz) = D\Sigma E_r(dN_r/dz)$$

if on the average  $D$  is independent of class (i.e., neglecting the Chapman correction). Integrating  $a_1$  over the distance  $z_0$  between the plates,

$$(N_r)_1 - (N_r)_2 = k_{N_r} z_0,$$

so that

$$Q = (D/z_0)\Sigma E_r[(N_r)_1 - (N_r)_2].$$

If equilibrium is fully established at the plates,

$$\Sigma E_r[(N_r)_1 - (N_r)_2] = NC_V(T_1 - T_2)$$

and

$$Q = NDC_V(T_1 - T_2)/z_0.$$

The standard formula is thus obtained.

We are, however, concerned with a degree of

<sup>3</sup> Landolt Bornstein Tabellen 5th ed.

<sup>4</sup> Richardson, Proc. Roy. Soc. A146, 56 (1933); Richards and Reid, J. Chem. Phys. 2, 194 (1934).

<sup>5</sup> M. Trautz, Ann. d. Physik 18, 833 (1933).

freedom for which  $(\partial N_1/\partial t)_{\text{coll}}$  is not negligible, on account of the finite lag  $L$ . The vibrational temperature  $T_V$  will be defined by  $N_1/N_0 = e^{-(E_1-E_0)/kT}$  and the calculation be made for a gas where the rate of relaxation is given by

$$\partial T_V/\partial t = \beta(T - T_V). \quad (b)$$

Furthermore, over the small intervals of temperature which have to be used in thermal conductivity experiments

$$\rho C_{\text{vib}} = (E_1 - E_0)(dN_1/dT_V) \quad (c)$$

will be appreciably constant, where  $C_{\text{vib}}$  is the vibrational specific heat/unit mass, and  $\rho$  is the density.

In the steady state, the heat transport  $Q$  through any layer is constant, i.e.,

$$-Q/NmD = C'(dT/dz) + C_{\text{vib}}(dT_V/dz) = b \quad (d)$$

where  $b$  is independent of  $z$ , so that

$$C'T + C_{\text{vib}}T_V = bz + d \quad (e)$$

where  $d$  is a constant. In (d) and (e), if we use the normal coefficient of diffusion,  $D$ ,  $C' = 2.5C_{\text{trans}} + C_{\text{rot}}$  in view of the Chapman correction. Combining (a) with (c), and using (b),

$$\begin{aligned} D(d^2 N_1/dz^2) &= [\rho C_{\text{vib}}/(E_1 - E_0)](\partial T_V/\partial t)_{\text{diff}} \\ &= [-\rho C_{\text{vib}}/(E_1 - E_0)](\partial T_V/\partial t)_{\text{coll}} \\ &= -[\rho C_{\text{vib}}/(E_1 - E_0)]\beta(T - T_V). \end{aligned} \quad (f)$$

Substituting for  $T$  by means of (e), and noting

$$\begin{aligned} d^2 N_1/dz^2 &= [\rho C_{\text{vib}}/(E_1 - E_0)](d^2 T_V/dz^2), \\ D(d^2 T_V/dz^2) &= -(\beta/C')((bz + d) - (C_{\text{vib}} + C')T_V). \end{aligned}$$

The solution to this equation is

$$T_V = Ae^{\alpha z} + Be^{-\alpha z} + (bz + d)/(C_{\text{vib}} + C'), \quad (g_1)$$

where

$$\alpha^2 = \beta(C_{\text{vib}} + C')/C'D,$$

or since  $L = T - T_V$ , from (e) the solution simplifies to

$$L = Ae^{\alpha z} + Be^{-\alpha z}, \quad (g_2)$$

where the arbitrary constants are different from those in (g<sub>1</sub>). The third term in (g<sub>1</sub>) is equivalent to a linear temperature gradient for  $T_V$ , and the

first two take account of relaxation effects, as measured by the constant  $\beta$  in the equation for  $\alpha^2$ .

In order to apply this solution to a concrete case, we have to evaluate the arbitrary constants by considering the boundary conditions. Since the system is symmetrical, when

$$z = 0, \quad L = L_1 = A + B$$

and when

$$z = z_0, \quad L = -L_1 = Ae^{\alpha z_0} + Be^{-\alpha z_0},$$

whence

$$B = -Ae^{\alpha z_0}, \quad \text{and} \quad L_1 = A(1 - e^{\alpha z_0}). \quad (h)$$

The constant  $A$  can be evaluated by considering the change in energy of the molecules by collision with the plates. If the lag is appreciable, the vibrational temperature of the molecules approaching the plate will be appreciably different from that of the plate itself, even at ordinary pressures. According to the theory of the accommodation coefficient<sup>7</sup> if  $T_V$  be the (vibrational) temperature of the molecules approaching the plate, and  $T_0$  that of the molecules leaving it,

$$T_D - T_V = a_{\text{vib}}(T_P - T_V),$$

where  $a_{\text{vib}}$  is the accommodation coefficient for vibrational energy. Little is known of the values of  $a_{\text{vib}}$ , but unless the material of the plates absorbs the molecules strongly,  $a_{\text{vib}}$  is probably very small because of the small duration of contact with the plate. By neglecting it altogether, the maximum value  $L_1$  can have will be obtained and can be calculated. The rate of increase of  $N_1$  in a layer of unit area and thickness  $dz$  next to the walls will be

$$\begin{aligned} &[\rho C_{\text{vib}}/(E_1 - E_0)]D(dT_V/dz)_0 \\ &+ [\rho C_{\text{vib}}/(E_1 - E_0)]\beta L_1 dz \\ &+ (N\bar{c}/4)[\rho C_{\text{vib}}/(E_1 - E_0)]a_{\text{vib}}(T_P - T_V) = 0. \end{aligned}$$

In this equation the first term represents the net increase of  $N_1$  by diffusion, which for this layer is equal to the net number of molecules crossing its boundary,  $D(dN_1/dz)_0$ . The second represents the change in  $N_1$  by collisions in the gas, and the third by collisions with the plate.  $N\bar{c}/4$  is the

<sup>6</sup> Rutgers, Ann. d. Physik **16**, 351 (1933).

<sup>7</sup> Knudsen, Ann. d. Physik **34**, 593 (1911).

number of molecules approaching the plate/unit time. If  $a_{\text{vib}}$  is negligible,  $(dT_V/dz)_0 = 0$ . Differentiating (g<sub>1</sub>) and writing

$$z=0, \quad (dT_V/dz)_0=0, \\ (dT/dz)_0 = \alpha(A-B) = \alpha A(1+e^{\alpha z_0})$$

and from (d), making the same substitution,

$$C'(dT/dz)_0 = -Q/NmD.$$

Using these equations, and substituting for  $A$  from (h),

$$\alpha L_1(1+e^{\alpha z_0})/(1-e^{\alpha z_0}) = -Q/NmDC'. \quad (i)$$

On inserting limits in (e),

$$C'\Delta T + C_{\text{vib}}\Delta T_V = Qz_0/NmD,$$

and since

$$\Delta T_V = T_{V_1} - T_V = T_1 - L_1 - T_2 + L_2 = \Delta T - 2L_1,$$

$$\Delta T(C' + C_{\text{vib}}) - 2L_1C_{\text{vib}} = Qz_0/NmD. \quad (j)$$

Eliminating  $L_1$  from (i) and (j),

$$\Delta T(C' + C_{\text{vib}}) = z_0Q(1+F)/NmD, \quad (k)$$

where

$$F = (2C_{\text{vib}}/\alpha z_0C')(e^{\alpha z_0} - 1)/(e^{\alpha z_0} + 1).$$

Since equation (k) may be written,

$$Q = (C_{\text{vib}} + C')(\Delta T/z_0) \cdot NmD/(1+F),$$

and

$$K_{\text{max}} = NmD(C_{\text{vib}} + C'),$$

we have

$$K = K_{\text{max}}/(1+F).$$

The only other correction, for the difference  $\Delta T_P - \Delta T$  is proportional to  $\lambda/z_0$  where  $\lambda$  is the mean free path, and is usually negligible at the pressures used.

For a concrete case, inspection of the above correction term  $F$  shows:

(1) When  $\alpha \ll 1$ , indicating a large time of relaxation,

$$F = (2C_{\text{vib}}/\alpha z_0C') \times (\alpha z_0/2) = C_{\text{vib}}/C'$$

In this case

$$K = K_{\text{max}}C'/(C' + C_{\text{vib}}) = NmDC'$$

as would be expected when vibration takes no part in heat transport.

(2) When  $\alpha$  is very large,  $F=0$ , as would be expected when vibration takes its full share in heat transport. It is important to know the region of pressures over which  $K$  is changing with pressure. Consider the case of  $\text{CO}_2$  at  $0^\circ\text{C}$  in an apparatus for which  $z_0=0.3$  cm

$$\beta = 8.1 \times 10^5 \text{ at } 30^\circ \text{ and } 760 \text{ mm},$$

$$C_{\text{vib}} = 1.7, \quad C_{TR} = 5.1 = C_{\text{rot}} + C_{\text{trans}}.^6$$

By using the data of Richards and Reid<sup>4</sup> for the activation energy of vibrational transfer,  $\beta = 2.7 \times 10^5$  at  $0^\circ$  and 760 mm and at a pressure  $p$  mm Hg,  $\beta = 2.7p \times 10^5/760$ .

$D$  at  $0^\circ$  and 760 mm = 0.1 and at  $p$  mm Hg,

$$D = 76/p.$$

Since  $C_{TR} = 5$  the molecule is taken as linear in calculating  $C'$ . From these data,

$$\alpha^2 = (2.7 \times 10^5/76)p^2 \times 11.2/9.5 = 4.2p^2$$

and

$$F = (e^{0.61p} - 1)/2p(e^{0.61p} + 1)$$

when  $p = 0.1$  mm, 1 mm, 10 mm and 100 mm, the values of  $F$  are 0.152, 0.148, 0.05 and 0.005, respectively. The experimental value of  $F$  calculated from

$$1 + F = f_{(\text{Eucken})}/K/\eta C$$

is approximately 0.05 for  $\text{CO}_2$ .

## DISCUSSION

A comparison of these figures with the experimental value 0.05 for  $\text{CO}_2$  which is obtained in the neighborhood of 200 mm, suggests that the value of  $\beta$  from acoustical experiments may have been overestimated. This is in part explained by assuming with Eucken and Mücke<sup>8</sup> that the vibration with  $\theta = 1830$  is not excited even at acoustical frequencies of  $10^3$  cycles. This would lead to a maximum of 0.02 to  $F$  at  $0^\circ\text{C}$  over the whole range of pressures considered above.

At present a more exact comparison is not possible, owing to the fact that the experimental methods commonly used for determining thermal conductivities are open to objection when used

<sup>8</sup> Eucken and Mücke, Zeits. f. physik. Chemie **B18**, 186 (1932).

for polyatomic gases. When concentric cylinders are used instead of parallel plates, Eq. (d) has to be modified to

$$-Q/2\pi rNmD = C'(dT/dr) + C_{vb}(dT_v/dr),$$

where  $Q$  is the heat transfer/unit length of axis. This leads to integrals in the solution which have to be evaluated for definite values of the variables. The solution is not given here, however, since most methods with concentric cylinders require a correction for the temperature jump, particularly at the surface with the smaller radius of curvature. According to Gregory and Archer<sup>9</sup> the most satisfactory form of the correction for simple gases is to write  $\Delta T/(z_0 + S)$  for the temperature gradient in place of  $\Delta T/z_0$ .  $S$  is taken as proportional to  $1/p$ . This correction is quite empirical and resembles the equation for  $F$  sufficiently to make a disentanglement of the

two effects somewhat problematical; for evidence that this empirical correction alone is not adequate for  $\text{CO}_2$  cf. M. Trautz.<sup>5</sup>

Independent evidence of the connection between thermal conductivities and the relaxation time for the various degrees of freedom can be obtained by considering the effect of small amounts of certain impurities. Thus the addition<sup>4</sup> of small amounts of  $\text{H}_2$  and  $\text{H}_2\text{O}$  can increase  $\beta$  by several powers of 10; this should have the effect of increasing the thermal conductivity and decreasing the pressure coefficient.<sup>10</sup> Such an effect has actually been observed<sup>11</sup> though here again the use of the vertical wire method makes it uncertain whether it is to be ascribed to convection effects, to a change of the accommodation coefficient in the presence of hydrogen, or to the effect discussed in this communication.

<sup>9</sup> Gregory and Archer, *Phil. Mag.* **15**, 301 (1933).

<sup>10</sup> Ubbelohde, *Proc. Roy. Soc. A* **146**, 271 (1934).

<sup>11</sup> M. Trautz and S. Weber, *Ann. d. Physik* **54**, 498 (1917).

## On the Definition of the Gibbs Potential

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(Received February 1, 1935)

IN a short note *On the Definition of the Gibbs Potential*<sup>1</sup> in which I commented on recent criticism by some authors as regards the introduction by Willard Gibbs of the chemical potential into thermodynamics, I included the following remarks concerning an article by L. J. Gillespie and J. R. Coe, Jr.:<sup>2</sup> "Quite recently thermodynamic relations of open systems have been deduced by L. J. Gillespie and J. R. Coe. They avoid intentionally the Gibbs potential as a basis for their deductions, on account of the fact that 'Gibbs' treatment has been held obscure by some authors.' They say that Gibbs provides a physical interpretation (of the potential), but

postpones it to a later part of his work." As Professor Gillespie has kindly called to my attention that these remarks might be interpreted as classing the two authors as critics of Gibbs, while the method adopted by them, avoiding the use of the potential, contained no such criticism, but was chosen for the sake of symmetry in the treatment, I am desirous to state that my remarks regarding the treatment of the two authors had no intention of such a classification.

On the contrary I am aware that the physical interpretation of the chemical potential, which follows from a rigid analysis of the mathematical definition by Gibbs suggests itself also as a consequence of an analogous interpretation of the energy and entropy functions of open systems given by Gillespie and Coe.

<sup>1</sup> J. N. Brønsted, *Det Kgl. Danske Videnskabernes Selsk. Mathem.-Fys. Medd.* **12**, No. 6, Copenhagen (1933).

<sup>2</sup> L. J. Gillespie and J. R. Coe, Jr., *J. Chem. Phys.* **1**, 103 (1933).