

## Sound Velocity in Reactive Mixtures of Real Gases

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Einstein's derivation of the dependence of sound velocity on frequency in a mixture of chemically reacting ideal gases of negligible absorption has been extended to mixtures of real absorbing gases. The results show that deviations of experiment from the earlier theory are probably due to departure of the gases from ideal properties. They also show that absorption is probably strong enough to render reaction rate determination by velocity measurements impossible, but that direct absorption measurements may be of some use. It is shown that extraneous phenomena may hide those considered.

NERNST and Keutel<sup>1</sup> suggested, in 1910, that the possibility of chemical reaction in a mixture of gases constitutes a mechanical "loading," or additional energy capacity, of the mixture and must cause the velocity of sound in the mixture to be less for sound of frequencies low enough to permit continual maintenance of chemical equilibrium than for sound of much higher frequencies; they pointed out that this acoustic dispersion seemed to offer a means of determining monomolecular gaseous reaction rates. Einstein<sup>2</sup> derived an expression for the dependence of sound velocity on frequency in a mixture of two acoustically transparent ideal gases, one being the dissociation product of the other. Considerable experimental work has been done on the nitrogen tetroxide-nitrogen dioxide mixture, notably by Grüneisen and Goens<sup>3</sup> in the audible region and by Kistiakowski and Richards<sup>4</sup> in the supersonic region; it has as yet failed to show evidence of dispersion but has shown deviation from the simple Einstein theory in the dependence of sound velocity at low frequencies on the temperature and pressure.

The Einstein method has therefore been applied to a mixture of acoustically absorbing real gases, one of which is the dissociation product of the other. The equations of propagation of acoustic disturbances in an absorbing gas show that, for a plane sinusoidal wave:

$$\left(\frac{\delta p}{\delta \rho}\right)_{adiab.} = \frac{\omega^2}{\left(\frac{2\pi}{\lambda} - \frac{i}{l}\right)^2} = \frac{u^2}{\left(1 - \frac{i}{2\pi} \frac{\lambda}{l}\right)^2} = \frac{u^2}{(1 - i\theta)^2} \quad (1)$$

where  $\omega$  is  $2\pi \times$  (sound frequency,  $f$ ),  $\lambda$  is wave-length,  $u$  is sound velocity and  $l$  distance in which amplitude is reduced by a factor of  $e^{-1}$ . The equation of state of the mixture, where  $\alpha$  is the fraction of the molecules dissociated, is:

<sup>1</sup> F. Keutel, Inaug-Diss. Berl. (1910).

<sup>2</sup> A. Einstein, Sitz. ber. d. Berl. Akad., p. 380 (1920).

<sup>3</sup> E. Grüneisen and E. Goens, Ann. d. Physik **72**, 193 (1923).

<sup>4</sup> G. B. Kistiakowsky and W. T. Richards, Jour. Am. Chem. Soc. **52**, 4661 (1930).

$$p = f(\rho, T, \alpha) \quad (2)$$

which for small acoustic disturbances gives

$$\frac{\delta p}{\delta \rho} = \frac{\partial p}{\partial \rho} + \frac{\partial p}{\partial T} \frac{\delta T}{\delta \rho} + \frac{\partial p}{\partial \alpha} \frac{\delta \alpha}{\delta \rho} \quad (3)$$

The first law of thermodynamics for the adiabatic acoustic process may be written:

$$C \frac{\delta T}{\delta \rho} + D \frac{\delta \alpha}{\delta \rho} = \frac{M p}{\rho^2} \quad (4)$$

where

$$C = (1 - \alpha)C_1 + 2\alpha C_2$$

is the total heat capacity per mole of the mixture at constant volume,  $D$  the heat of dissociation at constant volume and  $M$  the mass of one mole of the heavier constituent of the mixture. Finally, the conservation of mass in the reaction requires that

$$\left[ K_1(1 - \alpha) \frac{\rho}{M} - K_2 4\alpha^2 \frac{\rho^2}{M^2} \right] \frac{M}{\rho} = \frac{d\alpha}{dt} \quad (5)$$

where  $K_1$  is the average frequency of dissociation of a molecule of the heavier gas, the required monomolecular reaction rate, and  $K_2$  is the frequency of association of a pair of molecules of the lighter constituent. From variation of Eq. (5), remembering that the acoustic disturbances are small and sinusoidal and that for equilibrium

$$\frac{K_1}{K_2} = K = \frac{\rho}{M} \frac{4\alpha^2}{1 - \alpha} \quad (6)$$

(the concentration form of the mass action law) is true,

$$(1 - \alpha) \left( \frac{1}{K} \frac{\partial K}{\partial \rho} - \frac{1}{\rho} + \frac{1}{K} \frac{\partial K}{\partial T} \frac{\partial T}{\partial \rho} \right) = \left( \frac{2 - \alpha}{\alpha} + i \frac{\omega}{K_1} \right) \frac{\delta \alpha}{\delta \rho} \quad (7)$$

may be obtained. Combining Eqs. (3), (4), and (7), we find

$$\frac{\delta p}{\delta \rho} = \frac{\partial p}{\partial \rho} \left[ 1 + \frac{M \rho}{\rho^2 C} \frac{\partial p}{\partial T} \frac{\partial T}{\partial \rho} \right] + \frac{(1 - \alpha) \left( \frac{\partial p}{\partial \alpha} - \frac{D}{C} \frac{\partial p}{\partial T} \right) \left( \frac{M p}{\rho^2 C} \frac{\partial}{\partial T} \log K + \frac{\partial}{\partial \rho} \log K - \frac{1}{\rho} \right)}{\frac{2 - \alpha}{\alpha} + (1 - \alpha) \frac{D}{C} \frac{\partial}{\partial T} \log K + i \frac{\omega}{K_1}} \quad (8)$$

which may be combined with Eq. (1) and re-arranged to give

$$\frac{\left(\frac{u}{u_0}\right)^2}{(1-i\theta)^2} = \frac{1+i\gamma^2x}{1+ix} \quad (9)$$

where  $x = (2\pi/b)(f/K_1)$ ,  $\gamma = u_\infty/u_0$ ,  $u_0 = (\partial p/\partial\rho)(1+qa/b)$ ,  $u_\infty = (\partial p/\partial\rho)(1+q)$  ( $u_0$  = velocity of very low frequency sound,  $u_\infty$  = velocity of very high frequency sound.) Here

$$\left\{ \begin{array}{l} a = \frac{2-\alpha}{\alpha} + (1-\alpha) \frac{\frac{\partial p}{\partial\alpha}}{\frac{\partial p}{\partial T}} \frac{\partial}{\partial T} \log K + (1-\alpha) \frac{\rho^2 C}{pM} \left( \frac{\frac{\partial p}{\partial\alpha}}{\frac{\partial p}{\partial T}} - \frac{D}{C} \right) \left( \frac{\partial}{\partial\rho} \log K - \frac{1}{\rho} \right) \\ b = \frac{2-\alpha}{\alpha} + (1-\alpha) \frac{D}{C} \frac{\partial}{\partial T} \log K \\ q = \frac{\frac{\partial p}{\partial T} M p}{\frac{\partial p}{\partial\rho} \rho^2 C} \end{array} \right. \quad (9a)$$

Solving Eq. (9) for the quantities on the left hand side gives:

$$\theta = \frac{1}{2\pi} \frac{\lambda}{l} = \left[ 1 + \frac{(1+\gamma^2x^2)^2}{(\gamma^2-1)^2x^2} \right]^{1/2} - \frac{1+\gamma^2x^2}{(\gamma^2-1)x} \quad (I)$$

for absorption and

$$\frac{u}{u_0} = \frac{1+\theta^2}{(1-\theta^2)^{1/2}} \left( \frac{1+\gamma^2x^2}{1+x^2} \right)^{1/2} \quad (II)$$

for velocity, as functions of "relative frequency",  $x$ .

Letting the equation of state become

$$p = f(\rho, T, \alpha) = \left( \frac{R}{M} \right) \rho T (1 + \alpha) \quad (2a)$$

and the absorption,  $\theta$ , become negligible, we get

$$\left\{ \begin{array}{l} a = \frac{2-\alpha}{\alpha} + \frac{1-\alpha}{1+\alpha} \left( 2 \frac{D}{RT} - \frac{1}{q} \right) \\ b = \frac{2-\alpha}{\alpha} + \frac{1-\alpha}{1+\alpha} \frac{D^2}{R^2 T^2} q \\ q = (1+\alpha) \frac{R}{C} \end{array} \right. \quad (9b)$$

and

$$\frac{u}{u_0} = \left( \frac{1 + \gamma^2 x^2}{1 + x^2} \right)^{1/2} \quad (\text{II. a})$$

which is a complete reduction to the results of Einstein.

It is immediately apparent that the departure of a reacting gas mixture from ideal properties cannot change the type of sound velocity dependence upon frequency in the mixture, but can affect numerical values, and so can probably explain the discrepancies between experiment and the earlier theory. Unfortunately, this point cannot be tested, as the differential coefficients  $(\partial p/\partial \rho)_{\alpha, T}$ ,  $(\partial p/\partial T)_{\alpha, p}$  and  $(\partial p/\partial \alpha)_{p, T}$  are not at present accessible to experimental measurement, since, because of the rapid establishment of equilibrium, it is not now possible to secure independent control of density, temperature, and composition of a gaseous mixture.

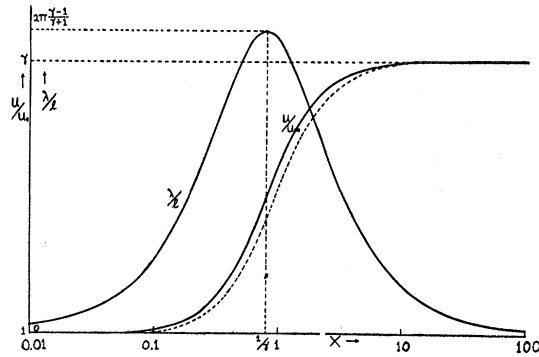


Fig. 1. Frequency dependence of velocity and absorption of sound in a mixture of two reacting gases.

Fig. 1 shows graphs of Eqs. (I), (II) and (IIa) (dotted) for  $\gamma = 1.25$ . It may be seen that the effect of absorption on velocity is slight (it is very much exaggerated in the figure by the large value of  $\gamma$  chosen;  $\gamma$  calculated from Eqs. (9b) for nitrogen tetroxide and nitrogen dioxide is about 1.05), in fact, for actual gases it is quite negligible. However, the practical effect of this absorption on the precise measurement of sound velocity in the dispersive frequency region is to render such measurement impossible. Precise velocity measurements in the dispersive region are essential for reaction rate determination since very small velocity differences are involved, but the absorption maximum should be sufficient in actual gases to reduce sound intensity to less than two percent of its initial value in fourteen wave-lengths, making the usual interferometric velocity measurements both very difficult and very inaccurate.

On the other hand, it may be seen from the graph that absorption measurements offer a promising means of determining the reaction rate. The curve of absorption against relative frequency shows a reasonably sharp maximum of height  $(\gamma - 1)/(\gamma + 1)$  at a relative frequency  $1/\gamma$  (when the sound fre-

quency,  $f$ , is of the same order of magnitude as the dissociation frequency,  $K_1$ , of the heavier molecules). At this absorption maximum

$$K_1 = \frac{2\pi}{b} \frac{1 + \theta}{1 - \theta} f, \quad (10)$$

so that a measurement of the frequency at this point and a rough measurement of the height of the maximum should yield a good value for  $K_1$ , since the scale constant  $b$  may be computed even for real gases.<sup>5</sup>

This work has been based entirely on the assumption that no other frequency dependent loading occurs beside that due to the chemical reaction. But Pierce<sup>6</sup> has found evidence of acoustic dispersion in air and carbon dioxide, and Herzfeld and Rice<sup>7</sup> have attributed this to a time lag in energy transfer from translational to internal molecular degrees of freedom. This phenomenon is presumably also present in nitrogen tetroxide and nitrogen dioxide and may well render completely invalid any conclusions regarding dissociation rate of the former derived from acoustic data.

<sup>5</sup> Noting that the absorption maximum lies almost at the center of the dispersive region and that  $\theta^2 \ll 1$ , Eq. (10) may be transformed into the directly measurable form

$$K_1 = \frac{2\pi}{b} \left( f + \frac{u_0}{\pi l} \right).$$

<sup>6</sup> G. W. Pierce, Proc. Am. Acad. Sci. **60**, 271 (1925).

<sup>7</sup> K. F. Herzfeld and F. O. Rice, Phys. Rev. **31**, 691 (1928).