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Ratio of Specific Heats of Air, N₂, and CO₂ as a Function of Pressure by the Ultrasonic Method

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Measurements have been made by Hodge of ultrasonic velocities at 27°C at pressures from 1 to 100 atmos. in air and N₂ and at 1 to 60 atmos. in CO₂. The results for air and N₂ combined with the respective compressibility data of Holborn and Otto give at 27°C for air, values of γ between 1.406 at 1 atmos. and 1.580 at 100 atmos., and for N₂, 1.403 at 1 atmos. to 1.564 at 100 atmos. The acoustic velocities in CO₂ combined with the compressibility data of Amagat, give for γ at 27°C values from 1.304 at 1 atmos. to 3.524 at 60 atmos. These and the other results between these limits are in excellent general agreement with the few results in this temperature and pressure region available for comparison.

AMONG the indirect methods for the evaluation of C_v , the specific heat at constant volume, or of γ , the ratio of specific heats, the acoustic method is the simplest and most convenient, and has accordingly been the subject of numerous and painstaking researches.¹ These studies have largely been confined to audible frequencies and have yielded only meager results, subject in most cases to very large errors. The determination of acoustic velocities at audible frequencies requires either the use of such large scale apparatus as to restrict the method to the commonest gases, or, if done by the more usual methods of resonators or of the Kundt's tube, correction factors are necessary. The determinations of the corrections have entailed a great deal of theoretical and empirical work and the results have been satisfactory in but few cases. An additional difficulty, only lately recognized, is the possibility of acoustic dispersion of the molecular type, in some cases amplified by traces of gaseous impurity.

The experimental resources which have lately become available through the development of ultrasonic methods of measuring acoustic velocity permit the use of small scale apparatus which at the same time is large enough in terms of wavelengths to reduce to a negligible amount the corrections made necessary by diffraction and the departure from the adiabatic condition encountered when a sound wave is confined to a tube of a diameter small compared to wave-

length. By a suitable choice of pressure and frequency the experiments can be carried out so as to explore the effects of dispersion of the molecular type.²

The ratio of specific heats, γ , may be found from the value of acoustic velocity, V , and the equation of state. Thus

$$V^2 = (\partial p / \partial \rho)_s = -v^2 \gamma (\partial p / \partial v)_T.$$

Since the equation of state is seldom known over more than a very narrow range of variables, a more direct course consists in using the isothermal values of $p v$. Thus, putting $(p v)_T = f(p)$, we have

$$\gamma = \frac{p v - p [\partial (p v) / \partial p]_T}{(p v)^2} V^2.$$

In the following a computation of γ has been made using Hodge's data for V , given in the preceding paper, and the compressibility data of Holborn and Otto³ for air and for N₂ and the compressibility data of Amagat⁴ for CO₂.

The compressibility data $(p v)_T = f(p)$, allow of interpolation to 27°C in the pressure ranges noted below. The interpolations were made algebraically, terms including the second order being usually sufficient. The interpolation equations were tested by extrapolation from them to temperatures not used in setting them up. From the curves $(p v)_{27} = f(p)$, thus obtained, values of $p v$ and of $d(p v) / d p$ were taken at

¹ For a summary, see Eucken, *Handbuch der Exp. Phys.* Vol. 8, Part 1 (1929), pp. 424-425.

² Richards and Reid, *J. Chem. Phys.* 2, 193 (1934).

³ Holborn and Otto, *Zeits. f. Physik* 33, 1 (1925).

⁴ Amagat, *Comptes rendus* 118, 450 (1891).

various pressures as desired. A large scale plot was made in the case of each gas of the values of acoustic velocity *vs.* pressure (*p*, *V*), and the best curves found by graphical methods. Values of *V* for use in the computations were then taken from the curves at desired pressure intervals.

AIR

The curve (*p*, *V*) was obtained by using Hodge's acoustic measurements at both 286 and 486 kc, since no dispersion is evident in the results. Computations of γ were made for pressures of 0, 1, and at intervals of 10 up to 80 m Hg. The results are shown in Fig. 1, pressures being given in atmos. For comparison, the following results are available by interpolation to 27°C from the work of Jacob,⁵ determined from thermodynamic data.

<i>p</i> . kg/cm ²	(Jacob)	(H and H)
0	1.400	1.404
50	1.485	1.491
100	1.562	1.574

NITROGEN

The results, similarly found, are shown in Fig. 1. No values have been found for comparison.

CO₂

The compressibility data of Amagat allow of the interpolation of $(pv)_T = f(p)$ to 27°C between 35 and 60 atmos. Hodge's acoustic data for CO₂ at 88 kc, where dispersion was least evident at atmospheric pressure, were chosen for computations. The results for γ are shown in Fig. 1. For comparison the following values have been

⁵ M. Jacob, *Zeits. f. tech. Physik* 4, 460 (1923).

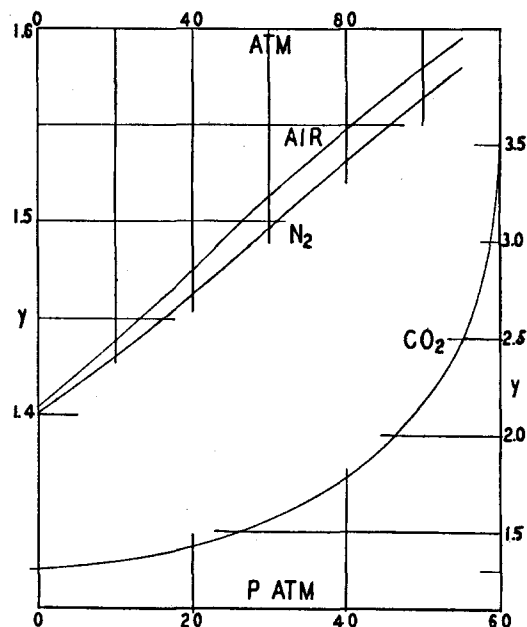


FIG. 1. Ratio of specific heats of air, N₂ and CO₂ at 27°C as a function of pressure.

computed from the results of Worthing.⁶

<i>p</i> . atmos.	(Worthing)	(H and H)
0	—	1.304
10	1.33	—
20	1.41	—
30	1.55	1.560
40	1.77	1.780
50	2.10	2.167
60	—	3.524

The results of this study show the feasibility of greatly extending, by relatively simple experimental means, the knowledge of γ and of C_v over the broad temperature and pressure ranges for which excellent data for $(pv)_T = f(p)$ are available for several gases. The precision measure of γ in the present results is, at atmospheric pressure, 2/10 percent, at other pressures, 4/10 percent.

⁶ A. G. Worthing, *Phys. Rev.* 32, 244 (1911); 33, 217 (1911).