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## Heat-Capacity Lag Measurements in Various Gases\*

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The impact-tube method of measuring relaxation times for the transfer of molecular energy from translational to internal degrees of freedom has been introduced in a previous report. This method has been applied to a series of gases to make measurements of relaxation times which would be difficult to measure quantitatively by sonic methods. Measurements of the relaxation times of the vibrational energy of  $\text{H}_2\text{O}$ ,  $\text{N}_2$ ,  $\text{N}_2$  catalyzed by  $\text{H}_2\text{O}$ , and  $\text{CCl}_2\text{F}_2$  are presented. The existence of a measurable lag in the adjustment of the rotational heat capacity of  $\text{H}_2$  has been confirmed, and measurements of its relaxation time are presented.

### INTRODUCTION

IN a previous report,<sup>1</sup> the impact-tube method of measuring the relaxation time of gases was introduced. In this method, measurements are made of the entropy change in a single cycle of adiabatic expansion and compression of the gas. The gas is expanded from a chamber through a nozzle, and compressed at the nose of an impact tube aligned with the jet from the nozzle (see Fig. 1 of reference 1). If the apparatus is large enough so that the portion of the stream which interacts with the impact tube is outside the boundary layer of the nozzle, then the process is adiabatic. If this apparatus is properly constructed and adjusted and a gas without internal heat capacity, such as helium is used, the pressure measured at the impact tube is found to be very close to the chamber pressure. In this case, practically no dissipation of energy occurs in this flow. Therefore, this apparatus provides a sensitive and accurate method of detecting dissipations caused by a lag in the adjustment of the internal heat capacity of a gas, to external conditions.

The energy dissipations involved are nearly always small compared to the kinetic energy of the gas in the jet, and so it is possible to calculate the thermal energy of the gas as a function of time from conventional hydrodynamics neglecting the heat-capacity lag effects. This calculation

can be simplified by choosing shapes for the nozzle and the impact tube for which hydrodynamic solutions are already available. Next, it is assumed that the rate of change of the internal molecular energy is directly proportional to its departure from equilibrium. Thus, only one type of lagging heat capacity with a single relaxation time is considered. Assuming a value for the relaxation time, it is then possible to calculate the departure from equilibrium at all times during a flow process, for which the thermal energy is known as a function of time from the hydrodynamic solution.

When a gas is not in equilibrium, a process analogous to heat conduction occurs in which heat flows from a temperature, which is appropriate to the internal energy of the molecules, to a temperature which corresponds to the translational energy. Now, when the departure from equilibrium and the relaxation time of the gas are known, the entropy increase in this "heat-conduction" process can be computed readily. In the case of the nozzle-impact-tube flow process, this entropy increase means that the stagnation pressure, measured by the impact tube, will be lower than the pressure of the gas in the chamber. The energy of the gas is, of course, identical with that of the chamber since these processes are adiabatic. The entropy, and the energy of the gas at stagnation conditions at the impact tube are thus known, and its pressure can readily be computed from standard thermodynamic formulae.

### Method for Short Relaxation Times

If the impact tube is made very small (of the order of 0.005 inch in diameter), the time in-

\* This work was done at the Langley Memorial Aeronautical Laboratory of the National Advisory Committee for Aeronautics. A somewhat more complete version was first published as a Restricted Bulletin No. L4E29 by the NACA. The restriction has since been removed, and the authors are grateful to the NACA for permission to publish this report.

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<sup>1</sup> A. Kantrowitz, *J. Chem. Phys.* **14**, 150 (1946).

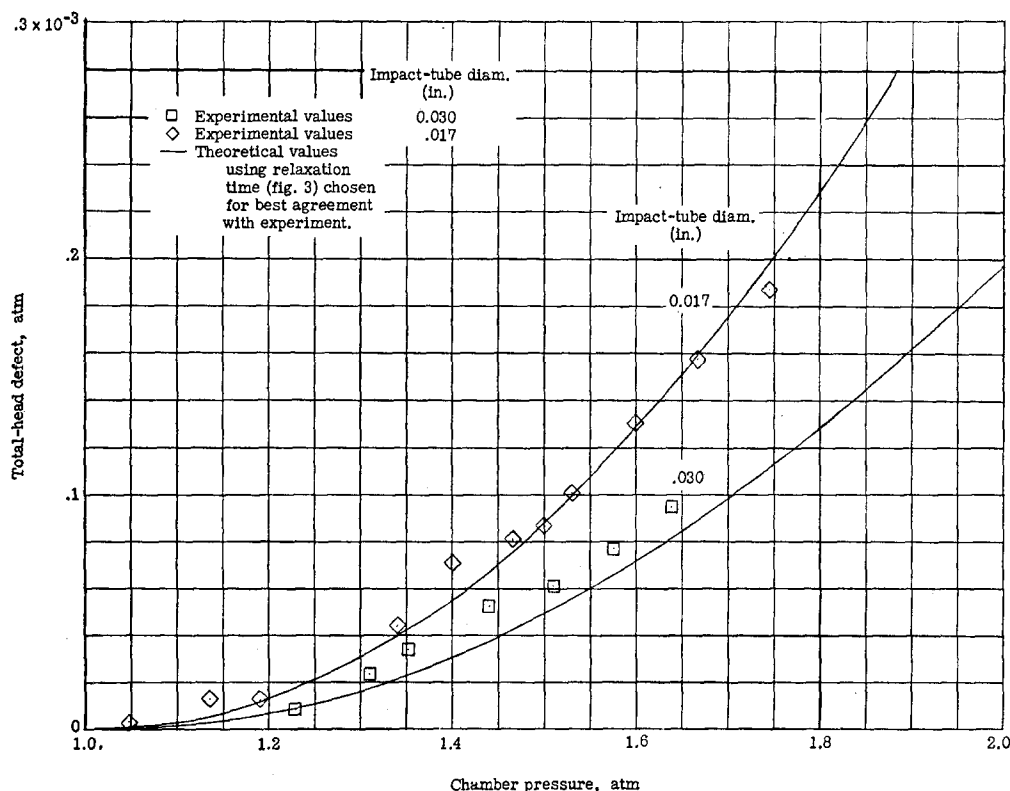


FIG. 1. Total-head defect of water vapor for chamber temperature of 585°K. From the departure of the experimental points from the theoretical curves, it can be concluded that the accuracy of these measurements is about  $\pm 20$  percent. Points taken with a total-head defect less than  $0.02 \times 10^{-3}$  atmos. were used only to establish the zero reading of the manometer.

volved in the compression at the nose of the impact tube can be made very short (of the order of 1 microsecond). On the other hand, the nozzle can be made long (e.g., 2 inches), so that the expansions take place in times of the order of  $\frac{1}{2}$  millisecond. Now, if the relaxation time of a gas is very short (compared to  $\frac{1}{2}$  millisecond), the internal energy will follow the expansion in the nozzle very closely, and the gas approaching the impact tube will be very close to equilibrium. Thus, only the departures from equilibrium and the dissipation in the compression process at the nose of the impact tube need be considered.

In reference 1, calculations of the total-head defect (that is, the difference between chamber pressure and impact-tube pressure) were made for the case where an equilibrium gas approaches a "source-shaped" impact tube. The calculations were made assuming various ratios  $K$  of the diameter of the impact tube, to the distance traveled by the undisturbed gas in its relaxation

time. Now, if it is desired to measure the relaxation time of a gas, known to have a short relaxation time compared to the time required for the expansion through the nozzle, experimental values of the total-head defect can be compared with these computations. Thus, values of  $K$  can be found for which the theoretical and experimental values of the total-head defect agree. In this way, a single measurement of the total-head defect yields a value of the relaxation time of the gas. If now a series of such measurements are made with different chamber pressures and different impact-tube sizes, the consistency of this method can be tested.

In this way measurements of the relaxation time of carbon dioxide were made. It was found that fairly consistent results for two impact tubes, and for a range of chamber pressures were obtained, thus establishing the general validity of this procedure.

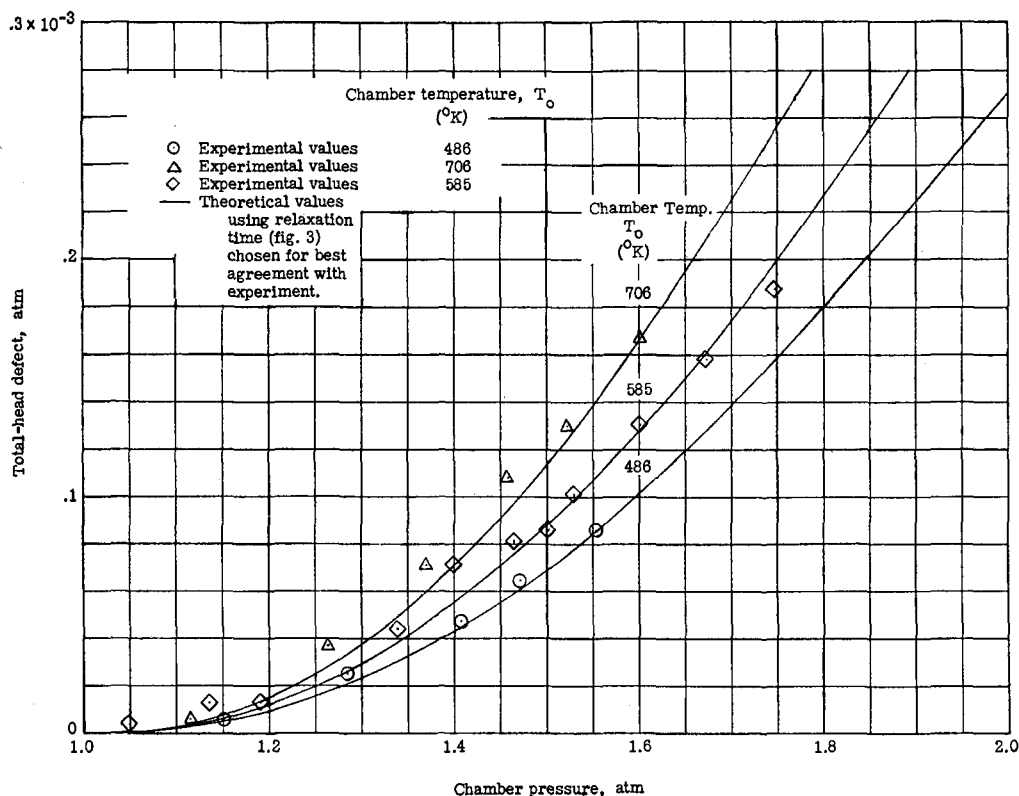


FIG. 2. Variation of total-head defects in water vapor with chamber temperature for 0.017-inch diameter impact tube.

### Method for Long Relaxation Times

If the relaxation time of a gas is very long compared to the time during which compressions take place at the nose of the impact tube, then the relaxation time cannot be obtained by the foregoing method. In this case, only negligible changes in the internal energy of the gas take place during the compression process, and the gas adjusts after the compression is over. The entropy increase and total-head defect will then be independent of the time of compression and, thus, of the impact-tube diameter.

If the relaxation time is long compared to both the times required for the expansion and the compression, no adjustment of the lagging internal energy will take place during the entire cycle. In this case, no entropy increase and no total-head defect will be observed. If, however, the relaxation time is long compared to the compression time but is comparable with the time required for expansion through the nozzle, then some adjustment of the lagging internal energy

will take place in the nozzle. In this case, an entropy increase will occur and, by measuring the resultant total-head defects, the relaxation time can be compared with the time required for the gas to flow through the nozzle. In this way, relaxation times up to the order of 0.01 second can be measured. This extension of the impact-tube method has been reported.<sup>2</sup> The necessary calculations together with some experimental details which may be helpful to those intending to apply impact-tube methods are given in the appendix.

### WATER VAPOR

An electric boiler and super heater were constructed which produced enough steam for an hour's run. The water-vapor boiler was carefully cleaned and then heated in a vacuum for some time before it was used. Distilled water was used at all times in the boiler, and only the middle

<sup>2</sup> A. Kantrowitz and P. W. Huber, NACA Restricted Bulletin No. L4E29 (1944).

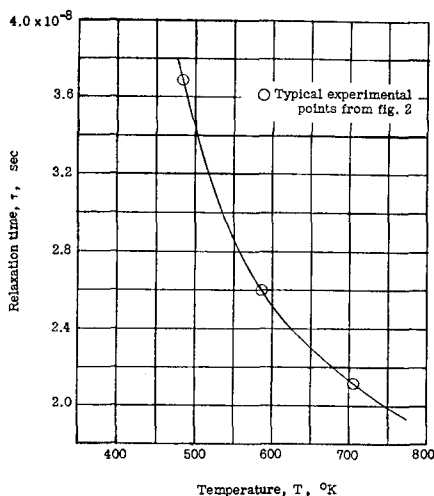


FIG. 3. Temperature variation of the relaxation time of water vapor (1 atmos.) chosen to give best agreement with measured total-head defects.

two-thirds of the water vapor generated was used in these experiments.

Total-head defects in water vapor were measured at three different temperatures and with two "source-shaped" impact tubes over a range of chamber pressures (see Figs. 1 and 2). It will be seen from Fig. 1 that the total-head defect is roughly inversely proportional to the impact-tube diameter. This fact, and the fact that the defects observed were small, means that water vapor has a relaxation time which is short compared with the compression time at the nose of the impact tubes. The relaxation times were then calculated by employing the method for short relaxation times discussed in the introduction. It was assumed that the total-head defects were caused by a lag in the vibrational heat capacity of water vapor and it was assumed that all of the vibrational heat capacity adjusted with a single relaxation time.

Choosing three typical experimental points, the relaxation times shown in Fig. 3 were found. Using these experimental values of relaxation time and the theory of reference 1, and presuming that the collisions responsible for the adjustment of vibrational energy are bimolecular (relaxation time  $\tau$  inversely proportional to pressure), we computed the theoretical total-head defects shown in Figs. 1 and 2. The agreement between the theoretical variations with chamber pressure, and impact-tube diameter with these measurements,

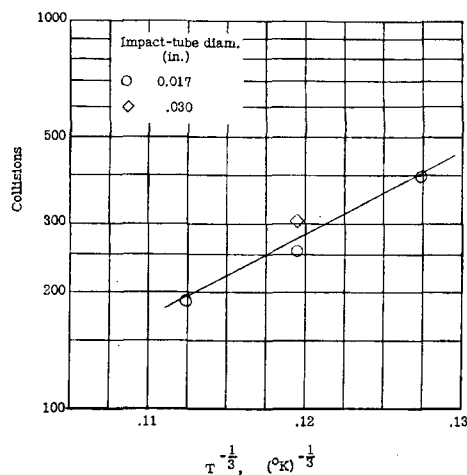


FIG. 4. Logarithmic plot of the relaxation time of water vapor in molecular collisions against  $T^{-1/3}$ . The theory of Landau and Teller (reference 3) indicates that a straight line should be obtained.

may be taken as an index of the accuracy of these results, which are probably of the order of  $\pm 20$  percent for relaxation time. Some experimental relaxation times for steam are shown in Table I. It can be seen that a very few collisions—of the order of 300—are required for adjustment of the vibrational energy.

Inasmuch as the water vapor employed probably had only slight impurities, and the adjustment involved only a few hundred molecular collisions, it seems very unlikely that these results could be appreciably affected by impurities. These measurements may therefore be presumed to apply to pure water vapor. The possibility exists that a part of the total-head defects measured may be attributable to a lag in the rotational heat capacity of water vapor, but vibrational and rotational effects cannot be separated in measurements of this kind (since both relaxation times are apparently very short compared to the compression time,  $K \approx 50$ ). If the total-head defects measured were partially caused by a lag in the rotational heat capacity, then less than 300 collisions are required for the adjustment of vibrational heat capacity in water vapor.

The results shown in Table I are next compared with the theory of Landau and Teller.<sup>3</sup> This theory indicates that the logarithm of the number of collisions necessary to transmit a

<sup>3</sup> L. Landau and E. Teller, *Physik. Zeits. Sowjetunion* **1**, 34 (1936.)

TABLE I. Experimental relaxation times of water vapor, hydrogen, and nitrogen.

Relaxation times for water vapor and hydrogen were calculated as shown in the tables\* on page 161 of reference 1, using the theory for very short relaxation times where the approximation  $K = 1.743/\Delta S'$  is valid. Relaxation times for the nitrogen points were calculated in a similar manner, but using the value of  $K$  from the part of the curve in Fig. 8 for long relaxation times. The relaxation times for hydrogen were reproducible to about  $\pm 5$  percent using different impact tubes. The relaxation times for water vapor were only reproducible to about  $\pm 20$  percent because of the very small total-head defects. The water-vapor content of the nitrogen was not measured closer than  $\pm 10$  percent.

Type and percent of impurities in gas	Diameter of impact tube (in.)	Temperature $\bar{T}$ ( $^{\circ}\text{K}$ )	Relaxation time, $\tau$ (sec.) at $\bar{T}$ and converted to 1 atmos.	Type of collision considered effective for adjustment	No. of collisions per molecule per sec. of the effective type (at 1 atmos. and converted to $\bar{T}$ )	No. of molecular collisions required for adjustment	No. of observations
Water Vapor							
Negligible	0.017	486	$3.7 \times 10^{-8}$	Bimolecular ( $13.92 \times 10^9$	$10.74 \times 10^9$	$4.0 \times 10^2$	5
Negligible	.017	585	2.6	$\text{H}_2\text{O}$ with $\text{H}_2\text{O}$ per mole-	9.78	2.6	8
Negligible	.030	585	3.1	cule per second at 1	9.78	3.1	6
Negligible	.017	706	2.1	atmos. and $288^{\circ}\text{K}$ )**	8.89	1.9	5
Normal Hydrogen							
0.5 $\text{O}_2$	0.0175	285	$1.04 \times 10^{-8}$	Bimolecular ( $1.48 \times 10^{10}$	$1.49 \times 10^{10}$	$1.55 \times 10^2$	10
0.5	.029	287	1.09	$\text{H}_2$ with $\text{H}_2$ per molecule	1.48	1.61	5
0.5	.064	284	1.15	per second at 1 atmos.	1.50	1.72	3
0.5	.0175	207	1.18	and $288^{\circ}\text{K}$ )**	1.74	2.05	5
Nitrogen							
0.05 $\text{H}_2\text{O}$	0.060	556	$5.9 \times 10^{-3}$	Bimolecular ( $74.3 \times 10^8$	$5.35 \times 10^8$	$3.1 \times 10^{7***}$	6
.05	.060	680	2.9	$\text{N}_2$ with $\text{N}_2$ per molecule	4.84	1.4***	5
.05	.060	686	2.7	per second at 1 atmos.	4.82	1.3***	5
.05	.060	694	3.4	and $288^{\circ}\text{K}$ )**	4.79	1.6***	6
.05	.060	761	2.6		4.58	1.2***	5
3.5 $\text{H}_2\text{O}$	0.017	413	$1.2 \times 10^{-4}$	$\text{N}_2$ with $\text{H}_2\text{O}$ ( $1.04 \times 10^8$	$30.8 \times 10^7$	$3.6 \times 10^4$	5
1.33	.060	560	3.7	$\text{N}_2$ with $\text{H}_2\text{O}$ per $\text{N}_2$	9.51	3.5	5
.66	.060	561	6.2	molecule, per percent	4.72	3.0	5
1.99	.017	575	2.3	$\text{H}_2\text{O}$ , per second at 1	14.70	3.4	5
2.97	.017	708	1.4	atmos. and $288^{\circ}\text{K}$ )**	19.70	2.9	6
1.41	.060	709	2.8		9.37	2.7	5
.97	.060	712	3.9		6.43	2.5	5
1.45	.017	733	2.6		9.46	2.4	5

\*  $\tau = d/Uk$  in column 8 of these tables should read  $\tau = d/UK$ .

\*\* Collisions per molecule per second at 1 atmosphere and  $288^{\circ}\text{K}$  were obtained from E. H. Kennard, *Kinetic Theory of Gases* (McGraw-Hill Book Company, Inc., New York, 1938), and were assumed to vary with  $T^{-1}$  and  $P$ .

\*\*\* Adjustment computed as resulting from collisions of  $\text{N}_2$  with  $\text{N}_2$  even though it is thought that the small amount of water vapor present was important.

vibrational quantum is inversely proportional to the cube root of the absolute temperature  $T$ . The number of collisions required for the relaxation of water vapor is plotted against  $T^{-1}$  in Fig. 4. The results presented herein, as well as those of other recent investigations on pure gases (see reference 1, p. 162), have been shown to fit the theory of reference 3 within experimental accuracy.

### HYDROGEN

The existence of anomalous absorption and dispersion of the velocity of sound in hydrogen have been reported by various workers.<sup>4-6</sup> These

effects have been attributed to a lag in the rotational heat capacity of hydrogen. Van Itterbeck and his collaborators found a relaxation time for the transfer of energy from translation to rotation of the order of  $2 \times 10^{-8}$  second at 1 atmosphere and  $288^{\circ}\text{K}$  from absorption measurements. Stewart<sup>6</sup> found relaxation times ranging from 1.1 to  $3.6 \times 10^{-8}$  second from velocity of sound measurements for the same conditions. Since the rotational heat capacity is a large fraction of the total heat capacity of hydrogen, it would be expected that considerable total-head defects (several cm of alcohol) would result from

<sup>4</sup> A. Van Itterbeck and P. Mariens, *Physica* **4**, 609 (1937); A. Van Itterbeck and L. Thys, *Physica* **5**, 889 (1938); and A. Van Itterbeck and R. Vermaelen, *Physica* **9**, 345 (1942).

<sup>5</sup> J. L. Stewart, Dissertation, Johns Hopkins University (1943); *Rev. Sci. Inst.* **17**, 59 (1946).

<sup>6</sup> E. S. Stewart, Dissertation, Johns Hopkins University (1946); *Phys. Rev.* **69**, 632 (1946).

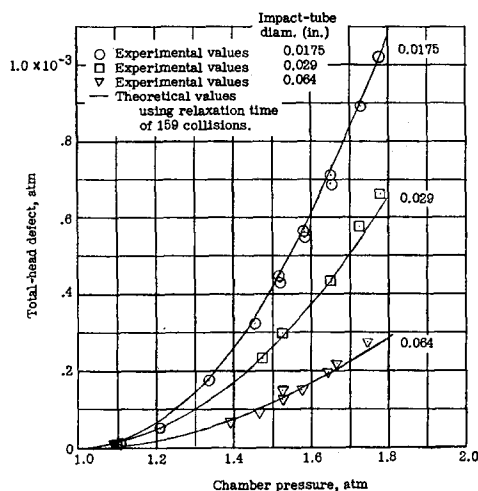


FIG. 5. Total-head defect of hydrogen for chamber temperature of 304°K. From the departure of the experimental points from the theoretical curves, it can be concluded that the accuracy of these measurements is about  $\pm 5$  percent. Points taken with a total-head defect less than  $0.15 \times 10^{-3}$  atmos. were used only to establish the zero reading of the manometer.

these lags. It seemed quite likely, therefore, that accurate values of the relaxation time could be obtained from the impact-tube method, and so a series of measurements was made on hydrogen.

The gas used was commercial hydrogen and the manufacturers reported that impurities were of the order of 0.5 percent of oxygen by volume, and perhaps 0.1 percent of nitrogen. The velocity of sound in this gas was measured at 1000~, and was found to be 4 percent below the value which would be expected for pure hydrogen. This agrees roughly with the impurity estimates.

Total-head defects were measured with three impact tubes over a range of chamber pressures at room temperature, and are given in Fig. 5. (A few measurements were also made at 207°K with the smaller impact tube, and are given in Fig. 6.) It can be seen (Fig. 5) that the total-head defect is inversely proportional to the impact-tube diameter, which shows that the method for short relaxation times should be used. Relaxation times for rotational heat capacity computed from each of these points averaged  $1.07 \times 10^{-8}$  second at 285°K, and  $1.18 \times 10^{-8}$  second at 207°K converted to atmospheric pressure on the assumption that the effective collisions were bimolecular. (The rotational heat capacities used were for equilibrium hydrogen,  $\frac{3}{4}$  ortho +  $\frac{1}{4}$  para, and were

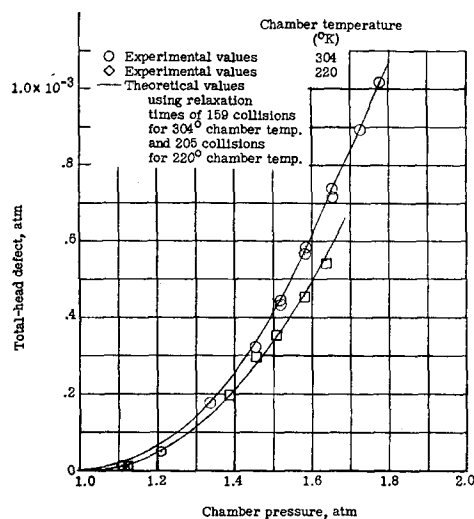


FIG. 6. Variation of total-head defects in hydrogen with chamber temperature for 0.0175-inch diameter impact tube.

taken from Fowler and Guggenheim.<sup>7</sup>) These computations were made on the assumption that all of the rotational heat capacity adjusted with a single relaxation time. This relaxation time was converted to molecular collisions and we obtained 159 collisions for the relaxation time at 285°K and 205 collisions at 207°K. Using 159 collisions, theoretical values for the total-head defect at 285°K for the three impact tubes were computed, and are plotted as solid lines in Fig. 5. The reproducibility of our measurements of the relaxation time can be estimated from the departure of individual points from the theoretical curves. Since an error in the relaxation time results in an error of the same percentage in the total-head defect in this case ( $K \gg 1$ ), it can be seen from Fig. 5 that the relaxation-time measurements are consistent to  $\pm 5$  percent. A few rough experiments were made to examine the effects of the impurities in our hydrogen. Several percent of nitrogen and then oxygen were added to the hydrogen and no large effect on the total-head defect was found. This indicates that our results were probably not affected by the presence of these impurities.

#### NITROGEN

The nitrogen used was commercial dry, 99 percent pure, obtained in high pressure cylinders.

<sup>7</sup> R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (University Press, Cambridge, 1939), p. 92.

Analysis of a sample of this nitrogen showed that it contained less than 0.1 percent oxygen by volume and less than 0.25 percent carbon dioxide. Passage of the gas through a dew point instrument indicated that roughly 0.05 percent water vapor was present. Additional water vapor was added to the nitrogen in some of the experiments by passing the gas through the boiler used in the water-vapor experiments. It was considered that the water-vapor content measurements were not accurate to better than  $\pm 10$  percent.

Total-head defects in nitrogen were measured at temperatures from 413 to 760°K over a range of chamber pressures with two different impact tubes. No change in total-head defect was found with change of diameter of the impact tube from 0.017 inch to 0.060 inch. This result indicated that the relaxation time of nitrogen was long compared with the compression time at the nose of the impact tubes used. The addition of small amounts of impurities in order to shorten the relaxation time, resulted in much larger total-head defects, and further established the fact that the relaxation time of nitrogen is of the same order as the time required for the expansion through the nozzle. The relaxation times were then calculated by employing the method for *long* relaxation times discussed in the introduction, assuming that all the vibrational heat capacity adjusted with a single relaxation time.

The relaxation times found for commercial nitrogen and nitrogen with various amounts of added water vapor are shown in Table I. It is clear from this data that not more than 1 collision in  $10^7$  between nitrogen molecules is effective in transforming translational energy into vibrational energy. Water vapor seems to be an effective catalyst for this transformation and about 1 collision in 30,000 between water vapor and nitrogen molecules is effective. As has been observed with some other gases,<sup>8</sup> the dependence of the number of collisions for relaxation on temperature is much smaller for a gas with impurities than for a relatively pure gas. Some evidence can be seen from the results in Table I, however, that the relaxation time in collisions decreases as the temperature increases.

An attempt was made to find evidence of a lag

in the rotational heat capacity of nitrogen from the very small total-head defects (of the order of 0.002 percent of the dynamic pressure) measured at room temperature. No component of these total-head defects which varied with the square of the dynamic pressure could be isolated. This indicates that the rotational relaxation time is shorter than  $10^{-9}$  second at room temperature and atmospheric pressure.

#### DICHLORODIFLUOROMETHANE

A few total-head defect measurements were made on dichlorodifluoromethane and have been reported.<sup>9</sup> Assuming that all the vibrational heat capacity lagged with a single relaxation time, a relaxation time of the order of  $2 \times 10^{-8}$  second at 297°K and 1 atmosphere was found.

#### APPENDIX

##### Symbols

- $l$ —nozzle length;
- $d$ —diameter of impact tube;
- $U$ —final velocity in nozzle;
- $u$ —velocity;
- $u'$ —non-dimensional velocity ( $u/U$ );
- $t$ —time;
- $t'$ —non-dimensional time ( $\frac{t}{l/U}$  or  $\frac{t}{d/U}$ );
- $\tau$ —relaxation time at average temperature and pressure of flow;
- $K$ —non-dimensional constant of flow referred to impact tube ( $d/U\tau$ );
- $K_N$ —non-dimensional constant of flow referred to nozzle ( $l/U\tau$ );
- $\epsilon'$ —excess of internal energy over that of equilibrium at the translational temperature (non-dimensional);
- $\Delta S'$ —non-dimensional entropy increase;
- $r$ —radius of nozzle cross section;
- $x$ —distance along nozzle axis;
- $T$ —temperature;
- $\lambda$ —constant ( $\frac{du'^2}{dt'}$ ) (non-dimensional);
- $\nu$ —kinematic viscosity;
- $\delta^*$ —boundary-layer displacement thickness.

#### Measurements of Heat-Capacity Lag for Gases with Long Relaxation Times by Means of a Nozzle of Special Design

In the measurements of heat-capacity lag of gases with the apparatus shown in Fig. 5 of reference 1, a nozzle is employed in which the gases expand and accelerate before meeting the impact tube. If the relaxation time of a gas

<sup>8</sup> L. Küchler, Zeits. f. physik. Chemie **41**, 199 (1938).

<sup>9</sup> P. W. Huber, NACA Technical Note No. 1024 (1946).



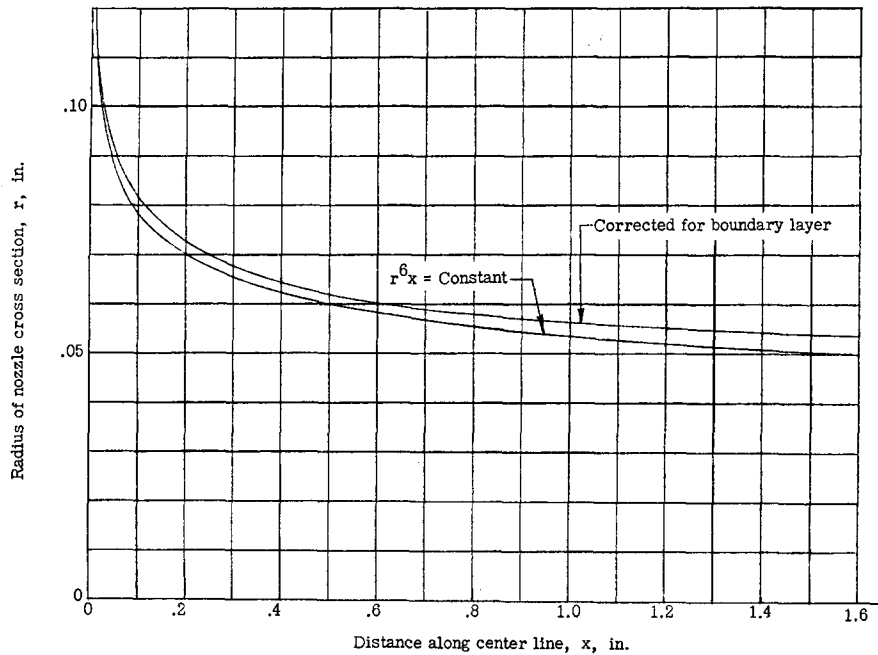


FIG. 7. Shape of nozzle, radius against distance along center line. Boundary-layer correction was computed as explained in the appendix.

is long enough to be of the same order as the expansion time through this nozzle, an entropy increase occurs in the nozzle. For ease of calculation, the nozzle used in these tests was so designed that

$$\frac{du^2}{dt} = \text{constant.} \quad (1)$$

The shape of a nozzle, of circular cross section, to meet the condition of Eq. (1) can be readily found if low velocity flow—that is, constant density—is assumed. When the velocity is assumed constant across the cross section, continuity yields

$$ur^2 = \text{constant.} \quad (2)$$

Also,

$$u dt = dx. \quad (3)$$

Combining Eqs. (1) to (3) gives

$$r^6 x = \text{constant.} \quad (4)$$

Equation (4) must be corrected for the presence of a boundary layer along the walls of the nozzle. The displacement thickness of this boundary layer—that is, the distance the streamlines just outside the boundary layer are displaced by its presence—can be found by standard methods.<sup>10</sup> It was assumed that this boundary layer would be laminar. Equation (1) of reference 10 was thus used to calculate the displacement thickness. This equation is an approximate formula for the laminar boundary-layer displacement thickness and is given as

$$\delta^* = 1.73 \sqrt{\frac{\nu s}{U}},$$

<sup>10</sup> A. E. von Doenhoff, NACA Technical Note No. 671 (1938).

where

$$s = \int_0^x \left( \frac{u}{U} \right)^{8.17} dx.$$

For these calculations  $\nu/U = 2.7 \times 10^{-5}$  cm was used. The distance  $\delta^*$  was then added to the nozzle radius. The radius of the nozzle cross section is plotted against the distance along the center line in Fig. 7.

We will now calculate the entropy increase in a nozzle of this design. It can be shown from definition that  $\lambda = \frac{3}{2}$ . From Eq. (11) of reference 1,

$$\epsilon' = \exp(-K_N t') \times \left( \int_0^{t'} \frac{2}{3} \exp(K_N t') dt' + \text{constant} \right),$$

where  $t' = 0$  is taken at the start of the expansion when  $\epsilon' = 0$ . The constant is then zero and integration yields

$$\epsilon' = \frac{2}{3K_N} [1 - \exp(-K_N t')]. \quad (5)$$

From Eq. (16) of reference 1 for the change in entropy as  $t'$  changes from 0 to  $t'_{\max}$

$$\begin{aligned} \Delta S' &= 2K_N \int_0^{t'_{\max}} \epsilon'^2 dt' \\ &= 2K_N \frac{4/9}{K_N^2} \int_0^{t'_{\max}} [1 - \exp(-K_N t')]^2 dt'. \end{aligned}$$

From Eq. (1), the non-dimensional time  $t'_{\max}$  for the gas to pass through the nozzle is  $\frac{1}{\lambda} = \frac{3}{2}$ ; hence,

$$\begin{aligned} \Delta S_N' &= \frac{4}{3K_N} - \frac{16}{9K_N^2} [1 - \exp(-\frac{3}{2}K_N)] \\ &\quad + \frac{4}{9K_N^2} [1 - \exp(-3K_N)]. \end{aligned}$$

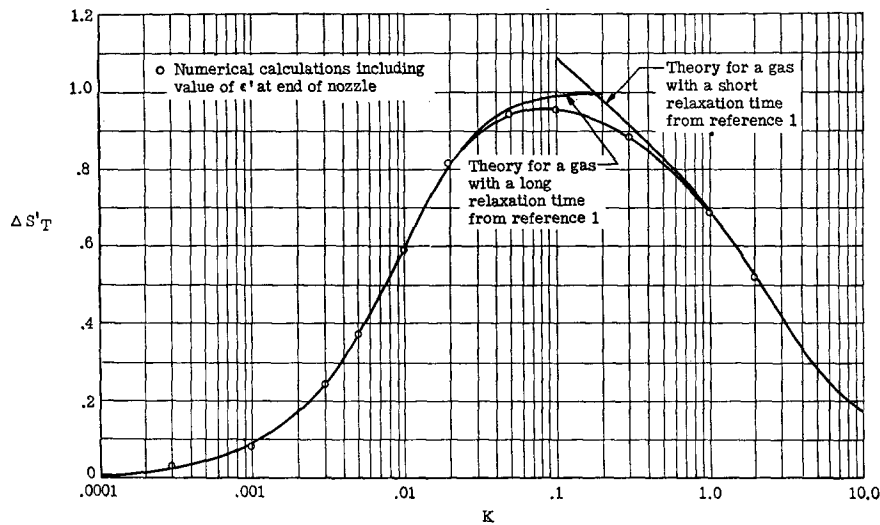


FIG. 8. The total non-dimensional entropy increase in nozzle and impact tube,  $\Delta S'_T = \Delta S'_{\text{tube}} + \Delta S'_N$ ;  $K = d/U\tau$ ;  $K_N = 94.1 \times K = (l/d)K$ .

This entropy increase in the nozzle must be added to the increase at the impact tube in order to obtain the total entropy increase in an expansion through a nozzle of this type, followed by a compression at the nose of a source-shape impact tube.

For the calculations of the entropy increase at the impact tube in reference 1, it was presumed that  $\epsilon' = 0$  initially. This assumption does not hold, however, for a gas with a long relaxation time which has reached a non-equilibrium condition at the end of the nozzle; consequently, the equations of reference 1 must be modified to fit this case as follows: In Eq. (22) of reference 1, for the variation of  $\epsilon'$  with time at the impact tube, the constant was zero because  $\epsilon'$  was assumed zero before compression. For a gas with a long relaxation time, the constant becomes Eq. (5) with  $t' = \frac{2}{3}$ , which is the value of  $\epsilon'$  at the end of expansion. This assumes that the impact tube is placed so close to the end of the nozzle that compression starts immediately after the gas leaves the nozzle. Equation (22) of reference 1 now becomes

$$\epsilon'(t') = -\exp(-Kt') \times \left[ \int_{t'_0}^{t'} 16u'^2(1-u')^{\frac{1}{2}} \exp(Kt') dt' - \frac{2}{3K_N}(1 - \exp[-\frac{2}{3}K_N]) \right]. \quad (6)$$

By integrating Eq. (6) by Simpson's rule and Eq. (16) of reference 1 by the planimeter, both between  $t' = 0$  and  $t' = \infty$ , the entropy increase in the compression at the impact tube is obtained for a gas with any relaxation time. The total entropy increase becomes

$$\Delta S'_T = \Delta S'_{\text{tube}} + \Delta S'_N,$$

which is plotted against  $K$  in Fig. 8 and compared with the theory of reference 1.

### Experimental Methods and Apparatus Details

It is apparent that the accuracy with which total-head defects caused by heat-capacity lag can be measured,

depends to a great extent on how well total-head defects caused by other factors can be eliminated. It might be helpful to list several sources of other effects on the total-head, and their method of elimination for the convenience of those intending to apply this measurement technique. The apparatus used in these experiments is essentially that shown in Fig. 5 of reference 1.

In constructing the apparatus, it is important to guard against high turbulence levels in the chamber which result in total-head defects. We found that these effects could be greatly reduced by the provision of two 200-mesh screens spaced 1 inch apart. Care must be taken to insure that the screens cover the whole chamber so that no jets, for example, are formed around the edges. The gas should be let into the chamber through small orifices which tend to smooth out fluctuations in the chamber pressure, which would otherwise lead to unsteadiness of the alcohol manometer. It is important to insure that no temperature differences exist in the gas, or between the gas and the chamber. Our practice was to run the gas around the chamber in spaces provided by two or three concentric liners, and further, to measure the temperature of the chamber and of the incoming gas, and to equalize these two temperatures by varying the electric heater currents. The nozzle, of course, should be made very smooth and the entrance should be well faired to the top of the chamber.

The technique for grinding the impact tube is essentially the same as that reported in reference 1, but perhaps it might be well to point out here that it is important that the end of the impact tube be flat and free from nicks.

The impact tube must be accurately aligned with the jet. It is convenient to provide an adjustment mechanism which keeps the end of the impact tube centered in the jet, while permitting the adjustment of its alignment in two perpendicular planes. A gas, such as nitrogen at room temperature, which shows no total-head defects caused by

heat-capacity lag, should be used for this adjustment. While the nitrogen is flowing through the apparatus, the alcohol manometer is observed through a microscope and the impact tube is then adjusted for minimum total-head defect. It is important to keep the impact tube carefully centered in the jet, especially when working with gases, such as hydrogen, having a high kinematic viscosity which results in thick nozzle boundary layers.

For the measurements of steam, an ethyl phthalate manometer was used. The manometer was heated to above the boiling point of steam to prevent condensation which

would produce spurious pressure readings. It was necessary to find the zero position of this manometer while a small flow of steam was going through the apparatus, because temperature differences occurred when no steam was flowing. It has been found that this procedure of taking zero readings with a small flow of gas generally gives more consistent results also in measurements of other gases.

When all of these adjustments are properly made, it is possible to reduce the total-head defect to about 0.002 percent of the dynamic pressure, using room temperature nitrogen.

## A Relation Between Bond Order and Covalent Bond Distance

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A relation between covalent bond distance and bond order of the form  $R = R_1[2/3 + 1/3 \times (n - 1/n + 1)^{p/2}]$  is proposed and tested against the available experimental data. A suitable expression for all covalent bond distances between atoms of the first row of the periodic table of the form  $R = Z - A/Z - B[2/3 + 1/3(1/3)^{p/2}]$  is also proposed. The agreement between calculated and observed values is well within the limits of the experimental errors.

A GREAT number of measurements of the CC bond distance<sup>1</sup> in different molecules show that it may have any value intermediate between 1.55Å, the single bond distance, and 1.205Å, the triple bond distance. These intermediate bond distances have been discussed on the basis of a quantum-mechanical treatment by Lennard-Jones,<sup>2</sup> Penney,<sup>3</sup> and Coulson.<sup>4</sup> These authors have introduced the concept of bond order, designated by  $p$ , where  $p$  is defined as zero for a single bond, one for a double bond, and two for a triple bond, and may have any intermediate value for bonds of so-called fractional order. In molecules such as benzene and naphthalene, for example, where the electrons are considered to be non-localized or mobile the links have intermediate lengths<sup>1</sup> corresponding to bonds of fractional order. In their papers the above

authors have calculated the bond orders of various links by the method of molecular orbitals and also by the bond pair method; practically identical values are obtained. From their definition of  $p$  which depends linearly on the interaction energy, values for the bond energies, and thus for the resonance energy, may be calculated. Also, as Coulson<sup>4</sup> points out, vibrational frequencies may be estimated.

Lennard-Jones<sup>2</sup> and Coulson<sup>4</sup> have derived a relation for the length of a link of order  $p$  in the form

$$R_p = R_1 - \frac{R_1 - R_2}{1 + \left(\frac{1-p}{p}\right) \frac{K_1}{K_2}}, \quad (1)$$

where  $R_p$  is the length of the link of order  $p$ ;  $R_1$  is the length of the link of order  $p=0$ , i.e., the single bond distance;  $R_2$  is the double bond distance; and  $K_1$ ,  $K_2$  are the single and double bond force constants, respectively.

Kavanau<sup>5</sup> has proposed an empirical relation

<sup>5</sup> J. L. Kavanau, *J. Chem. Phys.* 12, 467 (1944).

<sup>1</sup> J. M. Robertson, *J. Chem. Soc.* 131 (1938). L. R. Maxwell, *J. Opt. Soc. Am.* 30, 374 (1940).

<sup>2</sup> J. E. Lennard-Jones, *Proc. Roy. Soc. London* A158, 280 (1937).

<sup>3</sup> W. G. Penney, *Proc. Roy. Soc. London* A158, 306 (1937).

<sup>4</sup> C. A. Coulson, *Proc. Roy. Soc. London* A169, 413 (1939).