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HEAT-CAPACITY LAG IN TURBINE-WORKING FLUIDS

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SUMMARY

Gases require a finite time - the relaxation time - to adjust the vibrational part of their internal energy to a change in temperature. If changes in temperature occur in gas flow in times of the order of or shorter than the relaxation time, entropy increases occur. In order to evaluate partially the importance of these heat-capacity lags in turbines, the relaxation times of steam and nitrogen have been studied by the total-head-defect method.

The relaxation time of steam was found to be of the order of 3×10^{-8} second. It would be expected from this result that the vibrational heat capacity of steam would adjust to most of the temperature changes in engineering practice rapidly enough that little dissipation would be anticipated. Water vapor is known to be an efficient catalyst for combustion processes and the rapid adjustment of vibrational heat capacity may be important in its catalytic actions.

Adjustment of the vibrational heat content of nitrogen to a change in temperature was found to be a slow process and principally dependent on the action of impurities. Measurements were made of mixtures of steam with nitrogen and it was found that about 1 collision in 30,000 between steam and nitrogen molecules is effective in adjusting the vibrational heat content of nitrogen. Nitrogen at 1100° F absolute with 3 percent water vapor thus would have a relaxation time of 1.5×10^{-4} second at atmospheric pressure so that heat-capacity lag in nitrogen should be considered in the design of gas turbines.

INTRODUCTION

Turbine-working fluids such as steam, air, and exhaust gas have appreciable vibrational heat capacity at

high temperatures.   If these gases have relaxation times
of the order of or shorter than the intervals during
which temperature changes occur in the gas, losses attrib-
utable to heat-capacity lag must be anticipated.   Unfortu-
nately no measurements of the relaxation times of the
most important turbine-working fluids have previously been
made.   Measurements of the relaxation time of steam and
nitrogen are reported in the present paper.

The measurements were made by the total-head-defect
method, which was introduced in reference 1 and has been
herein extended to permit measurement in gases with long
relaxation times.

The symbols used throughout the present paper are
defined in appendix A.

TEST METHODS

A drawing of the basic apparatus used to obtain the
measurements presented herein is shown in figure 9 of
reference 1 and the apparatus is described in detail on
page 21 in reference 1.   An outer lining on the chamber
and fine-mesh screens inside the chamber were incorporated
in the apparatus used in these experiments.   An electric
boiler and superheater were constructed which produced
enough steam for an hour's run.   A heated manometer
system was used in the steam measurements to avoid con-
densation difficulties.   The boiler was also used to add
water vapor to the nitrogen and a dew-point instrument was
used during the nitrogen tests to measure the water-vapor
content.

The steam boiler was scrubbed and cleaned a number
of times 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 two-thirds of the steam
generated was used in these experiments.   Gases insoluble
in water were found in the steam to about one part in a
million.

The nitrogen used was commercial dry, 99 percent pure,
obtained in high-pressure cylinders.   Analysis of a
sample of this nitrogen showed that it contained less than
0.1 percent oxygen and less than 0.25 percent carbon
dioxide.   Passage of the gas through the dew-point instru-
ment indicated that roughly 0.05 percent water vapor was
present.

HEAT-CAPACITY LAG IN STEAM

Total-head defects of steam were measured at three
different temperatures and with two impact tubes over a
range of chamber pressure. The total-head defects
measured are plotted against chamber pressure in figures 1
and 2. The heated total-head-defect manometer used made
it difficult to obtain an accurate zero reading. The
zero readings were therefore obtained by extrapolating
the experimental curve to zero chamber pressure. The
results obtained are compared with the theory of refer-
ence 1 in figures 1 and 2. It will be seen from fig-
ure 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
steam 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 theory of total-head defects due to compressions at
the nose of an impact tube (reference 1). By choosing
three typical experimental points, the relaxation times
shown in figure 3 were found. By using these experi-
mental values of relaxation time and the theory of refer-
ence 1 and presuming that the collisions responsible for
the adjustment of vibrational energy are bimolecular
(collisions involving two molecules; relaxation time τ
inversely proportional to pressure), the theoretical total-
head defects shown in figures 1 and 2 were computed. The
agreement of the theoretical variations with chamber pres-
sure and impact-tube diameter and these measurements may
be taken as an index of the accuracy of these results,
which is probably of the order of ±20 percent for relaxa-
tion time. Inasmuch as the steam employed probably had
only slight impurities and the adjustment involved only a
few hundred collisions per molecule, these measurements
may be presumed representative of pure steam. Some
experimental relaxation times for steam are shown in
table I. It can be seen that a very short time - of the
order of 3×10^{-8} second - is required for adjustment.
The catalytic action of steam may be partly attributed to
this rapid interchange of energy.

The results shown in figures 1 and 2 are next com-
pared with the theory of Landau and Teller (reference 2).
This theory indicates that the logarithm of the number of
collisions necessary to transmit a vibrational quantum is

inversely proportional to the cube root of the absolute
temperature T.   The number of collisions required for

the relaxation of steam is plotted against $T^{-\frac{1}{3}}$ in
figure 4.   The results presented herein as well as those
of other recent investigations (see reference 1) have
been shown to fit the theory of reference 2 within experi-
mental accuracy.

HEAT-CAPACITY LAG IN NITROGEN

Total-head defects of nitrogen were measured at
different temperatures over a range of chamber pressure
with essentially the same apparatus as for the measure-
ments with steam.   No change in total-head defect was
found with change of diameter of the impact tube.   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 total-head defects were there-
fore computed for a flow of this type by extending the
theory of reference 1.   This calculation is reported in
appendix B and was used to find the relaxation time of
nitrogen.

The relaxation times measured for commercial nitrogen
and nitrogen with various amounts of added water vapor
are shown in table I.   It can be seen that, for the
relatively pure gas, a time longer than 0.005 second is
required whereas, in a steam and nitrogen mixture,
about 1 collision in 30,000 between steam and nitrogen
molecules is effective.   Nitrogen at 1100° F absolute
with 3 percent water vapor therefore would require

about 1.5×10^{-4} second at atmospheric pressure to adjust
its vibrational heat capacity.   It can also be seen that
the addition of water vapor shortens the relaxation time
by a factor roughly proportional to the amount added.
As has been observed with some other gases (reference 3),
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.

A short investigation was made to determine whether carbon dioxide in the presence of water vapor is an effective catalyst for the transformation of the vibrational energy of nitrogen into translational energy. The speculation was introduced by Mr. L. R. Turner of the Aircraft Engine Research Laboratory and was based on the fact that the frequency of one of the vibrational modes of CO_2 and that of nitrogen are about in resonance. Total-head defects were obtained with a 1.5-inch nozzle and 0.060-inch impact tube on a mixture of nitrogen with 3-percent water-vapor content at a temperature of about 800° F. Amounts of CO_2 up to 5 percent were added to this mixture and only small changes (less than one-twentieth of the defect) were noted. In a mixture of this kind, CO_2 is therefore considered to have only a small effect on the relaxation time of nitrogen.

APPLICATIONS

The long relaxation time found for nitrogen means that the vibrational energy of this gas lags behind the rapid temperature changes which occur in many engineering applications. As an illustration of the type of effect to be anticipated, the expansion of a mixture of hot gases through a converging-diverging nozzle from a pressure of 4 atmospheres to a pressure of 0.5 atmosphere has been analyzed. The mixture is composed of 70 percent air and 30 percent exhaust gas and components other than water vapor are assumed to have no effect on the relaxation time of nitrogen. (CO_2 has been shown to have little effect.) The relaxation times of the components other than nitrogen are assumed to be zero. In order to simplify the calculations, the nozzle was assumed to be so designed that the translational temperature decreased linearly with time. The translational and vibrational temperatures found are plotted against time in figure 5. (Translational temperature is defined as the temperature that would be measured in the gas at equilibrium having the same amount of translational kinetic energy. Vibrational temperature is defined as the temperature that would be measured in the gas at equilibrium having the same amount of vibrational energy.) It is seen that very little adjustment of the vibrational heat capacity occurs in the nozzle. The nozzle is 0.1 foot long, its area ratio in the diverging part is designed for an 8:1 expansion

ratio when isentropic flow is presumed, and the initial
temperature is 2460° F absolute.

The results of approximate calculations are presented .
in the following table:

	Losses in mechanical energy available (percent)	Pressure ratio across nozzle	Mass flow (slugs/sec/sq ft)	Velocity at nozzle exit (fps)
Isentropic flow	0	8	2.76	3723
Flow including heat-capacity lag	2	8.40	2.79	3712

CONCLUSIONS

The vibrational heat capacity of steam was found to
be adjusted very rapidly by bimolecular collisions in the
gas. A few hundred collisions per molecule or a time of
the order of 3×10^{-8} second is required. The rapidity
of this adjustment means that the vibrational heat capa-
city of steam follows the temperature changes in most
flow processes. This rapid interchange may be important
in the catalytic actions of steam.

The vibrational heat capacity of nitrogen was found
to be adjusted only slowly in the pure gas, a time longer
than 0.005 second being required. The adjustment is
materially accelerated by the presence of water vapor,
about 1 collision in 30,000 between steam and nitrogen
molecules being effective. Nitrogen at 1100° F absolute
and atmospheric pressure with a 3-percent water-vapor
content would have a relaxation time of 1.5×10^{-4}
second. The water vapor in exhaust gas thus does not

accelerate the adjustment of nitrogen enough that its
vibrational heat capacity can follow the rapid tempera-
ture changes in the flow through the gas turbines.

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APPENDIX A

SYMBOLS

l nozzle length

d diameter of impact tube

U final velocity in nozzle

u velocity

u' nondimensional velocity (u/U)

t time

t' nondimensional time $\left(\dfrac{t}{l/U} \text{ or } \dfrac{t}{d/U}\right)$

τ relaxation time at average temperature and pressure of flow

K nondimensional constant of flow referred to impact tube $(d/U\tau)$

K_N nondimensional constant of flow referred to nozzle $(l/U\tau)$

ϵ' excess of internal energy over that of equilibrium at the translational temperature (nondimensional)

$\Delta S'$ nondimensional entropy increase

r radius of nozzle cross section

x distance along nozzle axis

T temperature

APPENDIX B

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 figure 9 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 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

$$\frac{du^2}{dt} = \text{Constant} = \lambda \tag{1}$$

The shape of a nozzle, of circular cross section, to meet the condition of equation (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

$$ur^2 = \text{Constant} \tag{2}$$

Also,

$$u\,dt = dx \tag{3}$$

Combining equations (1) to (3) gives

$$r^6x = \text{Constant} \tag{4}$$

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 the methods of reference 4. It was assumed that this boundary layer would be laminar. Equation (1) of reference 4 was thus used to calculate the displacement thickness. By assuming typical flow conditions, this distance was then added to the nozzle radius. The radius of the nozzle cross section is plotted against the distance along the center line in figure 10 of reference 1.

The entropy increase in a nozzle of this design is now calculated. It can be shown from definition that $\lambda = 2/3$. From equation (11) of reference 1,

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

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

$$\epsilon' = \frac{2}{3K_N}\left(1 - e^{-K_N t'}\right) \tag{5}$$

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

$$\Delta S' = 2K_N \int_0^{t'_{max}} \epsilon'^2\, dt'$$

$$= 2K_N \frac{4/9}{K_N^2}\int_0^{t'_{max}}\left(1 - e^{-K_N t'}\right)^2 dt'$$

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

$$\Delta S'_N = \frac{4}{3K_N} - \frac{16}{9K_N^2}\left(1 - e^{-\frac{3}{2}K_N}\right) + \frac{4}{9K_N^2}\left(1 - e^{-3K_N}\right)$$

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
nonequilibrium condition in the nozzle; consequently, the
equations of reference 1 must be modified to fit this
case as follows: In equation (22) of reference 1, for
the variation of ϵ' with time at the impact tube, the
constant was zero because ϵ' was assumed zero before
compression.   For a gas with a long relaxation time,
the constant becomes equation (5) with $t' = 3/2$, which
is the value of ϵ' 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

$$\epsilon'(t') = -e^{-Kt'}\left[\int_{t_0'}^{t_1'} 16u'^2(1-u')^{\frac{3}{2}} e^{Kt'}dt' - \frac{2}{3K_N}\left(1 - e^{-\frac{3}{2}K_N}\right)\right] \quad (6)$$

By integrating equation (6) by Simpson's rule and
equation (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

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

which is plotted against K in figure 6 and compared with
the theory of reference 1.

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     Gas Dynamics.   NACA ARR No. 4A22, 1944.

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     the Position of the Laminar Separation Point.
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TABLE I.- EXPERIMENTAL RELAXATION TIMES OF STEAM AND NITROGEN

Type and per-cent of impurities in gas	Diam. of impact tube (in.)	Temperature (°F abs.)	Relaxation time at 1 atm, τ (sec)	Molecular collisions re-quired for adjustment	Type of collision considered effective for adjustment
Steam					
Negligible	0.017	874	3.7×10^{-8}	4×10^2	Bimolecular
Do----	.017	1053	2.6	2.6	Do.
Do----	.030	1053	3.1	3.1	Do.
Do----	.017	1271	2.1	1.9	Do.
Nitrogen					
0.05 H$_2$O	0.060	1001	5.9×10^{-3}	[a]3.1×10^7	Bimolecular
.05	.060	1224	2.9	[a]1.4	Do.
.05	.060	1236	2.7	[a]1.3	Do.
.05	.060	1250	3.4	[a]1.6	Do.
.05	.060	1370	2.6	[a]1.2	Do.
.7	.060	1009	6.2×10^{-4}	3.0×10^4	N$_2$ with H$_2$O
1.0	.060	1281	3.9	2.5	Do.
1.3	.060	1008	3.5	3.5	Do.
1.4	.060	1277	2.8	2.7	Do.
1.4	.017	1319	2.6	2.4	Do.
2.0	.017	1034	2.3	3.4	Do.
3.0	.017	1275	1.4	2.9	Do.
3.5	.017	744	1.2	3.6	Do.

[a]Adjustment computed as due to collisions of nitrogen with nitrogen even though it is thought that small amount of water vapor present was important.

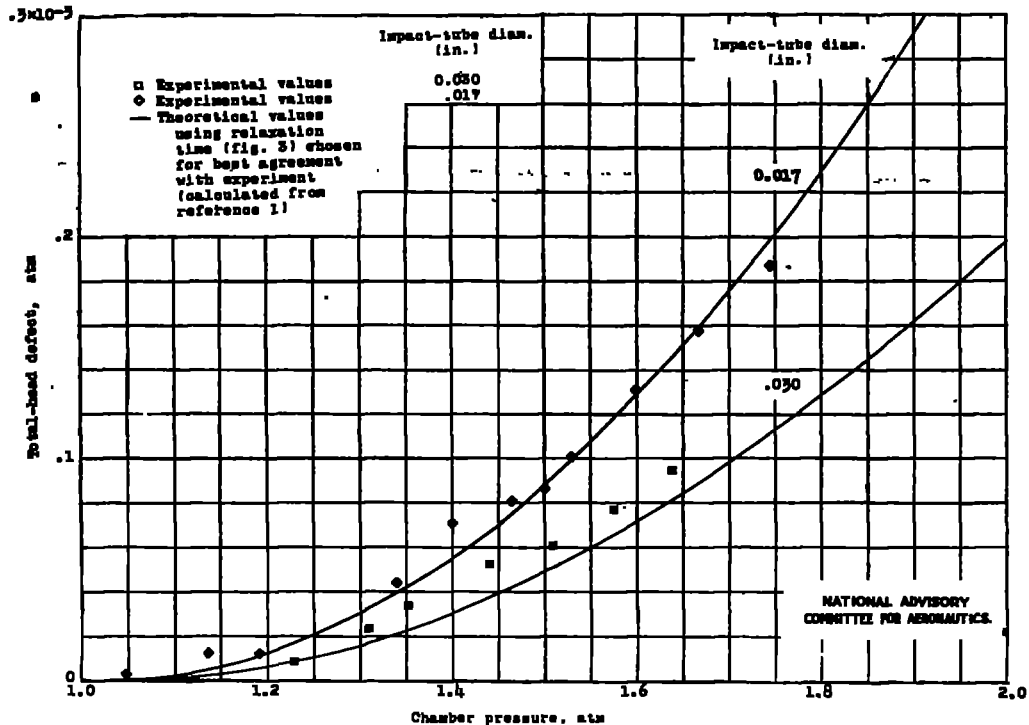NATIONAL ADVISORY
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Figure 1.- Total-head defect of steam, theoretical and experimental.
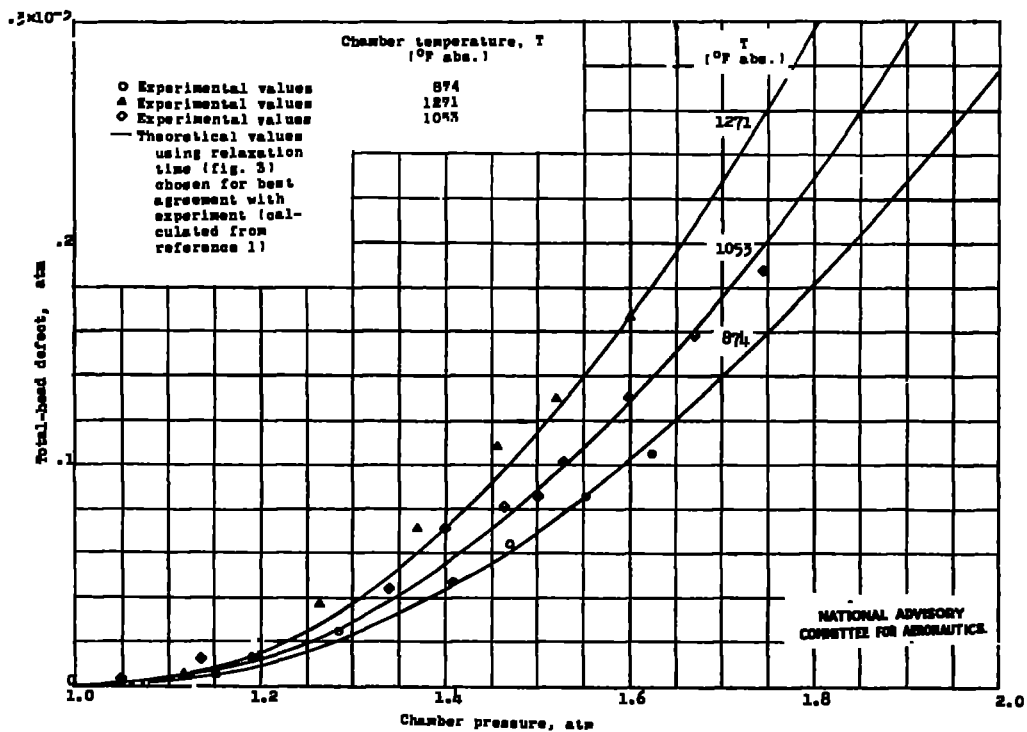Chamber temperature. 1053° F absolute.

Figure 2.- Total-head defect of steam, theoretical and experimental.
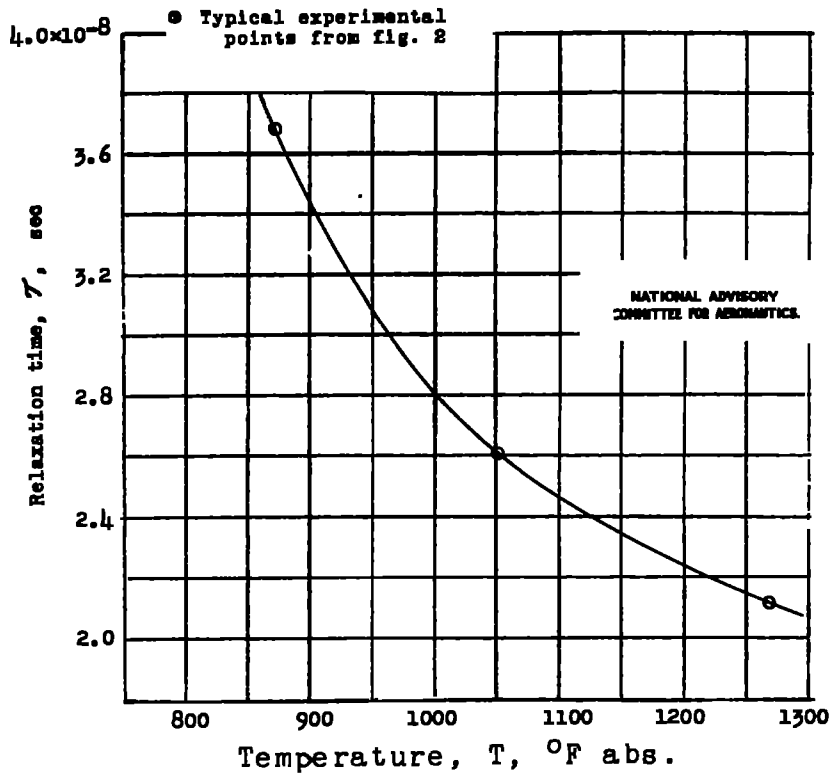Impact-tube diameter, 0.017 inch.

Figure 3.- Temperature variation of the relaxation time of steam (1 atm) chosen to give best agreement with measured total-head defects.
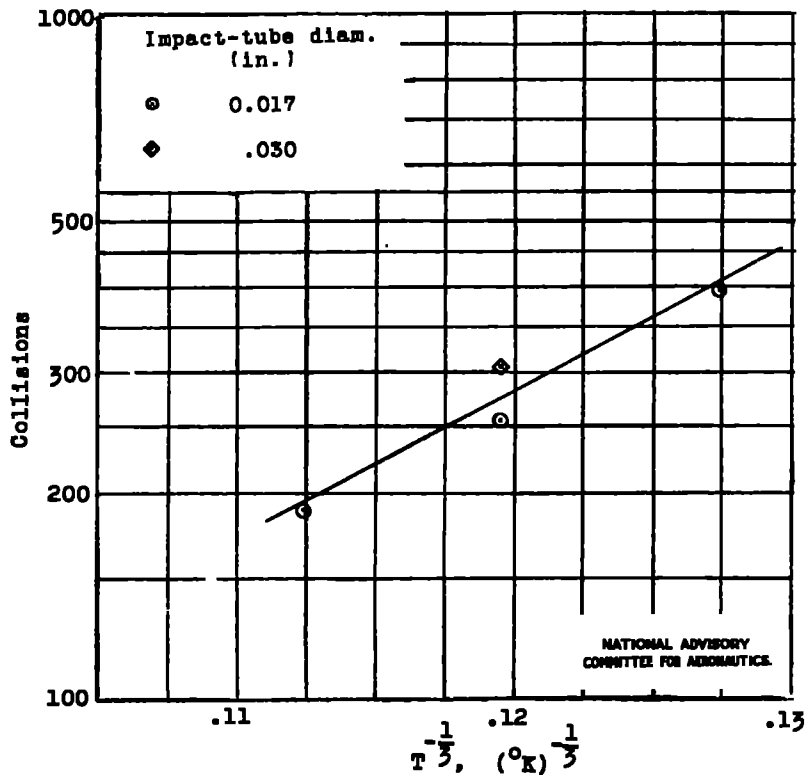

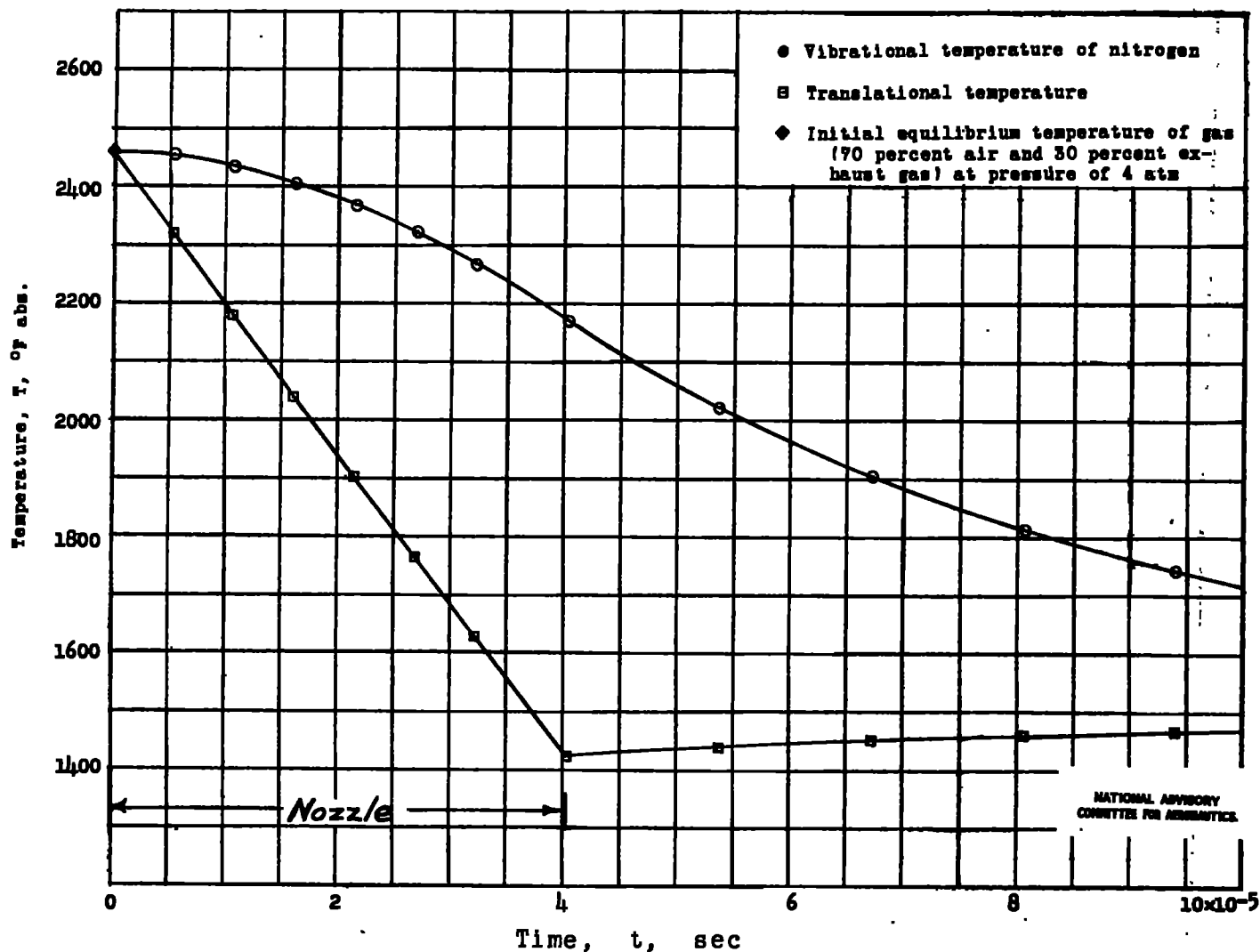Figure 4.- Measurements of the relaxation time of steam.

Fig. 5

Figure 5.- Theoretical departure of vibrational temperature of nitrogen from translational temperature in the flow of exhaust gas through a 1.2-inch nozzle having an 8:1 expansion ratio.
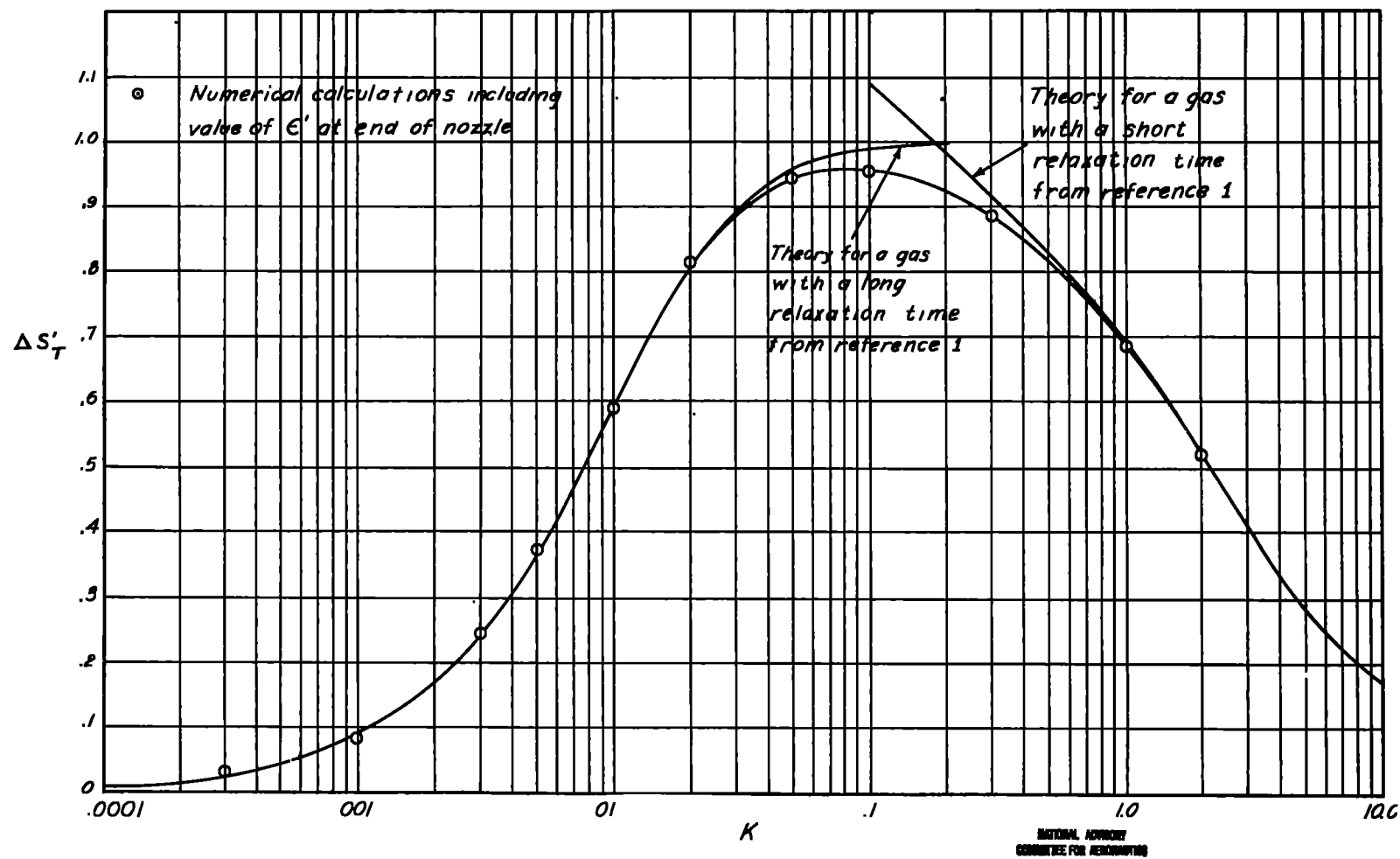
Fig. 6

Figure 6 - The total nondimensional entropy increase in nozzle and impact tube. $\Delta S'_T = \Delta S'_{tube} + \Delta S'_N$; $K = \frac{d}{UT}$; $K_N = 94.1 K = \frac{1}{d} K$.