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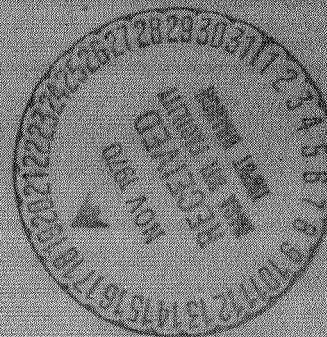
VIBRATIONAL RELAXATION MEASUREMENTS OF CARBON MONOXIDE IN A SHOCK-TUBE EXPANSION WAVE

T. Ian McLaren and John P. Appleton

May 1970

FLUID MECHANICS LABORATORY

DEPARTMENT OF MECHANICAL ENGINEERING

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

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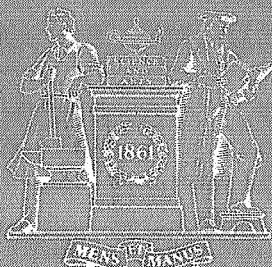
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Department of Mechanical Engineering
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ABSTRACT

A novel technique has been developed for use in the study of collisional energy transfer and chemical reaction rates in rapidly cooled gases. The principle feature is that the shock heated test gas sample is stationary during the cooling process so that the temporal behavior of a particular nonequilibrium property may be continuously monitored. The technique has been applied to the measurement of the vibrational de-excitation rate of carbon monoxide in an argon heat bath, using the fundamental infrared emission band of CO to follow its vibrational temperature throughout the expansion. In contrast to a number of recent reports indicating enhanced vibrational de-excitation rates for some diatomic molecules, the present experiments clearly indicate that the characteristic vibrational relaxation time of carbon monoxide in argon is the same no matter whether it is measured in a compression (shock wave) or expansion environment.

1. INTRODUCTION

This paper describes the development and initial operation
of a novel experimental method for use in the study of collisional
energy transfer and chemical reaction rates in rapidly cooled gases.
The principle feature of the method is that the shock heated test
gas sample is stationary during the cooling process so that the temporal
behavior of a particular non-equilibrium property may be continuously
monitored. Furthermore, the rate of cooling is a variable at the dis-
posal of the investigator.

In studies of collisional energy transfer in thermal systems at
high temperatures, the shock tube has been the most commonly used
apparatus for providing the required high temperature environment.
Observations have usually been made behind the incident or reflected
shock waves so that the rate determinations were made under conditions
where the predominant collision processes were those of excitation.
In many practical problems however, collisional de-excitation is the
process of major interest.

The desire to make pertinent de-excitation rate measurements to
complement the relatively large body of excitation rate data has long
been recognised. The scarcity of such data emphasizes the lack of a
generally acceptable experimental method. No counterpart to the relatively
simple one-dimensional flow produced behind a plane shock wave has been
devised to study these processes. In this paper we report the develop-
ment and initial operation of such an experimental method, and present
results of measurements made on the rate of vibrational de-excitation of
carbon monoxide highly diluted in argon.

In contrast to some earlier reports,[1,2] our results indicate no clear discrepancy between measurements of the rate of vibrational relaxation of carbon monoxide in argon obtained from shock wave experiments, and those obtained in an expanding flow environment.

2. EXPERIMENTAL APPARATUS

The experimental method which we have adopted to study vibrational de-excitation represents a development of a technique described by Jacobs, Hartunian, Geidt and Wilkins.[3] In their experiment a shock wave was reflected from the end wall of a shock tube to produce a stagnant gas in a state of thermochemical equilibrium. When the reflected wave passed a cylindrical diaphragm mounted flush with the inside diameter of the tube, the increased pressure behind the reflected wave caused the cylindrical diaphragm to burst, thus exposing the shock treated test gas to a vacuum chamber mounted outside the tube. The diaphragm opening resulted in an unsteady expansion wave which propogated into the test gas. Optical observations of the expanding gas were made across the tube close to the end wall where the time varying pressure profile was recorded using Kistler pressure transducers. Jacobs et al. reported some preliminary recombination rate measurements which were made using a dilute mixture of chlorine in argon. Although these appeared to prove the general utility of the technique, no subsequent work using this method has been reported.

The method as described above was subject to two drawbacks which limited its range of application. The closest distance of the cylindrical diaphragm to the observation position was restricted by the requirement that the expansion wave became one-dimensional by the time it reached the end wall. Since the magnitude of the pressure gradient decreases with distance from the origin in unsteady expansion waves, this minimum distance requirement set an upper limit to the cooling rate which could

be achieved. In addition, the overall expansion ratio which was obtained appeared to be about 2:1 which, for a gas consisting primarily of argon, only provided about a 20% reduction in the bulk gas temperature.

Our present facility consists of a new expansion assembly which couples on to the end of a 3 in. bore stainless steel shock tube. The shock tube is a conventional pressure driven device and has been previously described in the literature.[4] The whole system can be evacuated to 10^{-6} torr, with a typical degassing and leak rate equivalent to a rate of pressure rise somewhat less than 10^{-4} torr/minute. Helium was used as the driver gas.

A plan view of the expansion assembly is shown in Fig. 1. It consists of a 5 cm. square channel (A), about 30 cm. long, which is designed to allow the central core flow behind the primary shock wave to enter with minimal flow disturbance. The shock tube boundary layers thus spill out into the annular dump tank (B). There are two apertures, placed exactly opposite to one another, which are cut in the side walls of the channel toward its downstream end. The length of the apertures is determined by the replaceable inserts (C), which support secondary diaphragms mounted flush with the channel walls. The maximum aperture length is 15 cm. and the width of the apertures is 5 cm., i.e. they extend over the full channel width. These apertures allow open access from the channel into two expansion chambers (E_1, E_2) mounted on the side walls. The position of the end plug can be adjusted axially to locate at various positions downstream from the diaphragms.

The assembly is completely symmetrical about the vertical plane which contains the axis of the tube. Lithium fluoride windows are

positioned so that optical observations can be made across the channel, along the stagnation line close to the end wall. In operation, the secondary diaphragms (0.00025-0.0005 in. Mylar) were strong enough to withstand the pressure behind the incident shock wave but ruptured when subjected to the increased pressure behind the reflected shock. The subsequent rate of expansion at the end wall was measured using a flush mounted Kistler type 603L pressure transducer. Adequate time was allowed for the test gas to reach thermodynamic equilibrium before the arrival of the expansion waves by adjustment of the position of the end wall relative to the apertures. Pressure reduction ratios greater than 5:1 were consistently obtained within a time period of about 250 μsec, thus yielding cooling rates in excess of 10^7 $^\circ$K sec^{-1} and reductions in bulk gas temperature of about a factor of 2.

In our experiments, the vibrational temperature of the carbon monoxide was deduced by monitoring the infrared emission intensity of the CO fundamental band centred at 4.65μ. This was measured using a fast response indium-antimonide photovoltaic detector which, together with an interference filter, provided an effective pass band covering the spectral range from 4.0-5.5μ. Observation of the entire fundamental band ensured that the measured intensity was independent of changes in rotational temperature.[5] The performance of the detector, i.e. linearity of response and responsivity, was optimised by using a Perry type 720 current amplifier which allowed the detector to operate close to its ideal short circuit condition.

A collimation system consisting of suitably placed optical stops allowed the detector to view only the radiation emanating from a well

defined volume of gas in the vicinity of the stagnation line on the
end plug. The spatial resolution of the detector in both the axial
and lateral planes in the shock tube was less than 2 mm and the axis
of the collimation system was 2 mm in front of the plane of the end
wall.

The gas mixtures used in these experiments were prepared and
stored in stainless steel tanks at pressures of about five atmospheres.
The gases used were: argon, pre-purified grade supplied by Matheson,
with impurity concentrations < 20 ppm; carbon monoxide, research grade
supplied by Lif-O-Gen, batch analysis of which showed impurity levels
of 17 ppm oxygen, 5 ppm total hydrocarbons, and 260 ppm nitrogen.

3. CALIBRATION EXPERIMENTS

Before proceeding with the expansion experiments, subsidiary calibration tests were first carried out on both the infrared detection system and the pressure transducer.

A dynamic calibration of the pressure transducer in the shock tube using shock waves of known strength showed that its response sensitivity fell within the manufacturers specifications. In a second series of similar calibration tests, a 70 db per octave Tchebbycheff filter was used to damp out the high frequency (~300 Kc/s) microphony effects commonly observed when using this type of transducer. In addition, we found it necessary to place a light smear of vacuum grease on the exposed face of the transducer to eliminate heat transfer effects which distorted its response sensitivity.

A separate series of calibration experiments, with blank aluminum plates inserted in the expansion apertures, were carried out to measure the infrared emission intensity as a function of the temperature and the carbon monoxide concentration. Once such calibration record is shown in Fig. 2. This clearly illustrates the uniformity of the pressure and temperature in the vicinity of the end wall of the expansion assembly channel.

From records such as that shown in Fig. 2, the infrared emission intensity I, was found to closely follow the form expected for an optically thin system of harmonic oscillator molecules, viz.

$$I \alpha [CO]\{exp(\theta_v/T_v) - 1\}^{-1} \tag{1}$$

where [CO] is the carbon monoxide concentration, T_v is the vibrational
temperature, and θ_v the characteristic vibrational temperature of carbon
monoxide ($3090^\circ K$). Fig. 3 shows the results of the calibration experi-
ments as a plot of the infrared emission intensity per CO molecule
versus temperature. Comparison with the exact calculations of Young[6]
for the integrated fundamental emission intensity of carbon monoxide
showed that corrections due to anharmonicity of the molecule were not
important over the range of our experiments. In addition, detailed
estimates of the average absorption of the fundamental band for these
conditions, using the calculations of Young[6] and Plass,[7] confirmed
that our system was optically thin at all times.

By firing shocks into a pure argon test gas, it was possible
to determine the magnitude of any impurity radiation occuring within
our spectral pass-band. We found that after the system had been opened
to the atmosphere, for example, to replace the expansion assembly dia-
phragms, a subsequent shock fired into "pure" argon generated an apprecia-
ble level of radiation. However, after two, or at most, three shocks
had been fired without exposing the interior of the expansion assembly
to the atmosphere, the level of impurity radiation dropped below detectable
levels. Therefore, when preparing for an expansion experiment, support
plates were first fitted behind the newly inserted secondary diaphragms.
The requisite number of clean-up shocks were fired into pure argon until
no infrared output signal was detected, and the support plates were then
removed whilst maintaining a positive pressure of pure argon inside the
whole system. Subsequent firings into pure argon demonstrated that no
additional impurities had been introduced during the removal of the support
blanks.

4. EXPERIMENTAL RESULTS

Fig. 4 shows the pressure and infrared emission profiles recorded during an expansion experiment using a test gas consisting of 0.5% CO, 49.75% Ar and 49.75% He. It is evident from the infrared trace that vibrational equilibrium is fully established before the arrival of the expansion waves at the end wall. Since the enthalpy associated with the carbon monoxide represented a very small fraction of the total enthalpy of the mixture, the expansion at the end wall was assumed to be an isentropic process with $\gamma = 5/3$. Thus the measured pressure profile was used to compute the translational temperature and density profiles throughout the expansion. The vibrational temperature of the carbon monoxide was then calculated using Eq. (1). Fig. 5 shows the translational and vibrational temperatures thus determined. The error bar in Fig. 5 illustrates the maximum uncertainty in the measurement of T_v at the end of the expansion where the pressure and infrared signals are smallest.

For this test gas mixture and experimental condition, the vibrational temperature of the carbon monoxide should follow the varying translational temperature throughout the expansion, never lagging it by more than about 100 ^{o}K. This behavior is illustrated by the full line profile in Fig. 5 which was computed using the measured pressure profile and the vibrational relaxation rate data compiled by Millikan and White[8] from shock wave excitation experiments for CO-Ar, and CO-He systems. A number of such near-equilibrium expansion experiments were carried out over a range of conditions and it was found that, in general, the measured vibrational

temperature agreed to within 100 $^\circ$K of the translational temperature

throughout the expansions. The results of these near-equilibrium experiments

substantiate the view that our observations during the expansion were

made on a virtually stagnant gas sample having uniform properties along

the line of sight of the infrared detector.

The important results of our investigations were obtained from

a series of nonequilibrium expansion experiments conducted using test

gas mixtures of 0.25 and 0.5 mole per cent of carbon monoxide in argon.

A total temperature range from 4600 $^\circ$K to 1400 $^\circ$K was covered in which

the stagnation pressure varied between 0.5 and 2.5 atmos. Figs. 6-8

show representative results covering this range of conditions. As in

the near equilibrium experiments, the bulk gas temperature and density

were deduced from the measured pressure profiles by assuming isentropic

expansions, and the vibrational temperatures were derived from the infra-

red emission profiles. Again, the error bars illustrate the maximum

uncertainty in the measurement of T_v. The additional full-line profiles

in Figs. 6-8 illustrate the variation in the vibrational temperature

which was computed using the linear Laudau-Teller[9] vibrational relaxation

equation, viz.

$$\frac{dE(T_v)}{dt} = \frac{E(T) - E(T_v)}{\tau_v} \tag{2}$$

where $E(T_v)$ is the energy in the vibrational mode of the gas having

vibrational temperature T_v, and $E(T)$ is the equilibrium value correspond-

ing to the translational temperature of the gas, T. The characteristic

vibrational relaxation time, τ_v (sec), for the CO-Ar system was assumed

to be given by the empirical equation: [10]

$$\log(p\tau_v \phi_{CO-Ar}) = 101 \ T^{-1/3} - 11.45 \tag{3}$$

where p is the total pressure in atms. ϕ_{CO-Ar} is defined as the ratio of the characteristic vibrational relaxation time for carbon monoxide diluted in argon as measured in excitation (shock wave) experiments to that measured in expansion flow experiments.

It was found that for all of the expansions, the measured vibrational temperatures fell within bounds defined by $0.5 \lesssim \phi_{CO-Ar} \lesssim 1.5$, as illustrated in Figs. 6-8. It is not possible to say whether or not the marginal deviation of ϕ_{CO-Ar} from unity due to anharmonicity, as predicted by Bray[11] and Treanor,[12] is observed, but clearly the present results indicate that, within the uncertainty normally associated with shock tube experiments, vibrational excitation and de-excitation times are equal for carbon monoxide highly diluted in argon.

5. DISCUSSION

Table I presents a summary of the results obtained from previous investigations in which attempts were made to measure vibrational de-excitation rates in thermally excited systems of diatomic molecules. For completeness, we have included the results obtained for N_2 and O_2, although our present experiments were only concerned with CO. It is apparent from this summary that most investigators report values of ϕ greater than unity, i.e. characteristic vibrational de-excitation rates which were faster than the corresponding excitation rates. Only Russo's[1,2] investigations, which were conducted using a shock-driven nozzle expansion, are strictly comparable with our investigation, since the other investigators used undiluted CO. Russo obtained $\phi_{CO-Ar} \leq 10^2$.

It was suggested by von Rosenberg et al.[13] that the high values of ϕ reported by the Cornell workers[1,2] were possibly due to H atom impurities, since tests conducted in the Avco shock-driven nozzle facility had shown that the H atom appeared to be about 10^4 times more effective in relaxing the vibrational mode of CO than the CO molecule itself. However, Russo and Watt[14] refute this suggestion on the grounds that the concentration of H atoms required to explain their results would still be considerably larger than they estimated to have been present.

The remainder of the investigations referred to in Table I, in which pure CO was used as the test gas, indicate values of ϕ_{CO-CO} which range between 1 and 5. Holbeche and Woodley's[15] result, i.e. $\phi_{CO-CO} \simeq 1$, merits special mention since this was also deduced from vibrational temperature measurements (sodium line reversal) which were made in an unsteady shock-tube expansion flow. However, in contrast to our technique,

their expansion was produced by arranging for the primary shock wave
to rupture a secondary weak diaphragm which originally separated the
test gas from a region of virtual vacuum at the downstream end of the
shock-tube. The unsteady backward facing rarefaction wave thus produced
was convected passed their observation station, i.e. they did not ob-
serve a stagnant gas sample. Consequently, the interpretation of their
measurements required a relatively complex numerical solution of the
flow which was performed on a computer; see Appleton[18]. Departures
from the ideally assumed unsteady, one-dimensional, centered rarefaction
wave, caused by the non-ideal rupture of the secondary diaphragm and
the possible boundary layer effects, probably introduced some uncertain-
ties of interpretation into their measurements.

In the light of the concern shown over possible impurity effects
in the earlier investigations, precautions were taken during the initial
stages of our investigation to minimise the impurity problems. The
test gas mixtures were passed through a copper coil immersed in a liquid
nitrogen trap, and through an alumina pellet trap which was cooled in
a bath of acetone and solid carbon dioxide (see Millikan[19]). However,
when it was established that the impurity radiation which was observed
was due to contaminants, apparently scavenged from the shock-tube walls
(see Section 3), the cold traps were eliminated from the gas-handling
system and the final series of experiments were conducted using test
gases taken directly from the mixing tanks. It was estimated that the
maximum impurity levels in the CO-Ar mixtures used in our experiments,
based on the manufacturers' specifications, was less than 40 ppm.

The test gas was normally introduced into the shock tube through
the expansion assembly channel at the downstream end so as to flush

any degassed contaminants away from the observation region. However, test shots conducted with the gas-feed direction reversed, and at other times with a continuous flow system in operation, showed no evidence of any effects due to impurities. Thus, the former, more convenient system, was adopted for general use. The only impurity problem encountered in these experiments was that discussed in Section 3.

The series of experiments reported here were conducted with a fixed expansion aperture length of 12 cm and with the end plug located 5 cm downstream from the apertures. The high temperature limit of our data range was imposed only because at temperatures close to or above 5,000 $^{\circ}$K, an appreciable fraction of the fundamental emission band occured at wavelengths above the fall-off point on the responsivity curve of our indium antimonide detector. The low temperature limit was set by the excessive time required for the vibrational energy mode of CO to equilibrate with the bulk gas temperature in the constant pressure region behind the reflected shock. Neither of these represent fundamental limitations to our basic method of investigating de-excitation processes.

6. CONCLUSIONS

The explanation for the high values of ϕ reported for nitrogen and carbon monoxide in the earlier work, particularly the values of ϕ_{CO-Ar} reported by Russo,[1,2] is not clear. It may be significant that the present technique is the first one applied to making these de-excitation rate measurements which permits observations to be made on a stagnant gas sample. No a priori calculations of the variations in the gas dynamic properties through the expansion are required. Confirmation of the fluid mechanical behavior of our system was provided by the equilibrium expansion experiments. The results of the non-equilibrium expansions clearly indicate that the vibrational relaxation of carbon monoxide in an argon diluent is adequately described by a linear rate equation in which the characteristic vibrational relaxation time is the same no matter whether it is measured in a compression (shock wave) or expansion environment.

ACKNOWLEDGMENT

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Investigators	Test Gas	Measuring Technique	Experimental Facility	Stagnation Conditions	Result
Hall & Russo [1]	100% N_2	Sodium line-reversal (SLR)	Nozzle expansion	2800-4600°K 24-82 atms.	$\phi_{N_2-N_2} \approx 70.$
"	5% CO 95% Ar	SLR	"	3600-5200°K 45 atms.	$\phi_{CO-Ar} \leq 10^2$
Russo [2]	5% CO 95% Ar	Infrared emission	"	"	$\phi_{CO-Ar} \approx 10^3$
Holbeche & Woodley [15]	100% N_2	SLR	Unsteady expansion flow	2500-2800°K † 8 atms.	$\phi_{N_2-N_2} \approx 15$
"	100% CO	SLR	"	†	$\phi_{CO-CO} \approx 1$
"	100% O_2	SLR	"	2000-2500°K † 1 atms.	$\phi_{O_2-O_2} \approx 10^{-1}$
von Rosenberg, Jr., Taylor & Teare [13]	100% CO	Infrared emission	Nozzle expansion	up to 4000°K 15 atms.	$\phi_{CO-CO} \approx 5$
Russo & Watt [14]	5% CO 95% N_2	Infrared band reversal	Nozzle expansion	2800-4000°K up to 50 atms.	$\phi_{CO-N_2} \leq 10^2$
Blom & Pratt [16]	100% CO	Infrared band reversal	Prandtl-Meyer expansion	1200-2200°K	$\phi_{CO-CO} \approx 3$
Teare, Taylor, & von Rosenberg Jr. [17]	5% CO 95% N_2	Infrared emission	Nozzle expansion	2000-3000°K 6-10 atms.	$\phi_{N_2-N_2} \leq 5$ * $\phi_{CO-CO} \leq 5$ *
McLaren & Appleton (this work)	0.5% CO 99.5% Ar	Infrared emission	Unsteady expansion	2600-4600°K 0.5-2.5 atms.	$\phi_{CO-Ar} \approx 1$

† Conditions behind incident shock.   * Upper limits to ϕ allowed by these experiments

TABLE I

FIGURE CAPTIONS

Figure 1   Plan view of expansion assembly

Figure 2   Pressure and infrared signals from a calibration experiment
in 0.5% CO, 99.5% Ar. Incident shock Mach number, M_s = 3.63,
initial test gas pressure, p_1 = 14.0 torr. Reflected shock
temperature, T_5 = 3020°K, reflected shock pressure, P_5 = 1.41
atms.

Figure 3   Calibration curve showing infrared emission intensity per CO
molecule as a function of temperature for 0.5% CO, 99.5% Ar.
Full line given by Eq. (1).

Figure 4   Pressure and infrared responses from an expansion experiment
conducted in test gas mixture: 0.5% CO, 49.75% He, 49.75% Ar.
M_s = 3.81, p_1 = 13.9 torr, T_5 = 3325°K, P_5 = 1.59 atms.

Figure 5   Translational and vibrational temperatures deduced from the
measured pressure and infrared profiles in the expansion
illustrated in Fig. 4.—O— , translational temperature assum-
ing an isentropic expansion; Δ, vibrational temperature.
Upper full curve shows the vibrational temperature profile
calculated using the vibrational relaxation rate data from
Millikan and White.[8]

Figure 6   Results from non-equilibrium expansion in 0.5% CO 99.5% Ar.
—O— , translational temperatures computed from the pressure
profile; Δ, vibrational temperatures from the infrared record.
Full curves show the vibrational temperature profiles calcu-
lated for the values of ϕ as indicated. M_s = 4.50, p_1 = 3.9
torr, T_5 = 4600°K, P_5 = 0.65 atms. Insert shows actual oscillos-
cope record.

Figure 7   Results from non-equilibrium expansion in 0.5% CO, 99.5% Ar.

—○— , translational temperatures computed from the pressure

profile; Δ, vibrational temperatures from the infrared record.

Full curves show the vibrational temperature profiles calcu-

lated for the values of ϕ as indicated. M_s = 4.25, p_1 = 10.0

torr, T_5 = 4100°K, P_5 = 1.50 atms. Insert shows actual oscillo-

scope record.

Figure 8   Results from non-equilibrium expansion in 0.5% CO, 99.5% Ar.

—○— , translational temperatures computed from the pressure

profile; Δ, vibrational temperatures from the infrared record.

Full curves show vibrational temperature profiles calculated

for the values of ϕ as indicated. M_s = 3.35, p_1 = 23.0 torr,

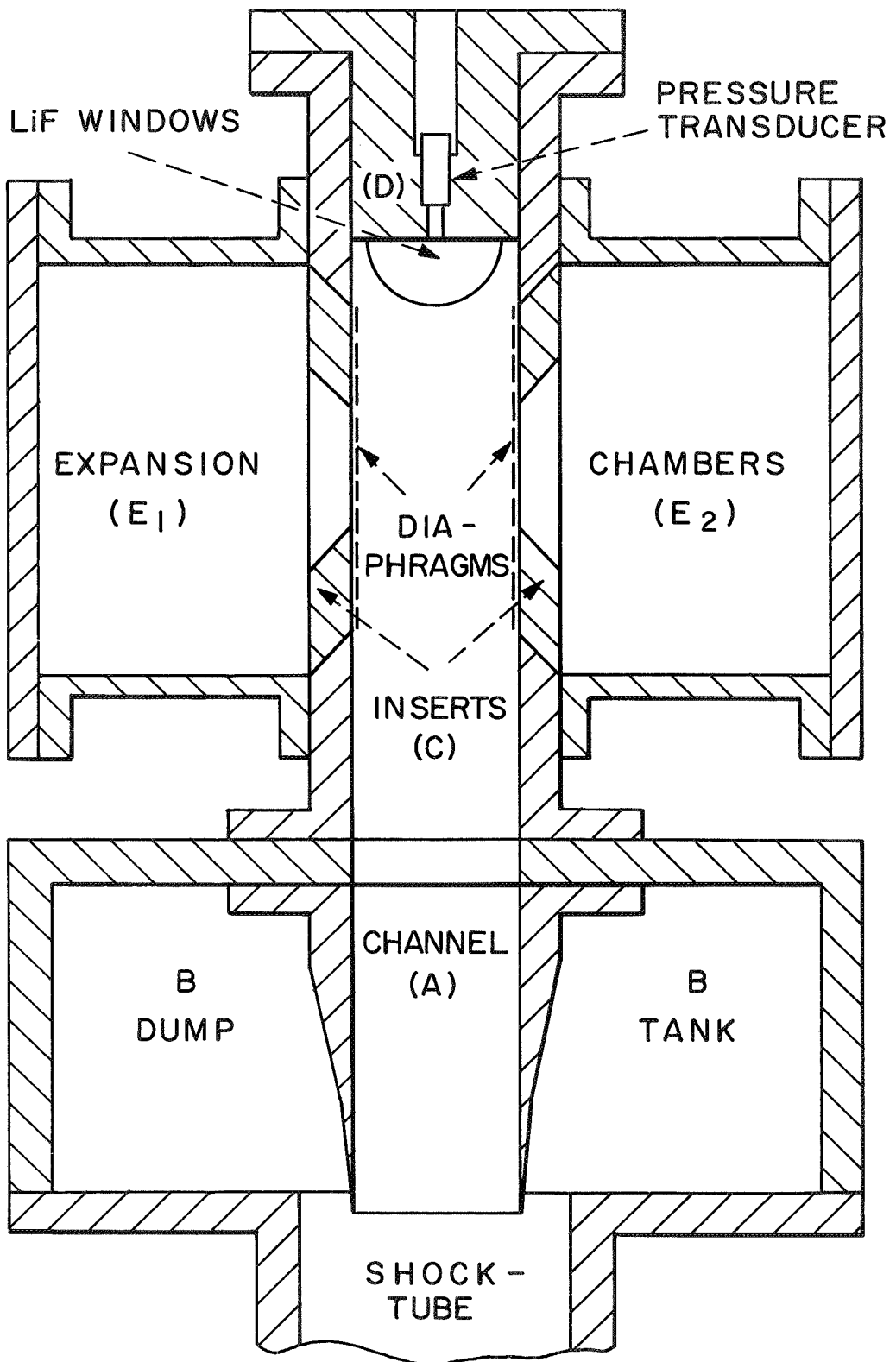T_5 = 2600°K, P_5 = 1.90 atms. Insert shows actual oscilloscope

record.

FIGURE 1

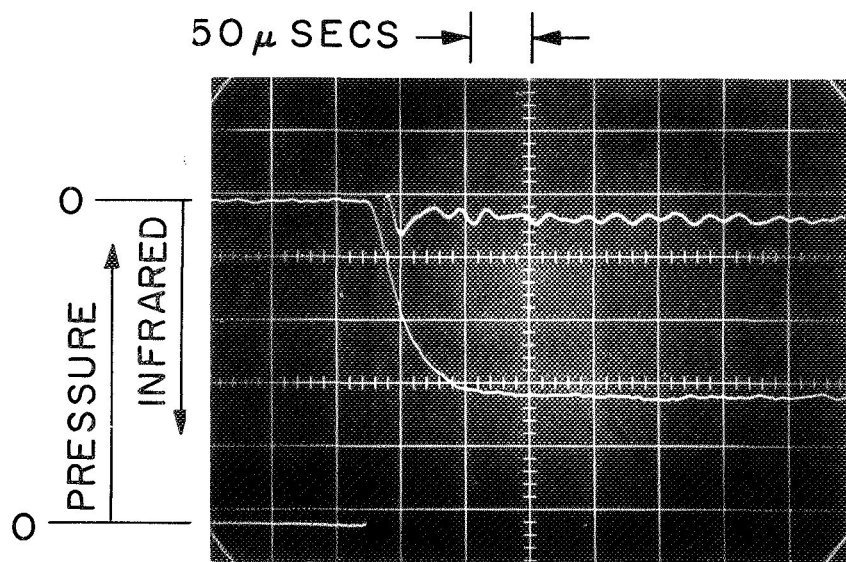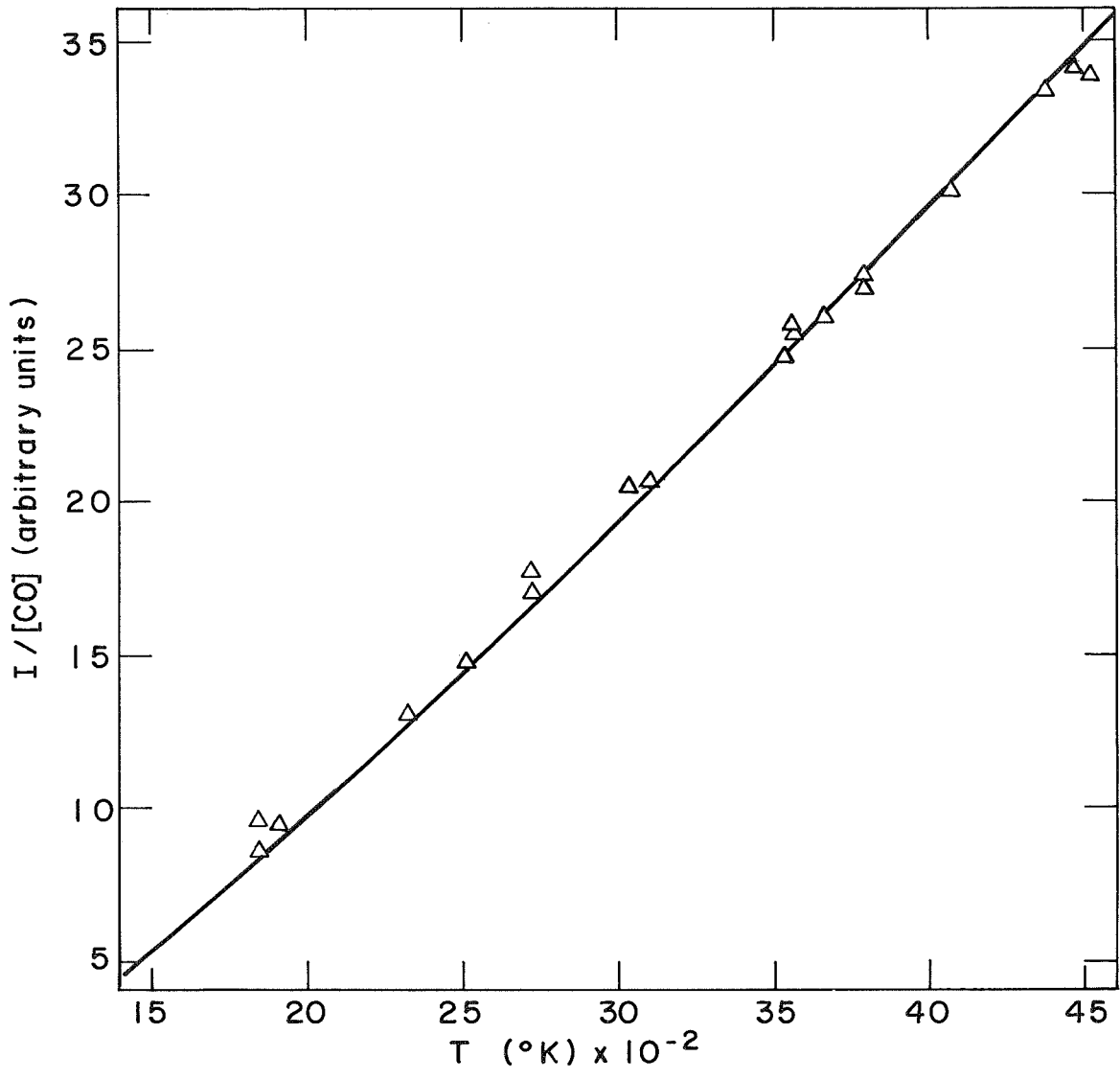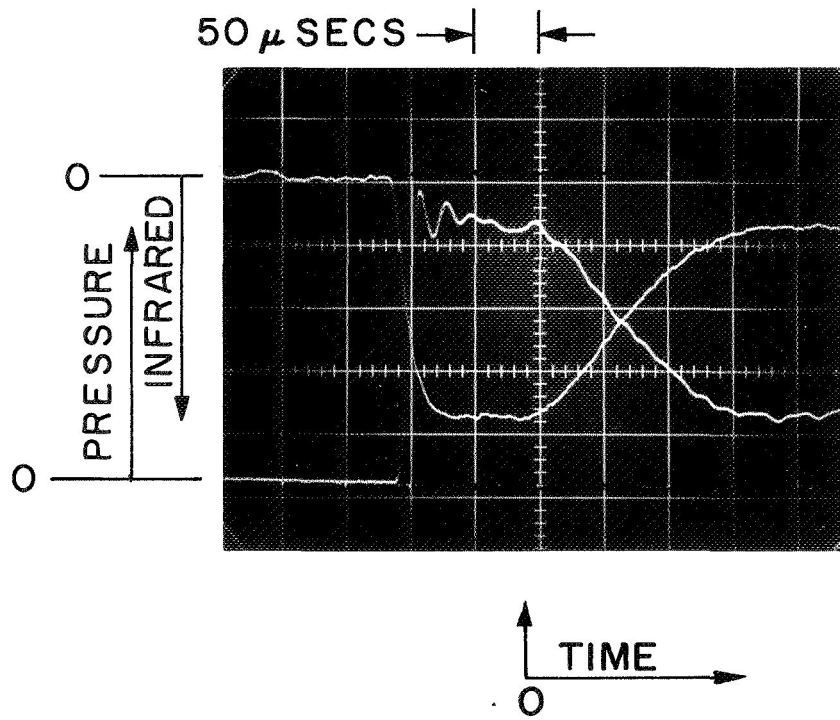FIGURE 2

FIGURE 3

FIGURE 4

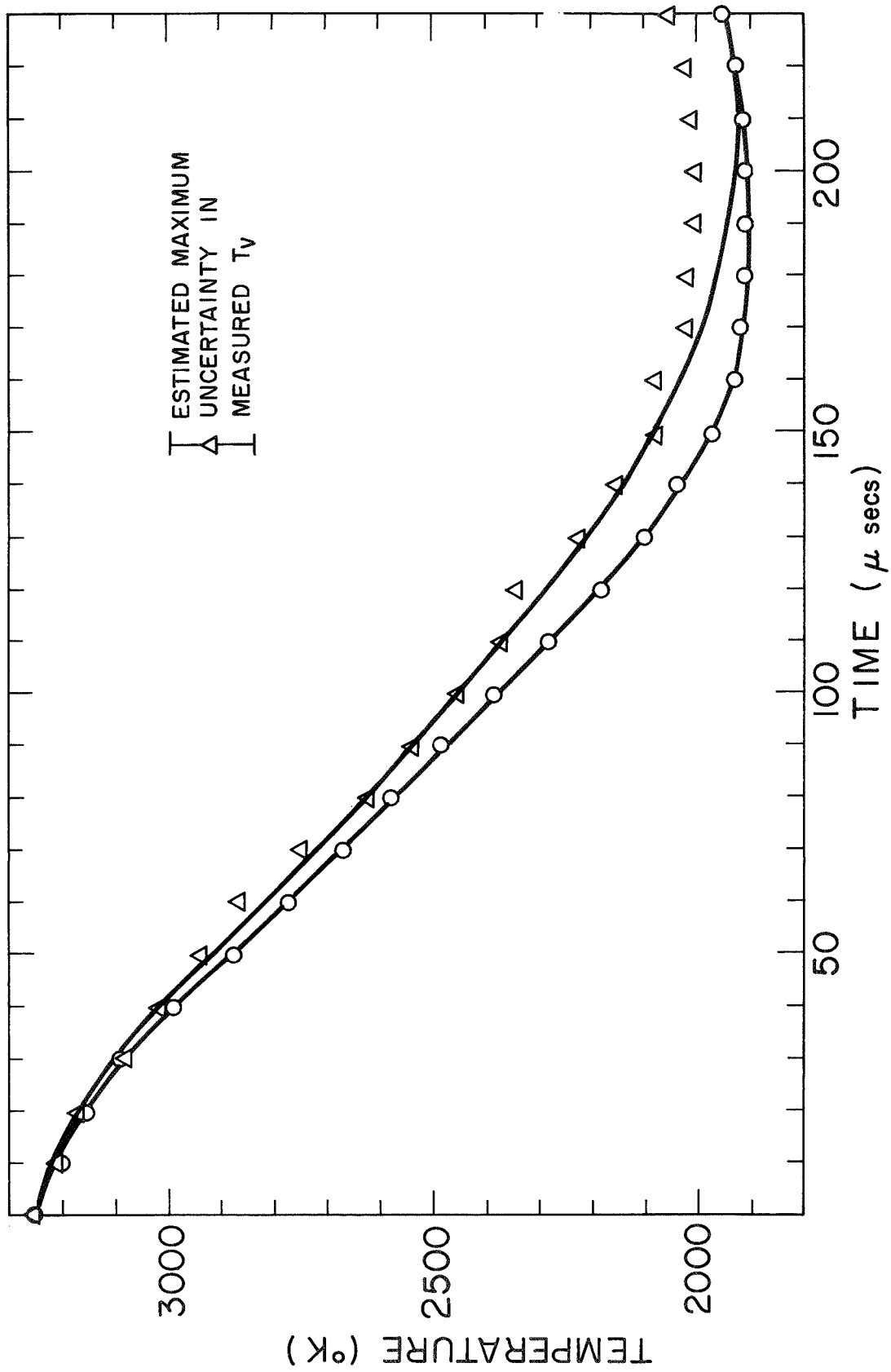TIME (μ secs)

TEMPERATURE ($^\circ$ K)

FIGURE 5

ESTIMATED MAXIMUM
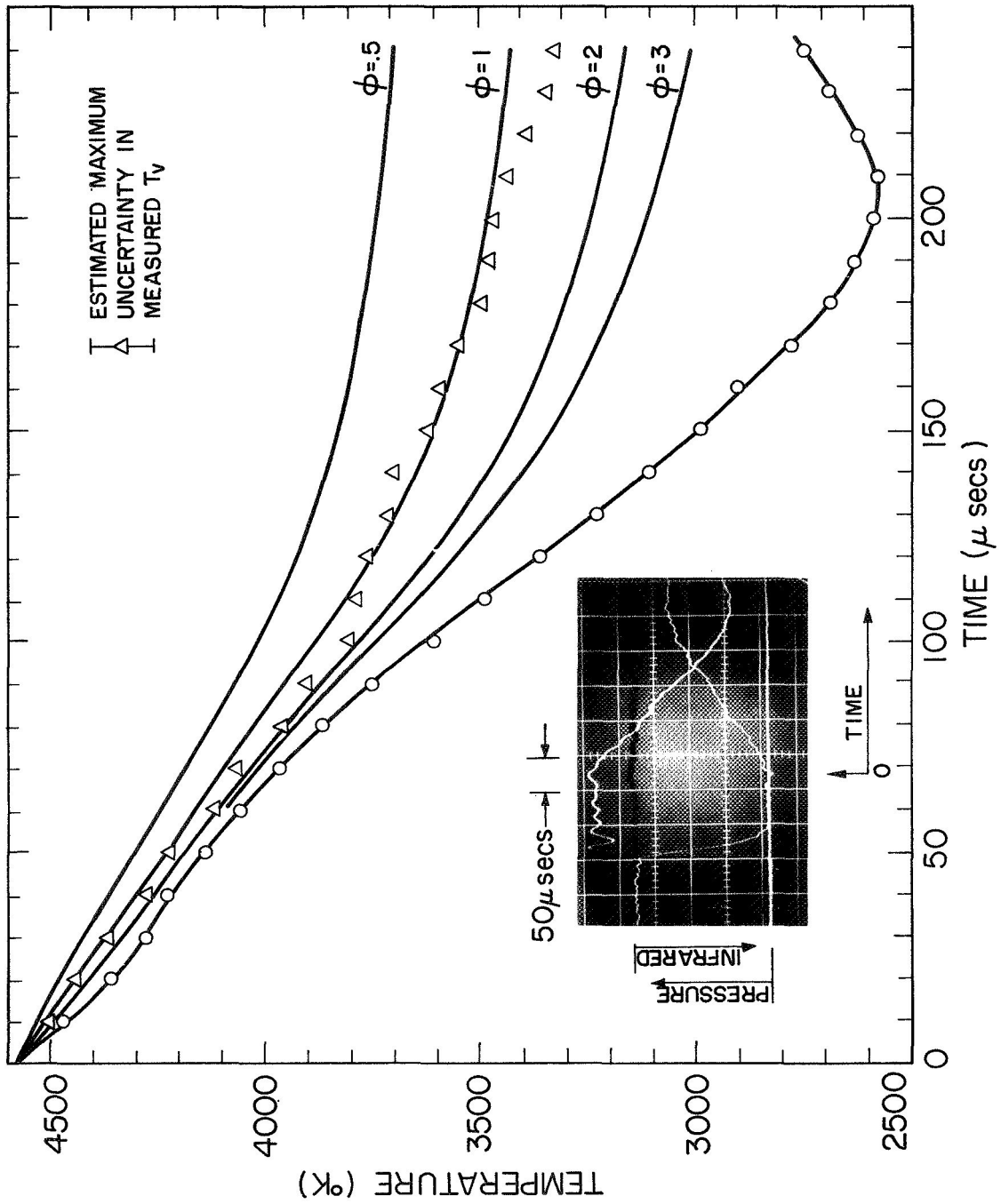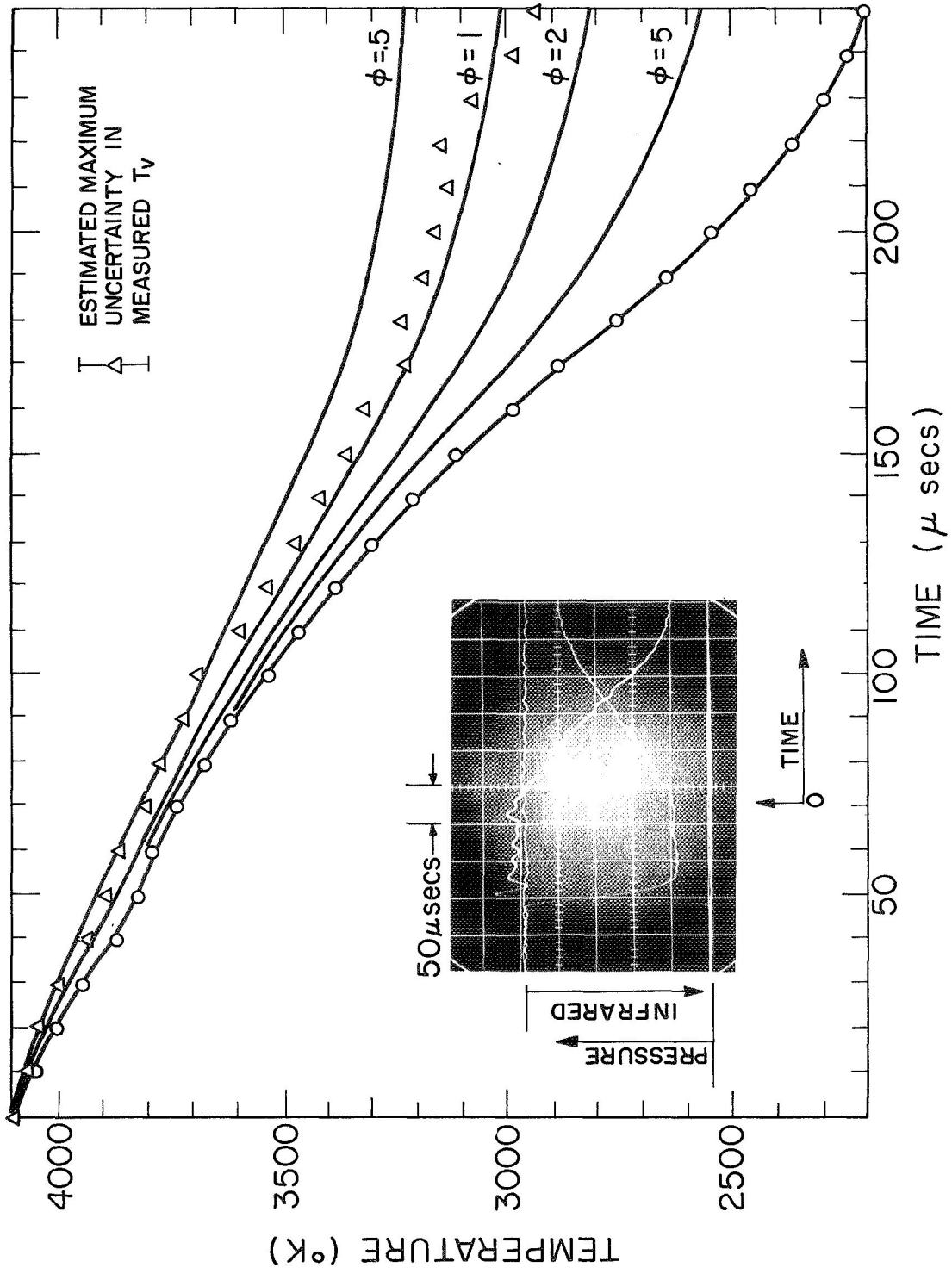UNCERTAINTY IN
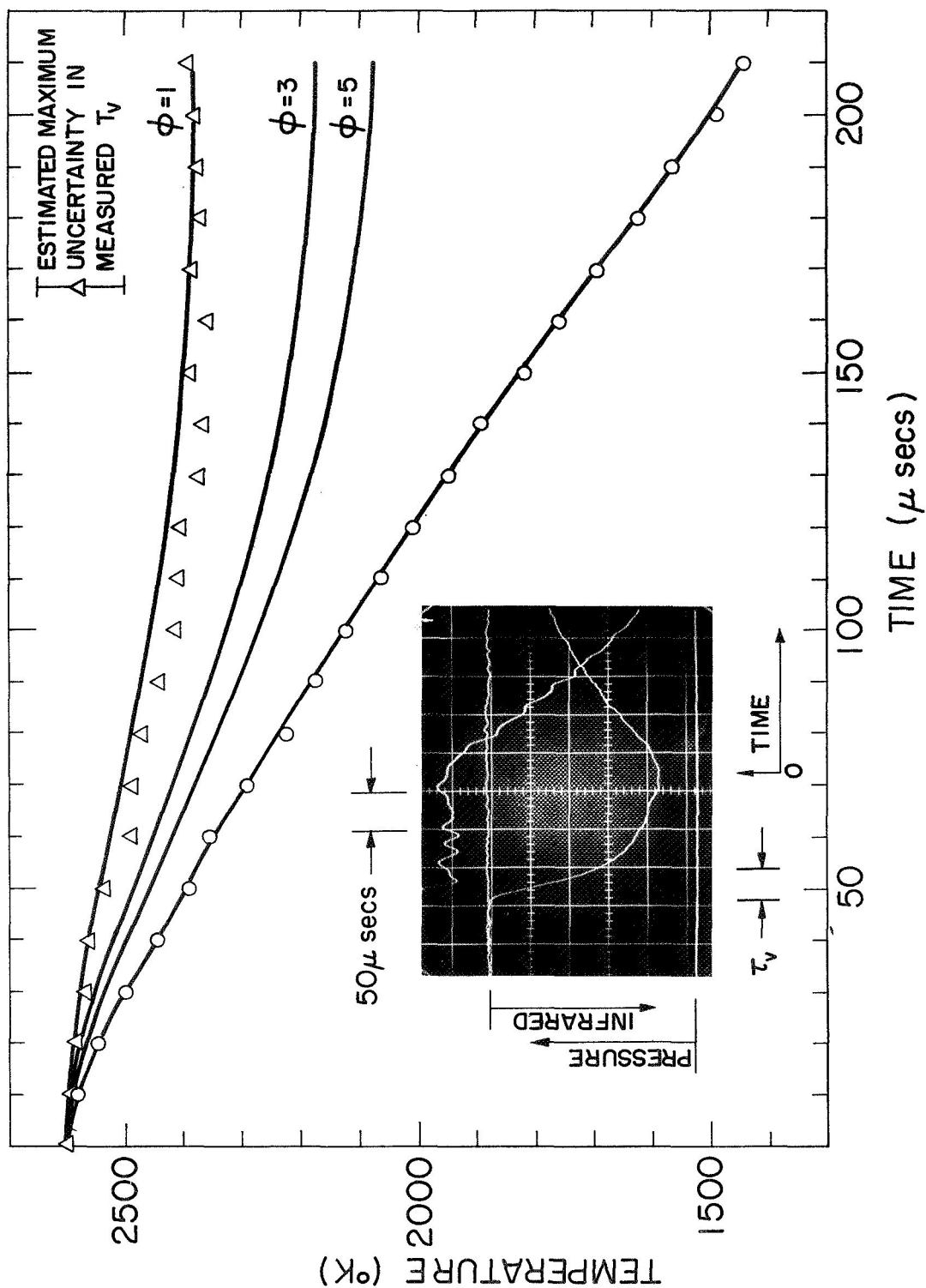MEASURED T_V

FIGURE 6

FIGURE 7

FIGURE 8

DOCUMENT CONTROL DATA - R&D

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13. ABSTRACT

A novel technique has been developed for use in the study of collisional energy transfer and chemical reaction rates in rapidly cooled gases. The principle feature is that the shock heated test gas sample is stationary during the cooling process so that the temporal behavior of a particular nonequilibrium property may be continuously monitored. The technique has been applied to the measurement of the vibrational de-excitation rate of carbon monoxide in an argon heat bath, using the fundamental infrared emission band of CO to follow its vibrational temperature throughout the expansion. In contrast to a number of recent reports indicating enhanced vibrational de-excitation rates for some diatomic molecules, the present experiments clearly indicate that the characteristic vibrational relaxation time of carbon monoxide in argon is the same no matter whether it is measured in a compression (shock wave) or expansion environment.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
vibrational relaxation carbon monoxide shock-tube						

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