NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

PROPOSED ARTICLE FOR SYMPOSIUM PROCEEDINGS

MINIMIZATION OF ERRORS IN SHOCK TUBE INVESTIGATION OF BROMINE DISSOCIATION RATES IN PRESENCE OF NOBLE GASES

by Marvin Warshay

Lewis Research Center
Cleveland, Ohio

N66   22203
(ACCESSION NUMBER)   (THRU)

14
(PAGES)   /
                          (CODE)

TMX-56448   06
(NASA CR OR TMX OR AD NUMBER)   (CATEGORY)

FACILITY FORM 602

Prepared for

Proceedings of Fifth Shock Tube Symposium
May 14, 1965

65-36

E-3014

MINIMIZATION OF ERRORS IN SHOCK TUBE INVESTIGATION OF BROMINE

DISSOCIATION RATES IN PRESENCE OF NOBLE GASES

by Marvin Warshay

Lewis Research Center

National Aeronautics and Space Administration

Cleveland, Ohio

$2 \ 2203$

ABSTRACT

A shock tube with a glass driven section was employed to obtain reliable dissociation rates of bromine in dilute mixtures (1 percent) with various noble gases (Ar, Ne, and Kr) at temperatures of 1200° to 1900° K. Extensive theoretical treatments have recently been applied to dissociation and recombination of gases; however, evaluation of these theories and continued progress has been hampered by the lack of sufficiently precise experimental data. This investigation attempts to partly fill this need by using a carefully designed apparatus and a procedure that would produce reliable kinetic data. Using dilute bromine mixtures and successfully avoiding bromine-metal contact eliminated two serious problems that have plagued other investigators, namely, large temperature changes during dissociation and bromine-metal reactions. The driven section and gas mixture bottles were made of glass and were strengthened (as much as tenfold) by external fiber glass bonding; all valves, lines, and a novel shock-tube transition section were made of TFE fluorinated polymer. Bromine concentrations were measured by a light absorption technique in which highly stable power supplies and incandescent light sources (< 0.05 percent change/hr) were employed. The photomultiplier system developed for this work produced low fatigue rates (0.1 percent/msec), high signal-to-noise ratios (100), and rapid response (0.7 μsec).

INTRODUCTION

In the past decade the shock wave method has been used extensively in the field of chemical kinetics; it has been of particular value in the measurement of the rates of dissociation of diatomic molecules. These experimental results have heightened interest in the theory of dissociation and recombination (refs. 1,2,3,4, and 5). However, in spite of the large number of shock tube investigations that have been made in this area the experimental rate data are still not sufficiently reliable to adequately test present theoretical assumptions nor to provide a solid basis for future

theories. Palmer (ref. 6) stated the problem succinctly in saying that shock tube measurements of rate constants have been notoriously imprecise.

The results of past investigations of the dissociation of bromine in the presence of argon clearly fit this description. As can be seen in Figure 1, the agreement among the four different investigations (refs. 7, 8,9, and 10) is not good and the scatter of the data of several of the investigations is pronounced. For example, in spite of the fact that the fourth investigation (ref. 10) is a repeat of the third investigation (ref. 9), using the same equipment, there is a 50 percent discrepancy between the data.

Despite the previous inadequacies, the outlook for making reliable measurements of bromine dissociation rates is not bleak. Bromine in many respects is a convenient substance to work with. It dissociates at relatively low temperatures. It absorbs light strongly in the visible region providing a good means of following the course of reaction. Secondly from careful analysis of the past bromine shock tube experiments the major trouble areas could be uncovered. These areas, as it develops, are associated with bromine-metal contact, light absorption measurements, and cooling of the gas as dissociation proceeds.

In the present investigation of bromine dissociation, the problems that had plagued past investigations were tackled and largely overcome. An apparatus and a procedure were carefully designed to obtain reliable bromine dissociation rate data. A shock tube with a glass driven section was employed to measure dissociation rates of bromine in dilute mixtures (1 percent) in the presence of argon, neon, and krypton, at temperatures of 1200° to 1900° K.

EXPERIMENTAL CONSIDERATIONS

In the following discussion of experimental apparatus and procedures many points are treated only briefly because they are well understood and have been discussed at length in other papers (refs. 8,11, and 12). However, at the beginning of each subsection an effort is made to stress the pertinent aspects of the design and/or procedure.

Materials Considerations - Bromine Reactivity

Shock Tube

The significant feature of the shock tube design was the avoidance of all contact of bromine with metal surfaces. Since bromine reacts with all common metals, the actual concentration of bromine in a mixture would be in doubt if it were in contact with metal surfaces. Several experiments have confirmed this. Palmer and Hornig (ref. 8) reported an observable reaction when aluminum diaphragms were used with pure bromine. They did not use aluminum diaphragms with bromine mixtures. In the present study, preliminary experiments indicated that bromine has a strong affinity

2

for both copper and stainless steel. A rather surprising phenomenon was
the fact that the walls of a stainless-steel shock tube have a chromato-
graphiclike effect on the bromine in the 1 percent Br_2-99 percent Ar mix-
ture. In these experiments it required about 20 minutes, after the mixture
was injected into one end of the 12-foot stainless-steel driven section, for
the bromine concentration of the mixture at the opposite end to stop increas-
ing and to attain its ultimate value. (See Figure 2, which shows a typical
response.)

Therefore, with metals completely ruled out and with TFE fluorinated
polymer commercially unavailable in the size needed, the logical choice for
driven section was glass. Palmer and Hornig (ref. 8), Davidson and Britton
(ref. 7), and Britton (refs. 8 and 10) all used driven sections that were
at least partly glass. With a glass driven section the previously mentioned
chromatographiclike effect was not observed.

The main components of the shock tube used in this investigation were a
6-foot stainless-steel driver section and a 9-foot driven section made of
borosilicate glass pipe, (Fig. 3). Both sections had an inner diameter of
4 inches. Placed between the two sections, on the low-pressure side of the
diaphragm, was a 1-inch-long transition section made of TFE. The vacuum
and gas sample lines were connected to this section rather than directly to
the glass driven section. Cutting through the glass wall of the driven sec-
tion would have weakened the walls and presented a sealing problem[*].

The face of the transition section was cut to mate with the flange used
to clamp the diaphragm into place. A 4-inch hole was cut into the center
together with eight properly located bolt holes. Drilled and tapped radially
in this piece were the inlets for vacuum and for the gas mixtures.

The entire gas mixture line and the initial portions of the vacuum lines
leading from the shock tube consisted of TFE tubing, fittings, and valves.
These TFE valves were used to prevent the bromine gas samples from coming
into contact with the metal portion of the vacuum lines.

The glass wall of the driven section was strengthened; this was necessary
in order to increase the pressure range over which the tube could be used.
As was discovered separately by Britton (ref. 9) and by this investigator,
glass can break when subjected to too severe a shock. Therefore, using a
glass driven section over a reasonable range of pressures necessitates find-
ing a way to strengthen the glass walls. This investigator's solution to
the problem was to join materials to the outside of the glass, which added
tensile strength to the glass walls. Three materials were joined to the
outside of the glass at different places along the pipe. A steel tube cov-
ered the first $1\frac{1}{2}$ feet of driven section, being bonded to the glass with

---

[*]The transition piece is advantageous from other standpoints as well.
it has room for several additional inlets that can easily be machined in the
TFE. Furthermore, sealing is no problem. The TFE glass pipe O-ring type
gaskets that were used form their own impression in the TFE transition piece.

epoxy cement. This cement was forced into the annulus through grease fittings in the metal tube. The next 12 inches of glass were strengthened by means of fiber glass tape wound in a crisscross fashion. The remaining length of driven section was strengthened by a 1/2-inch-thick polymethyl methacrylate tube that had been split lengthwise to allow it to fit over the conical end of the glass pipe. Several clamps kept the polymethyl methacrylate tightly pressed against the glass. Polymethyl methacrylate is convenient because it is transparent. Of the three methods, the fiber glass method is considered to impart the greatest strength to the glass due to its intimate contact. Fiber glass was also used to strengthen the glass mixture bottles. This will be discussed in the next section.

At the beginning of the driven section, connected to the metal tube, was a stainless-steel flange. This flange was installed as a substitute for the conical end of glass pipe that had broken off during preliminary experiments[†]. The very small area of flange that was exposed to the gas mixture was covered with monochlorotrifluoroethylene polymer grease which is inert to bromine.

Instead of an end plate at the far end of the driven section, a thin Mylar diaphragm was used as a closure. Beyond this diaphragm was a pipe which led to the stack. By breaking through the end diaphragm, the shock itself provided the means to dispose of the shock tube contents.

The driver section was fitted with a solenoid-operated piercing mechanism which was used to pierce the mylar type D diaphragms. Multiple diaphragms were used to obtain the desired rupture strength. The pressure of the helium driver gas was raised to a pressure within 3 psig or less of the diaphragm bursting pressure, 80 psig in most experiments. In practically all cases, Mach number and temperature variation was produced by varying the initial driven gas pressures.

Gas Mixtures

In the preparation of the mixtures of bromine and noble gas in a gas-handling apparatus, bromine did not come into contact with any metals, only glass or TFE surfaces. The valves, fittings and tubing were TFE.

The 1-percent-bromine mixtures were prepared by the partial pressure method. A calibrated Wallace and Tiernan FA160 (0-220 mm) pressure gage was used to measure the bromine pressure. To keep bromine out of the gage and metal line a buffer of the noble gas was used. The total gas mixture pressure was measured with a calibrated (0 - 100 psig) gage.

[†]Before this mishap, only polymethyl methacrylate was used to strengthen the glass; however, the polymethyl methacrylate tube only covered to within 2 inches of the conical end, and this area is where the glass broke during a preliminary experiment in which pressure bursting was used. The pressure was 140 psig.

The gas mixture bottles were large borosilicate glass boiling flasks whose walls were strengthened by bonding fiber glass gauze to them with epoxy cement. With the use of the measured tensile strength of a test specimen of the glass epoxy bond, it was calculated that the strengthened walls of the glass bottle would withstand pressures up to 800 psi. Gas bottle pressure was now limited by the TFE valve connected to the bottle, which was capable of withstanding 150 psig. This provided ample confidence to prepare samples at pressures of 80 psig. If properly applied to the glass portion of the shock tube, this method of glass strengthening could allow the shock tube, which has a glass driven section, to be used at far greater pressures than are presently being considered. Because the number of coatings determine the wall strength, practical considerations such as covering the conical end and still attaching the flange would govern ultimate strength.

Reagent grade Br_2 (99.5 percent minimum purity) was further purified by distillation before being used. The argon, neon, and krypton purities were 99.998, 99.96, and 99.994 percent, respectively. Before being used the two components of the mixtures were allowed to mix for 1 week.

Light Absorption Measurements - Determination of I_0

Keeping I_0, the incident light intensity, within narrow bounds was the single most important part of the measurements of the Br_2 concentration by the light absorption technique. Wray (ref. 13) has pointed out that the largest source of error in the use of absorption spectrometry for the present type of application is the measurement of I_0. Jacobs and Giedt (ref. 14), who used an expression for calculating the dissociation rate of Cl_2 involving the term log log (I_0/I), estimated that a maximum error of 30 to 40 percent in k_D could result from an error of only ±2 percent in I_0. The magnitude of the error in k_D that results from an error in I_0 depends on the particular expression used to calculate this rate constant as well as the initial bromine concentration. The error is lower for lower bromine concentrations.

The determination of I_0 hinges on both the apparatus and the procedures used. The critical features of apparatus are stable power supplies and light sources, a photomultiplier system that produces stable signals with high signal-to-noise ratios, and a good device to measure the I_0 signal. These features will now be described in the following paragraphs.

The incandescent light source (6.5 V, 2.75 A) powered by a highly regulated power supply gave extremely good stability, <0.05 percent change/hr for either the power supply voltage or the bulb current. The light beam was made parallel by placing the bulb at the focal point of a converging-diverging lens. This lens was mounted in a camera shutter, which served to regulate the exposure of the light beam to the shock tube and to the detection system. A fixed 1-mm slit was used where the beam entered the shock tube. The light emerging from the shock tube passed through an interference filter that fed monochromatic light into the 931A photomultiplier. The mea-

sured peak and band width used at the filter half peak were 4400Å and 80Å, respectively. The high voltage required to operate the photomultiplier was produced by a very stable power supply (<0.01 percent change/hr). The photomultiplier output was recorded by the lower beak of a dual beam oscilloscope. An oscilloscope camera was used to photograph the oscilloscope traces.

The ideal photomultiplier system would respond instantaneously to an input light signal and would produce a stable signal with no noise. Unfortunately, time response, minimization of phototube fatigue and high signal-to-noise ratios are goals which often require opposing actions. For example, to minimize fatigue and still maintain a high output would require a high load resistance in the circuit; however, good time response requires a low load resistor. To solve the apparent dilemmas associated with the use of the photomultiplier required not only a good compromise in designing the system, but also a proper procedure for its use. The photomultiplier system developed for this work produced low fatigue rates (0.01 percent signal change per msec) good rate response (0.7 μsec) and good signal to noise ratios (up to 100). The photomultiplier circuit diagram is shown in Figure 4.

With respect to procedure, it was important not to expose the photomultiplier indiscriminately to the light. The shutter blocking light from the phototube was controlled by a solenoid connected to a timing mechanism. (This timing mechanism also controlled the solenoid that operated the piercing mechanism.) Keeping the duration of each light exposure as low as possible was not the only thing that was necessary to minimize fatigue. It was learned that intervals between exposures that were too short resulted in erratic rates of decay of I_0. Therefore, the exposure duration was <0.1 second and the interval between exposures was on the order of 15 minutes. (The higher the anode current, the greater the required interval between exposures.) Measurements of I_0 were made both before and after each shock; the I_0 at the time of the shock was calculated by interpolation. This value deviated by no more than ±0.5 percent in most cases. The traces were measured on a time-motion analyzer.

Two additional light beams (at stations A and C) together with associated optical equipment, like that just described, were located 6 in. on either side of the beam (station B) that was used to measure Br_2 concentration. The signal from station A, which was 24 in. from the end of the shock tube, was used to trigger the oscilloscope. Photomultiplier signals from stations A and C were used to measure the shock velocity. With the aid of a cathetometer, all three beams were carefully alined perpendicular to the shock tube axis.

Temperature Drop During Dissociation

Br_2 Concentration

The dissociation of Br_2 is an endothermic reaction; consequently,

the gas mixture cools as dissociation proceeds. This leads to a change in all the parameters characterizing the gas in the reaction zone and must be taken into account to properly evaluate the rate constants. Palmer and Hornig (ref. 8) derived a factor, which they called F, to make this enthalpy correction (defined in the next section). However, for their 1 to 10 Br_2 - Ar mixture, their corrections varied nonlinearly with temperature between the extremes 50 and 870 percent ($1.50 \leq F \leq 9.70$). Though theoretically correct, the determination of F involves uncertainties that are a reflection of the uncertainties associated with the components that make up F, for example, temperature and extinction coefficient. Therefore, the most satisfactory solution is to minimize temperature drop thereby making its influence minor. By properly designing the experiment, gas mixtures containing only 1 percent Br_2 could be used. At these concentrations the enthalpy corrections were both small and varied little with temperature ($1.07 \leq F \leq 1.13$).

Calculations

The rate of dissociation of bromine is determined from the initial slope of the oscilloscope trace. The rate constants were calculated from the following expression

$$k_D = \frac{\left(\dfrac{dI_2}{d\tau}\right)\left(\dfrac{V_2}{V_1}\right)F}{I_0(I_2/I_0)\epsilon_2 l [Br_2][M]} \tag{1}$$

where $[Br_2]$ and $[M]$ are the concentrations of bromine and the noble gas, respectively, I_0 and I_2 are the incident and transmitted light intensities, V_1 and V_2 are the particle velocities relative to the shock front, ϵ is the extinction coefficient, τ is the reaction time on the oscilloscope trace, l is the path length of the light in the gas, and F is the Palmer and Hornig enthalpy correction factor (ref. 8) due to dissociation. The subscripts 1 and 2 refer to the unshocked and shocked gases, respectively. Hiraoka and Hardwick (ref. 16) have written a convenient expression for the F correction factor

$$F = \frac{1}{\dfrac{\dot{\rho}_2}{\rho_2}\dfrac{1}{\dot{f}} - \dfrac{d \ln(\epsilon_2 l)}{d T_2}\dfrac{\dot{T}}{\dot{f}}} \tag{2}$$

For the case of a very small fraction of Br_2 dissociated, they derived equations for the changes in density ρ and temperature T as the dissociation progresses, assuming the ideal gas law and using the conservation laws for mass, momentum, and energy.

$$\frac{\dot{\rho}_2}{\rho}\frac{1}{\dot{f}} = \frac{X_0(\Delta H - C_V T_2)}{C_\rho T_2 - (M/R)V_2^2 C_V} \tag{3}$$

$$\frac{\dot{T}_2}{\dot{f}} = \frac{\dot{f}_2}{\rho_2}\frac{1}{\dot{f}}\left(\frac{M}{R}V_2^2 - T_2\right) - X_0 T_2 \tag{4}$$

where $\Delta H = D_0 - RT_2/2$. The dissociation energy at 0° K is D_0, f is the fraction of dissociation, and X_0 and M are the mole fraction of Br_2 and mean molecular weight, respectively, of the driven gas.

In these calculations the shock wave parameters were calculated with the standard one-dimensional relations(ref. 12).

RESULTS

Extinction Coefficients of Br_2

The static measurement of the room temperature extinction coefficient ϵ served to test the efficacy of the optical and electronic equipment that were to be used later in the shock wave measurements. The value of ϵ found for the log form of the Beer - Lambert law was 144.5 ± 1.6 liter/(cm)(mole).

The measurements of ϵ were considerably less scattered than those made by other investigators (refs. 7,8, and 9), who reported uncertainties as high as ±15 percent. Part of the reason for their poorer precision lies in the fact that these measurements were done directly in the shock tube, in some cases prior to the shocks, while those of the present investigation were carried out in a precision absorption cell connected to the gas handling apparatus. In the latter case, better control of the measured parameters that determine ϵ is achieved. Also, the bromine is never in contact with any metal surfaces.

The experimental determination of ϵ at elevated temperatures was conducted from shock tube experiments in the conventional manner, that is, from the initial absorption of light caused by the shock wave. These data are shown in Figure 5. The solid line was calculated from the theoretical expression of Sulzer and Wieland (ref. 15). The agreement is good. Furthermore, the scatter of the data is lower than that of most other investigations of this kind.

Measured Rate Constants

With the aid of equations(1) through (4), bromine dissociation rate constants were calculated for each of the three systems, Br_2-Ar, Br_2-Ne, and Br_2-Kr. These data are presented in Figure 6, in the traditional manner, log k_D against $\frac{1}{T}$. The least square lines representing the data were calculated by assuming the simple collisional form for k_D, that is $AT^{1/2}\exp(-E/RT)$. The data for each of the three systems exhibit definite linear trends over wide temperature ranges. Furthermore, the precision of

the data is significantly higher than that of most published data for bromine dissociation rates in the presence of argon. If figures 6(a) to (c) are compared with figure 1, the mean $\dfrac{|k_{obs} - k_{cal}|}{k_{obs}}$ values for the Br_2-Ar, Br_2-Ne, and Br_2-Kr systems are seen to be 12, 11, and 8 percent, respectively.

In separate experiments conducted with the light source turned off it was determined that emission from the shock heated gas could be ignored in the absorption experiments. Also, Britton (ref. 9) reported that below 1900° K bromine emission is negligible.

DISCUSSION

The improvement in the reliability of these results is attributed to the efforts made to uncover and improve weaknesses in past investigations. Major efforts were devoted to the avoidance of bromine-metal contact, to the maintenance of a stable incident light source I_0, and to the reduction of the enthalpy effect to a minor influence. Of the remaining sources of error, two that are difficult to eliminate completely are associated with the non-ideal shock-wave behavior and the measurement of initial slopes from oscilloscope traces.

While not the subject of this present paper, it is proper to make two brief statements regarding the relative influences of Ar, Ne, and Kr upon the Br_2 dissociation rate. A comparison of the least-square lines representing the data indicate that Br_2 dissociation is approximately 15 percent lower in Ne than in Ar. In the Kr system Br_2 dissociates at higher rates than it does in the Ar system at high temperatures, while the reverse is true at low temperatures.

REFERENCES

(1) D. L. Bunker and N. Davidson, J. Am. Chem. Soc. 80, 5090 (1958).

(2) J. C. Light, J. Chem. Phys. 36, 1016 (1962).

(3) S. E. Nielsen and T. A. Bak, J. Chem. Phys. 41, 665 (1964).

(4) E. E. Nikitin and N. D. Sokolov, J. Chem. Phys. 31, 1371 (1959).

(5a) S. W. Benson and T. Fueno, J. Chem. Phys. 36, 1597 (1962).

(5b) S. W. Benson and G. C. Berend, J. Chem. Phys. 40, 1289 (1964).

(6) H. B. Palmer, Project Squid Tech. Report PSU-11-P, August (1964).

(7) D. Britton and N. Davidson, J. Chem. Phys. 25, 810 (1956).

(8) H. B. Palmer and D. F. Hornig, J. Chem. Phys. 26, 98 (1957).

(9) D. Britton, J. Phys. Chem. 64, 742 (1960).

(10) C. D. Johnson, and D. Britton, J. Chem. Phys. 38, 1455 (1963).

(11) D. Britton, N. Davidson, and G. Schott, Discussions Far. Soc. 17, 58 (1954)

(12) I. I. Glass, W. Martin, and G. N. Patterson, UTIA Report 2, November (1953).

(13) K. L. Wray, J. Chem. Phys. 37, 1254 (1962).

(14) T. A. Jacobs and R. R. Giedt, J. Chem. Phys. 39, 749 (1963).

(15) P. Sulzer and K. Wieland, Helv. Phys. Acta 25, 653 (1952).

(16) H. Hiraoka and R. Hardwick, J. Chem. Phys. 36, 1715 (1962).
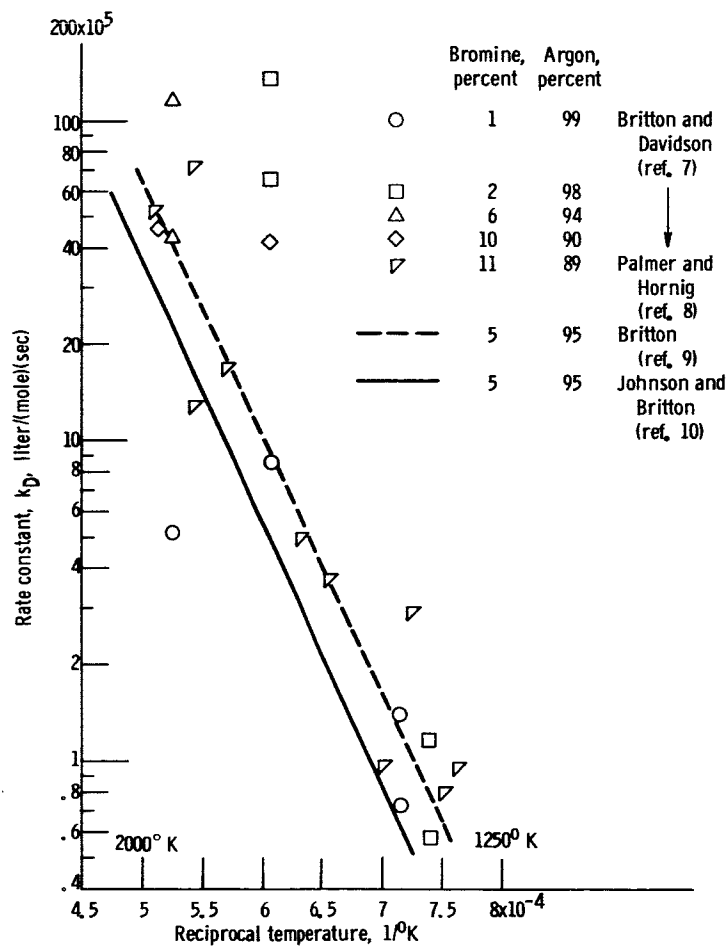
Figure 1. - Rate constants for dissociation of Br_2 in Br_2 - Ar
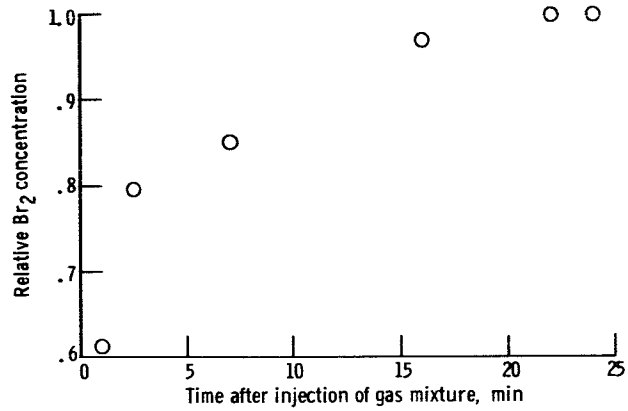mixtures. (Not all experimental data included for ref. 7.)

Figure 2. - Measured Br_2 concentrations of 1 percent Br_2 - 99 percent Ar mixtures in stainless-steel shock-tube driven section.
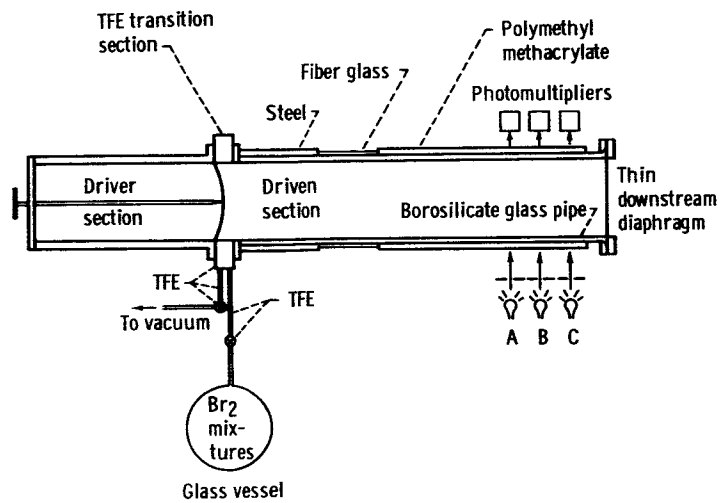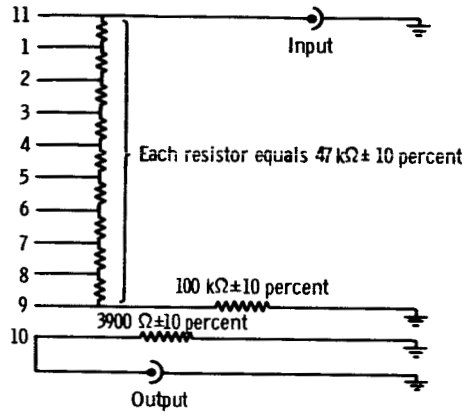

Figure 3. - Schematic of shock tube.

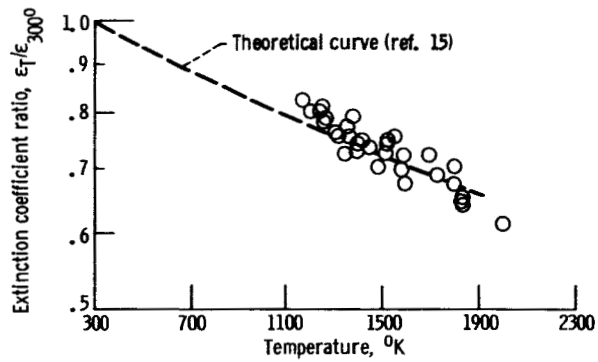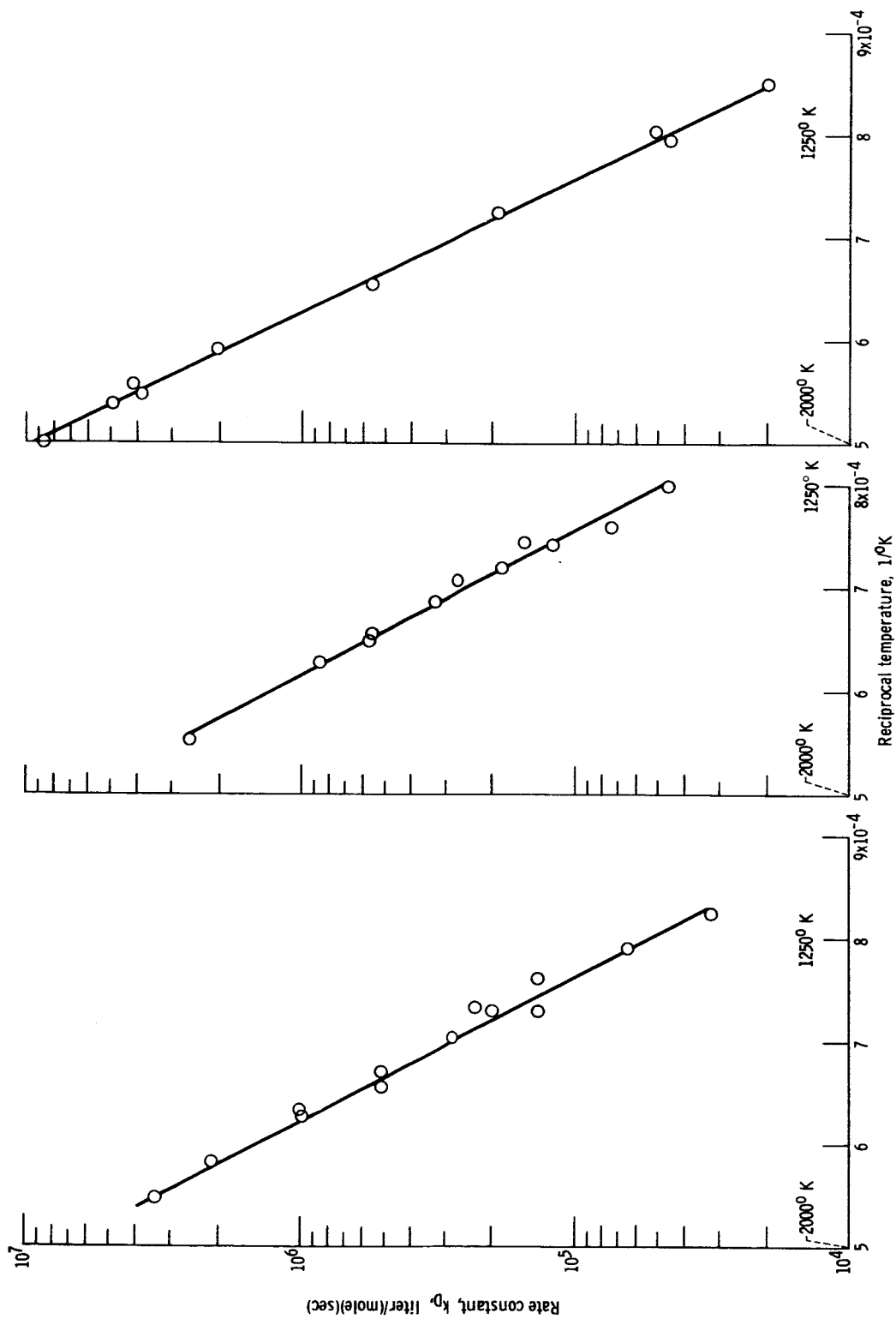Figure 4. - 931A Photomultiplier circuit diagram.

Figure 5. - Temperature dependence of Br_2 extinction coefficient at 4400 Å.

Reciprocal temperature, $1/^\circ K$

(a) 1 Percent Br_2 - 99 percent Ar.

(b) 1 Percent Br_2 - 99 percent Ne.

(c) 1 Percent Br_2 - 99 percent Kr.

Figure 4. - Rate constants for dissociation of Br_2.

Rate constant, k_D, liter/(mole)(sec)