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Author

Valentini, James J.

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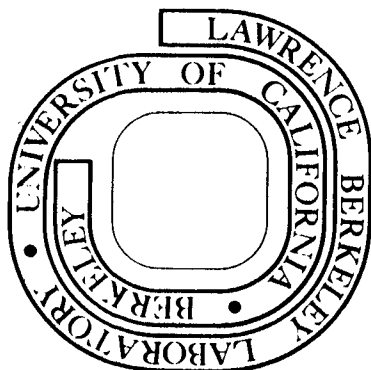
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A SUPERSONIC ATOMIC AND MOLECULAR HALOGEN NOZZLE BEAM SOURCE

James J. Valentini, Michael J. Coggiola and Yuan T. Lee

Materials and Molecular Research Division
Lawrence Berkeley Laboratory

and

Department of Chemistry
University of California
Berkeley, California 94720

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ABSTRACT

A reliable, resistance heated, nozzle beam source is described which is capable of producing high intensity supersonic atomic and molecular beams of chlorine, bromine, and iodine. The use of a high density graphite nozzle eliminates corrosion and allows for operation up to 2100K. The performance of this source is reported using seeded halogen gas mixtures which extend the accessible kinetic energy region to several eV.

Introduction

Supersonic nozzle sources are now frequently used to produce beams of atoms or molecules for collision experiments.¹ The high intensities, narrow velocity distributions and small angular divergences which characterize supersonic beams are obvious reasons for the desirability of nozzles as beam sources.² One particularly advantageous feature of nozzle sources is the "seeding" technique,³ in which the species of interest, the "seed" gas, is mixed in a large excess of a diluent gas.

In a seeded beam the seed species and diluent are characterized by velocity distributions which have the same peak velocity. For very dilute mixtures, a few mole percent seed gas, this peak velocity is nearly equal to that in a pure beam of diluent gas. By varying the mass of the diluent gas the seed species can be accelerated or decelerated. The seeding technique has been used to produce hyperthermal energy beams of more than 30 eV kinetic energy. Such beams have been used in studies of collisional dissociation,^{4,5} the energy dependence of reactive cross sections,⁶⁻⁸ and rotational energy transfer.⁹ However, the seeding technique has been almost exclusively limited to beams of molecular or stable atomic species.

We have constructed a nozzle source which can be used to produce beams of halogen molecules or halogen atoms by thermal dissociation. The source employs a graphite nozzle which can be heated to temperatures above 2000 K to produce beams of chlorine, bromine, or iodine molecules or atoms seeded in rare gas diluents. Both hyperthermal and hypothermal energy beams have been produced for crossed beam studies of reactive

collisions of chlorine molecules and atoms¹⁰ and elastic scattering of chlorine atoms.¹¹

Source Construction

The nozzle source shown partially sectioned in Figure 1, is resistively heated by low voltage, high current AC power (up to 7 volts rms and 450 amps). This low voltage, high current power is provided by winding 4/0 welding cable as the secondary around a toroidal primary coil. A rheostat controls the primary voltage (0-117 VAC), which is supplied by a line voltage regulator. Figure 2 is an enlarged and simplified axially sectioned view of the source showing the heating current path.

The outer graphite tube and nozzle are machined from a special high-density graphite.¹² The nozzle orifice (.079 mm) is hand drilled after final machining. The outer graphite tube (2.22 cm O.D., .32 cm wall) is screwed into the copper mounting block and a graphite nut is screwed onto the tube and tightened down against the copper mounting block to hold the outer graphite tube firmly in place. The nozzle itself (1.27 cm O.D., .32 cm wall) is supported at two points. At the front it fits snugly into the conical bore of the outer graphite tube. At the rear it is securely mounted in a two piece copper supporting block which is split along the axis of the nozzle. The two halves of the supporting block are tightened down on the two halves of a cylindrical graphite sleeve in which the nozzle can slide. This arrangement give stable support to the nozzle

while allowing axial movement due to thermal expansion of the nozzle upon heating. The nozzle supporting block is rigidly fixed to the copper mounting block by means of two screws which are electrically insulated from the mounting block by mica washers and teflon sleeves. The supporting block and mounting block are separated by several thicknesses of mica sheet.

At its end the nozzle is attached to a .32 cm O.D. stainless steel gas feed line by means of an "O"-ring type fitting.¹³ A thin copper plate is attached to the rear of this fitting, and two steel springs connecting the plate to the copper supporting block apply a small axial force to the nozzle. This spring loading keeps the nozzle firmly seated in the conical bore of the outer graphite tube, despite thermal expansion and contraction of the nozzle when repeatedly heated and cooled. The gas feed line is wound in a large radius helix to allow for the expansion and contraction of the nozzle.

The source must be extensively cooled due to the large power dissipation in the nozzle. Both the copper mounting block and nozzle supporting block are internally drilled with channels to allow passage of cooling water. The "O"-ring fitting is cooled through a copper block which clamps to the fitting, and which is internally drilled with cooling water channels. This cooling allows the "O"-ring temperature to be maintained at less than 425 K while the nozzle may be more than 2000 K.

The nozzle assembly is precisely mounted on the front plate of the source chamber (Fig. 3, L) so as to be accurately aligned with the skimmer which is also mounted on the front plate.

Figure 3 shows the nozzle assembly mounted in the source chamber. The end plate of the source chamber has several feedthroughs for electrical power, cooling water, gas mixture, and thermocouples. The two pairs of copper tubes (.64 cm O.D.) which provide cooling water for the copper mounting block and nozzle supporting block also carry the heating current for the nozzle. They are attached to external power cables via bus bars. Vacuum feedthroughs are made by drilling out "O"-ring fittings¹³ to accomodate .64 cm O.D. copper tubes. These fittings are attached to lucite flanges which electrically insulate the copper tubes from the end plate. Because of the large radiative flux, the front of the source chamber is also cooled. For this purpose, water is passed through a .64 cm O.D. copper tube soldered to the front surface of the source chamber. Monel, stainless steel and graphite skimmers of .51 to 1.02 mm orifice diameter have been used with the source. Visible deterioration of the metal skimmers occurs after extended use due to the high temperature and corrosive nature of the beam. The graphite skimmers have proved highly resistant to physical deterioration, especially at the skimmer lip. For the data reported here a stainless steel skimmer of .94 mm diameter was used, with a nozzle to skimmer distance of .57 cm.

Beam Characterization

Velocity distributions of seeded beams of halogen atoms and molecules produced by expansion from the graphite nozzle have been determined from

time-of-flight velocity analysis. For this analysis the beam was gated on and off by a rotating (150 to 300 cps) aluminum disk of 17.78 cm diameter with eight slots of .165 cm width equally spaced around the periphery. The rotating disk was located at the entrance aperture (0.028 cm diameter) of an electron bombardment ionizer/quadrupole mass spectrometer detector which has been described in detail elsewhere.¹⁴ The flight path from the rotating wheel to the ionizer was 17.3 cm. A computer controlled 256 channel scaler was used to record the signal intensity as a function of flight time. The start pulse for the multichannel scaler was generated by an LED-phototransistor pair which is also gated on and off by the rotating aluminum disk, and which was located 90° around the wheel from the beam path. The channel width is variable, a width of 4 μ sec was used for this analysis.

This arrangement gave an instrumental velocity (time) resolution of 7 to 15%, depending on flight time. This instrumental broadening is due to the width of the gating function and the ionizer length. The actual time-of-flight spectra were recovered by deconvoluting the observed distributions using the known ionizer geometry and geometrically correct gating function. Corrections to the flight times were made for the ion flight time in the detector and the 90° phase difference between the multichannel scaler start pulse and the gating of the beam. The time scale of the scaler was calibrated by recording the time-of-flight distributions of supersonic beams of pure rare gases expanding from the graphite nozzle at a known temperature (300 K), and comparing them with the calculated spectra. The time-of-flight distributions

were then converted to flux velocity distributions and the peak flux velocities determined. This procedure gave velocities which are accurate to between 1.5% and 7%, the largest uncertainty being that for the fastest beams of chlorine seeded in helium at the highest temperatures, about 1700 K.

Figure 4 shows the variation of the peak flux velocities for chlorine atoms, chlorine molecules and diluent gas as a function of nozzle temperature for various seeded mixtures. The accessible range of particle energies for this source using these seeded mixtures is quite large. For chlorine atoms energies as low as .10 eV and as high as 1.4 eV are possible. For chlorine molecules the energy range is even wider, from .02 to 2.2 eV. By contrast, an effusive graphite source would have an energy range of about .1 eV to .2 eV for chlorine atoms and .03 to .2 eV for molecules.

The light curve drawn for each seeded mixture gives the expected temperature dependence of the peak velocity assuming an ideal seeded beam expansion, i.e. one in which all species attain the same peak velocity. This expected temperature dependence of the peak velocity is only approximate, due to an uncertainty in the nozzle temperature which is discussed later. The curve is scaled at one temperature to the mole fraction weighted average of the diluent gas and chlorine molecule velocities. For $\text{Cl}_2|\text{Ar}$ the observed and ideal peak velocities are scaled at 300 K, for $\text{Cl}_2|\text{Xe}$ the scaling was done at 880 K, since the Xe velocity distribution at room temperature was not recorded. For dilute seeded mixtures such as these, the diluent peak velocities should

follow very closely the curve even for a non-ideal expansion. Deviation from this behavior is evident in Figure 4 and is probably due to the uncertainty in the gas temperature in the nozzle. Despite this non-ideal behavior, the observed velocities of the $\text{Cl}_2|\text{Ar}$ and $\text{Cl}_2|\text{Xe}$ mixtures the velocities observed roughly follow the peak velocities expected of an ideal expansion. A slight amount of "slippage" is evident, especially at higher temperatures, where the particle number density in the beam may be too small to produce sufficient collisions to effect momentum and energy equilibration between seed and diluent species in the expansion. No curve of ideal velocity versus nozzle temperature is shown for the $\text{Cl}_2|\text{He}$ mixture, as the helium velocities were not measured and scaling of the curve is not possible. However, the slippage in this mixture is considerable. For a .98% Cl_2 in He seeded mixture the peak velocities expected in an ideal expansion are about 38×10^4 cm/sec at 1650 K, while the measured velocity is 24×10^4 cm/sec. Velocity slippage is expected to increase as the seed-diluent mass ratio deviates further from unity.

Since this slippage is due to insufficient seed-diluent collisions in the expansion an increase in nozzle pressure should lead to an increase in the peak velocity of the heavy species and a decrease in slippage. Such behavior has been observed with this nozzle as can be seen in Figure 5. Similar, though less pronounced behavior also has been observed for the $\text{Cl}_2|\text{Ar}$ and $\text{Cl}_2|\text{Xe}$ mixtures.

No points corresponding to chlorine atom peak velocities are shown for temperatures below about 1300 K where the $\text{Cl}|\text{Cl}_2$ ratio is

less than 10. Although the chlorine atom velocity distributions were measured for all temperatures, the distributions are complicated by the contribution to the m/e 35 (Cl^+) signal from Cl_2^+ fractionation in the detector ionizer. Using the measured Cl_2 fractionation ratio (Cl_2^+/Cl^+) corrections to the chlorine atom velocity distribution can be made, but this has not been done. For temperatures above 1300 K chlorine atoms are 10 to 1000 times more abundant than molecules, hence Cl_2^+ fractionation makes an insignificant contribution to the Cl^+ signal and need not be taken into account.

The narrow velocity distributions characteristic of supersonic nozzle sources are observed with this graphite nozzle. For 1% Cl_2 in Xe and 10% Cl_2 in Ar the Mach numbers measured range from 7 to 9 (12-16% FWHM). For 1% Cl_2 |He the chlorine atom Mach numbers are also in this range, as are the high (> 1400 K) temperature chlorine molecule Mach numbers. However, Mach numbers as high as 25 are observed for chlorine molecules at lower temperatures.

The performance of the graphite nozzle as a source of bromine molecules and atoms has also been evaluated. Figure 6 shows the variation of peak velocities as a function of temperature for all species in a 6.3% Br_2 in Ar mixture. This mixture was generated by passing the argon diluent gas through a temperature controlled reservoir containing liquid bromine. The curve showing the temperature dependence of the peak velocity for an ideal expansion is scaled to the mole fraction weighted sum of the argon and bromine molecule peak velocities at 635 K. As for the chlorine seeded mixtures, velocity

slippage is evident. Bromine atom and molecule energies of approximately .3 eV to .5 eV can be produced with this nozzle and seeded gas mixture. Although velocity distributions for $\text{Br}_2|\text{Xe}$ and $\text{Br}_2|\text{He}$ mixtures were not measured, the expected range of bromine molecule (atom) energies available from this source even allowing for slippage, is .04 eV to ~3.3 eV (.08 eV to ~2.0 eV). The Mach numbers observed for bromine molecules and atoms range from about 7 to 15, comparable to those for the chlorine seeded mixtures.

As can be seen in Figures 7 and 8 total dissociation of bromine molecules and nearly total dissociation of chlorine can be achieved with the graphite nozzle at halogen partial pressures which give intensities large enough to be useful for collision experiments. The atom:molecule ratios for 10.1% Cl_2 in Ar are naturally not as large as those shown for the .98% Cl_2 in He seeded mixture. However, nearly complete dissociation is also seen in the 10% mixture, the Cl: Cl_2 ratio being about 200 at 1600 K.

Determination of Nozzle Temperature

Figures 4 through 8 have abscissas giving the nozzle temperature, or more correctly, the temperature of the gas in the nozzle. That these two temperatures are not identical is a consequence of the dynamic nature of the heating of the nozzle and of the gas flow through the nozzle. For a resistively heated nozzle such as this one which must make good electrical, and hence thermal contact with a cooled surface a large

temperature gradient along the nozzle is inevitable. Radiative losses will of course considerably reduce this gradient. Such a gradient perforce makes the nozzle "temperature" ill-defined. Furthermore, since the flow velocity through the nozzle is quite large, about 6 cm/sec for this source, the gas temperature will be a complicated function of the nozzle temperature and temperature gradient.

For Figures 4 through 8 we have used a temperature scale based on the effective temperature of the gas in the nozzle. This temperature scale is determined from analysis of the measured time-of-flight distributions of beams of pure neon produced by expansion from the graphite nozzle at several different values of the heating power. The variation of this gas temperature with heating power is shown in Figure 9. For comparison the temperature of the nozzle was independently determined. These measurements were made by placing the nozzle source in a small vacuum chamber fitted with an observation window on the axis of the beam. The source was then operated under normal conditions with the skimmer removed, and a calibrated optical pyrometer was used to view the nozzle tip. The gas temperatures fall significantly below the tip temperatures determined in this way, especially at high temperatures. This disagreement is not unexpected as the nozzle design makes the tip region one of large resistance (and hence high temperature) due to the mating of the outer graphite tube and nozzle. By varying the gas pressure in the nozzle we have also observed the pressure dependence of the effective gas temperature. At a nozzle tip temperature of 1500 K a 10% change in gas temperature occurs as the pressure is raised from 500 torr to 1300 torr.

Discussion

Beams of halogen atoms are usually produced by thermal dissociation in an effusion source¹⁵ or by low pressure electric discharge.^{16,17} Electric discharge sources can only be used to produce low energy (less than .04 eV) halogen atom beams, while thermal dissociation sources are limited by the melting point of the containing material to about .3 eV. The velocity distributions in beams produced in these ways are Maxwell-Boltzmann. If a narrower velocity distribution is required a mechanical velocity selector must be used, with a concomitant drastic reduction in beam intensity.

The seeded supersonic nozzle source we have described produces a beam of halogen atoms with a narrow velocity distribution, about 15% FWHM. By varying the nature and composition of the diluent gas the beam energy can be varied from about .1 eV to about 1.5 eV for chlorine atoms and .1 to 2.0 eV for bromine atoms. This nozzle source can easily produce a seeded beam with an intensity 10 to 100 times greater than that possible with an effusive source - mechanical velocity selector combination.

The graphite nozzle was not tested using seeded iodine beams. To produce an adequate vapor pressure molecular iodine must be heated to about 350 K. In order to prevent subsequent condensation of the iodine vapor the gas inlet line to the nozzle must also be heated. No provision for such heating was made in the initial construction of the source, designed primarily as a chlorine source. With this simple addition however, hyperthermal beams of both atomic and molecular iodine could

be easily produced. Since the bond dissociation energy of molecular iodine is only 60% of that of chlorine, total dissociation of iodine could be easily achieved.

Due to its high reactivity, fluorine cannot be used in this graphite source. However, using this same design, a reliable atomic and molecular fluorine source has been successfully operated¹⁸ wherein the graphite nozzle components were replaced by pure nickel pieces of somewhat smaller size.

In its present form this source has been used at pressures of two atmospheres or less. It is limited in operating pressure by the "O"-ring fitting which attaches the stainless steel gas feed line to the graphite nozzle, although we have not determined the actual maximum operating pressure of this fitting. By metal plating the end of the nozzle and brazing the gas feed line to it, the safe operating pressure of the nozzle could probably be increased, limited only by the bursting strength of the graphite tube. Operation of the nozzle at higher pressures should result in less slippage and higher energies for seeded mixtures of halogens in light carrier gases, such as Cl_2 in He, at high temperatures. At a given pressure the gas number density ($\propto 1/T$) is considerably reduced at high temperatures so operation of the nozzle at pressures of several atmospheres will not impose an unmanageable load on the pumping system.

We have not operated the nozzle at temperatures higher than 2100K. This limitation is due to a limit on the heating power available. Since the maximum working temperature of graphite in vacuum is about 2300K

0 0 0 0 4 6 0 3 9 1 7

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considerable increase in beam energy can be achieved with this source,
if the heating power can be further increased.

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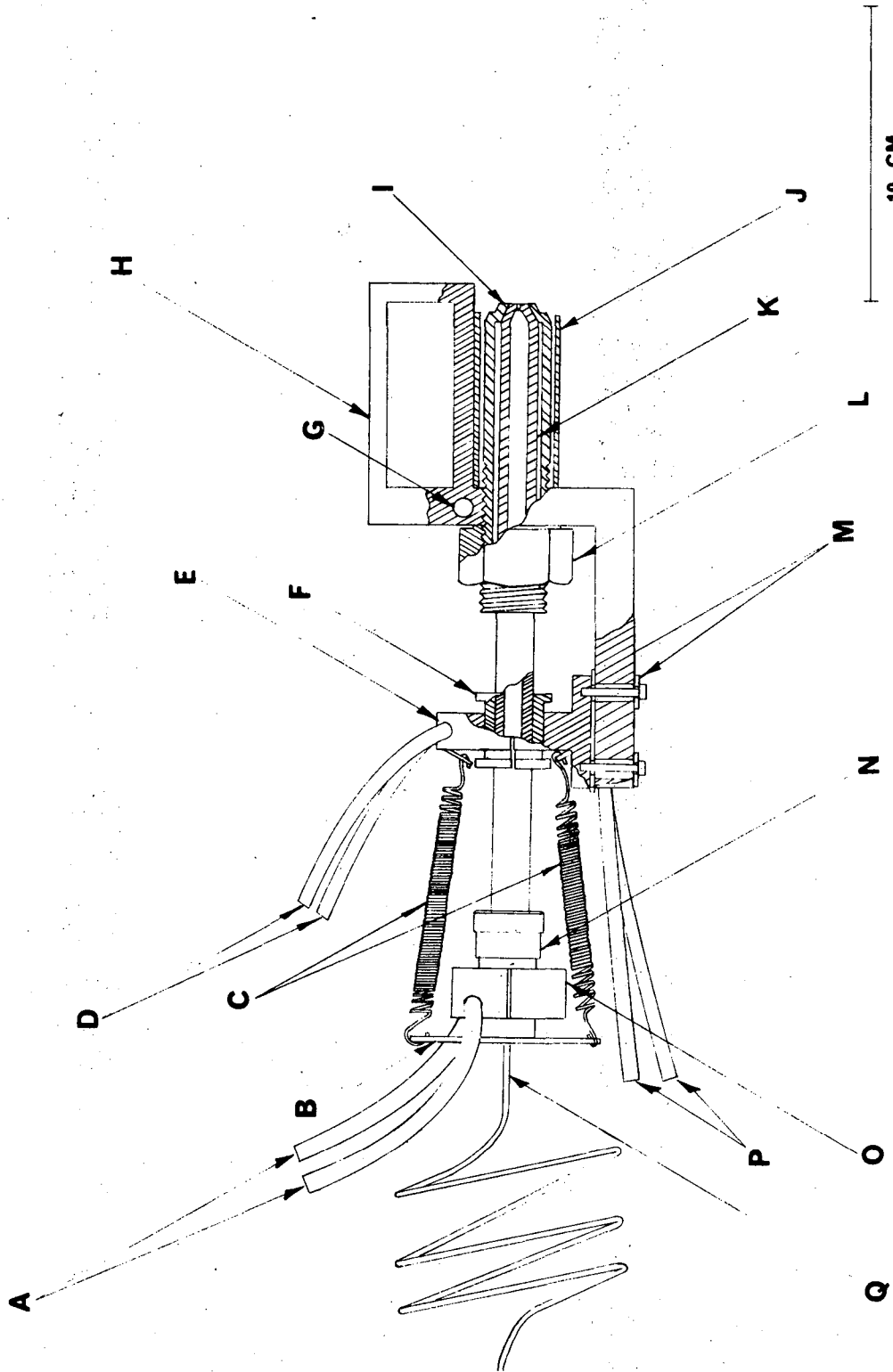
FIGURE CAPTIONS

- Fig. 1. Partially sectioned view of graphite nozzle source. A - water cooling lines for O-ring cooling block; B - nozzle retaining plate; C - springs; D - water cooling lines for support block; E - copper support block; F - graphite sleeve; G - water cooling channel; H - copper mounting block; I - outer graphite tube; J - tantalum radiation shield; K - inner graphite tube; L - graphite retaining nut; M - mica insulation; N - Cajon ultratorr fitting; O - copper O-ring cooling block; P - water cooling lines for mounting block; Q - gas inlet line.
- Fig. 2. Heating current paths for graphite nozzle. E - copper support block and current return; F - graphite sleeve; H - copper mounting block and current supply; I - outer graphite tube; K - inner graphite tube; L - graphite retaining nut.
- Fig. 3. Sectioned view of graphite nozzle source mounted in a differentially pumped chamber. A - Lucite insulating feedthroughs; B - water cooling for mounting block, and current supply; C - gas inlet line; D - water cooling for support block, and current return; E, J - Cajon ultratorr fittings; F - water supply for O-ring cooling block; G - nylon insulating feedthroughs; H - stainless steel outer source chamber; I - front plate water cooling lines; K - stainless steel inner source chamber; L - 1200

ℓ/sec diffusion pump, differential region; M - 2400 ℓ/sec diffusion pump, source region.

- Fig. 4. Peak flux velocities for chlorine atoms (■) chlorine molecules (●) and diluent gas (▼) as a function of source temperature for three seeded gas mixtures. Solid curves indicate expected velocity dependence assuming an ideal seeded beam expansion, see text.
- Fig. 5. Peak flux velocities for chlorine atoms (■) and chlorine molecules (●) as a function of source stagnation pressure. Seeded mixture was 0.98% Cl₂ in He at a source temperature of 1470K.
- Fig. 6. Peak flux velocities for bromine atoms (■), bromine molecules (●) and diluent gas (▼) as a function of source temperature. The seeded mixture was 6.3% Br₂ in Ar. The solid curve shows the expected velocity dependence assuming an ideal expansion, see text.
- Fig. 7. Br:Br₂ ratio as a function of source temperature. Gas mixture was 6.3% Br₂ in Ar at a stagnation pressure of 1000 torr. Data has been corrected for electron impact fractionation of Br₂ occurring in the detector ion source.
- Fig. 8. Cl:Cl₂ ratio as a function of source temperature. Gas mixture was 0.98% Cl₂ in He at a stagnation pressure of 1000 torr. Data has been corrected for electron impact fractionation of Cl₂ occurring in the detector ion source.

Fig. 9. Nozzle source temperature as a function of input heating power. (\square) - effective source temperature derived from rare gas time-of-flight distributions, (\circ) nozzle tip temperature determined from optical pyrometry.



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Fig. 1

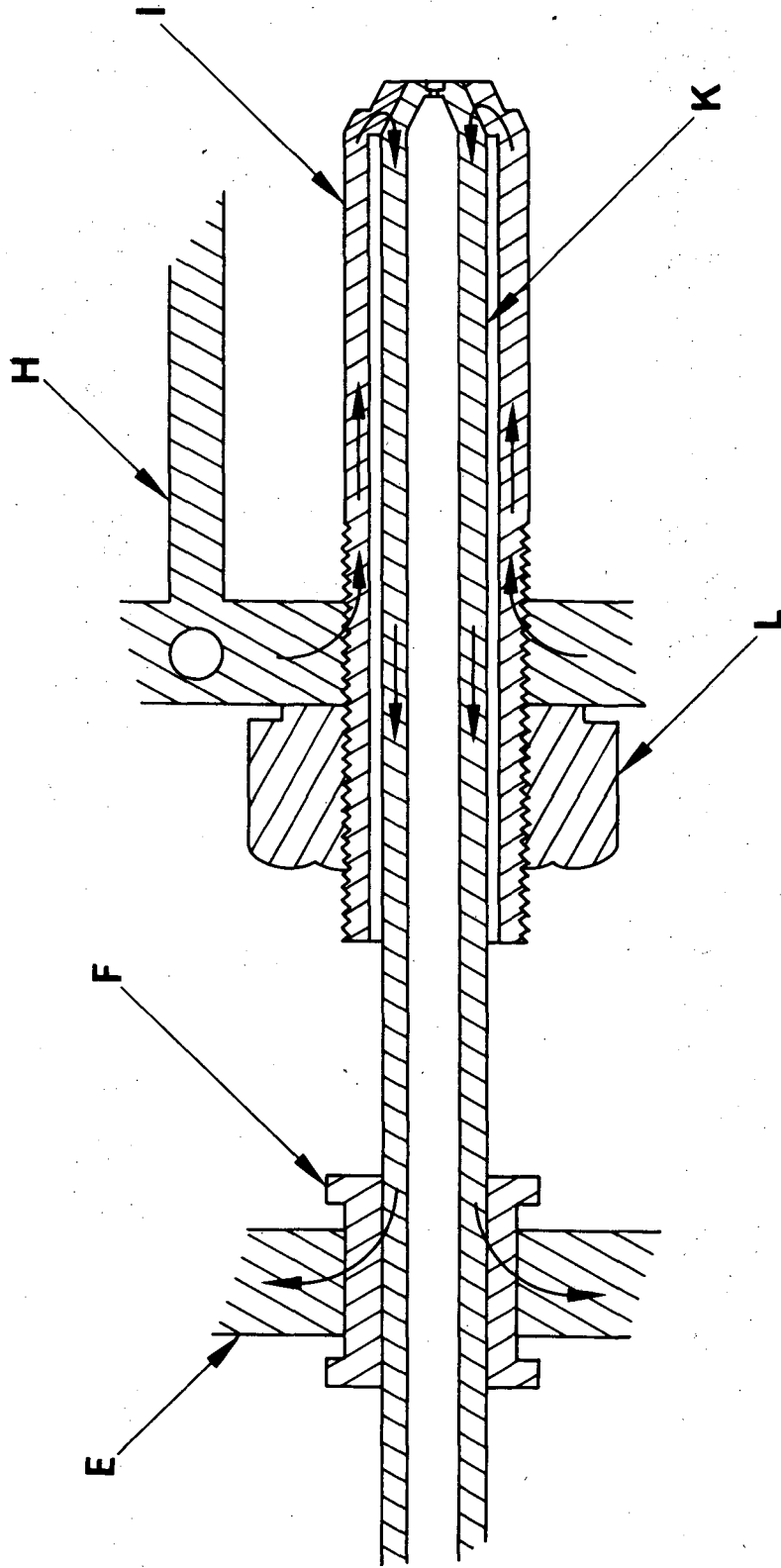
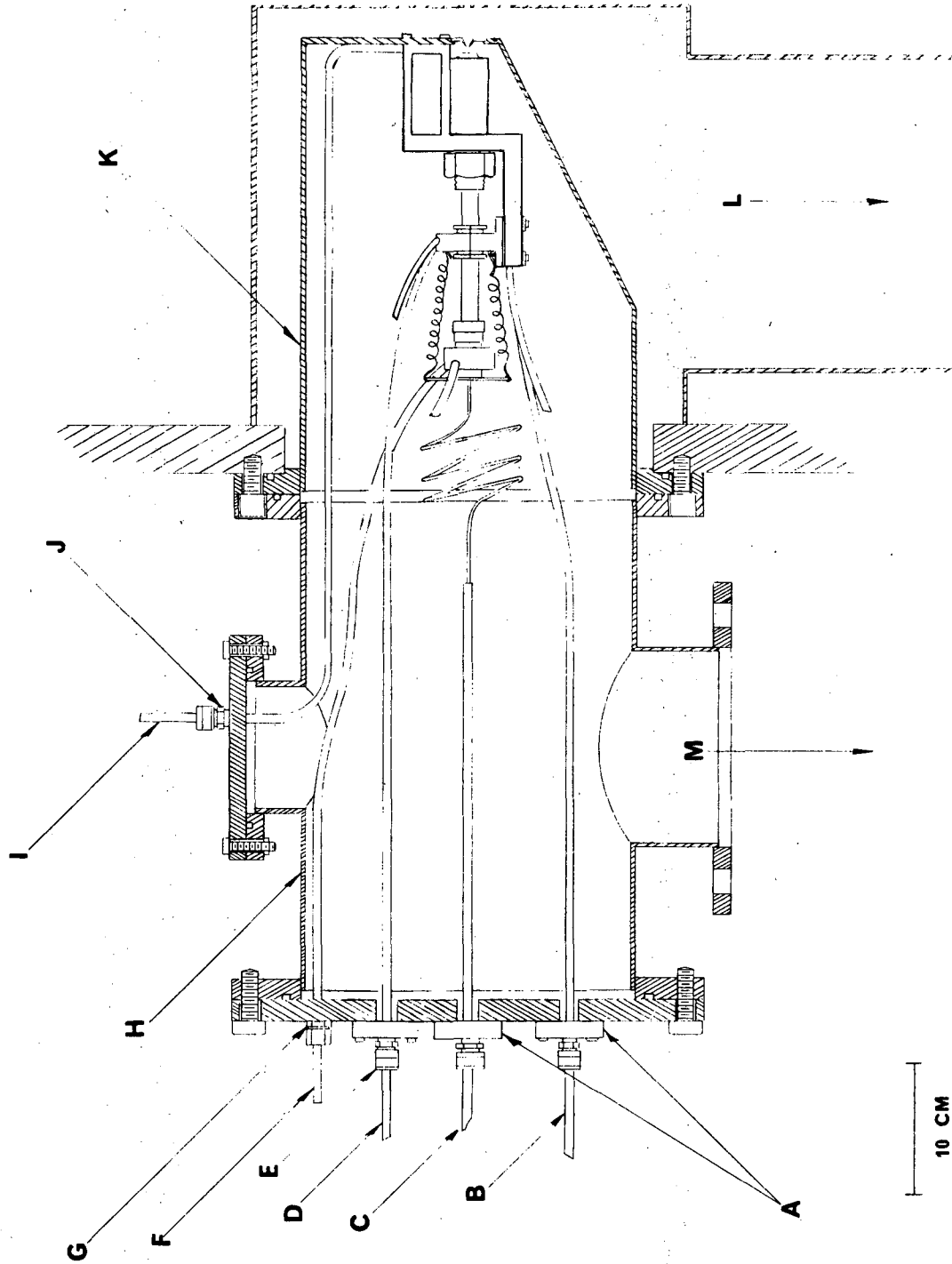


Fig. 2

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Fig. 3

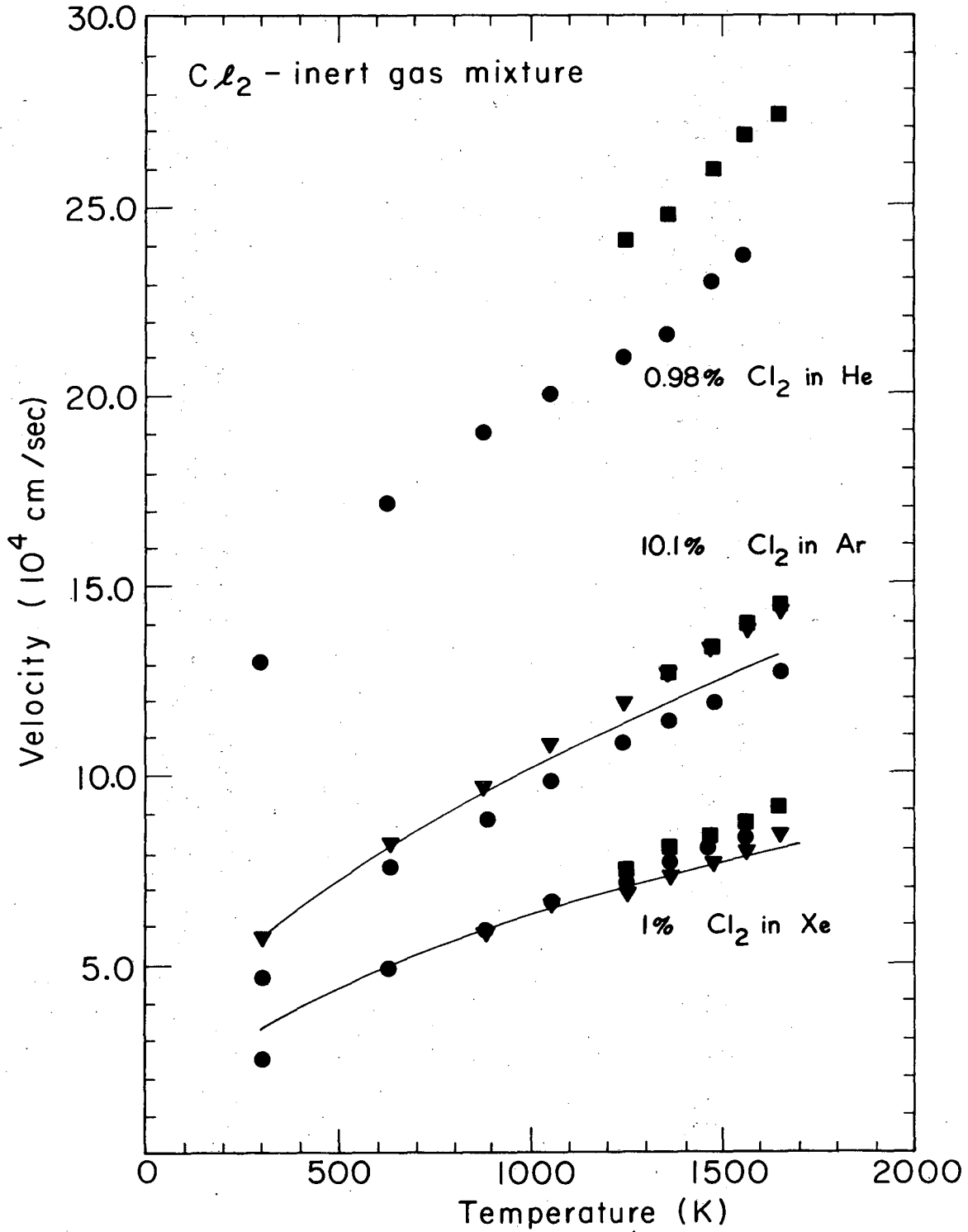


Fig. 4

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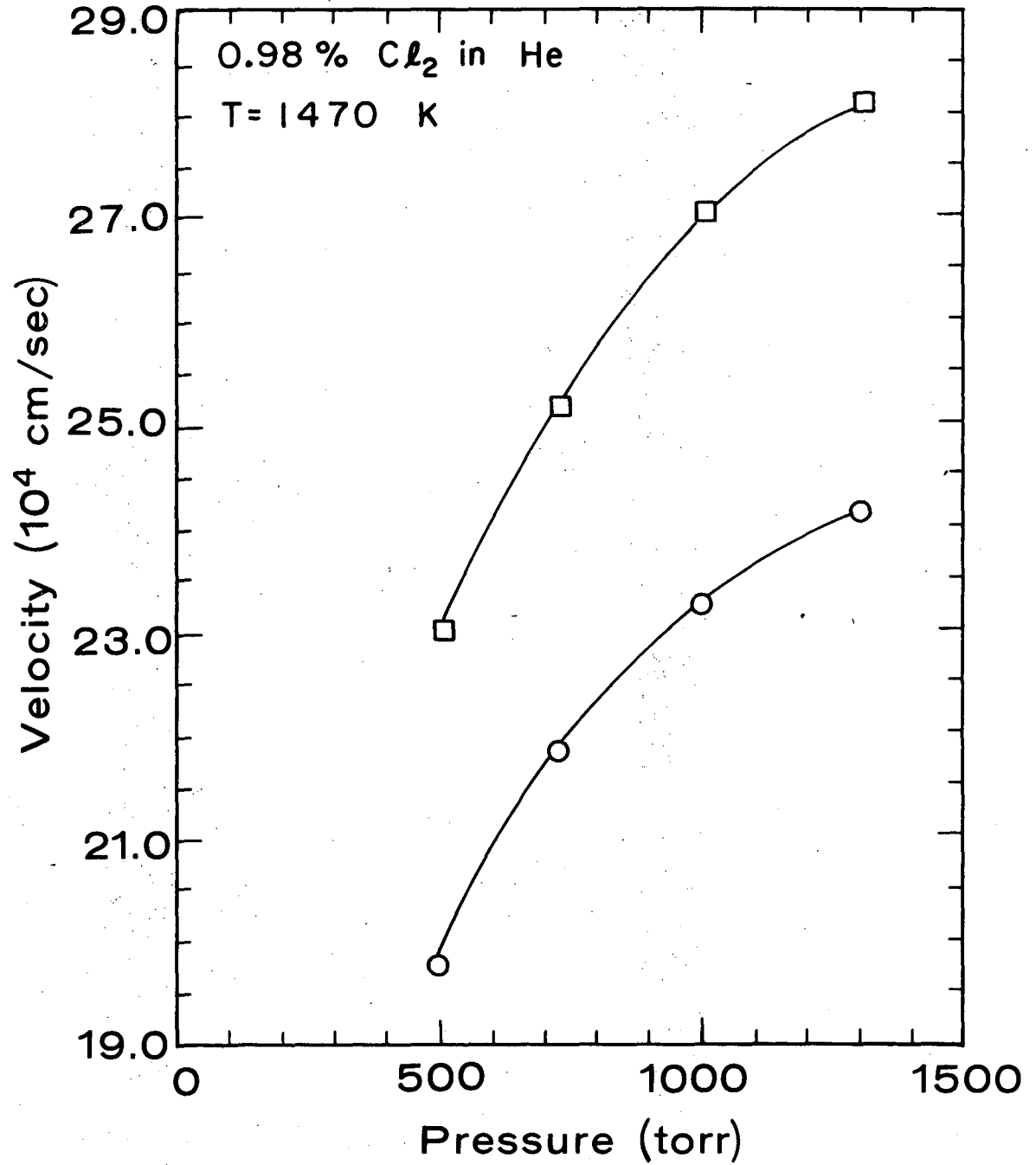


Fig. 5

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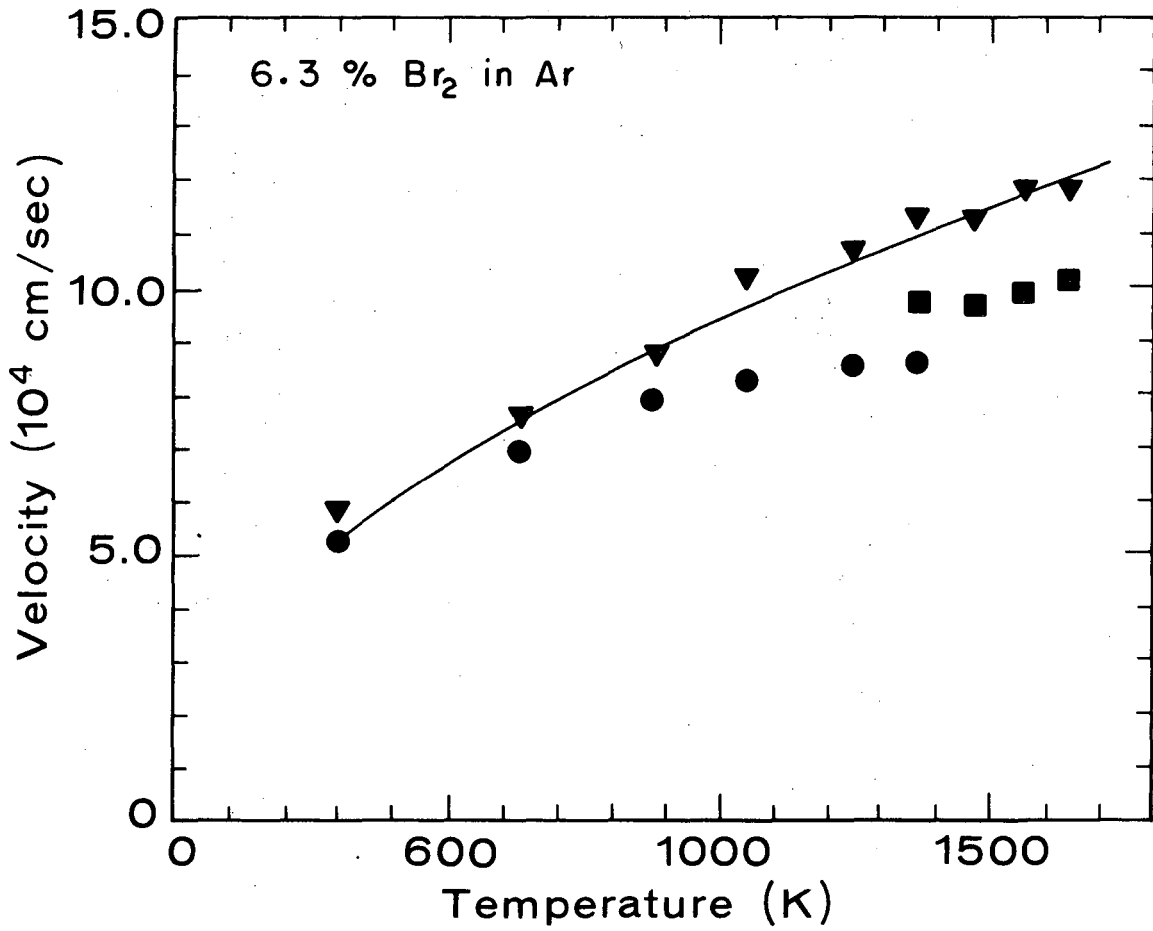


Fig. 6

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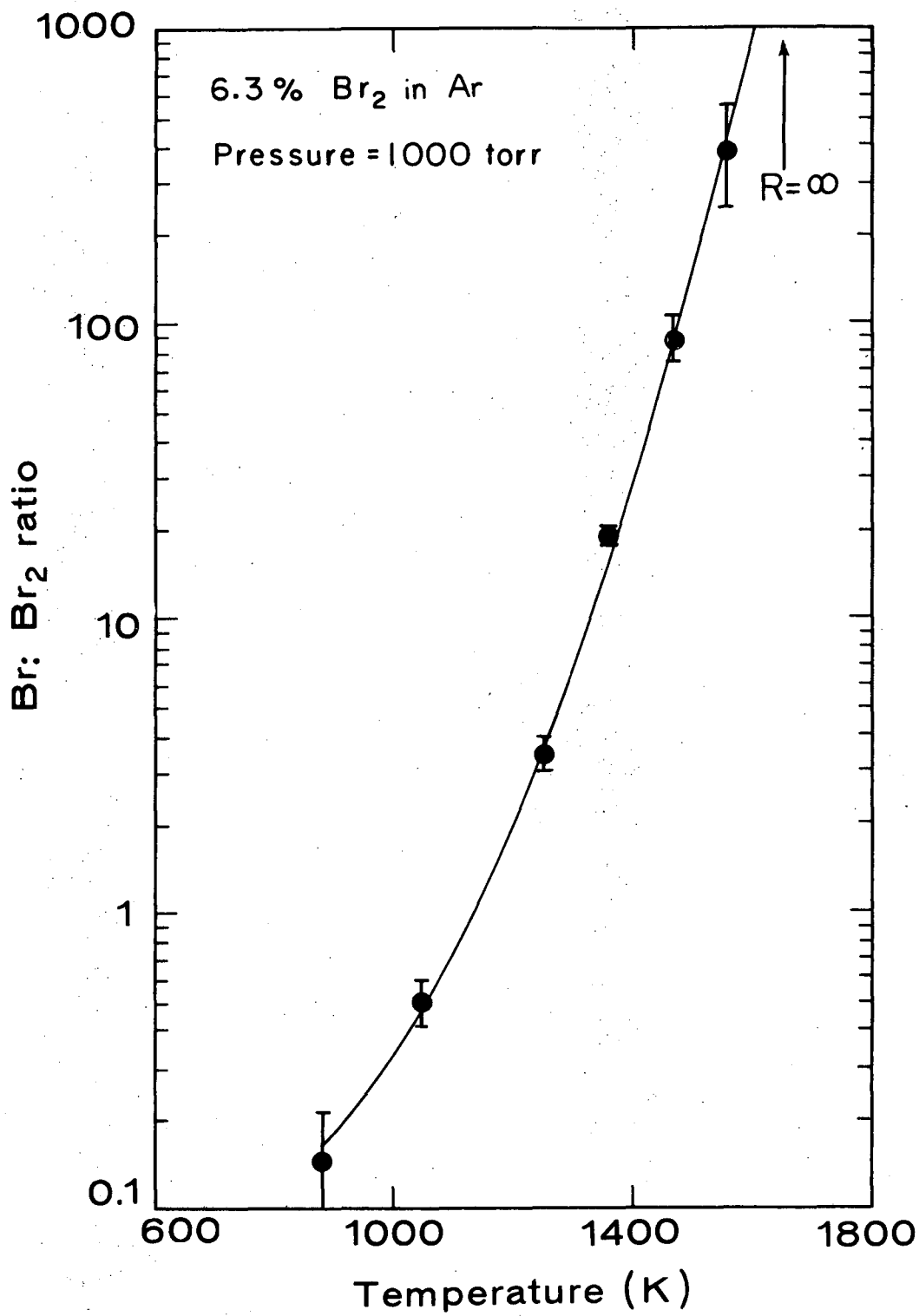


Fig. 7

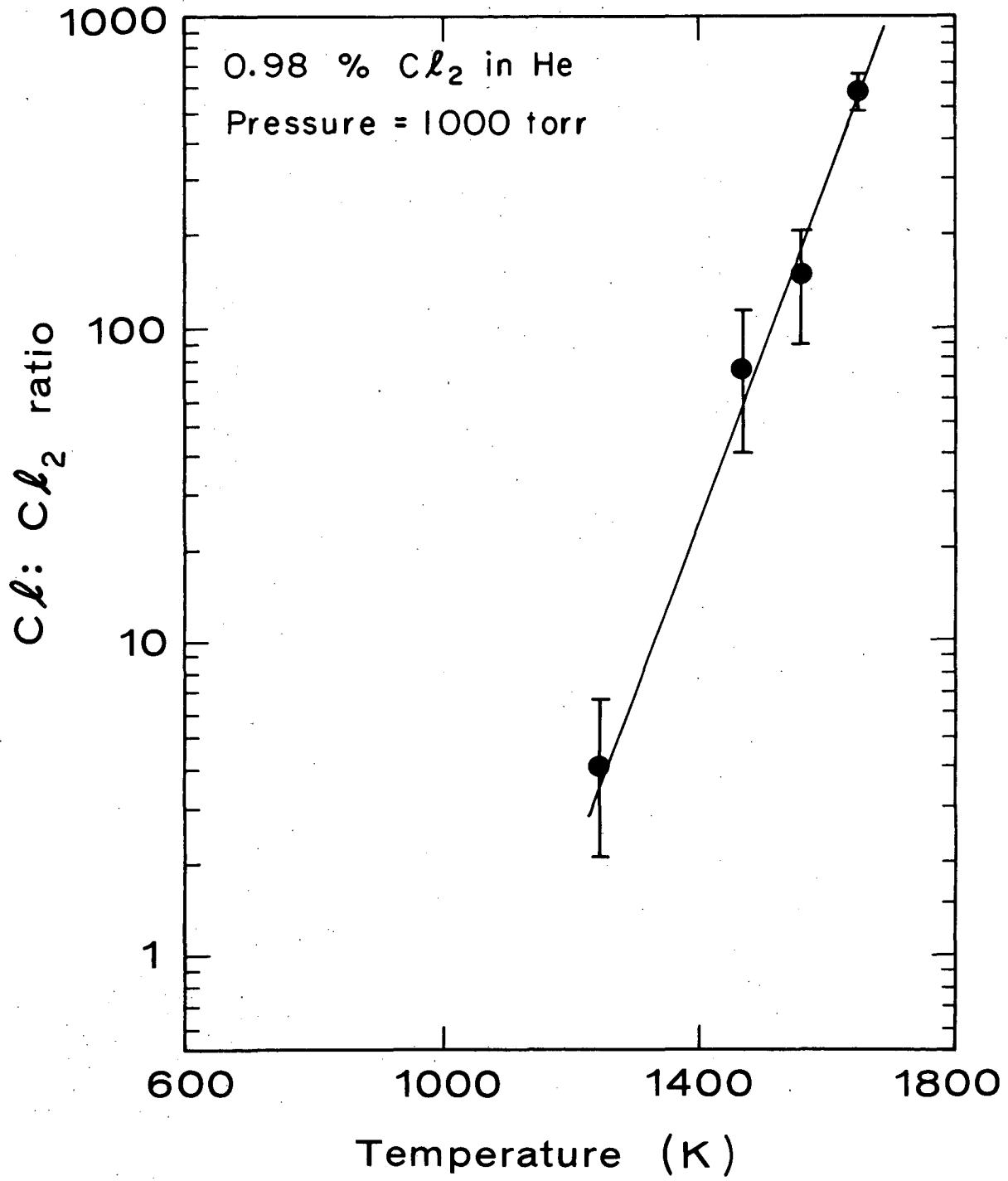


Fig. 8

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