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The Acoustic Properties of Methane Hydrate by Brillouin Spectroscopy.

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Abstract

Under certain conditions of pressure and temperature hydrocarbon gases combine with water to form ice-like solids, gas hydrates. Such conditions are encountered in the permafrost areas of the far north and beneath the offshore waters surrounding us. Very little information is available on the physical properties of such deposits which pose a danger to northern drilling and may, in the future, provide an unconventional source of natural gas. This report describes the methods and techniques used to produce single crystals of hydrate in the laboratory and determine its acoustic properties.

Résumé

Sous certains conditions de pression et de température le gaz naturel se combinent pour former une substance semblable à la glace, les hydrates de méthane. Au Canada nous rencontrons de telles conditions dans les zones de pergélisol et sous les mers qui nous côtoient. Présentement, très peu de données sur les proprietés physiques de telles dépôts qui pose un danger au forage du nord et qui, dans le futur, peut pouvoir une source non-conformiste de gaz naturel. Ce rapport décrit les méthodes et techniques utilisé pour produire un cristal unique d'hydrate dans un laboratoire et de déterminer ces propriétés acoustiques.

THE ACOUSTIC PROPERTIES OF METHANE HYDRATE

BY

BRILLOUIN SPECTROSCOPY

A Report

by

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It is the purpose of the present work to determine acoustic velocities in pure methane hydrate utilizing the method of Brillouin spectroscopy. This information is clearly of considerable value if seismic techniques are to be used for detection of methane hydrate in the natural environment. As explained in a previous report (Dec. 8/79) Brillouin spectroscopy probes thermally induced (i.e. not artificially excited) elastic waves and requires only very small sample sizes (as small as 1 mm^3). This is an obvious advantage for samples which are relatively difficult to obtain and require high pressures.

The previous report also gave a description of methane hydrate and possible methods of formation. The theory of Brillouin scattering and the necessary apparatus were also discussed and illustrated (see also Fig. 1). A detailed account of the sample cell, cryostat, gas handling system (see Fig. 2), various successfull attempts (3 methods) of sample preparation, and proposed modifications was given and shown on diagrams. The basic results of the work up to Dec. 8/79 are described in the next paragraph.

It was found that a gas flow system was necessary to ensure a sufficient supply of water-saturated methane gas in the hydrate formation region. Hence the system was at first modified to permit a continuous flow of methane through water in a high pressure reservoir. If any part of the hydrate sample region, at the tip of the hypodermic feed through tube, was above the hydrate formation temperature at the methane pressure used, then liquid water would readily condense. Consequently it was, in general, necessary to reduce the temperature to below $-10^{o}C$ at methane pressures near 700 psi. For slow flow conditions (a few cm^3 per hr at STP) hydrate formed around the cell walls immediately below the exit tube, whereas at faster flow rates the gas mixture was forced deeper into the cell and bulk

samples could be formed, which at some point would block up the quartz cell. By introducing a copper cold point in the bottom of the cell it was verified that methane hydrate will grow in the coldest region in the immediate proximity (within 1 mm) of the hypodermic tip, that is, the coldest point first encountered by the gas mixture.

On the basis of the above results and according to the proposals in the Dec. 8/79 report, the apparatus was considerably modified. In fact, the entire cell and cryostat system was rebuilt, also to make assembly and adjustments easier and more reliable (see Fig. 3). By removing the 1.3 cm thick plexiglass bottom plate and outer plexiglass cover (8.8 cm I.D. and 9.4 cm O.D.) the cell and cooling system, which is supported by the top brass cover, is exposed. The water-cooling tubes for the thermoelectric molecule, the electrical leads and vacuum port exit via the top cover. The quartz-metal high pressure seal is an integral part of the top cover.

The cell dimension were increased to 1.5 mm I.D. and 6.5 mm O.D. and the hypodermic tube decreased to 0.5 mm O.D. and offset to one side of the cell to allow for passage of the incoming laser beam along the cell (see Fig. 4). Laser beam access also necessitated the insertion of a quartz window into the bottom of the cell. This was accomplished by ultrasonically drilling out the bottom 6 mm of the quartz all to accomodate a highly polished, 3 mm diameter, 7 mm long, fused quartz plug. After very thoroughly cleaning the quartz tube and plug, the plug was carefully epoxied into the bottom of the sample tube. A 5 mm wide brass cooling clip was positioned and spring mounted slightly below the top surface of the quartz plug. The clip was connected to the thermal module via of a flexible copper braid. Accurate temperature control (within 0.1 C^{o}) was accomplished by means of a heater and GaAs Diode, mounted on the clip, in conjunction with

a Lakeshore Cryotronics Indicator/Controller Model DTC 500.

As before, the sample cell was flared and ground to provide for pressure sealing to the gas handling system. The appropriate Teflon seals and the tightening coupling is shown in figure 3. The pressure sealing, however, this time is considerably more intricate in that the hypodermic tube (as previously proposed) is now adjustable in a vertical position so that the end of the tube can be kept very close (20.5 m) to the hydrate surface at all times to ensure that the gas mixture first encounters the coldest horizontal surface rather than the cell walls. The tube is adjustable from the cell bottom through a height of about 1.5 cm. The appropriate O-ring seals, seats and adjusters are shown in the figure. Hence it is now possible to initiate hydrate growth on the surface of the window and, by slowly adjusting the position of the hypodermic tube, to allow a bulk sample of methane hydrate to grow vertically up the sample tube.

Progress, however, has not proceeded as rapidly as expected, or at least as hoped. There are several reasons for this. (1) The modified apparatus was designed and drawn up just before Christmas. Unfortunately Christmas and New Years' (and some time thereafter) is not the most efficient time in the machine shop. (2) There were leakage problems in the quartz-metal high pressure seals. The reason was concluded to be due to thermal recycling and the differential thermal expansion between Teflon and brass. This problem arose because there is now direct thermal contact between the cooling water and the high pressure seal via the brass cover. However, once discovered the problem was easily overcome by simply keeping the system cold at all times. (3) At one point there was a leakage problem at the epoxy joint at the cell bottom. After several repair attempts

it was necessary to replace the cell and plug. (4) The above problem was in fact initiated when it was necessary to temporarily move the equipment to another laboratory due to (otherwise very beneficial) renovations in the existing laboratory. (The equipment is presently being moved back). (5) In addition to breakdowns caused by the flue, the Ar^+ laser, which was to provide the incident radiation, burned out about 6 weeks ago. A new tube was installed 1 week ago, and another delayed and very pressing project is now being completed with the light scattering equipment - this work would otherwise have been finished.

Nevertheless the project is back in operation.. Other than one existing problem, the equipment is working well and several bulk samples (~few mm^3) have been produced. Although usable, they are still somewhat cloudy. The problem (which is not too serious) that still remains is one of freeze-up and consequently blockage at the tip of the hypodermic tube, even at relatively fast flow rates. Although there is reluctance to re-open the system, it may be necessary to lift the end of the hypodermic tube off the cell walls to prevent too much cooling of the tip.

Despite some set backs, the results have been encouraging in that the presently existing equipment appears to be quite adequate for the job. Another positive sign is the acquisition of an NSERC equipment grant for a new Ar^+ laser (which is now on order) for the renovated laboratory. This will releave the pressure, for essentially having to wait to free one of the other existing light scattering systems. It is estimated that Brillouin scattering and hence sound velocity data for methane hydrate will be forth-coming during the summer months. It is also the intention to widen the scope of this work to other similar (structure I) gas hydrates, particularly

to the much easier to form xenon and ethylene oxide hydrates. By forming clear crystals, and possibly single crystals, of these similar hydrates and subsequently completing light scattering experiments and analysis, much additional knowledge, especially of the elastic properties, of methane hydrate will be gained.

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FIGURE CAPTIONS

Fig. 1 Overall arrangement of the apparatus in a Brillouin scattering experiment: L, lenses; M, mirror; A, aperture; COL, X-ray collimator; S, sample site; P, Polaroid X-ray camera; PM, photomultiplier tube; AD, amplifier-discriminator; DAS, data acquisition and control system.

Fig. 2 The high pressure gas handling system.

Fig. 3 Schematic drawing of the "new" modified cryostat

Fig. 4 Detail A Magnified drawing of the sample cell region.

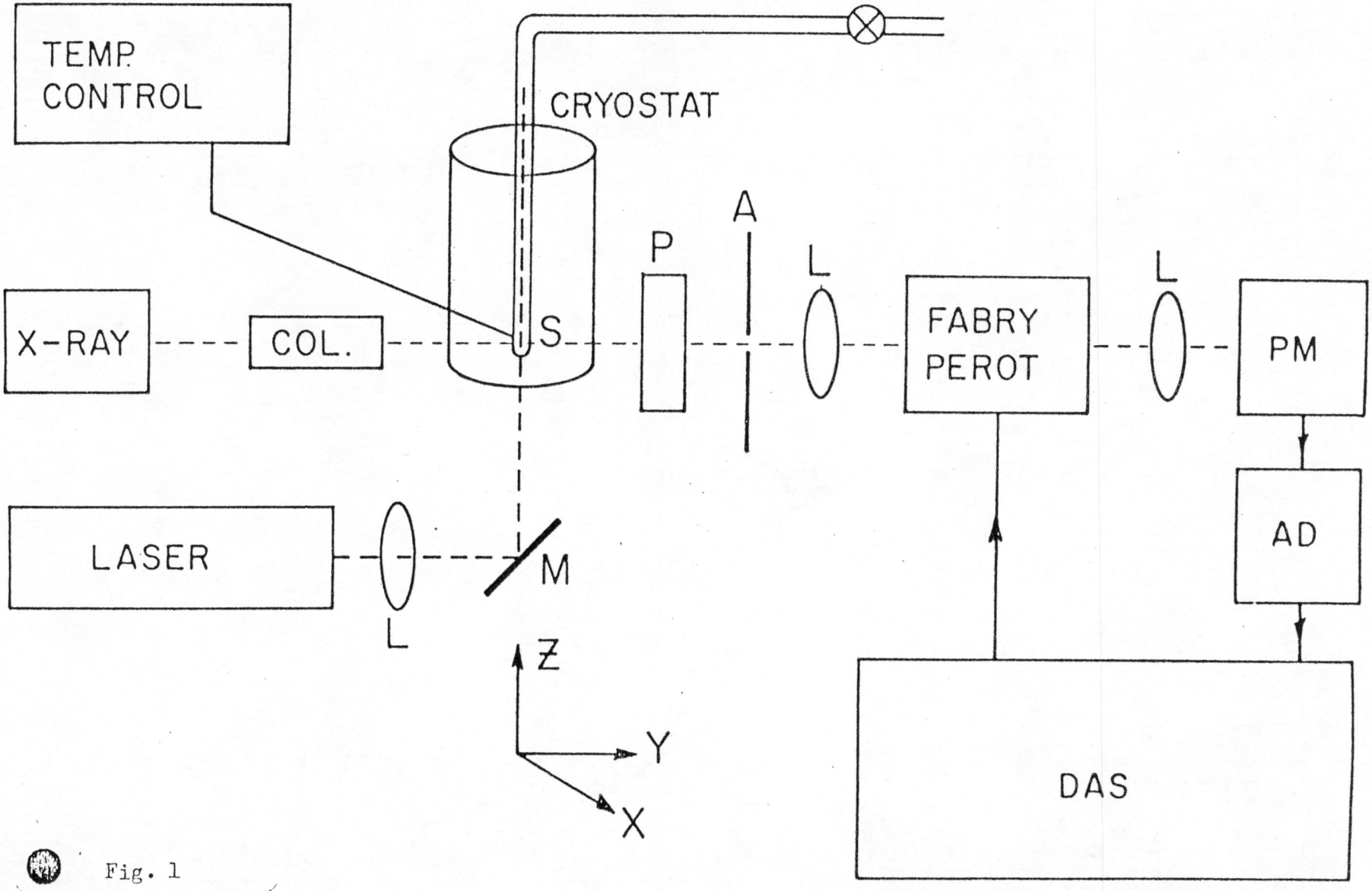
TEMP.
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Fig. 1

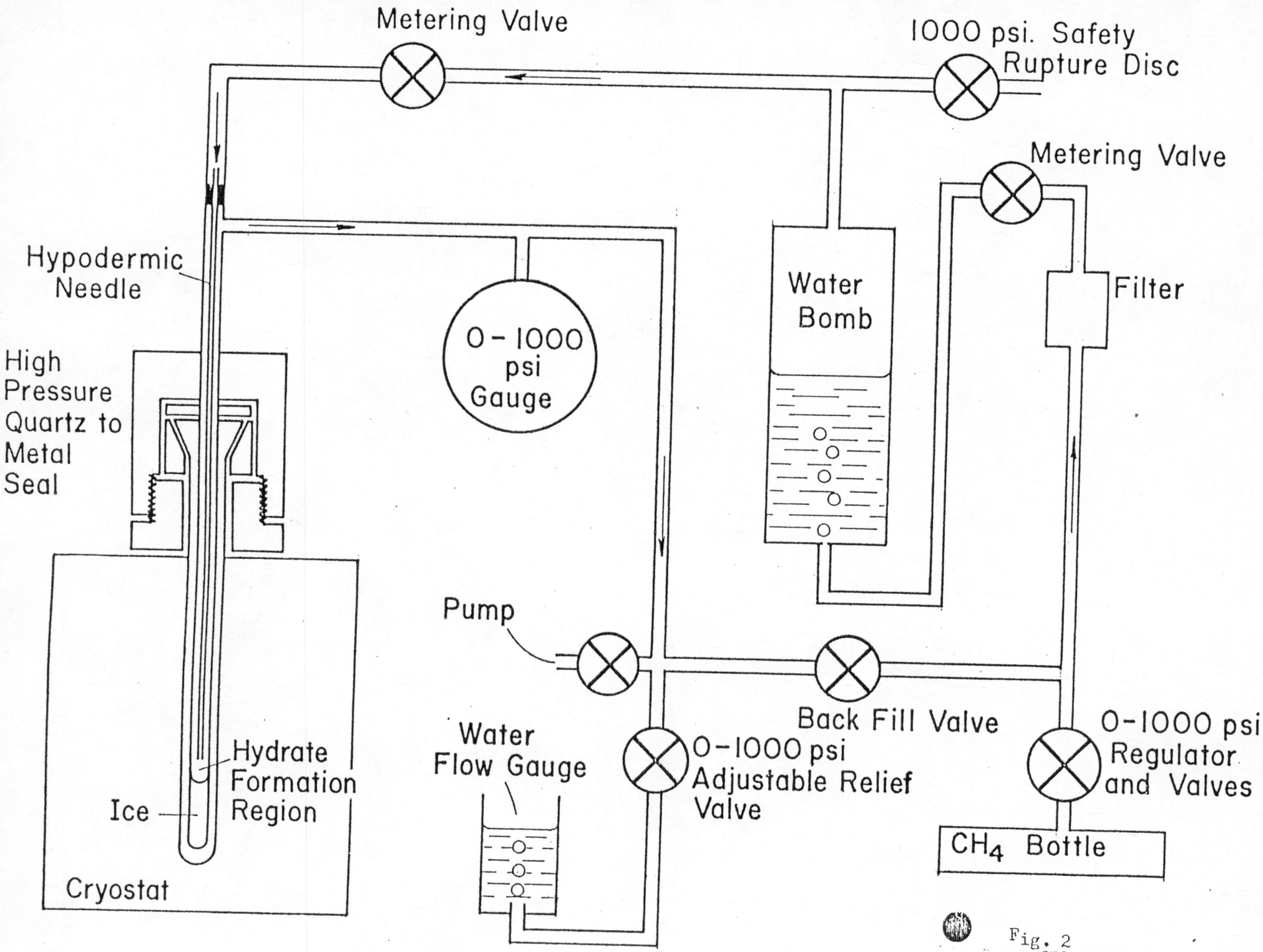

Metering Valve
1000 psi. Safety Rupture Disc
Metering Valve
Hypodermic Needle
High Pressure Quartz to Metal Seal
0 - 1000 psi Gauge
Water Bomb
Filter
Pump
Back Fill Valve
0-1000 psi Regulator and Valves
Water Flow Gauge
0-1000 psi Adjustable Relief Valve
Hydrate Formation Region
Ice
Cryostat
CH_4 Bottle

Fig. 2

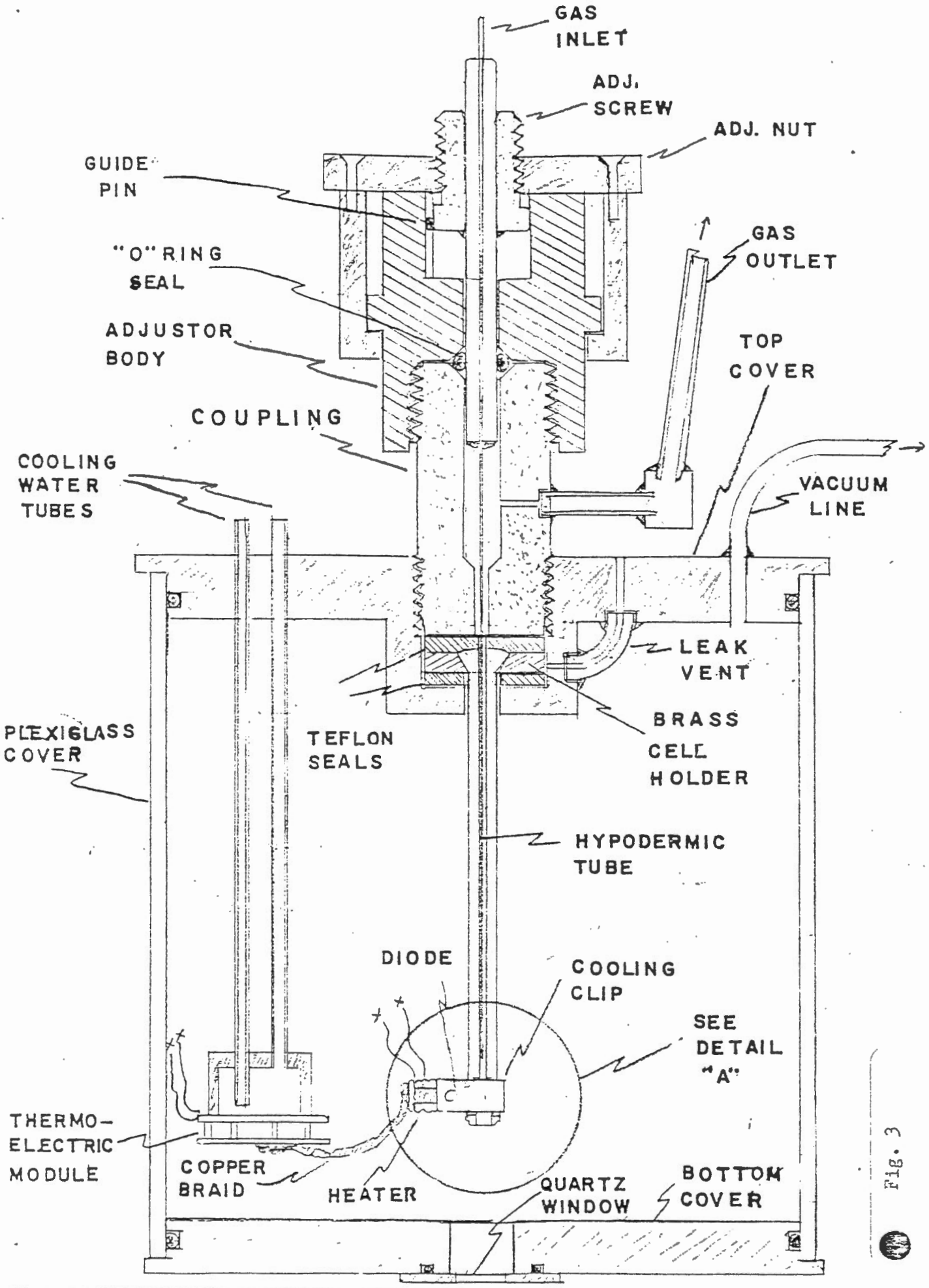
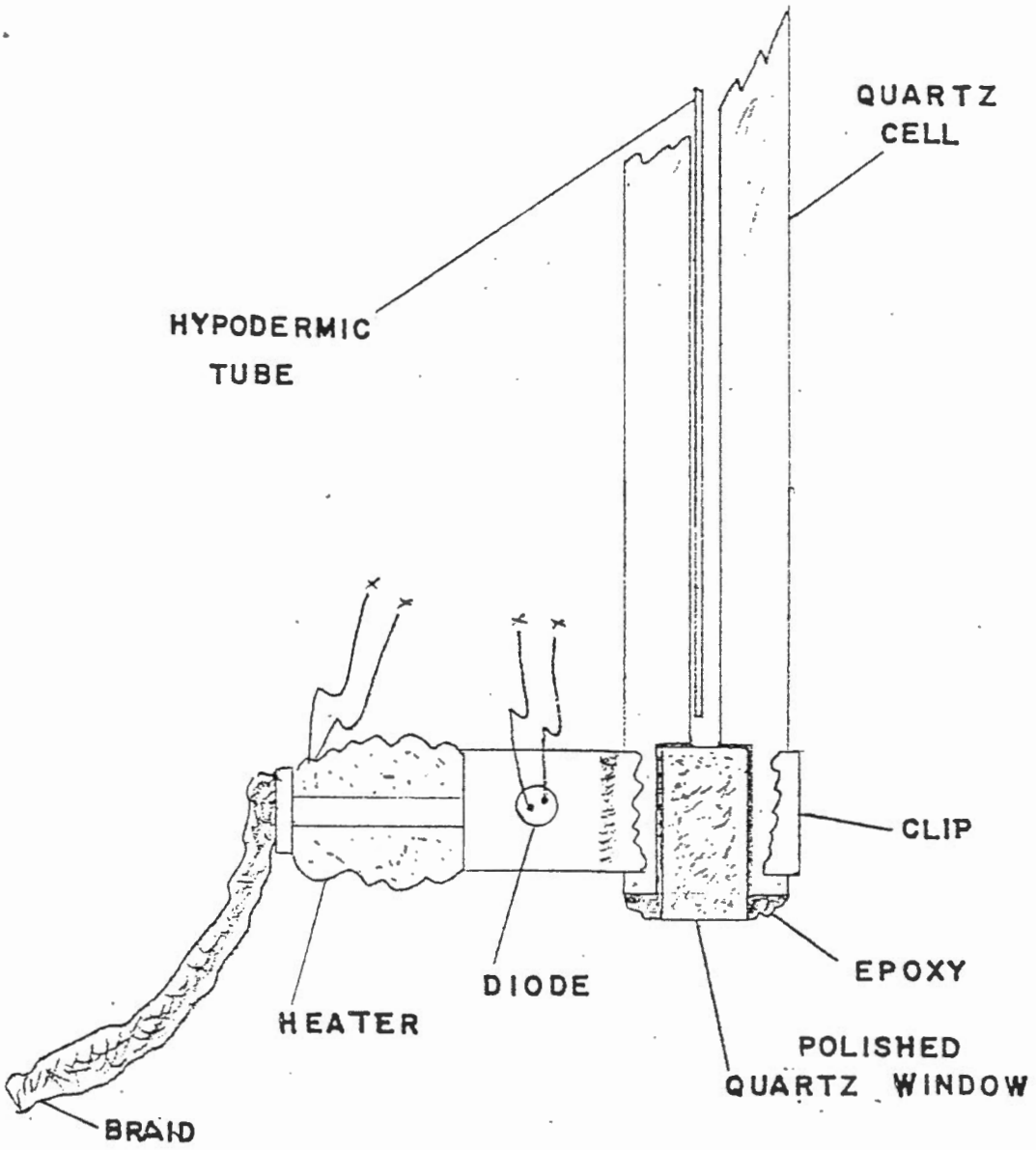

GAS INLET
ADJ. SCREW
ADJ. NUT
GUIDE PIN
"O" RING SEAL
GAS OUTLET
ADJUSTOR BODY
TOP COVER
COUPLING
COOLING WATER TUBES
VACUUM LINE
LEAK VENT
PLEXIGLASS COVER
TEFLON SEALS
BRASS CELL HOLDER
HYPODERMIC TUBE
DIODE
COOLING CLIP
SEE DETAIL "A"
THERMO-ELECTRIC MODULE
COPPER BRAID
HEATER
QUARTZ WINDOW
BOTTOM COVER

Fig. 3



SAMPLE CELL

Fig. 4

DETAIL "A"