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ACOUSTIC PROPERTIES OF CLATHRATE HYDRATES
AND HYDRATE-SATURATED POROUS ROCKS.

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Abstract

Preliminary studies of the elastic wave velocities in a structure II hydrate over a temperature range of -17.4°C to $+2.4^{\circ}\text{C}$ have shown both p and s-wave velocities to be lower than for ice, the p-wave measurement lies 10% below a theoretical estimate made. Some interesting qualitative relationships have been observed in comparing the seismic wave attenuation with that in ice. These will be investigated further as a possible down-hole detection tool to discriminate unambiguously between hydrate and ice.

Résumé

Des études préliminaires de la vitesse de propagation des ondes élastiques dans un hydrate de type structure II, entre les températures de -17.4°C et $+2.4^{\circ}\text{C}$, ont révélé que les ondes primaires et secondaires se propagent plus lentement que dans la glace. La mesure pour les ondes primaires est 10% en dessous d'une valeur théorique calculée. Quelques rapports qualitatifs intéressants ont été observés en comparant l'affaiblissement des ondes sismiques dans l'hydrate avec celui dans la glace. Ces rapports seront étudiés de plus près afin de déterminer leur potentiel comme outil de sondage pouvant distinguer sans ambiguïté entre l'hydrate et la glace.

Acoustic Properties of Clathrate
Hydrates and Hydrate-Saturated
Porous Rocks

A Progress Report

DSS Contract No. OSU80-00354

"Study to investigate the elastic, electrical and thermal properties of propane gas hydrates and hydrate-saturated sands, over a range of temperature and pressure."

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30 March 1981

1. A preliminary study of the elastic wave velocities of propane gas hydrates has been completed. Results of this study are summarized as follows:
 - (i) A bulk specimen of propane gas hydrate necessary for velocity measurements can be prepared by adding appropriate amounts of liquid propane and distilled water under hydrate forming pressure and temperature conditions.
 - (ii) Compressional (P) and shear (S) wave velocities of propane gas hydrates and (for comparison) ice were measured as a function of temperature and axial stress. The temperature range extended from -17.4°C to $+2.4^{\circ}\text{C}$, and the axial stress varied from 0.53 MPa to 2.1 MPa.
 - (iii) Below 0°C , the temperature dependence of both compressional and shear wave velocities was weak; the respective values being 3.25 km/sec and 1.65 km/sec for propane hydrate and 3.86 km/sec and 2.04 km/sec for ice.
 - (iv) No significant variation of velocity with axial stress was observed below 0°C .
2. (a) The above results were presented at the 4th Canadian Permafrost Conference in Calgary, Alberta (March 2-6, 1981) in a paper entitled "Compressional and Shear wave velocities of Propane gas hydrates" by B. I. Pandit and M. S. King.
(b) Also, a paper entitled "Elastic wave velocities of propane gas hydrates" by B. I. Panidt and M. S. King has been submitted for publication in the proceedings of the symposium on "Unusual Gas Resource and Recovery Technology" organized by the American Chemical Society in August 1980. A copy of the above paper is enclosed as part of this report.
3. As a continuation of the above study, the 'P' and 'S' wave signals for the propane hydrate and the ice specimens have been now digitized in order to determine the respective amplitude and phase spectra. From these spectra, it is hoped to draw some conclusions on the relative attenuation of elastic waves in hydrates and ice respectively.

A paper incorporating all of the above results is in preparation now for submission (in April) and publication in the Proceedings of the 4th Canadian Permafrost Conference.

4. In addition to the above, specimens of Tetrahydrofuran (THF) hydrate have been successfully prepared in a bulk form. At room temperature (25°C) and atmospheric pressure, THF is a liquid and, more importantly, soluble in water. It is, therefore, possible to saturate a porous rock with a solution containing THF and water. IF the relative amounts of THF and water are appropriate to pure hydrate formation it should be possible to form and thus fill the pore spaces of the rock the THF hydrate.

In order to examine the differences in elastic wave velocities and attenuation between a water (ice) saturated rock and a hydrate saturated rock, it is intended to proceed with the following experiment.

Two 'identical' specimens of a high porosity (≈ 0.20) rock will be saturated, one with distilled water and the other with a solution of THF + water. The specimens will then be assembled in pressure cells for velocity measurements in a manner described by Pandit and King (1979). The cells will then be placed in a cold room whose temperature can be varied from -18°C , to say, $+10^{\circ}\text{C}$. At -18°C and atmospheric pressure, the pore spaces of one specimen will be filled with (essentially) ice and the other with THF hydrate. Velocity measurements will be made as a function of temperature and axial stress. Above 0°C but below $+4^{\circ}\text{C}$, the velocity of the specimen containing ice will drop sharply while that of other specimen is expected to show no change as THF hydrate is stable up to $+4^{\circ}\text{C}$ at atmospheric pressure. Above 4°C , however, a sharp drop in velocity will occur in this specimen, too.

As mentioned earlier, 'P' and 'S' wave signals for both specimens will be digitized to obtain the amplitude and phase spectra, and thus the attenuation.

Also, the present set up allows the study of hysteresis in velocities as a result of thermal cycling. This will be studied too.

Reference

1. B. I. Pandit and M. S. King. A study of the effects of pore-water salinity on some physical properties of sedimentary rocks at permafrost temperatures. Canadian Journal of Earth Sciences, vol. 16, no. 8, 1979, pp. 1566-1580.

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Elastic Wave Velocities

of

Propane Gas Hydrates

by

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Abstract

Compressional (P) and shear (S) wave velocities of propane gas hydrates and ice were measured as a function of temperature and axial stress. The temperature range extended from -17.4°C to $+2.4^{\circ}\text{C}$, and the axial stress varied from 0.53 MPa to 2.1 MPa. Below 0°C , the temperature dependence of both compressional and shear wave velocities was weak; the respective values being 3.25 km/sec and 1.65 km/sec for propane hydrate and 3.86 km/sec and 2.04 km/sec for ice. Also, no significant variation of velocity with axial stress was observed below 0°C .

Introduction:

The results presented here constitute the initial phase of a program to study the velocities and attenuation of elastic waves in gas hydrates and hydrate saturated sands and sedimentary rocks at temperatures encountered in northern Canada. Such information is needed in the interpretation of seismic data obtained over areas where gas hydrates occur in the underlying rock formations.

Choice of hydrate:

The experimental set up used in this study is such that the preparation of the hydrate specimen and the measurement of elastic wave velocities are carried out in different pressure cells. This necessitates the exposure of the hydrate to atmospheric pressure while being assembled for velocity measurements. Figure 1 shows the phase diagram for propane hydrate. It is clear from the figure that there is a pressure-temperature region (marked A) within which the hydrate is stable at atmospheric pressure. Consequently, the present study has been confined to propane hydrates only.

Preparation of hydrate specimens:

Figure 2 shows the pressure cell in which the hydrate specimens are prepared. The cell consists of a plexiglass cylinder bounded by brass plates at the top and bottom. Distilled water and propane gas are introduced through an opening in the top brass plate.

The purpose of the spiral groove behind the teflon insert was to aid in specimen recovery. It was planned to circulate pressurized gas through the groove thus compressing the hydrate specimen sufficiently so that it could be pushed out of the cell easily after the bottom plate was removed. This approach was not followed, however. Instead, the inner surface of the teflon insert was coated with a thin layer of RTV 910 lubricant before introduction of water or gas. The procedure was successful in recovering the hydrate specimen.

Figure 3 shows the schematic diagram of the complete apparatus used in hydrate preparation. The procedure adopted was as follows:

- (i) The temperature of the preparation room was lowered to approximately 2°C.
- (ii) The pressure cell was then evacuated.
- (iii) Distilled water at about 2°C was then introduced in the cell.
- (iv) Propane gas was added to it at a pressure of 0.5 MPa.

The pressure and temperature conditions in the cell are adequate for forming a hydrate. In fact, a layer of hydrate slurry was observed floating over the water layer. However, it was not possible to produce sufficient quantity of hydrate to prepare a bulk specimen needed to perform velocity measurements.

To prepare bulk specimens used in this study the procedure followed by Stoll and Bryan (1) was adopted. Essentially, it consists of mixing liquid propane and water to prepare large quantities of hydrate. Consequently, after addition of the propane gas, as in

step (iv), a pressure intensifier was used to liquefy the gas present in the cell. On stirring, a hydrate slurry was formed immediately. Repeated cycles of addition of gas and its subsequent liquefaction enabled the preparation of bulk specimens of propane hydrate.

In order to prepare pure specimens of propane hydrate, the volume of liquid propane should bear a certain ratio to the volume of water in the cell. Taking the molecular formula for propane hydrate to be $C_3H_8 \cdot 17H_2O$, and the density of liquid propane at $2^\circ C$ as 530 kg/m^3 , it can be shown easily that the volume of liquid propane should be 0.27 times the volume of water. In practice, it is difficult to achieve this ratio exactly; one of the components is very likely to be in excess. The two hydrate specimens involved in the present study had a water (or ice) content in excess of the above formula.

Once the hydrate slurry had been formed, it was left undisturbed for about 24 hours. The slurry then formed a fairly coherent mass. The temperature of the cell was reduced to approximately $-18^\circ C$, and so maintained for at least 12 hours. The cell was then disassembled, and the hydrate specimen was pushed out from it. It was then machined, keeping it at a temperature of $-18^\circ C$, to produce parallel flat surfaces. The final dimensions and masses of the two hydrate specimens as well as for an ice specimen are given below.

Table I

	Hydrate I	Hydrate II	Ice
Length (mm)	35.82	25.40	35.31
Diameter (mm)	49.81	49.94	49.15
Density (kg/m^3)	850	750	920
Purity	10-20% ice content	5% ice content	pure

The ice contents of the hydrate specimens are qualitative estimates based on the liquid propane/water ratio in the preparation cell.

Velocity measurements:

The specimen was first mounted between piezo-electric transducer holders. It was then surrounded by double jackets of tightly fitting thin rubber, over which overlapping vinyl tape was wrapped. This ensured that the DC 200 silicone fluid exerting the confining pressure did not invade the specimen.

A block diagram of the ultrasonic velocity apparatus is shown in Figure 4. The piezo-electric transducer holders are designed to measure compressional (P) and shear (S) wave velocities sequentially on the same specimen, and are similar to those described by King (2). The specimen is surrounded in the triaxial cell by DC 200 silicone fluid. Compressed nitrogen is employed to pressurize the DC 200 silicone fluid applying the confining pressure and to apply the axial stress on the specimens. Velocity measurements were made by measuring the time of propagation of a sinusoidally decaying pulse at 820 kHz through the specimen. Velocities were generally measured with an accuracy of ± 1 percent. Temperature of the specimens were measured by platinum resistance sensors placed in the triaxial cell close to the specimens.

The confining pressure was maintained at 0.35 MPa throughout the course of the measurements. At any given temperature, the axial stress was varied from 0.53 MPa to 2.1 MPa in two steps. The

temperature range over which the velocities were measured extended from -16.5°C to $+2.4^{\circ}\text{C}$. About 24 hours were allowed for the specimens to reach thermal equilibrium with its surroundings at a specific temperature.

Results:

Figures 5-8 show typical compressional (P) wave and the shear (S) wave signals through the specimens, namely, propane hydrate I and ice at successively higher temperatures. The time of travel through the specimen for either P or S wave is the time corresponding to the arrows shown, minus the travel time for the respective waves when the transducer holders are in face-to-face contact. As is evident from these figures, P wave arrival times can be determined with greater precision throughout the temperature range covered in this study. This is not so for the S wave, especially at temperatures close to 0°C . The P wave signal for 'ice' at 0.2°C corresponds almost to the travel time for transducers when they are face-to-face indicating that the specimen has melted. Also, there is no 'S' wave propagating through the specimen any more.

The hydrate specimen at -0.1°C shows a marked increase in P wave travel time (that is, a decrease in velocity); however, the specimen still retains its coherence. This is so even at 2.4°C (Figure 8). It is very difficult to determine the travel time for the S wave in these two cases.

Figures 9 and 10 show the variation of the compressional and shear wave velocities as a function of temperature and at an axial stress of 0.53 MPa. The variation of velocities with axial stress attained in this study was almost within the error of measurement.

Hydrate I shows insignificant variation with temperature for both velocities as long as the temperature is below 0°C . Above 0°C , a marked drop in the velocities is observed. This drop may be explained due to the melting of the excess ice (10-20%) within the specimen. It is worth noting here that on lowering the temperature of the hydrate once again to -17.4°C , the compressional and shear wave velocities rose to 3.38 km/sec and 2.03 km/sec respectively. When these values are compared with those initially obtained at -16.5°C , namely, 3.24 km/sec and 1.65 km/sec, there is an indication that the hydrate specimen had undergone a reduction in length. This specimen was recovered after the velocity measurements were completed. Its length was now 35.13 mm which means a reduction of 0.69 mm from its initial length. Using this new value, the compressional and shear wave velocities now become 3.23 km/sec and 1.98 km/sec. These velocities corresponds to increases of 2.5% and 20% respectively over the initial values at -16.5°C . Furthermore, the very small reduction in length indicates that above 0°C , the hydrate was stable and essentially coherent.

The velocity measurements on propane hydrate II had to be abandoned beyond -5°C due to refrigeration failure in the room in which the velocity cells were kept. The increase in velocity may be

due to specimen compaction. The same reason may also explain the slight increase in velocities for the ice specimen as the temperature was brought close to 0°C.

Bulk modulus 'K' and the rigidity modulus ' μ ' can be calculated from the velocity and density data. Table II gives the values of the above parameters for the hydrate specimen I and ice at (i) -16.5°C and (ii) -1.1°C respectively.

Table II

Specimen	K GPa	μ GPa
Hydrate I	(i) 5.82	(i) 2.32
	(ii) 5.64	(ii) 2.36
Ice	(i) 8.34	(ii) 3.85
	(ii) 8.78	(ii) 3.98

Acknowledgements

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1. Stoll, R. D. and Bryan, G. M.: J. Geophys. Res., 1979, 84,
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2. King, M. S.: "Rock Mechanics: Theory and Practice"
(Somerton, W. H., ed.), American Institute of Mining,
Metallurgical and Petroleum Engineers, New York, NY, 1970
p. 333.

FIGURE CAPTIONS

- Figure 1. Phase diagram for propane hydrate.
- Figure 2. Pressure cell for hydrate preparation.
- Figure 3. Schematic diagram of the complete apparatus.
- Figure 4. Block diagram of ultrasonic velocity apparatus.
- Figure 5. Compressional (P) and shear (S) wave signals through hydrate and ice.
- Figure 6. Compressional (P) and shear (S) wave signals through hydrate and ice.
- Figure 7. Compressional (P) and shear (S) wave signals through hydrate and ice.
- Figure 8. Compressional (P) and shear (S) wave signals through hydrate and ice.
- Figure 9. Variation of compressional (P) wave velocity with temperature. Axial stress: 0.53 MPa.
- Figure 10. Variation of shear (S) wave velocity with temperature. Axial stress: 0.53 MPa.

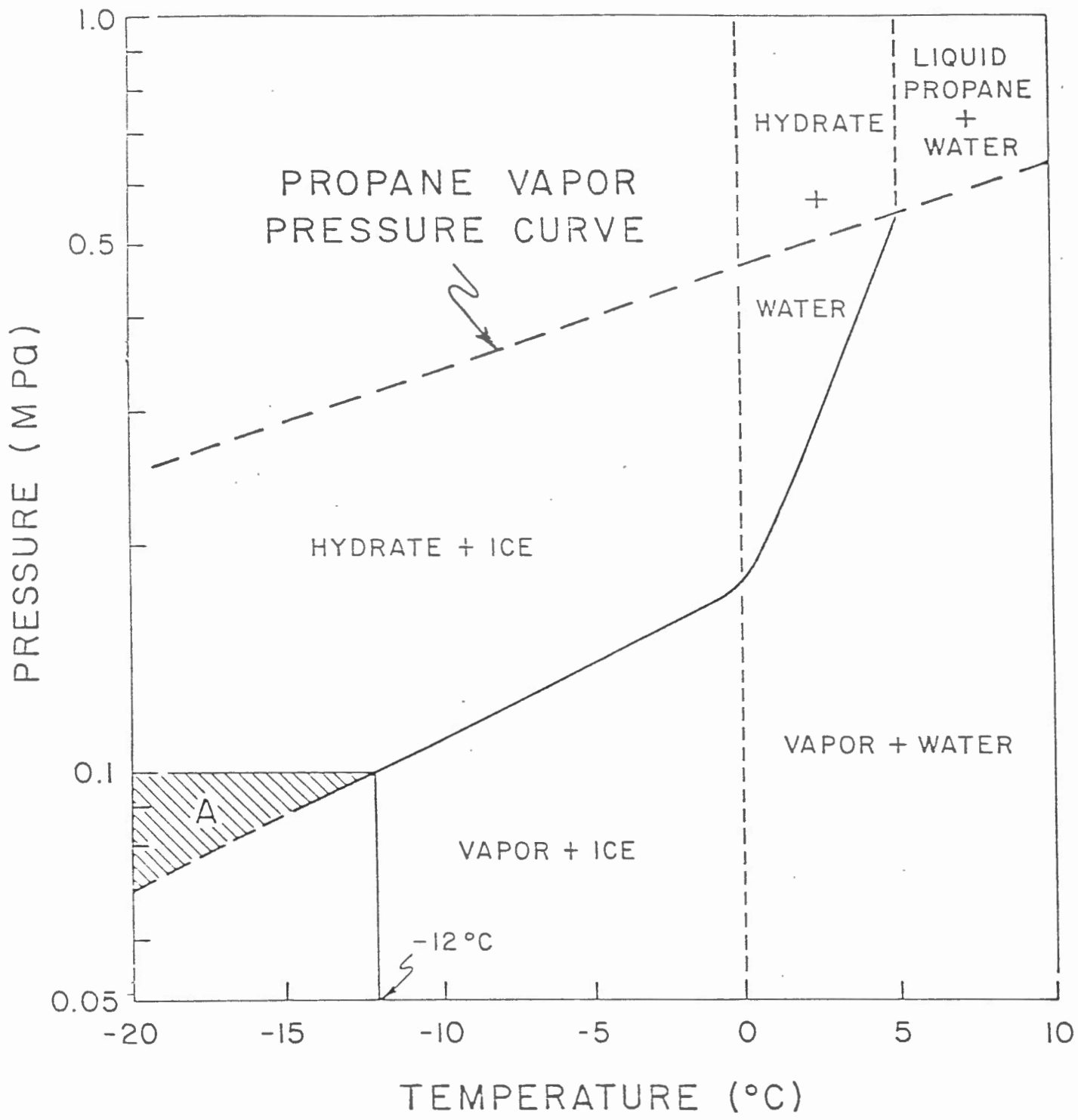
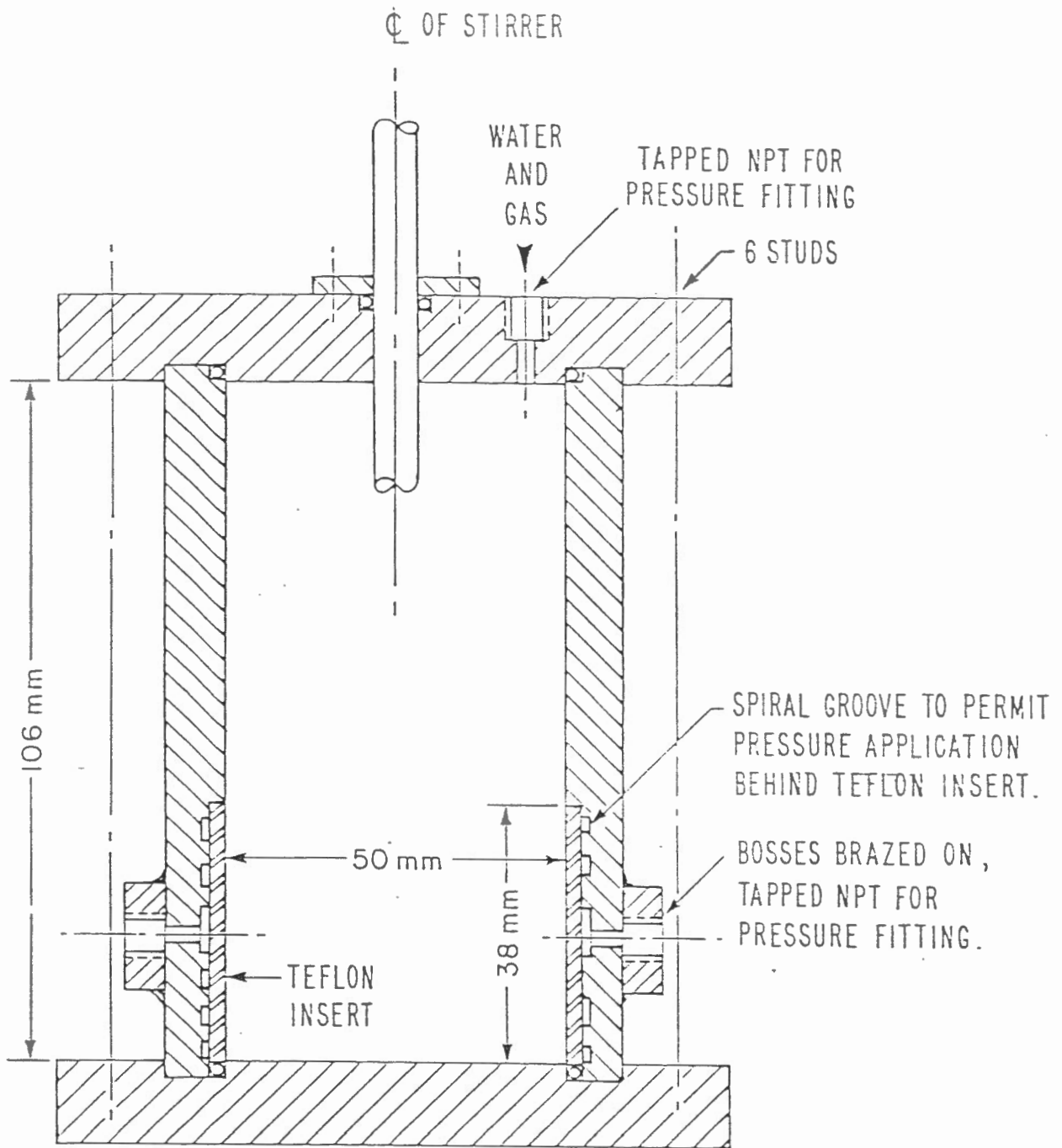
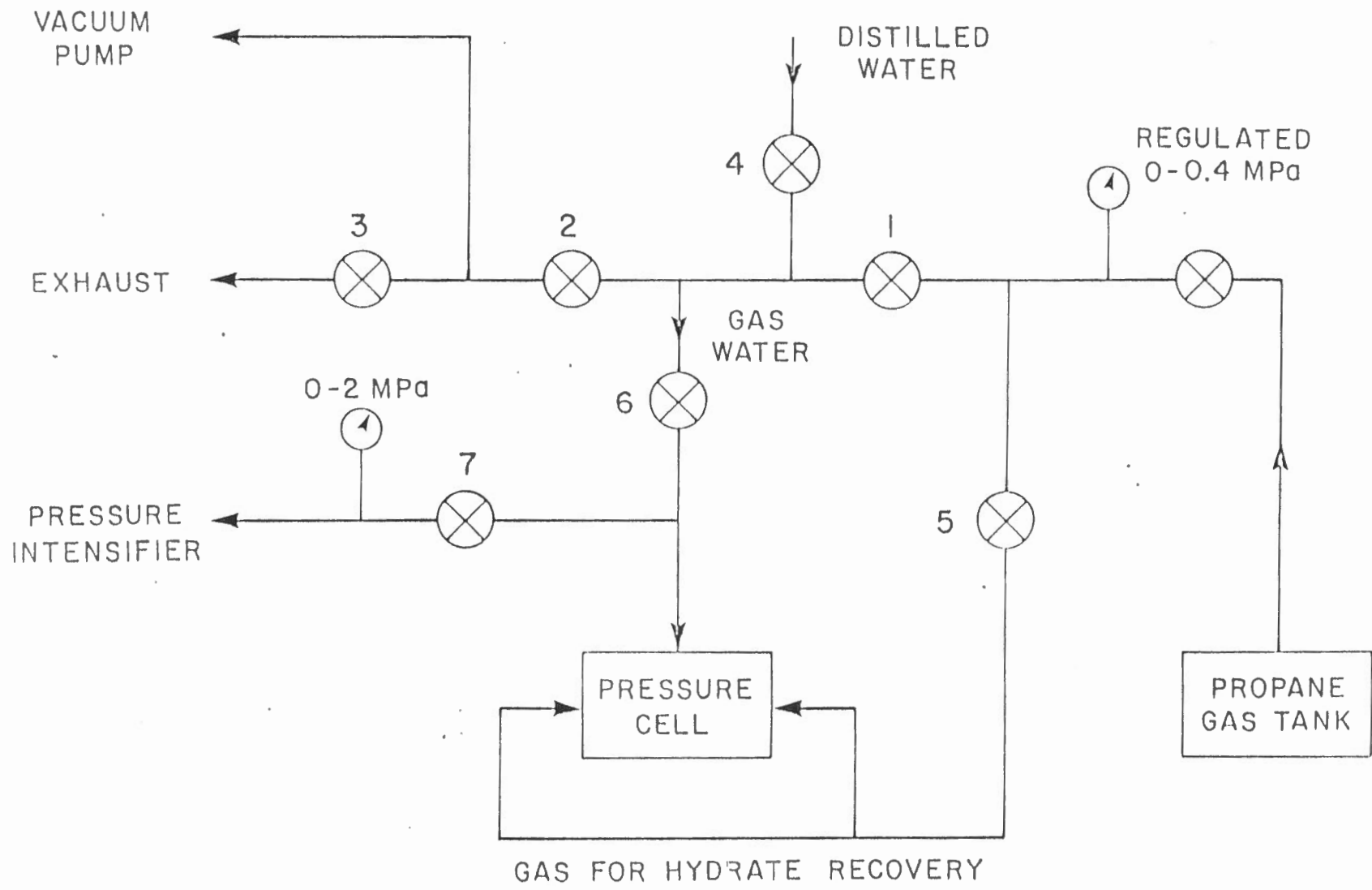
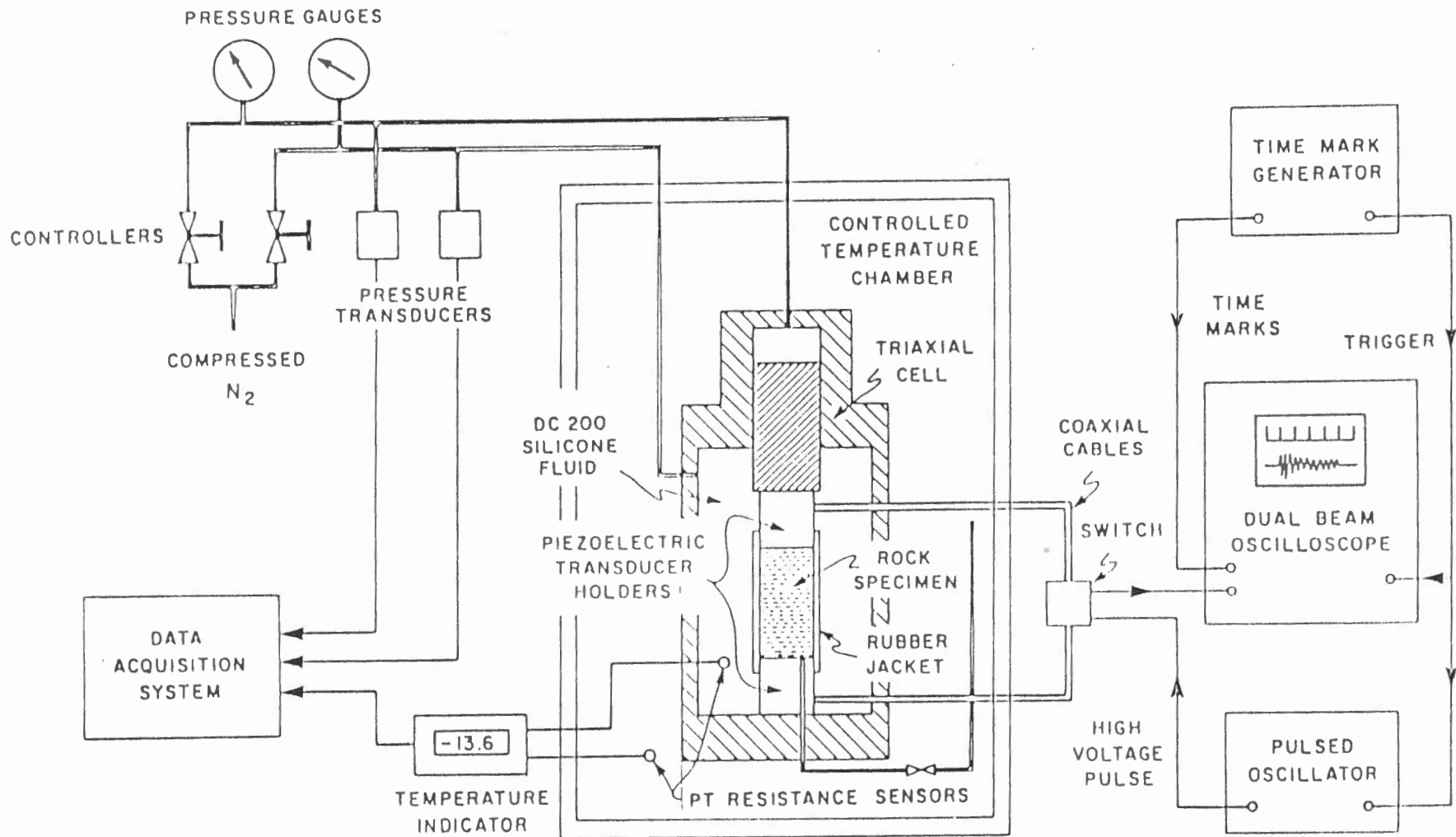


Fig. 1.

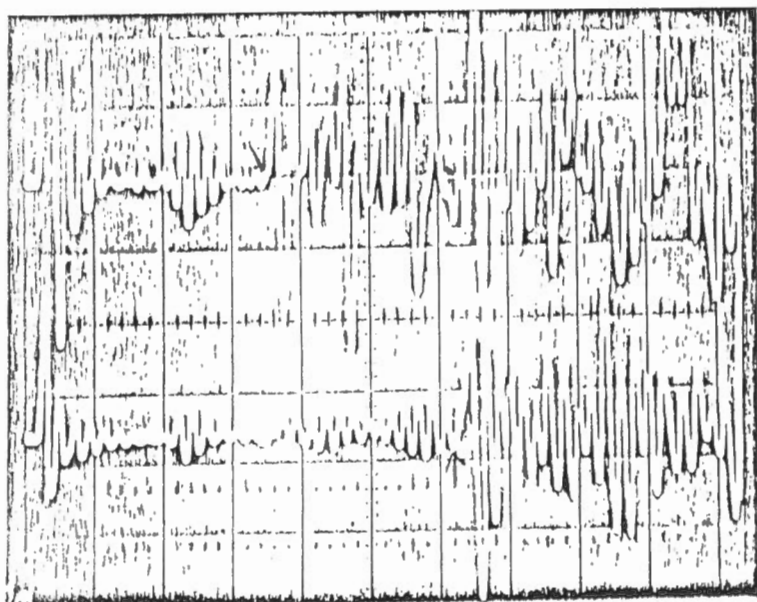






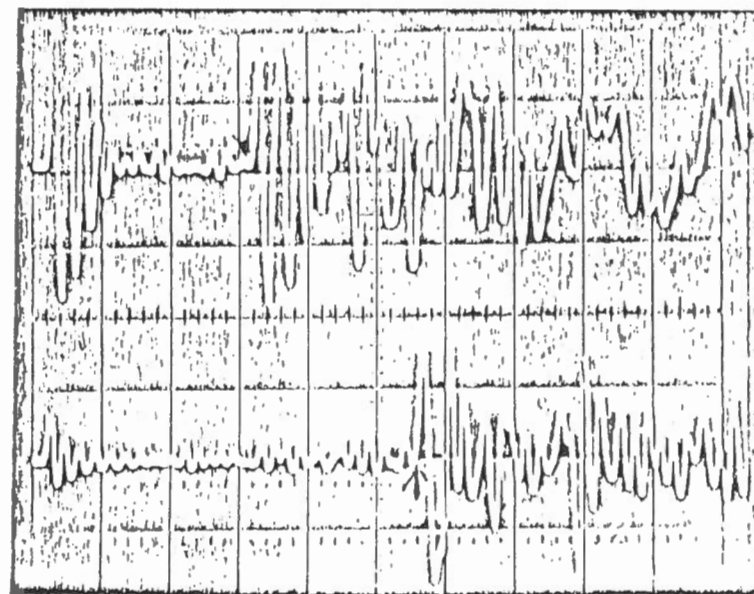
PROPANE HYDRATE I

ICE



P

S



TEMPERATURE -16.5°C

TIME PER DIV. 5 μs

X 100

AMPLIFICATION

X 100

P 0.1

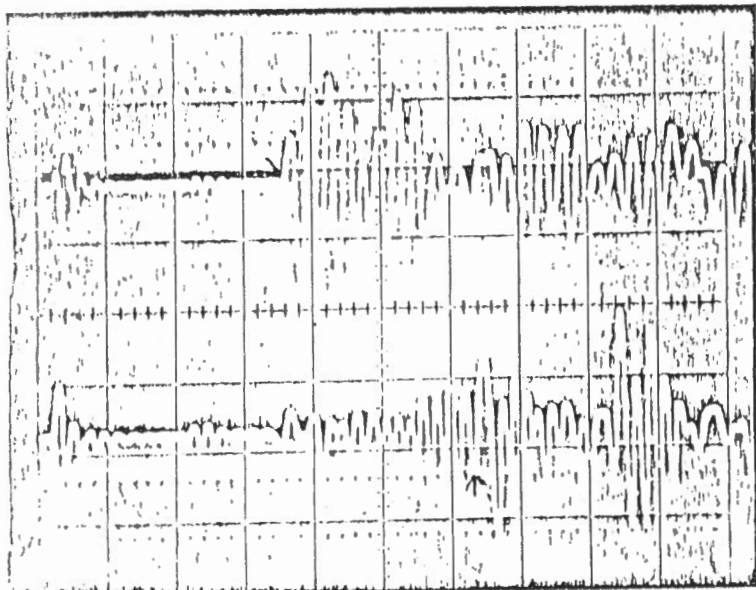
S 1.0

VOLT PER DIV.

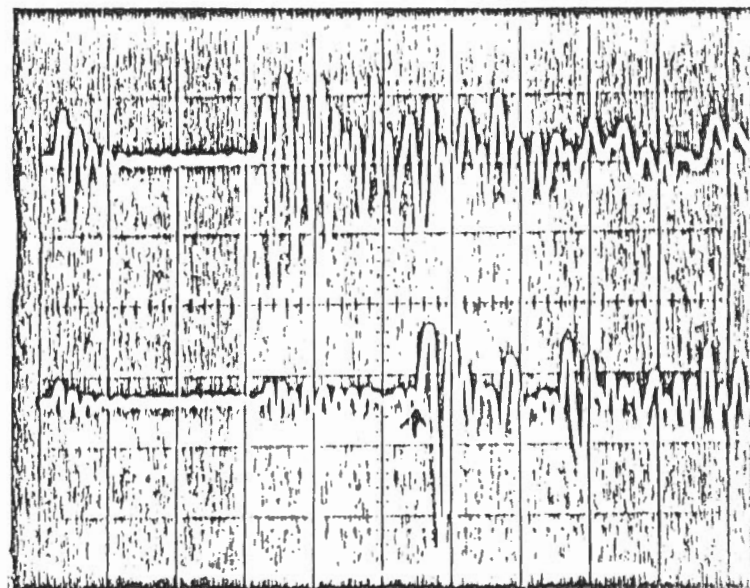
P 2.0

S 2.0

PROPANE HYDRATE I



ICE



TEMPERATURE, -8.1°C

TIME PER DIV. $5\mu\text{s}$

X 100

AMPLIFICATION

X 10

P 1.0

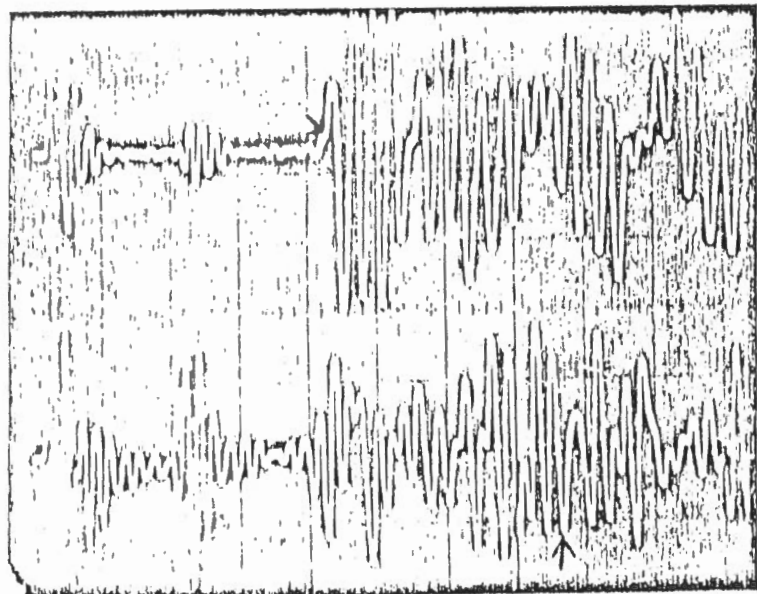
VOLT PER DIV.

P 1.0

S 2.0

S 0.5

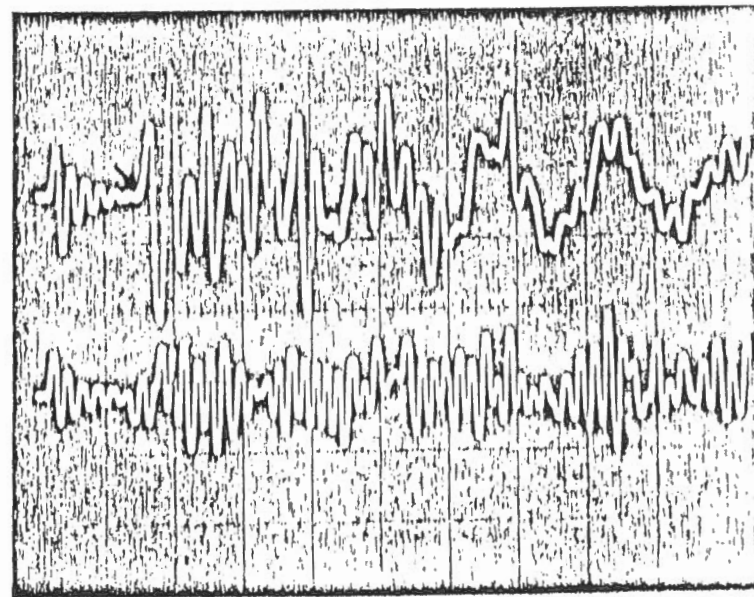
PROPANE HYDRATE I



-0.1°C

ICE

P



S

+0.2°C

TEMPERATURE
TIME PER DIV. 5 μs

X 100

AMPLIFICATION

X 10

P 0.2

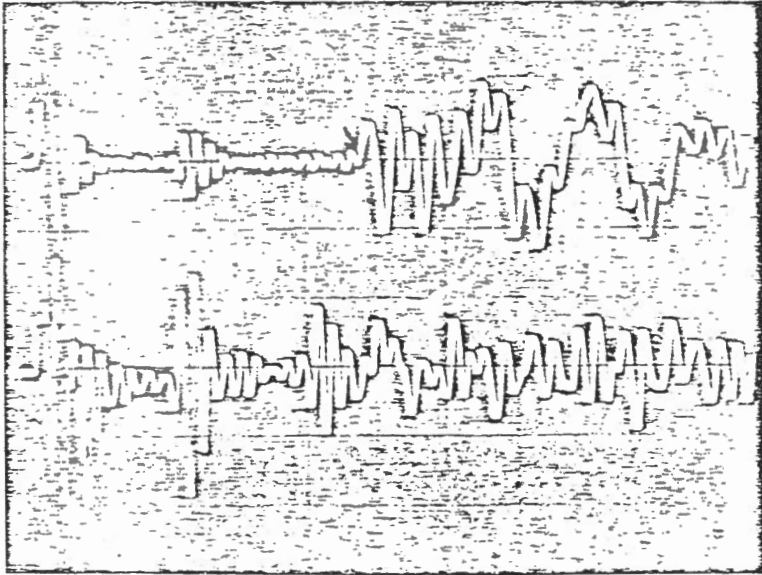
VOLT PER DIV.

P 1.0

S 0.2

S 0.2

PROPANE HYDRATE I



P

S

TEMPERATURE + 2.4 °C

TIME PER DIV. 5 μ s

AMPLIFICATION X 100

VOLT PER DIV. $\left\{ \begin{array}{l} P \ 0.2 \\ S \ 0.2 \end{array} \right.$

