$q_1,q_2,\mathrm{q}_1,\mathrm{q}_2$ = General quantities given by Equation (5), Part I
$R$ = ratio of cylinder speeds
$r$ = radius or coordinate
$r_1$ = radius of inner cylinder
$r_2$ = radius of outer cylinder
$r_m$ = mean radius
$S$ = shape function given by Equation (23), Part I
$T$ = temperature
$\overline{T}$ = average temperature in annulus
$T_1$ = temperature of inner cylinder
$T_2$ = temperature of outer cylinder
$N_{Ta^*}$ = Taylor number
$N_{Ta}$ = Taylor number $(\sqrt{N_{Ta}{}^*})$
$N_{Tac^*}$ = critical Taylor number
$N_{Tac}$ = critical Taylor number $(\sqrt{N_{Tac}{}^*})$
$t$ = time
$t_1$ = first harmonic component of temperature disturbance
$u$ = velocity in $r$ direction
$u_1$ = first harmonic component of $u$ disturbance
$u_s$ = velocity at edge of boundary layer
$v$ = velocity in $\theta$ direction.
$v_1$ = first harmonic component of $v$ disturbance
$\overline{v}$ = average velocity of flow in potentially unstable region of annulus
$w$ = velocity in $z$ direction
$w_1$ = first harmonic component of $w$ disturbance
$Z$ = constant given by Equation (22), Part I
$z$ = coordinate

**Greek Letters**

$\alpha$ = dimensionless constant
$\beta$ = constant in Equation (11), Part I
$\beta^1$ = coefficient of volume expansion
$\delta$ = potentially unstable region of gap
$\delta_M$ = momentum boundary-layer thickness
$\delta_M{}'$ = $\delta_M/d$
$\delta_T$ = thermal boundary-layer thickness
$\delta_T{}^1$ = $\delta_T/d$
$\nu$ = kinematic viscosity
$\tau$ = dimensionless coordinate
$\theta$ = coordinate
$\lambda$ = dimensionless wave length
$\sigma$ = dimensionless constant given in Equation (13), Part I
$\Omega$ = speed of rotation of cylinder (rad./sec.)
$\Omega_1$ = rotational speed of inner cylinder
$\Omega_2$ = rotational speed of outer cylinder

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# Hydrates at High Pressures: Part I. Methane-Water, Argon-Water, and Nitrogen-Water Systems

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A gas hydrate may be defined as the stable crystalline icelike complex formed from the lower molecular weight nonpolar and slightly polar compounds and water when a mixture of these is subjected to external pressure. Gas hydrates may occur above and below the ice point and fall in a subdivision of the class of compounds known as *inclusion compounds*.

The first hydrate of this type, chlorine hydrate, was discovered by Davy in 1810. After this discovery considerable work was done by Villard (*17*) and De Forcrand (*9, 10*) on the direct determination of hydrate formulas and formation conditions.

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After this initial research on the hydrates the main impetus to the study of gas hydrate systems stemmed from Hammerschmidt's discovery (*11, 12*) that gas hydrates were responsible for the plugging of gas transmission lines. Consequently research was carried out on the phase behavior of gas hydrates, including studies in regard to the inhibition of hydrate formation (*8, 14, 15*).

Recent research on the gas hydrates includes the use of hydrate formation as a water desalting method (*1*), the development of the crystal structure of gas hydrates (*6, 16*), and the statistical mechanical description of gas hydrates as solid solutions (*18*).

This study is concerned with the determination of the gas hydrate equilibrium locus in the three-phase region; water-hydrate-gas for methane, argon, and nitrogen hydrates with the effect of high pressure on the hydrate equilibrium curve.

## EXPERIMENTAL EQUIPMENT

Basically the experimental equipment consisted of a pressure cell in which hydrate formation took place, a pressure generating and measuring system, and a temperature control and measuring system. Figure 1 presents a schematic diagram of the apparatus.

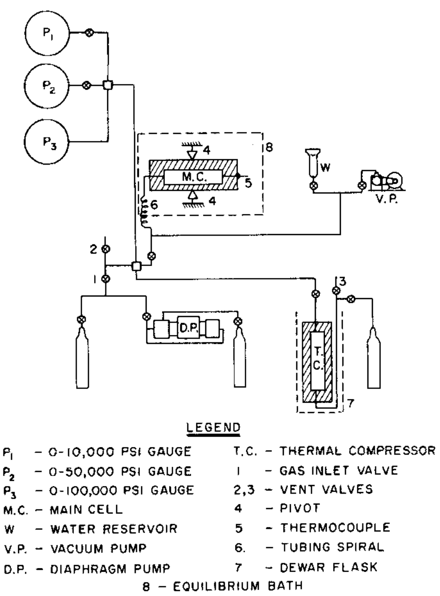

**Fig. 1. Schematic diagram of system.**

The main cell was the vessel in which hydrate formation took place. The cell was tested to a pressure of 100,000 lb./sq. in. abs. This vessel was fabricated from type 4340 steel and had a volume of 95 cc.

In order to insure equilibrium of the phases present within the main cell the vessel was rocked about its horizontal position using a gear head motor and a variable speed cam.

A dual pressure generating system was used. Pressures to 10,000 lb./sq. in. abs. were generated through the use of an air-operated, double-ended diaphragm compressor. A gas cylinder which contained the hydrate-forming gas was connected through a drying tube of silica gel to the inlet side of the compressor.

Pressures to 60,000 lb./sq. in. abs. were generated through the use of a thermal compressor. The thermal compression cell was a high-pressure vessel of welded construction. This cell was built from a special steel alloy, type 4815, which retains most of its impact strength at liquid nitrogen temperatures.

In operation the outlet side of the compressor was opened to the inlet side of the thermal compression. Then the thermal compression cell was immersed in liquid nitrogen. Since the compressor was applied to the thermal compression cell, the thermal compression cell was filled with liquified hydrate forming gas. Then the gas inlet valve was closed, and the thermal compression cell was brought into contact with ambient air. Thus, any high pressure desired could be generated.

The pressure measuring system consisted of three 16-in. diameter Heise gauges connected in parallel with each other and in series with the main cell. These three gauges were a 0 to 10,000, a 0 to 50,000, and a 0 to 100,000 lb./sq. in. abs. gauge. The accuracy of the gauges was 0.1% of their maximum reading over their entire range of application.

Temperature control was achieved through the use of a thermal regulator and a refrigeration unit. The combined use of heat and refrigeration allowed control of the bath temperature to 0.007°F.

All temperature measurements made on the system were made through the use of a thermocouple and a potentiometer. The thermocouple was a special probe type chrome-alumel thermocouple for use at high pressures. The probe length of this thermocouple was 5 in. which insured that the temperatures measured were the actual temperatures of the main cell contents.

## EXPERIMENTAL METHOD

The experimental method which was employed in this study was a departure from the method used by other workers (*5, 7, 8, 12*) in the field of gas hydrates. It was based on the determination of the hydrate equilibrium curve through direct pressure and temperature measurements of a constant volume system rather than a visual method of determining the equilibrium conditions.

Initially the system was evacuated, flushed with the hydrate-forming gas, and re-evacuated. Then water was charged into the system and followed by the hydrate-forming gas. The system temperature was held constant at a point above the hydrate-forming conditions during the charge of material into the system. Next the system was supercooled relative to the hydrate equilibrium conditions, and the hydrate was allowed to form at a constant temperature.

After the hydrate had formed, an auxiliary heater was employed to change the system temperature at a rate of 1° to 2°F./hr. The experimental points recorded in this region in which the system temperature was below the temperature of the three-phase equilibrium condition water-hydrate-gas fell on a constant volume line in the P-T plane.

When the equilibrium conditions for the system gas-water-hydrate were reached, the hydrate broke down rapidly with incremental increases of temperature, liberating the hydrate-forming gas. Since the theoretical composition of methane, argon, and nitrogen hydrates was about six molecules of water to one molecule of gas, and since the solubility of the hydrate-forming gas in water at the system temperature and pressure ranged betweeen 0.1 and 1 mole %, the excess gas passed directly into the gas phase. The movement of the gas from the hydrate to the gas phase showed up experimentally as a sharp break in the system pressure as a function of temperature. At this point the heating rate was readjusted to fall between the limits of 0.2° and 0.5°F./hr., and observations of the system temperature and pressure were made at 15-min. intervals.

Eventually the supply of hydrate in the main cell was decomposed entirely, and the system conditions then approached the conditions existing at the initial charging of the main cell. The points representing the system temperature and pressure once again followed a two-phase constant volume line in the P-T plane.

Thus each experimental run generated a segment of the equilibrium curve for the equilibrium system, water-hydrate-gas.

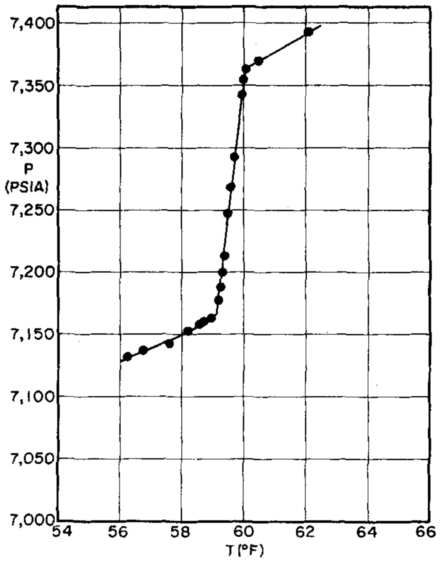

Fig. 2. Typical data for argon hydrate (run 7).

After the initial charging conditions had been reached, the temperature controller was readjusted to a higher equilibrium temperature. Upon the attainmeent of this temperature the system pressure was raised to the pressure of the next experimental run through the charging of more hydrate-forming gas into the system.

The data produced during a typical experimental run are shown in Figure 2.

In order to test the validity of this method the following checks were carried out.

First several duplicate experimental runs were carried out over the entire experimental pressure range. In all cases the segments of the hydrate curve so produced agreed to within ± 0.1°F.

Second the experimentally determined hydrate equilibrium curve was compared with the results of other workers in the field and was found to agree with these results within the limits of accuracy of the experimental equipment.

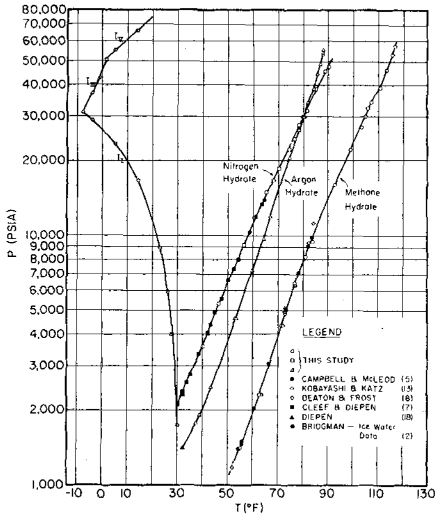

Fig. 3. Hydrate curves.

Third in order to determine if the use of a small temperature gradient during the breakdown of the hydrate approximated the equilibrium situation in a practical sense, a special experimental run was carried out. Instead of a temperature drift, equilibrium conditions were achieved at all points during the run. The results of this run duplicated the results of a run with a temperature drift.

## EXPERIMENTAL RESULTS AND DISCUSSION

The hydrate equilibrium curves were determined experimentally for methane hydrate from 2,310 lb./sq.in.abs. and 62.7°F. to 57,580 lb./sq.in.abs. and 116.4°F., for argon hydrate from 1,545 lb./sq.in.abs. and 34.1°F to 55,550 lb./sq.in.abs. and 88.0°F. and for nitrogen from 3,616 lb./sq.in.abs. and 40°F. to 47,700 lb./sq.in.abs. and 90.2°F. The midpoints of the breaks typified by Figure 2 are presented as the experimental data and are tabulated in Table 1 and presented in Figure 3.

Table 1. Hydrate Equilibrium Curve Data

| Methane | | | Argon | | | Nitrogen | | |
|---|---|---|---|---|---|---|---|---|
| Run | *R* (°F.) | *P* (lb./sq. in. abs.) | Run | *T* (°F.) | *P* (lb./sq. in. abs.) | Run | *T* (°F.) | *P* (lb./sq. in. abs.) |
| 1 | 62.7 | 2,310 | 1 | 34.1 | 1,545 | 1 | 40.0 | 3,616 |
| 2 | 63.2 | 2,312 | 2 | 38.7 | 1,915 | 2 | 46.5 | 5,340 |
| 3 | 71.7 | 4,350 | 3 | 37.3 | 1,785 | 3 | 56.4 | 9,240 |
| 4 | 71.5 | 4,340 | 4 | 43.3 | 2,465 | 4 | 65.1 | 14,790 |
| 5 | 72.7 | 4,895 | 5 | 53.2 | 4,655 | 5 | 67.7 | 16,750 |
| 6 | 76.8 | 6,427 | 6 | 52.9 | 4,630 | 6 | 70.0 | 18,680 |
| 7 | 77.0 | 6,350 | 7 | 59.5 | 7,265 | 7 | 74.1 | 22,260 |
| 8 | 80.6 | 8,255 | 8 | 64.1 | 9,705 | 8 | 76.2 | 24,550 |
| 9 | 83.1 | 9,490 | 9 | 66.8 | 11,875 | 9 | 78.2 | 27,900 |
| 10 | 83.2 | 9,490 | 10 | 74.4 | 20,590 | 10 | 79.8 | 30,135 |
| 11 | 92.4 | 16,075 | 11 | 78.1 | 26,580 | 11 | 81.3 | 31,850 |
| 12 | 98.9 | 22,150 | 12 | 80.1 | 30,010 | 12 | 84.9 | 38,915 |
| 13 | 103.2 | 27,165 | 13 | 80.3 | 30,145 | 13 | 88.8 | 46,070 |
| 20 | 104.9 | 29,927 | 14 | 81.9 | 34,325 | 14 | 90.2 | 47,700 |
| 19 | 105.9 | 32,475 | 15 | 84.0 | 39,150 | | | |
| 14 | 107.4 | 34,440 | 16 | 85.5 | 44,580 | | | |
| 15 | 110.6 | 39,400 | 17 | 86.8 | 49,070 | | | |
| 16 | 113.3 | 46,365 | 18 | 87.9 | 54,665 | | | |
| 17 | 115.6 | 53,340 | 19 | 88.0 | 55,550 | | | |
| 18 | 116.4 | 57,580 | 20 | 87.7 | 54,840 | | | |

Bridgeman (*2, 3, 4*) has studied the ice-water equilibrium curve up to 576,000 lb./sq.in.abs. Over this range of pressure he found six different varieties of ice, five of which are evidenced by discontinuities in the slope of the ice-liquid water equilibrium curve. These discontinuities are indicative of the change of the crystal structure of ice under the effect of high pressure.

The structures of the ice lattice and the hydrate lattice are similar with respect to the bond angles between water molecules in the lattice. Thus the appearance of a discontinuity in the slope of the hydrate equilibrium loci was expected. But from the experimental results of this study the hydrate equilibrium curves showed no abnormalities in their behavior. If hydrate crystal structure changes did occur at high pressures, the effects on the pressure-temperature curve may have been completely masked by the presence of the gas phase in the foregoing experiments.

From about 10,000 lb./sq.in.abs the methane hydrate equilibrium locus became somewhat more concave down toward the temperature axis than had been expected. Kobayashi and Katz (*13*) predicted that at 40,000 lb./sq.in.abs. the hydrate would exist at a temperature of 100°F. However it was found experimentally that the hydrate existed at a temperature of 100°F. at a pressure of 24,000 lb./sq.in.abs.

The minimum pressure at which experimental data were taken was 2,200 lb./sq.in.abs. for methane hydrate. Below this pressure the hydrate has been well studied by Deaton and Frost (*8*) and Villard (*17*). The experimentally determined equilibrium locus for methane hydrate between 2,200 and 10,000 lb./sq.in.abs. agreed with the curves determined by Campbell and McLeod (*5*) and Kobayashi and Katz (*13*).

The pressure coordinate of the extrapolated curve at 32°F. was 1,400 lb./sq.in.abs. which agreed with the values of 1,404 lb./sq.in.abs. reported by Diepen (*18*).

The experimentally determined equilibrium curve for nitrogen hydrate below 14,000 lb./sq.in.abs. agreed with the data of van Cleef and Diepen (*7*). The equilibrium curves of argon and nitrogen hydrates intersected each other on the P-T projection in the neighborhood of 30,000 lb./sq.in.abs.

## FUTURE MODIFICATIONS

At present the entire experimental system with the exception of the thermal compressor is designed for a maximum pressure of 100,000 lb./sq.in.abs. To date the experimental pressure range is limited to 60,000 lb./sq.in.abs. which is the upper limit of the thermal compressor. In order to use the experimental system to its upper pressure capabilities, a special pump has been designed and constructed to operate at a maximum pressure of 100,000 lb./sq.in.abs.

A search for materials of construction for a thermal compression cell capable of handling a working pressure of up to 100,000 lb./sq.in.abs. is underway. Such a cell combined with a diaphragm compressor capable of generating 30,000 lb./sq.in.abs. should enable pressures up to 100,000 lb./sq.in.abs. to be generated at room temperature by thermal compression.

## FUTURE USES OF THE INDIRECT METHOD

Another use of the indirect method which was investigated was the direct determination of the hydrate formula. Thus for a closed system such as was used experimentally the number of moles of hydrate-forming gas present in the gas phase at the point of decomposition is given by

$$n_1 = P_1 V_{s1}/Z_1 R T_1 \qquad (1)$$

where $V_{s1}$ is the system volume available to the gas phase.

After the complete decomposition of the hydrate has been completed, the number of moles of gas in the system is given by

$$n_2 = P_2 V_{s2}/Z_2 R T_2 + S n_w \qquad (2)$$

where $V_{s2}$ is the system volume available to the gas phase, $S$ is the solubility of the gas in water in the moles/mole of water, and $n_w$ is the number of moles of water present.

It should be noted that $V_{s1}$ is not equal to $V_{s2}$, since the specific volume of the hydrate and liquid water are not precisely the same. However if the amount of water in the system is small, the volume difference $V_{s1} - V_{s2}$ becomes negligible.

Therefore $(n_2 - n_1)$ must be equal to the number of moles of gas associated with $n_w$ moles of water in the hydrate, with the assumption of complete conversion of the water to the hydrate. Therefore $n_w/(n_2 - n_1)$ gives the hydrate number. Likewise $(n_2 - n_1)/n_w$ is a measure of the occupation of the cavities in the hydrate lattice by the hydrate former.

This procedure was tested with methane hydrate data between 2,200 and 10,000 lb./sq.in.abs. The results showed that 100% conversion of the water to hydrate did not take place with the experimental apparatus in its present state. This result was not unexpected, as the experimental procedure involved supercooling a mixture of water and the hydrate former. The occlusion of water by the hydrate crystals evidently prevents the reaction of the water with the hydrate-forming gas.

If the formation of methane hydrates could be carried to completion through refinement of the experimental apparatus, the method should provide a means of directly determining the hydrate number.

## ACKNOWLEDGMENT

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