

DYNAMIC GAS HYDRATE FORMATION
IN THE PRESENCE OF NON-
HYDRATING PARAFFINS

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A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Petroleum Engineering.

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ABSTRACT

An attempt was made to find an inexpensive means of preventing formation of gas hydrates in offshore Gulf Coast production facilities. Conditions existing in the offshore production environment were duplicated as closely as possible in the experimental apparatus. Existing literature was surveyed to determine what had previously been done and what to expect in the course of this research.

Natural gas, water, and various liquid paraffins (propane, isobutane, normal butane, normal pentane, and normal hexane) were passed through the test apparatus and made to form gas hydrates under dynamic, two- and three-phase flow conditions. Results of these tests showed that increasing mole percentages of propane, isobutane, and normal butane contributed to and facilitated the formation of gas hydrates. Contrarily, increasing mole percentages of normal pentane and normal hexane inhibited the formation of hydrates, but only in the presence of liquid normal pentane and hexane. In the absence of the liquid, these heavier paraffins had no effect.

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INTRODUCTION

Gas hydrates are solid solutions of gases in water, and form under pressure from mixtures of water and various gases including the paraffinic gases--methane through normal butane and isobutane. X ray analysis of the hydrate crystals has shown that they consist of a framework of water molecules with the hydrate-forming gas molecules included in voids in the lattice. X ray analysis has also shown that the hydrates have particular hydrate numbers depending upon the length of the hydrate-forming gas molecule. The hydrate crystals resemble ice or wet snow and in the absence of excess water have a peculiar popcorn-like appearance. (See figure 1).

The fact that gas and water under pressure could form a solid solution at temperatures above freezing became of economic significance with the initiation of gas transmission in pipelines at relatively high pressure, and with the realization that hydrates could plug a line as effectively as ice. As is noted in the literature

survey, much work has been done with gas hydrates, but not much recently with actual field conditions.

The objective of this thesis was to study hydrate formation under conditions very similar to those existing in the field. With the hope of making the results of some practical significance, a problem situation commonly encountered in offshore production in the Gulf Coast was simulated in the experimental apparatus. That problem is the occurrence of hydrates in the vertical riser carrying scrubbed-but-unprocessed gas from a sea-floor transmission line to the gas processing platform. From the production platform scrubbers, the gas enters the sea saturated with water and gasoline vapor. Part of this water and gasoline then condenses out of the gas as it cools to the temperature of the sea water. The condensed water in particular can become a problem when it is mixed in turbulent flow with the gas. At favorable temperature and pressure conditions, hydrates form and can plug the line, particularly at a restriction in the line.

With the production conditions simulated, the components of the flowing gas-water-gasoline mixture were varied in an attempt to see what effect the variation would have on the temperature of hydrate formation in the flowing mixture. It was here, in varying particularly

the amount of pentanes plus (gasoline) in the flow stream, that some useful knowledge was anticipated. In some situations this knowledge might permit more economic prevention of hydrate formation in production lines than is now accomplished with the use of glycol, or other anti-freeze agents.

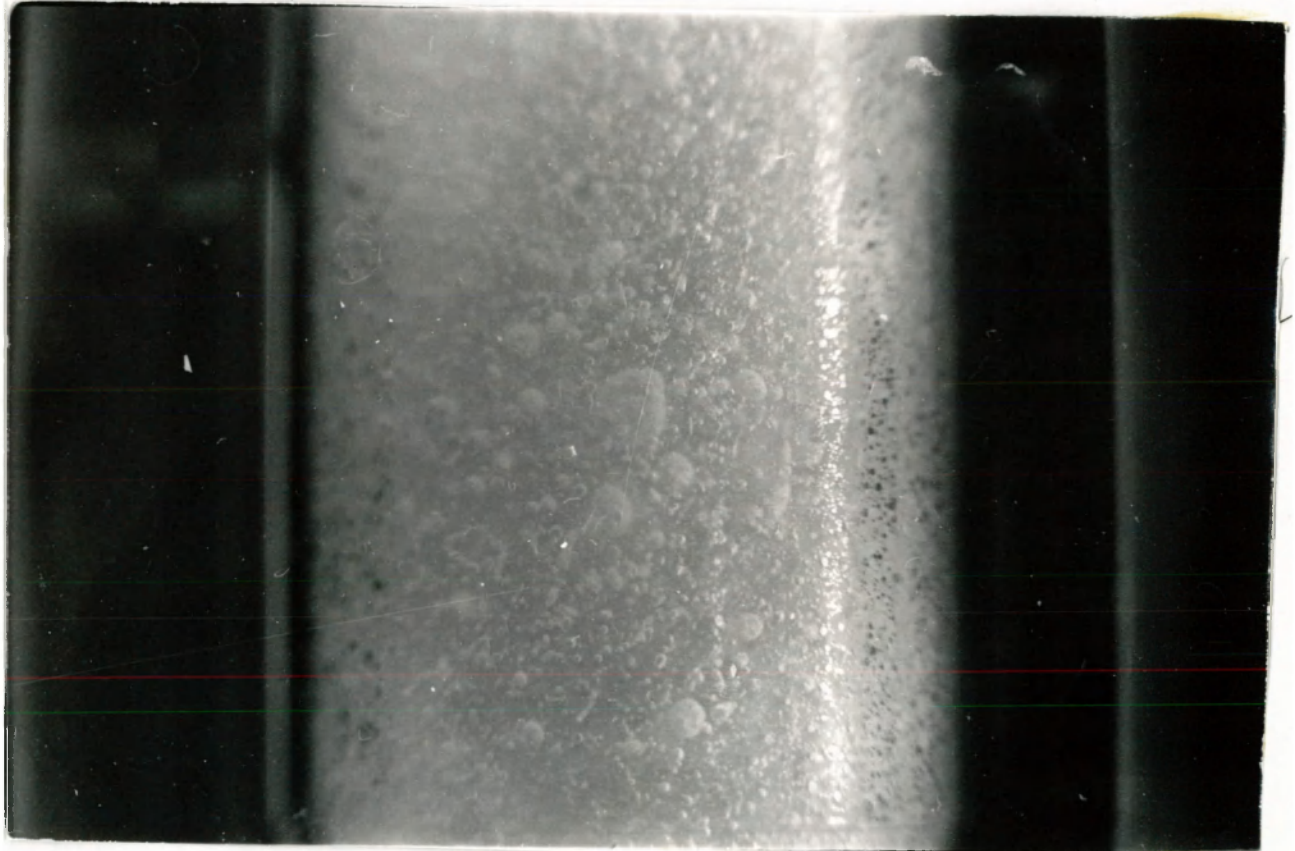


Figure 1. "Popcorn" Hydrates
on Walls of Hydrate Chamber-
Enlarged 6 Times

LITERATURE SURVEY

Investigation of gas hydrates began in 1810 with the discovery of the first known gas hydrate, a crystalline compound of chlorine and water, by Humphrey Davy (Hammerschmidt, 1934). Others continued to develop information in the hydrates of various gases throughout the 19th century, with Villard making perhaps the most significant contribution in the late 1800's. His data on the hydrates of methane, ethane, acetylene, and ethylene were the basis of early hydrate studies in the natural gas industry. The work of Villard, DeForcrand, and other early investigators of gas hydrates was summarized by Schroeder in 1927.

Hammerschmidt (1934) published the first investigation into the occurrence of hydrates in natural gas pipelines. This work included the experimental formation of hydrates by flowing gas and water through a glass tube as well as investigation of the field occurrence of gas hydrates. He

noted that two primary conditions were necessary for the formation of hydrates:

1. Certain combinations of pressure and temperature, dependent on gas composition.
2. Liquid water.

When the primary conditions for hydrate formation were met, the secondary condition initiating the formation of hydrates was agitation of the gas-water mixture. In the absence of any initial "seed" hydrate crystal, this agitation is necessary for hydrate formation. Indeed, in the turbulence of high-rate gas flow through water, hydrates form very quickly.

Hammerschmidt also noted that the formation of hydrates lowered the dew point of the parent gas, and that hydrates had definite decomposition temperatures depending upon their pressure and gas composition. A hydrate he removed from a pipeline was found to contain six times the propane and ten times the isobutane of the parent gas--indicating the predominance of propane and isobutane in the hydrate structure. Also, as a result of his experimentation, Hammerschmidt came to the conclusion that normal butane did not participate in the hydrate structure and that only lighter hydrocarbons--methane through isobutane--formed hydrates.

Deaton and Frost (1937, 1938, 1940, 1946), in their work for the U. S. Bureau of Mines, investigated a range of natural gases as well as their pure components and found that the hydrate decomposition curves for all the gases ran parallel (on semi-log paper) in the pressure range investigated-- 60 psig to 1600 psig. Their work was similar to Hammerschmidt's in that they investigated pipeline flow conditions and tried to apply their laboratory findings in the field. Their results differed from Hammerschmidt's in that they felt normal butane did contribute to the formation of the hydrates.

Work done on gas hydrates since Hammerschmidt and Deaton and Frost has almost all been more theoretical than practical, at least in that it deals with hydrates under static conditions rather than dynamic. Roberts and associates (1940) published phase diagrams for the hydrates of the pure gases methane and ethane and for their mixtures (see figure 2). Reamer and co-workers investigated the hydrates of ethane, ethene, propane and propene and their mixtures in 1952 (see Figures 3 and 4). The phase diagrams of the pure gases shown together with the hydrate equilibrium curves published by Deaton and Frost in 1946 (see figure 5 and table 1) clearly show the effect of gas composition on hydrate formation characteristics. Other authors have investigated the hydrate effects of the non-

hydrocarbon natural gas components as hydrogen sulfide (Noaker and Katz, 1954), carbon dioxide (Unruh and Katz, 1949), and nitrogen (Jhaveri and Robinson, 1965). In summary of their articles, the addition of hydrogen sulfide to a gas tends to reduce the pressure at which hydrates will form for a given temperature and gas composition. The addition of nitrogen or carbon dioxide will increase the hydrate equilibrium pressure for the same gas and temperature.

In a series of articles, Katz and co-workers investigated natural gas hydrates, and proved that they obeyed the Phase Rule (thus could be considered solid solutions). They developed vapor-solid equilibrium constants for use in predicting the hydrate formation condition of natural gas mixtures (Wilcox, Carson, and Katz, 1941 and Carson and Katz, 1942). Trekell in 1965 developed hydrate temperature displacement curves from his study of binary hydrate forming gases. His curves permit the prediction of the hydrate temperature of natural gases for pressures from 1000 to 10,000 psia. However, the work of neither Katz and associates nor that of Trekell considers nitrogen which Jhaveri (1965) found did participate in the hydrate structure. It is probable that both their techniques would be improved by the additional consideration of nitrogen. No attempt was made in the following experimental work to compare actual

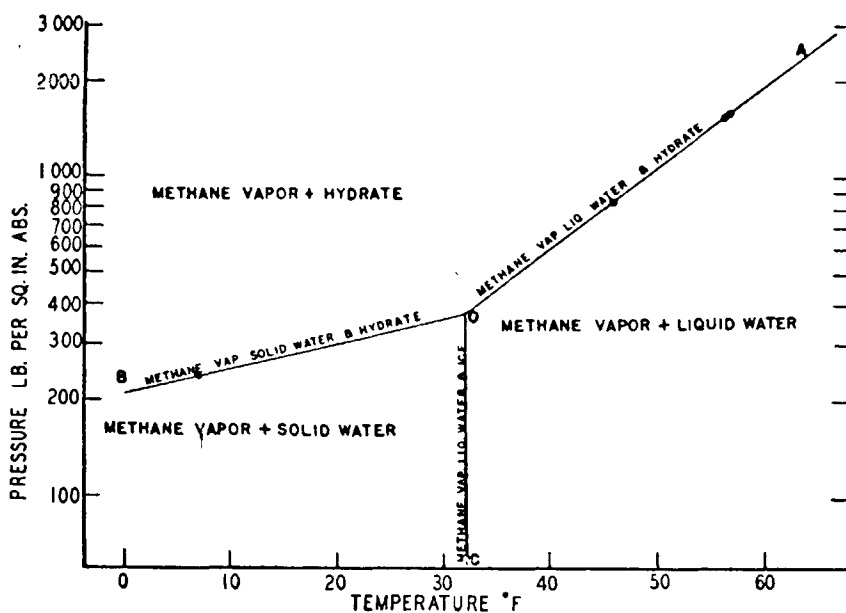


Figure 2. Three-Phase Diagram for Methane-Water System (Roberts, et al, 1940)

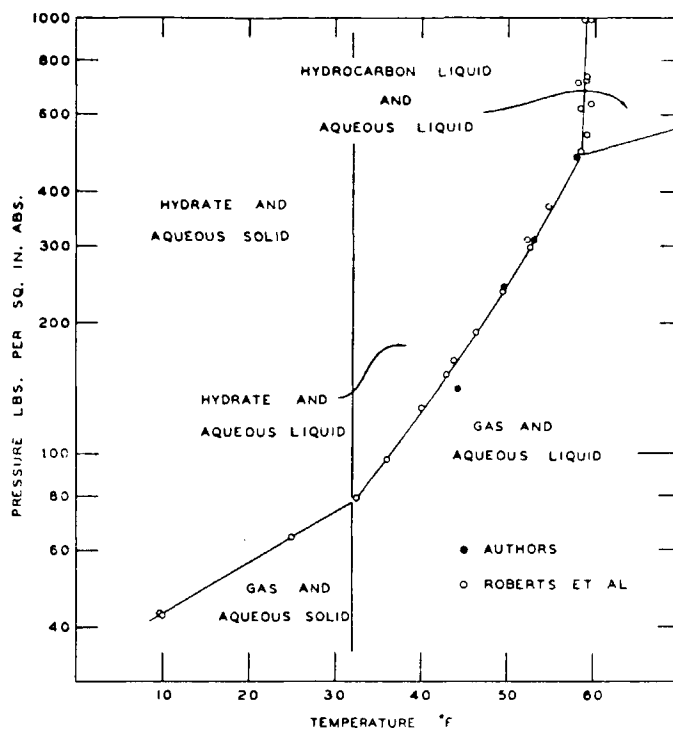


Figure 3. Three-Phase Diagram for Ethane-Water System (Reamer, et al, 1952)

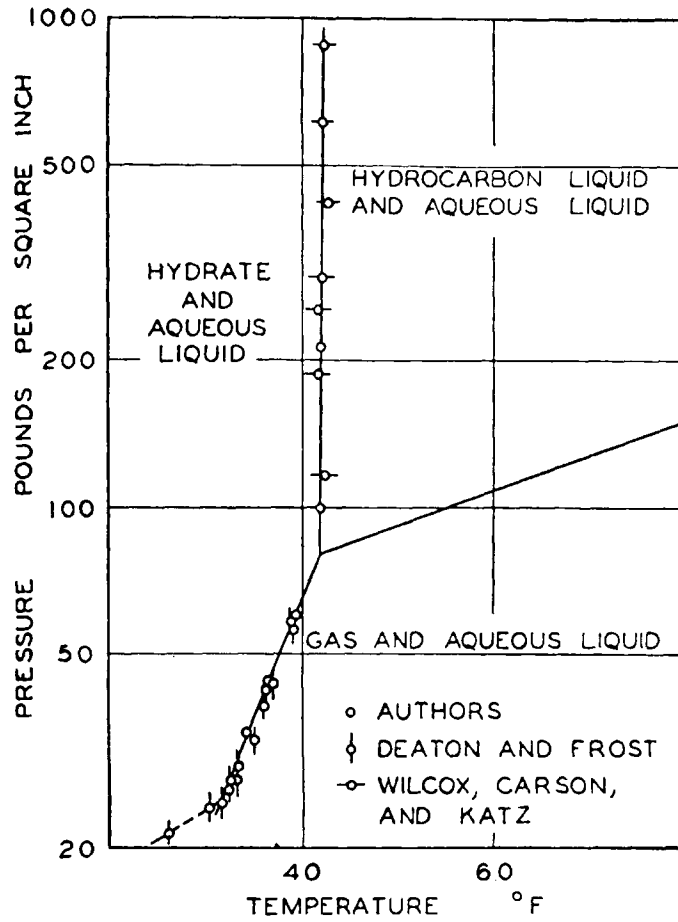


FIG. 4 — LOCUS OF THREE-PHASE STATES FOR PROPANE-WATER SYSTEM.

Figure 4. Three-Phase Diagram for Propane-Water System (Reamer, et al, 1952)

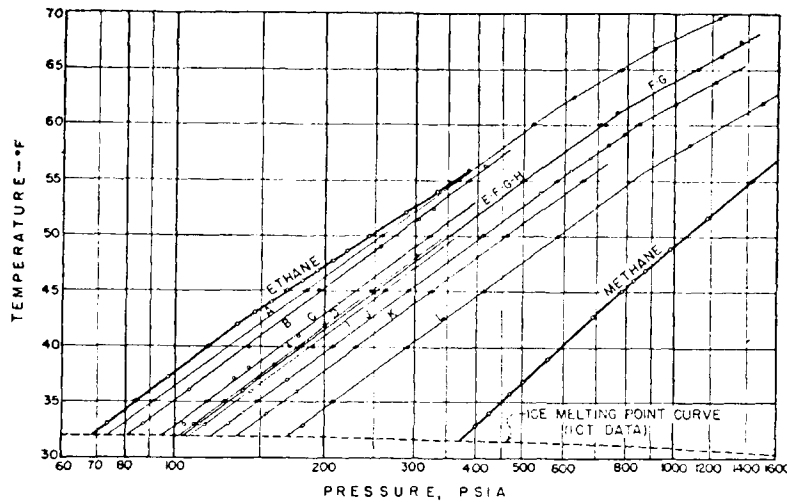


Figure 5. Gas-Hydrate Equilibrium Curves for Natural Gases. Letters refer to natural gases in Table 1. (Deaton and Frost, 1946)

Component	Natural cases											
	A	B	C	D	E	F	G	H	I	J	K	L
Carbon dioxide	0.2	0.2	0.2	0.3	3.25	0.4	0.0	0.2	0.0	0.9	0.8	0.6
Hydrogen sulfide					.25							
Nitrogen	7.7	1.1	9.4	9.5	1.1	.3	1.0	14.3	3.4	1.2	25.0	.2
Methane	65.4	87.9	78.4	79.4	87.8	91.0	90.8	75.2	88.5	90.6	67.4	96.5
Ethane	12.7	4.4	6.0	5.8	4.0	3.2	3.0	5.9	4.3	3.8	3.7	.9
Propane	10.3	4.9	3.6	3.6	2.1	2.0	2.1	3.3	2.0	1.5	1.9	1.8
Butane and heavier	3.7	1.5	2.4	1.4	1.5	3.1	3.2	1.1	1.7	2.0	1.2	
	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
B.t.u. (cal.) total	1,283	1,147	1,077	1,049	1,067	1,138	1,135	990	1,086	1,095	839	1,056

	Pure gases	
	Methane	Ethane
Carbon dioxide	0.3	0.0
Methane	99.7	.8
Ethane		97.1
Propane		2.1
Isobutane		
Normal butane		
Total	100.0	100.0

Table 1. Analysis of Gases Used in Obtaining Figure 5, in percent by Volume. (Deaton and Frost, 1946)

hydrate formation temperatures with calculated ones due to the continually varying gas composition and lack of knowledge of that exact composition.

As this work is intended to study the effects of various components of the gas stream on the formation of hydrates under dynamic conditions, consideration lastly should be given to the previous work which applies here. Hammerschmidt (1936) noted a test in which 4.5 gallons of water per thousand cubic feet of gas were added to a gas stream flowing at hydrate forming conditions. The result of this addition of water was the almost complete plugging of the apparatus within thirty minutes. He also mentioned, however, that calcium chloride brines of concentration 18 percent or greater would prevent hydrates or decompose those formed in tests run at 575 psig and temperatures from 35 to 38°F. Trekell (1965) noted that as the concentration of pentanes plus approached 1 mole percent of the gas stream, they noticeably retarded the formation of hydrates. He also felt that the presence of a hydrocarbon liquid phase would, by the Phase Rule, reduce the variance to zero preventing the formation of hydrates in the presence of a hydrocarbon liquid. It is the purpose of this thesis to test these observations and thoughts under dynamic conditions.

EXPERIMENTAL APPARATUS AND MATERIALS

The experimental apparatus as set up and used in developing the data presented herein is shown in figure 6. The individual systems and equipment utilized within the overall system are described in the following text.

The base gas supply with which the experiments were run was public-utility gas taken from the Public Service Company lines. The gravity of this gas varies from 0.65 to 0.68, depending upon the gas source, according to Public Service Company personnel. The gravity of the same gas, as determined by the Schilling apparatus used in these experiments, varied from 0.620 to 0.653. One analysis of the gas used is shown in the appendix.

The base gas was compressed by a Rix three-stage compressor and stored in four 11 by 47 inch bottles (about 7.6 std. cu. ft. of storage volume) at from 2000 to 2500 psig pressure prior to a run.

Gas was then bled out of the bottles through a downstream pressure regulator, and the flowing pressure maintained as nearly as possible at 400 psia. The gas rate

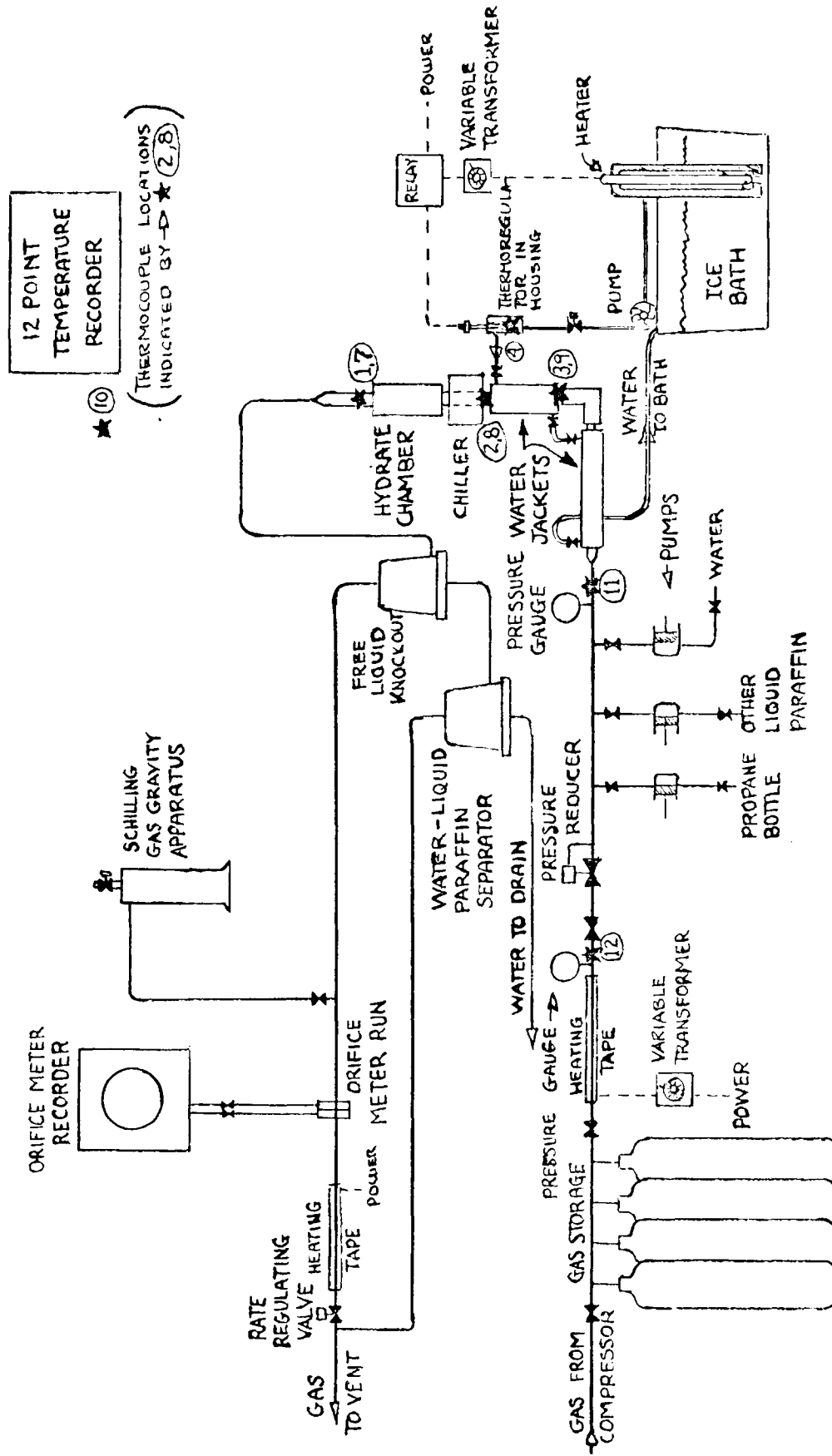


FIGURE 6 EXPERIMENTAL APPARATUS

was controlled by a regulating valve just downstream of the orifice meter run.

The gas was prevented from freezing in the pressure regulator, by wrapping the pipe leading to the regulator with a 384-watt heating tape and insulating it. Power to the heating tape was then controlled with a variable transformer which was set depending upon the upstream gas storage pressure and the downstream gas temperature desired. A nomograph to facilitate the transformer settings was developed from Brown's natural gas enthalpy-entropy diagrams (presented in Katz et al, 1959, p. 143-144) and experimentally obtained data. Freezing in the rate regulating valve was prevented by the similar installation of a 96-watt heating tape just upstream of the valve. Full power was maintained to this tape throughout all runs.

The gas rate was measured in a 0.5 in. Daniels honed orifice flange unit holding a 0.1225 in. orifice. Differential and static pressure were recorded on a circular 4-hour chart by a standard field orifice meter recorder with 100 inches of water differential and a 500-psig bourdon static. An orifice meter coefficient was determined for the base gas and then used for all gas mixtures. It was not recalculated for different gas

gravities as knowledge of the exact gas rate was considered unnecessary for these tests. The important factors were a constant 400-psia flowing pressure and a constant gas rate well above turbulent flow conditions. Gas gravities were measured with a Schilling gas gravity apparatus; an air measurement was taken as close as possible to each gas measurement to prevent variations in atmospheric pressure from affecting the interpretation.

Water and hydrocarbon fluids were metered into the gas stream by a battery of pumps. Water was added as necessary to maintain water splashing in the hydrate chamber by a 1500-psig American Meter pump with a variable stroke length. Propane, and one of the following paraffins, isobutane, normal butane, normal pentane, or normal hexane, were added continuously by dual piston 3000-psig Wallace and Tiernan, variable-stroke-length pumps, hooked up to a Reeves variable speed drive. This combination permitted maximum hydrocarbon liquid rates of 100 times the minimum; although at a set prime mover speed, measured rates of one piston could not exceed 15 to 20 times that of the other piston. Maximum capacity of the American Meter pump was 3.2 gph at 1500 psig, while that of a single cylinder of the Wallace and Tiernan pump was an estimated 3.0 gph at 3000 psig.

Materials used in addition to the public utility gas were Phillips Petroleum technical grade isobutane, technical grade normal butane, high purity grade normal hexane, and commercial grade normal pentane. The propane used was commercial grade propane donated by the Refinery Corporation of Denver. The water used was tap water.

In order to prevent cavitation of the hydrocarbon liquid (thus varying rates of injection) as it was pumped into the gas stream, the suction lines from the propane and butane bottles and from the hexane and pentane cans were chilled in coils in an ice bath just prior to the pump. It was felt that by using the vapor pressure of the liquid in room temperature (70⁰ F) storage vessels to drive chilled (and thus lesser vapor pressure) liquid into the pump suction, even and continuous flow would be insured. Using this technique, pump displacement efficiency was found to be 85 percent. (This is the displacement efficiency of the pump rate of hydrocarbon liquids versus the pump rate of water.)

The 1.0-in. outside diameter flow lines prior to the hydrate chamber were water jacketed and temperature controlled by constantly circulating water. A small centrifugal pump drew water from an ice bath and up concentrically around a 1000-watt Vycor heater. The water was then pumped through a regulating valve, across

an adjustable mercury bulb thermoregulator, and into the water jackets. The water circulation in the jackets was in series and counter to the gas flow in order to cool the gas to the lowest temperature just prior to the hydrate chamber. The power to the Vycor heater was controlled by a variable transformer whose setting was determined by the amount of power required to heat the circulation water from the ice-bath temperature to the temperature desired. The thermoregulator was wired to an electric relay which shut off the power to the heater when the water temperature exceeded the set temperature. The variable transformer was used in an attempt to keep the circulation water at a constant temperature and prevent large variations in the circulation water temperature about the set point.

Temperatures of the gas stream were sensed through the copper flow-tube at the points indicated in the diagram every three minutes by iron-constantan thermocouples and recorded on a Honeywell 12-point temperature recorder. By placing two correctly selected thermocouples at a point, temperatures were recorded every 1.5 minutes rather than every 3 minutes.

The assembly in which the gas-liquid was cooled to a condition at which hydrates would form is 0.90-in. internal diameter and can be seen in part in figure 7. The entire

apparatus consists first of a 37-in. water jacketed horizontal flow tube leading into a machined lucite right-angle turn. From the lucite "ell" a second 12-in.-long water-jacketed flow tube leads upward into a "chiller" in which about 5.5 in. of the flow tube is maintained at a constant 32° F by an ice bath. Immediately downstream and above the "chiller" is the hydrate chamber, a lucite tube with the internal diameter machined out from 0.90-in. to 1.30-in. From the hydrate chamber the gas passes into a short piece of 1.0-in. tubing.

The apparatus, as it is set up, is intended to simulate a vertical riser from a horizontal pipe line on the sea floor. The water jackets cool that gas-liquid mixture to a desired temperature. The "chiller" simulates the splash line, cooling the gas a fraction of a degree more. Then the hydrate chamber, while permitting observation of the hydrate formation, allows the gas to expand slightly, cooling it, while inducing turbulence.

The gas flow is taken from the flow assembly in 0.5-in. tubing through a free liquid knockout, and is then metered before being vented. The free liquid passes from the knockout into a dual gravity separator from which any liquid hydrocarbons evaporate and vent to the gas stream downstream of the regulating valve while the water is dumped down the drain.

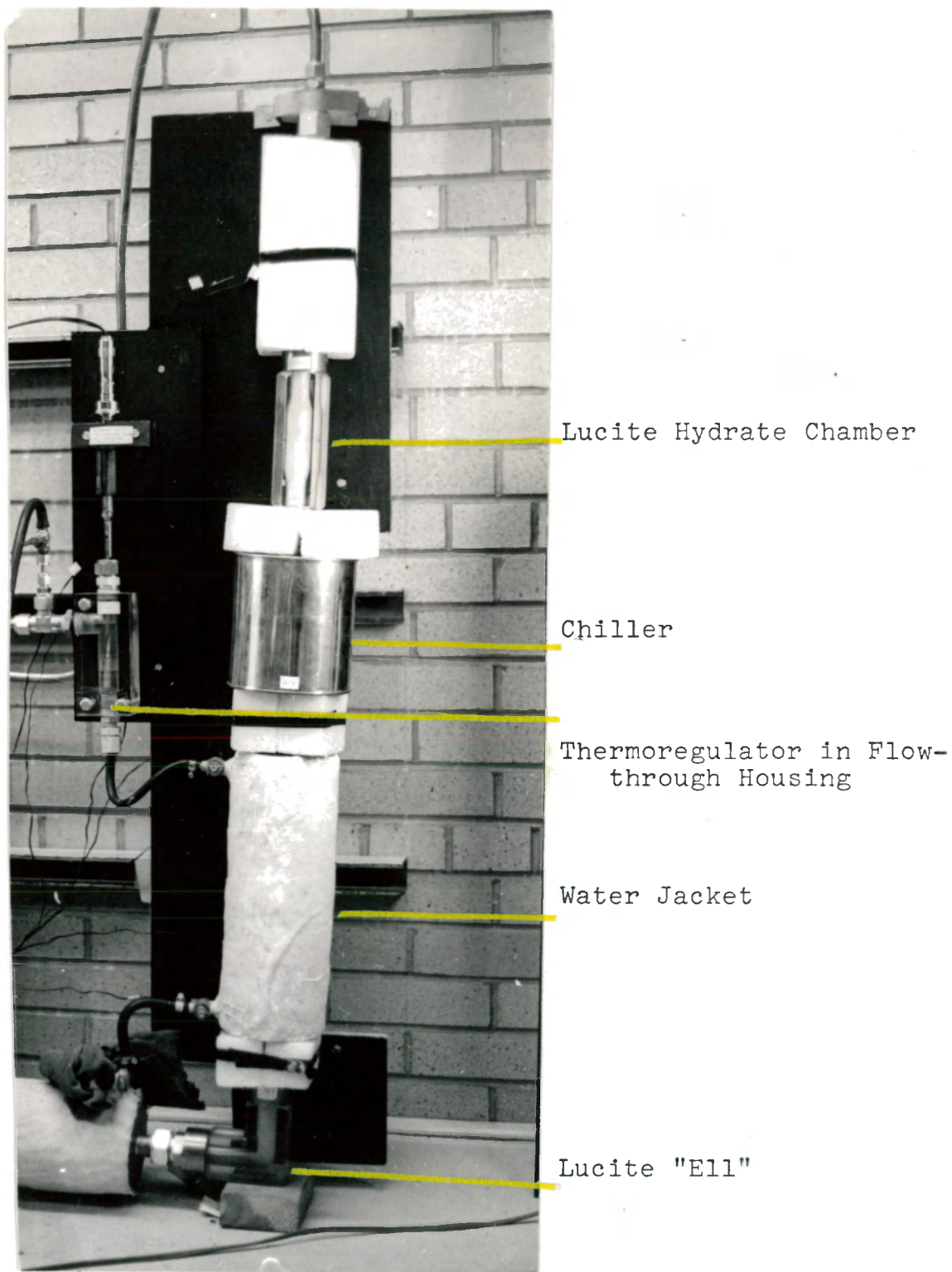


Figure 7. Main Portion of One Inch Flow Assembly-- Including Hydrate Chamber

EXPERIMENTAL PROCEDURE

The experimental procedure outlined below insured the smoothest possible operation of the equipment used and therefore the most reliable analysis of the data obtained. This procedure can be considerably simplified and the results obtained possibly improved in reliability with sophistication of the apparatus. This sophistication is reserved, however, until the value of further work on hydrates under dynamic conditions is determined, and until the cost and work involved can be justified.

Preparation of the system for a series of runs began with charging the gas storage bottles to 2000 to 2500 psig with public utility gas. The pressure reducer and liquid hydrocarbon pumps were cleaned with benzene. This was done to remove the fine rust particles carried in the gas which had accumulated in the regulator during the previous series of tests and which did cause malfunctioning of the regulator in early runs. Also the check valves in the hydrocarbon pumps tended to stick if they were not cleaned regularly.

Water, propane, and the hydrocarbon to be considered were checked to be in adequate supply; and their containers hooked into the system.

The temperature recorder was kept on continuously during the period in which experimental data were gathered to prevent any variation in recorded temperatures as the equipment warmed up.

To start a run, the gas was turned on initially at a very low rate. The heating tape installed just upstream of the pressure reducer was turned on about ten minutes prior to beginning the test so that adequate heat would be available to prevent any initial freezing in the reducer. As soon as the 400-psia stabilized flow pressure was reached, the manifold between the orifice meter run and the recorder was opened, and the gas rate was set with the regulating valve. At this point the regulating valve heating tape was turned on, the water bath thermoregulator was set, and the water bath pump and heater were turned on.

Then while the system temperatures were coming to equilibrium, the gravity of the public-utility gas in use was measured. And sufficient water was added to the gas to get water splashing in the hydrate chamber as the gas flowed through it. When the incoming gas temperature and flowing gas temperatures in the apparatus had

stabilized at temperatures safely above the anticipated hydrate temperature, the propane and other liquid hydrocarbon pumps were turned on; and their injection rates were set for the run to be made.

When the liquid hydrocarbon injection began, the gas flowing temperature was again watched--especially as the incoming liquid propane and butane absorbed considerable heat from the gas. If necessary, the power to the heating tape above the pressure reducer was increased or reduced in order to bring the temperature of the gas mixture as it entered the flow apparatus to a point 10°F above the anticipated hydrate temperature. If the gas temperature was too much higher, the water jackets would have difficulty in reducing the temperature enough to form hydrates. And if the gas temperature was too much lower, there would be a danger of hydrates forming where they could not be observed and noted.

When the gas temperature of the mixture to be tested was stabilized, the water bath temperature was reduced either gradually or quickly to a point 4°F to 6°F below the anticipated hydrate temperature. A gradual reduction in temperature (about 0.5°F per minute) permitted hydrocarbon liquids to accumulate with the water in the hydrate chamber prior to hydrate formation. The "quick" reduction

in temperature (1.0° F plus per minute) which brought the flowing mixture to hydrate temperature as quickly as possible, conserved gas for additional tests. In a "quick" test, hydrocarbon liquids accumulated only at pump rates above about 5.0 mole percent.

As the flowing temperature gradually dropped, the gas mixture gravity was measured. Then as the hydrate formed, the time of hydrate formation was noted and a note made on the temperature record. The hydrate formation temperature was taken as the average of the temperatures upstream and downstream of the hydrate chamber at the time hydrates were observed.

Following hydrate formation the water-bath temperature was increased, again either gradually to observe the hydrate as it decomposed or quickly to get the system back up to equilibrium conditions for another test. If quick destruction of the hydrates was desired, the gas and hydrocarbon pumps were turned off; and the dropping pressure was used to destroy the hydrate crystals. At the same time the water-jacket temperature (and gas heat if necessary) was increased to ready the system for the next test.

Bringing the system back on for another test after shutting it down to destroy the hydrates also purged

nearly all the water and cumulated liquids from the chamber, and rendered negligible the effect of residual hydrocarbon liquids on the next test.

If hydrate decomposition was to be observed, the water-bath temperature was brought gradually back up to a point about 10^0 F above the hydrate formation temperature and the behavior of the hydrates was observed. It was occasionally necessary during this period of rising temperatures to add water to maintain liquid splashing in the chamber. This addition had to be made as soon as required to prevent the water causing a sudden temperature increase and interrupting the smooth destruction of the hydrates. Observation of the hydrate decomposition more than halved the number of runs obtained on a charge of gas as the flow assembly had to be warmed until all hydrate crystals were destroyed lest the following test be contaminated.

Following the decomposition of all hydrate crystals, another run could be begun, leaving the accumulated hydrocarbon liquid in place; or it could be purged to permit an entirely fresh test to be made.

THEORETICAL DEVELOPMENT

As noted in the introduction, this experiment was initiated with its objective, the investigation of gas hydrates as they occur under field-like conditions. In particular an offshore, Gulf Coast, hydrate problem area was selected.

The apparatus in which the hydrate was actually formed was designed to simulate conditions found in a vertical riser coming from a sea-floor production line to a sales gas platform. Water and liquid hydrocarbons were added to the gas stream to simulate the liquid products condensing from the gas as it is cooled by the water on the sea floor. The effect produced on the hydrate formation temperature of a gas by adding varying amounts of selected hydrocarbons to the flow stream was the main point of the study. A lesser objective of this research was to determine whether hydrate formation could be experimentally controlled under actual flowing conditions.

Gas rates as high as possible were sought to

approximate as closely as possible the turbulent flow conditions actually existing in the field. The gas rates actually used during the experiment had single-phase flow Reynolds numbers of from 15,000 to 20,000. In the two and three-phase flow conditions actually existing in the apparatus, the effective Reynolds numbers of flow would be much higher. A flowing gas pressure of 400 psia was selected as representative of a typical field operating pressure.

The base gas rate and mixture of 458 scf/hr plus plus 0.4 gph of propane (about 2.6 mole percent propane when corrected for the pump displacement efficiency) was selected as a standard for the experiment because it gave a hydrate formation temperature of about 49⁰ F. The base gas alone had a low hydrate temperature ranging from 47⁰ F to 48⁰ F, depending upon its gravity. The higher formation temperature of the blend made depression of the hydrate temperature more evident with the apparatus used.

Again, the primary objective of the experiment was to determine the effect of increasing the heavier hydrocarbon components of the gas stream on the hydrate formation temperature. The effect of increasing propane and isobutane content of the gas has been well documented in the literature, and tests were run to confirm the increasing hydrate

temperature with increasing propane and isobutane content. The effects of increasing amounts of normal butane, pentane, and hexane were less certain. It was hoped to determine if these heavier hydrocarbons would depress the hydrate formation temperature and to what extent.

Since the objective was to investigate trends, the exact composition of the gas was not a concern as long as it was constant over a series of runs and did not vary much from series to series. The public utility gas met these requirements when the storage bottles were used as the gas supply for a series of runs. For then the whole gas supply could be assumed to have come to an even composition by diffusion prior to beginning a test. One base gas gravity measurement was taken as a valid base for all data gathered in that series of runs.

EXPERIMENTAL RESULTS

The results obtained in this research are shown graphically in figures 8 and 12, and are discussed in the following text. The underlined headings indicate the gas mixtures considered.

PROPANE-BASE GAS

The first experiments were carried out with propane and base gas alone during the testing of the equipment and while attempting to find the best base gas-propane mixture for testing of the other hydrocarbon mixtures. Due to the variation in the base gas gravity, all results are not directly comparable. However, figure 8 shows the results obtained and the trend of increasing hydrate temperature with increasing propane content. By coincidence, the results for base gas gravities of about 0.65 line up on a single trend similar to that found later with isobutane and normal butane.

ISOBUTANE-PROPANE-BASE GAS

The standard base gas-propane mixture developed, 458 SCF/hr of base gas plus 0.4 gph of propane (2.5 mole percent propane), was used in a single series of tests made to demonstrate the effect of increasing the isobutane content of the gas stream. These tests were made by purging the apparatus of accumulated liquid between each run. Because of this purging, and because of the volatile nature of isobutane, no liquid isobutane was detected during the tests although the rate at which isobutane was added was up to 4.25 mole percent during the tests.

The trend shown in figure 9 is that anticipated from previously published work.

NORMAL BUTANE-PROPANE-BASE GAS

These tests which were some of the first made, were run slowly to observe both hydrate formation and decomposition points and associated temperatures. As a result, considerable liquid normal butane was evident during the two runs made while adding 4.4 mole percent normal butane to the base gas-propane mixture. This liquid butane was evident only at temperatures less than 54°F. Once hydrates were formed (at about 50.5°F for this mixture), liquid normal butane would appear as the water was used up in

hydrates, but then would disappear again as additional water was added to the system. When water was added, the slushy hydrate-normal butane mixture would thicken and adhere to the sides of the hydrate chamber much more firmly.

These observations plus the apparent upward trend of the hydrate formation temperature with added normal butane content of the gas mixture, indicate that normal butane does indeed form hydrates. With the few data points obtained, the trend indicated in figure 10 may not necessarily be valid (in its slope). The published work of Trekell (1965), Hammerschmidt (1934) indicate that the slope should be near horizontal.

NORMAL PENTANE-PROPANE-BASE GAS

Both types of data runs were made for both this case and that of normal hexane. The first series of runs were made without purging the liquid from the system between runs, and both hydrate formation and decomposition temperatures were noted. These runs were made in sequence, adding 0.96, 1.98, 2.86, 3.83, and then 4.32 mole percent normal pentane to the constant flowing base gas and propane volume. As the runs were made, liquid pentane continued to accumulate in the flow assembly. The hydrate formation

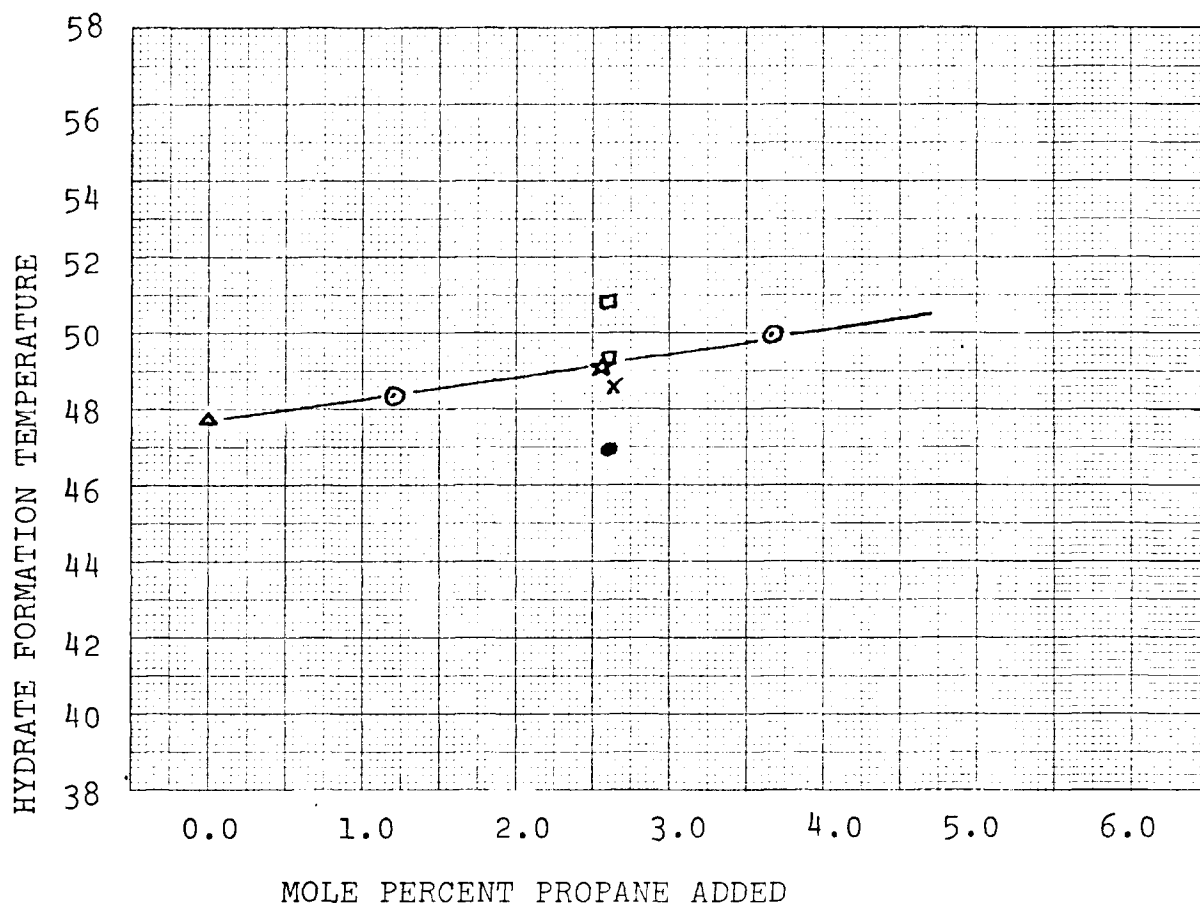
temperature gradually declined as the mole percent normal pentane flowing increased. The data points shown in figure 11 for these first runs are erratic, but still show the same trend more clearly demonstrated later in the normal hexane run series.

The second group of data runs were made by purging the system of most liquids between each run. The temperatures were also dropped quickly and hydrates formed quickly (in an average of 8 minutes from pumps-on to hydrate formation, compared to the slower non-purge run average of 20 minutes from pumps-on to hydrate formation). Because of the quickness with which these runs were made, liquid normal pentane was not observed prior to hydrate formation except at the highest rate used--5.67 mole percent normal pentane. As can be seen in figure 11, the hydrate formation temperatures in this series were uniformly about 47°F, except where liquid pentane appeared. There the hydrate formation temperature was suppressed to 42.8°F.

NORMAL HEXANE-PROPANE-BASE GAS

The first series of data runs made with normal hexane were made as with normal pentane in a continuous sequence without purging the liquid from the apparatus between runs.

As with runs of this type made with normal pentane, the runs were made quickly; and no liquid hexane was observable except at the highest rate of 5.03 mole percent. And here again, where no liquid hydrocarbons were observable, the hydrate formation temperature was a nearly constant 47°F without regard to the mole percent hexane in the flow. But when the liquid hexane appeared in the system prior to the appearance of hydrates, the temperature of hydrate formation was suppressed to 43.2°F (for the 5.03 mole percent normal hexane rate).

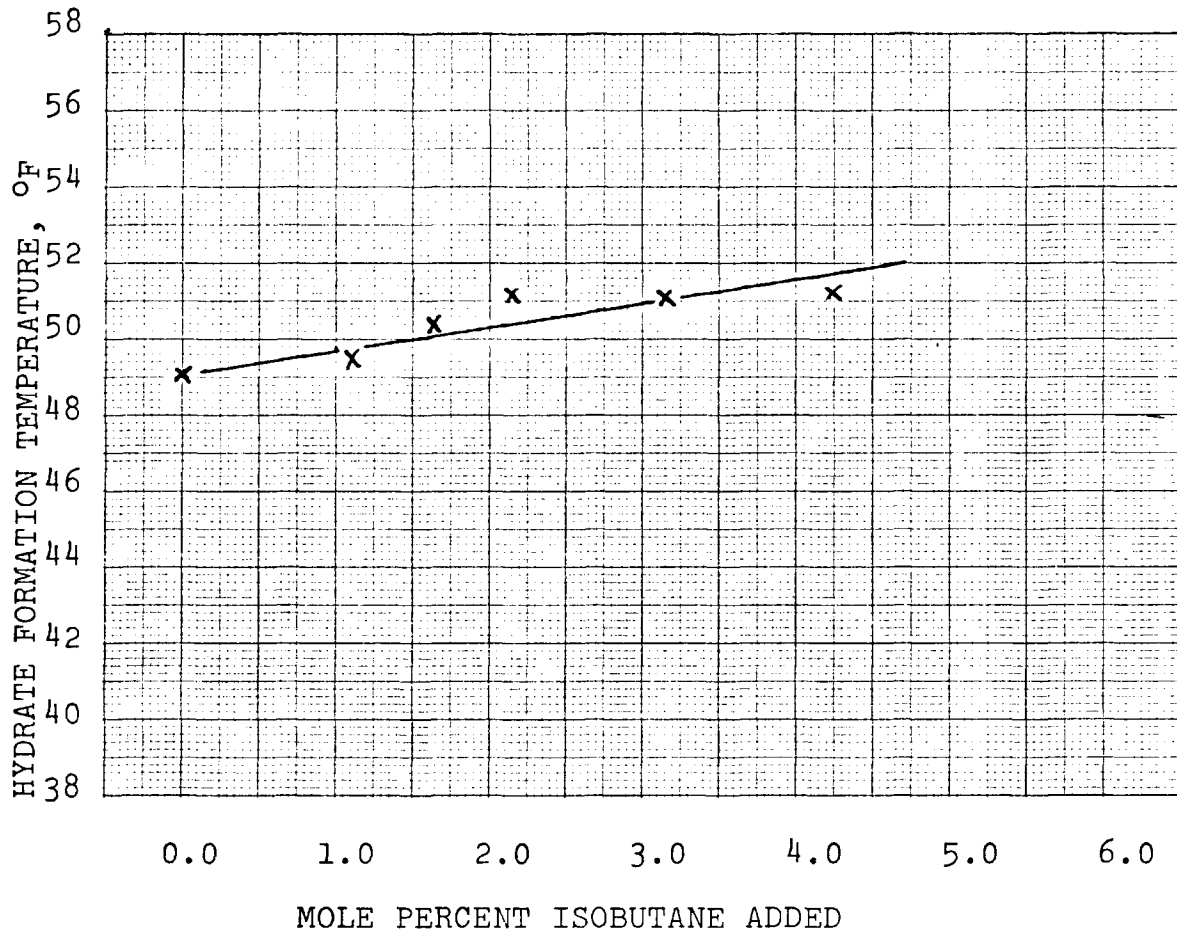


DATA USED IN PREPARING CURVE

- x --2/ 8/72, 0.634 GRAVITY BASE GAS
- △ --2/10/72, 0.651 GRAVITY BASE GAS
- ⊙ --2/11/72, 0.653 GRAVITY BASE GAS
- --2/15/72, 0.634 GRAVITY BASE GAS
- ☆ --2/21/72, 0.649 GRAVITY BASE GAS
- --2/22/72, 0.627 GRAVITY BASE GAS

FIGURE 8 PROPANE-BASE GAS CURVE

DYNAMIC HYDRATE FORMATION TEMPERATURE
VERSUS MOLE PERCENT PROPANE ADDED

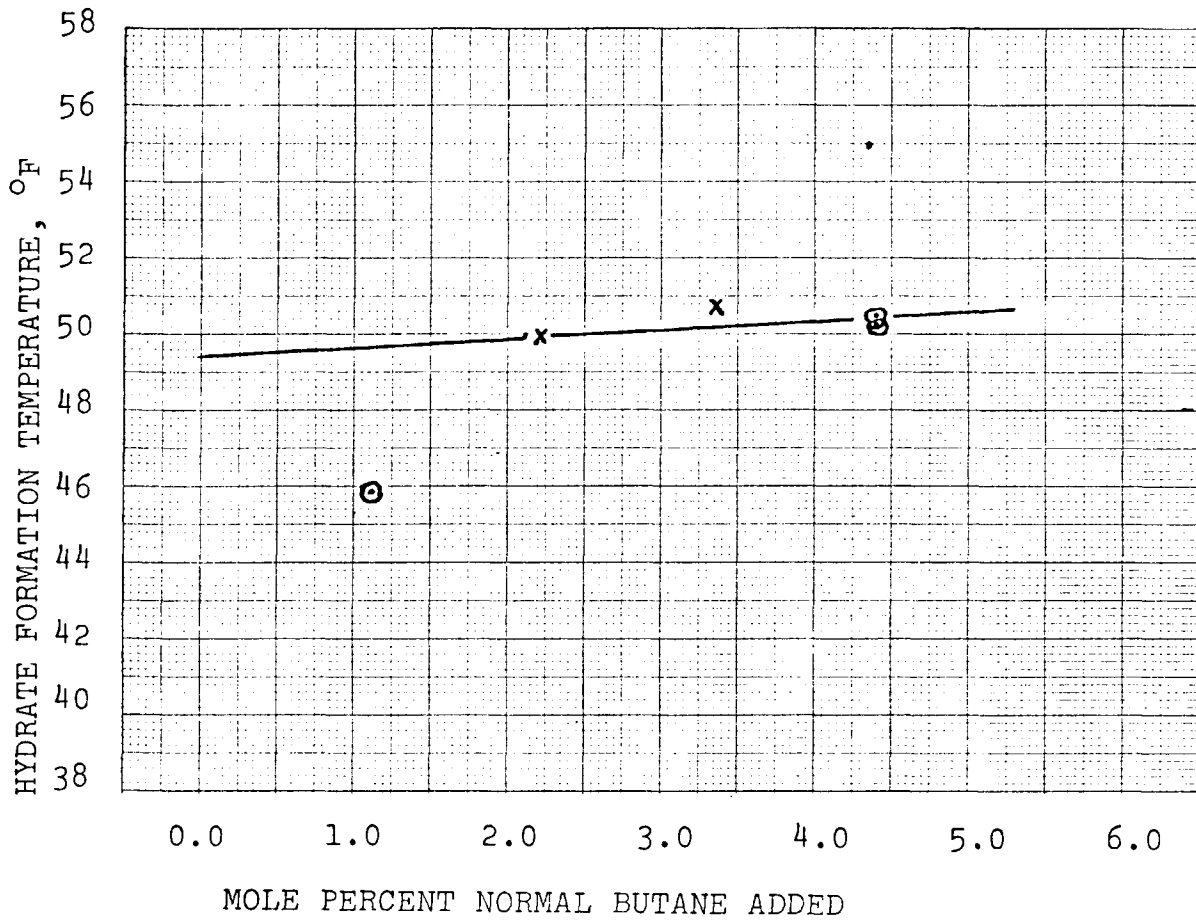


DATA USED IN PREPARING CURVE

X --2/21/72, 0.649 GRAVITY GAS WITH
2.5 MOLE PERCENT PROPANE ADDED

FIGURE 9 ISOBUTANE-PROPANE-BASE GASE CURVE

DYNAMIC HYDRATE FORMATION TEMPERATURE
VERSUS MOLE PERCENT ISOBUTANE ADDED

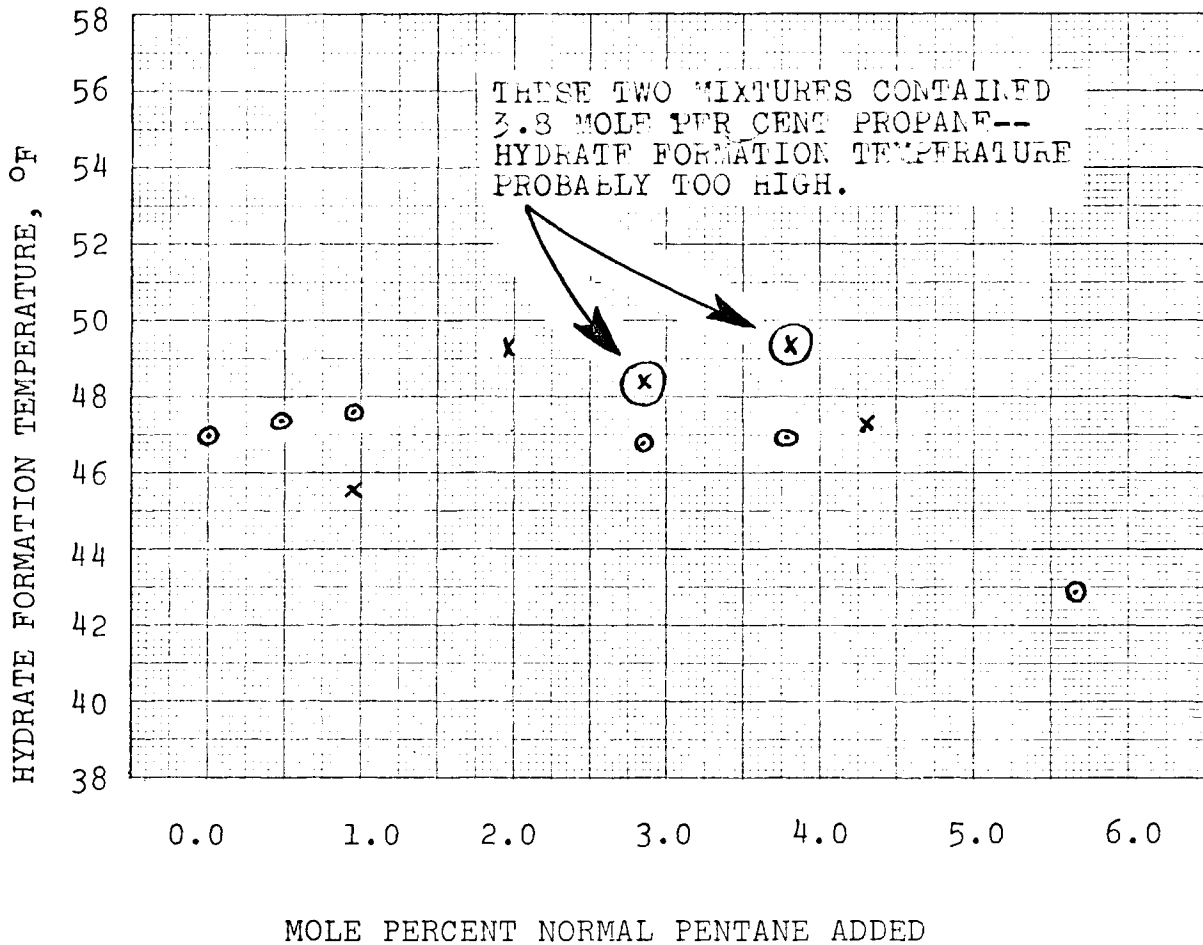


DATA USED IN PREPARING CURVE

- x --2/16/72, 0.654 GRAVITY GAS WITH 2.5
MOLE PERCENT PROPANE ADDED
- ⊙ --2/17/72, 0.620 GRAVITY GAS WITH 2.5
MOLE PERCENT PROPANE ADDED

FIGURE 10 NORMAL BUTANE-PROPANE-BASE GAS CURVE

DYNAMIC HYDRATE FORMATION TEMPERATURE
VERSUS MOLE PERCENT NORMAL BUTANE ADDED

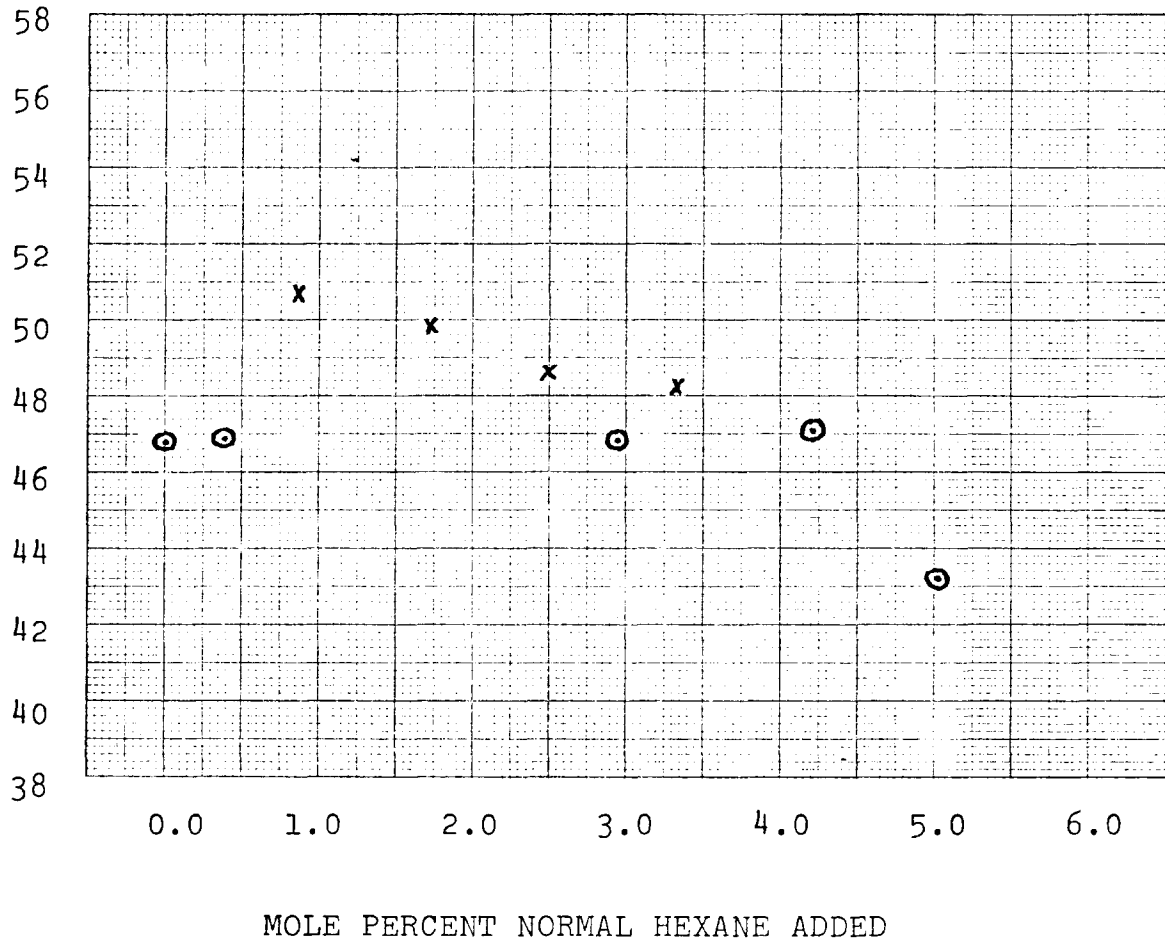


DATA USED IN PREPARING PLOT

- x --2/19/72, 0.636 GRAVITY GAS WITH 2.5 MOLE PERCENT PROPANE ADDED (LIQUID ALLOWED TO ACCUMULATE THROUGHOUT RUNS).
- o --2/22/72, 0.627 GRAVITY GAS WITH 2.5 MOLE PERCENT PROPANE ADDED (LIQUID PURGED FROM SYSTEM AFTER EACH RUN).

FIGURE 11 NORMAL PENTANE-PROPANE-BASE GAS PLOT

DYNAMIC HYDRATE FORMATION TEMPERATURE
VERSUS MOLE PERCENT NORMAL PENTANE ADDED



DATA USED IN PREPARING PLOT

- X** --2/18/72, 0.623 GRAVITY GAS WITH 2.5 MOLE PERCENT PROPANE ADDED (LIQUID ALLOWED TO ACCUMULATE THROUGHOUT RUNS).
- O** --2/22/72, 0.627 GRAVITY GAS WITH 2.5 MOLE PERCENT PROPANE ADDED (LIQUID PURGED FROM SYSTEM AFTER EACH RUN).

FIGURE 12 NORMAL HEXANE-PROPANE-BASE GAS PLOT

DYNAMIC HYDRATE FORMATION TEMPERATURE
VERSUS MOLE PERCENT NORMAL HEXANE ADDED

SUMMARY OF EXPERIMENTAL RESULTS

Results of the addition of propane and isobutane to the base gas and base gas plus propane mixture were as anticipated from prior published work. Increasing the richness and gravity of the gas by adding more propane and isobutane raised the maximum temperature at which hydrates would form at a given pressure. As various authors have expressed differing opinions on the participation of normal butane in the formation of hydrates, the results obtained with this hydrocarbon are interesting. Probably further data runs should be made to determine whether an increasing percentage of normal butane does raise the temperature at which hydrates will form in a gas mixture.

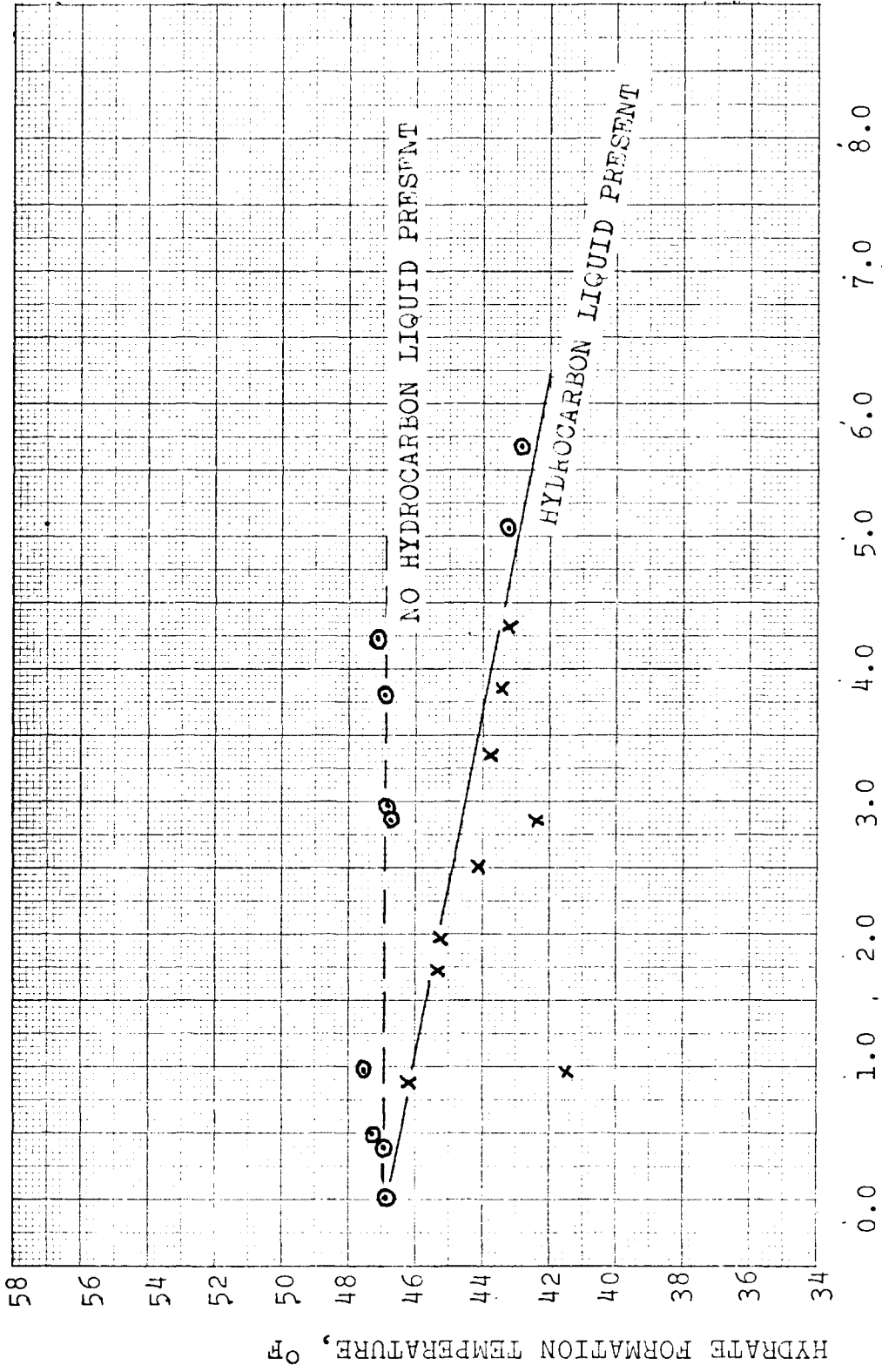
The data obtained with normal pentane and normal hexane were essentially identical and are shown together in figure 13 for comparison. The three separate runs have all been normalized to a common base gas plus propane

hydrate temperature of 47°F. The two normal pentane hydrate formation temperatures reached with the high 3.8 mole percent propane added have been adjusted to what they would have been had they contained only 2.5 mole percent propane as did the other tests. When the data are normalized and shown together, the two trends--one with hydrocarbon liquid present and one without--are evident.

It may be noted here in regard to previous mention made of observing hydrate decomposition and decomposition temperatures that no trends were noted. This lack of any definite trends is in accordance with other authors' comments that hydrate decomposition is a function of time and temperature--the higher the temperature is above the hydrate formation temperature the more quickly the hydrate crystals are destroyed.

During the tests made for this research, the elapsed test times, the hydrate-water or hydrate-liquid hydrocarbon mixture ratios, and the rate of temperature increase following the decision to destroy the hydrates--all of these test parameters--varied considerably from test to test. The mixture of hydrate and liquid churning in the hydrate chamber made determination of a consistent end point impossible. The inconsistency of the other

parameters in these series of tests made any attempt of questionable value. In the author's opinion the hydrate formation temperature is equivalent to the hydrate decomposition temperature under the intensely turbulent conditions at which these test hydrates were formed. The difference being whether net heat flow is out of the system (forming hydrates) or into the system (destroying hydrates).



MOLE PERCENT PENTANES PLUS ADDED

FIGURE 13 PENTANES PLUS-PROPANE-BASE GAS CURVES

DYNAMIC HYDRATE FORMATION TEMPERATURE VERSUS MOLE PERCENT PENTANES PLUS ADDED--COMPARISON OF TWO FLOW REGIMES

CONCLUSIONS

The main point to be noted from the preceding experimental results is that increasing percentages of pentanes plus in the gas stream reduce the hydrate formation temperature for a given gas only in the presence of pentane plus liquids. This reduction is primarily due to the Phase Rule which applies to these solid solutions. The addition of a liquid hydrocarbon to the mixture of gas and water prevents the hydrate from forming as hypothesized by Trezell (1965), but only to the extent determined by the mole percent pentanes plus flowing in the gas stream. Hydrates will still form in the presence of liquid pentanes plus, but at a lower temperature than before.

It is also concluded from this research that hydrates can be formed and observed under flowing conditions and that their formation or destruction may be controlled to a degree. It is recognized that the rate of flow used in the 0.90-in. internal diameter flow assembly is

equivalent to only 217,000 std. cu. ft. of gas per day in a 4.0-in. internal diameter pipeline. Still the two-phase flow conditions were duplicated to as great an extent as the experimental apparatus would permit, and this simulation should permit some application of the knowledge gained here.

RECOMMENDATIONS

The only recommendation that can be firmly made at this time is that additional work should be done, using the apparatus as assembled or modified as below.

The apparatus may be modified to permit higher rates of flow by the installation of a two-stage pressure-reducing assembly with two separate heating tape installations. Also the actual flow stream (and thus hydrate formation) temperature could be sensed by the insertion of a thermistor into the flow stream, connecting the thermistor to a continuous temperature recorder. There was some evidence during very early testing of the apparatus that hydrates release a small but sudden amount of heat upon first forming. If so, this should be quite apparent on a continuous temperature recorder and clearly signal hydrate formation.

The additional research that should be considered is enumerated as follows:

1. Work with higher gas flow rates and with much higher mole percentages of pentanes plus to confirm the data included herein and extend it to an end point.
2. Work with higher gas gravities to determine to what extent the presence of pentanes plus affects rich gas hydrate temperatures, whether more or less than the lean gas used here.
3. Work with the various antifreeze agents currently in use in the field and those under consideration. The effect of various percentage concentrations could be checked closely and possibly an optimum determined.
4. Work to confirm the contribution of normal butane to hydrate formation to determine if it increases the tendency for hydrates to form.

One other recommendation that could be made is for a field test. Gasoline could be added to gas flow lines in which hydrates have been a problem. These should be gas lines where the additional pressure loss caused by the

addition of gasoline in the mole percentages here indicated would not be serious. A record should be kept of the rates of flow, pressures, temperatures, and the occurrence of hydrates in these and nearby comparable facilities in order that some field experience in the practicality of the use of gasoline to inhibit hydrates might be obtained.

If gasoline does indeed significantly inhibit hydrate formation, the simple recombination of a portion of the gasoline previously scrubbed from a well gas stream with the liquid-free-but-saturated gas could provide an inexpensive means of preventing hydrates. This procedure might eliminate the costly necessary use of antifreeze on some offshore production platforms.

Figure 14

SAMPLE ANALYSIS OF PUBLIC SERVICE COMPANY GAS

(Analysis made 9/7/71, received by phone 10/19/71
from Public Service Company)

<u>COMPONENT</u>	<u>MOLE PERCENT</u>
Methane	83.61
Ethane	7.06
Propane	1.70
Isobutane	0.13
Normal Butane	0.23
Isopentane	0.07
Normal Pentane	0.08
Nitrogen	5.85
Carbon Dioxide	1.18
Helium	0.09
	<hr/>
	100.00

CALCULATED GRAVITY OF ABOVE GAS = 0.648

Table 2

HYDRATE FORMATION EXPERIMENTAL TEST DATA

DATE	RATE SCF/HR	PRESSURE PSIA	SCHILLING		MOLE/HR RATES		MOLE PERCENT		HYDRATE TEMPERATURE		
			Base Gas	Mixture	Base Gas	Propane	Other	Other	Before Chiller	After Chiller	Average
2/ 8/72	570.	395.	0.634	0.657	1.503	0.041	0.0	2.65 C ₃	48.8°F	48.3°F	48.5°F
2/10/72	560.	402.	0.651	0.651	1.477	0.0	0.0	0.0	48°	47.5°	47.7°
2/11/72	627.	400.	0.653	0.656	1.654	0.020	0.0	1.2 C ₃	48.1°	48.6°	48.3°
2/11/72	607.	395.	0.653	0.675	1.601	0.061	0.0	3.67 C ₃	49.6°	50.2°	49.9°
2/15/72	456.	400.	0.634	0.656	1.203	0.032	0.0	2.6 C ₃	48.9°	49.7°	49.3°
2/15/72	456.	400	0.631	0.638	1.203	0.032	0.0	2.6 C ₃	49.4°	52.2°	50.8°
Normal Butane											
2/16/72	456.	400.	0.654	0.677	1.203	0.032	0.028	2.22nC ₄	49.4°	50.2°	49.8°
2/16/72	456.	400.	0.654	0.677	1.203	0.032	0.043	3.36nC ₄	49.5°	51.9°	50.7°
2/17/72	457.	400.	0.620	0.647	1.204	0.032	0.014	1.12nC ₄	44.5°	47.2°	48.8°
2/17/72	457.	400.	0.620	0.695	1.204	0.032	0.057	4.41nC ₄	49.1°	51.0°	50.5°
Normal Hexane											
2/18/72	461.	404.	0.623	0.658	1.216	0.032	0.011	0.87nC ₆	50.2°	51.2°	50.7°
2/18/72	461.	404.	0.623	0.662	1.216	0.032	0.022	1.73nC ₆	49.4°	50.2°	49.8°
2/18/72	461.	404.	0.623	0.650	1.216	0.032	0.032	2.5 nC ₆	47.8°	49.3°	48.6°
2/18/72	461.	404.	0.623	0.643	1.216	0.032	0.043	3.33nC ₆	47.6°	49.0°	48.3°

Table 2

HYDRATE FORMATION EXPERIMENTAL TEST DATA
(Continued)

DATE	RATE SCF/HR	PRESSURE PSIA	SCHILLING		MOLE/HR RATES			MOLE PERCENT Other	HYDRATE TEMPERATURE			
			Base Gas	Mixture	Base Gas	Propane	Other		Before Chiller	After Chiller	Average	
2/19/72	458.	400.	0.636	0.664	1.208	0.032	Normal Pentane	0.012	0.96	44.8°F	46.2°F	45.5°F
2/19/72	458.	400.	0.636	0.667	1.208	0.032	0.025	1.98	48.3°	50.5°	49.4°	49.4°
2/19/72	458.	400.	0.636	0.675	1.208	0.049	0.037	2.86nC ₅	47.5°	49.3°	48.4°	48.4°
2/19/72	458.	400.	0.636	0.674	1.208	0.049	0.050	3.83nC ₅	48.8°	50.0°	49.4°	49.4°
2/19/72	458.	400.	0.636	0.674	1.208	0.032	0.056	4.32nC ₅	46.3°	48.3°	47.3°	47.3°
2/17/72	457.	400.	0.620	0.695	1.206	0.032	Normal Butane					
2/21/72	463.	402.	0.649	0.662	1.221	0.032	0.057	4.4nC ₄	49.7°	51.0°	50.3°	50.3°
2/21/72	463.	402.	0.649	0.657	1.221	0.0	0.0	0.0	47.8°	50.4°	49.1°	49.1°
2/21/72	459.	402.	0.649	0.663	1.211	0.032	Isobutane					
2/21/72	454.	398.	0.649	0.679	1.198	0.032	0.014	1.13iC ₄	45.7°	48.5°	47.1°	47.1°
2/21/72	465.	398.	0.649	0.692	1.227	0.032	0.014	1.11iC ₄	47.2°	49.3°	48.0°	48.0°
2/21/72	457.	398.	0.649	0.709	1.206	0.032	0.027	2.15iC ₄	49.8°	52.5°	51.1°	51.1°
2/21/72	462.	400.	0.649	0.670	1.219	0.032	0.041	3.15iC ₄	50.1°	52.1°	51.1°	51.1°
2/21/72	458.	399.	0.649	0.679	1.208	0.032	0.055	4.25iC ₄	49.9°	52.1°	51.2°	51.2°
							0.021	1.65iC ₄	49.3°	51.5°	50.4°	50.4°
							0.014	1.12iC ₄	48.8°	50.1°	49.4°	49.4°

Table 2

HYDRATE FORMATION EXPERIMENTAL TEST DATA
(Continued)

DATE	RATE SCF/HR	PRESSURE		SCHILLING		MOLE/HR RATES		MOLE PERCENT		HYDRATE TEMPERATURE	
		PSIA	Base	Gas	Mixture	Base	Gas	Propane	Other	Before Chiller	After Chiller
2/22/72	454.	402.	0.627	0.648	1.198	0.032	0.074	5.67nC ₅	43.5°F	42.2°F	42.8°F
2/22/72	470.	411.	0.627	0.646	1.240	0.032	0.050	3.78nC ₅	46.1°	48.7°	46.99
2/22/72	464.	400.	0.627	0.659	1.224	0.032	0.037	2.86nC ₅	46.0°	48.6°	46.8°
2/22/72	458.	402.	0.627	0.662	1.208	0.032	0.012	0.96nC ₅	46.9°	49.3°	47.6°
2/22/72	455.	404.	0.627	0.667	1.200	0.032	0.006	0.48nC ₅	46.3°	48.4°	47.3°
2/22/72	453.	398.	0.627	0.647	1.195	0.032	Normal	Hexane	42.6°	43.8°	43.2°
2/22/72	447.	400.	0.627	0.650	1.179	0.032	0.065	5.03nC ₆	46.0°	48.3°	47.1°
2/22/72	458.	400.	0.627	0.635	1.208	0.032	0.054	4.23nC ₆	45.9°	47.8°	46.8°
2/22/72	463.	400.	0.627	0.633	1.221	0.032	0.038	2.97nC ₆	46.3°	47.6°	46.9°
2/22/72	453.	400.	0.626	0.635	1.195	0.032	0.005	0.39nC ₆	46.0°	47.9°	46.9°
							0.0	0.0	46.0°	47.9°	46.9°

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* In items after this, the abbreviation "Compt. Rend." will be used for this publication.

ADDITIONAL REFERENCES NOTED

Due to the many additional references noted, they have been separated into the following five subject groups and arranged alphabetically by author within the groups:

1. Hydrates of Gases.
2. Phase and Equilibrium Behavior of Hydrocarbons and Hydrocarbon-Water Mixtures.
3. Gas Dehydration and Hydrate Inhibition
4. Water Content of Gases
5. General Texts

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