Phase Behavior of Propane and Propene Hydrates

Thesis by

Russell A. Thompson, Jr.

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I. ABSTRACT

The compositions of propane, propene, and propane-propene hydrates varied from 5 to 15 mols of water per mol of hydrocarbon. No appreciable separation of the propene from the propane was found between the excess liquid hydrocarbon phase and the hydrate phase. These facts represent the results of twenty experiments at 400 psia and 33 - 39° F.

While the variations in apparent compositions are over one hundred times the experimental error as demonstrated by material balances, no theoretical explanation is offered to interpret this behavior.

II. INTRODUCTION

The existence of apparent compounds, termed hydrates, which are formed from water and some substance (other than a salt) that exists as a gas or liquid was first discovered by Davy in 1810. Several investigators have worked on the hydrates of chlorine, sulfur dioxide, ammonia, methane, ethane, ethylene, propane, phosgene, hydrogen sulfide, carbon dioxide and others. Villard (1,2) determined experimentally the boundary curves for methane, ethane, and ethylene hydrates. De Forcand (3) attempted to calculate the composition of the hydrates by thermodynamic methods. In 1934 Hammerschmidt (4) reopened the subject of hydrates. His work is primarily concerned with the prevention of formation of hydrates in natural gas transmission lines. Deaton and Frost (5,6,7) have studied boundary temperatures and the composition for several hydrocarbons. They give the following compositions: $CH_4 \cdot 7H_2O$, $C_2H_6 \cdot 8H_2O$ and $C_3H_8 \cdot 18H_2O$. For boundary temperatures of hydrate in the condensed propane region there is the paper of Wilcox, Carson and Katz (8). Roberts, et al (9) present phase diagrams for methane and ethane basing the composition of the hydrate on thermodynamic calculations. In this laboratory there is the unpublished data of Taylor (10,11,12,13).

The boundary curves for methane, ethane, propane, propene, and for two mixtures of the latter two hydrocarbons are given in

FIG. I

METHANE - WATER SYSTEM
ETHANE - WATER SYSTEM

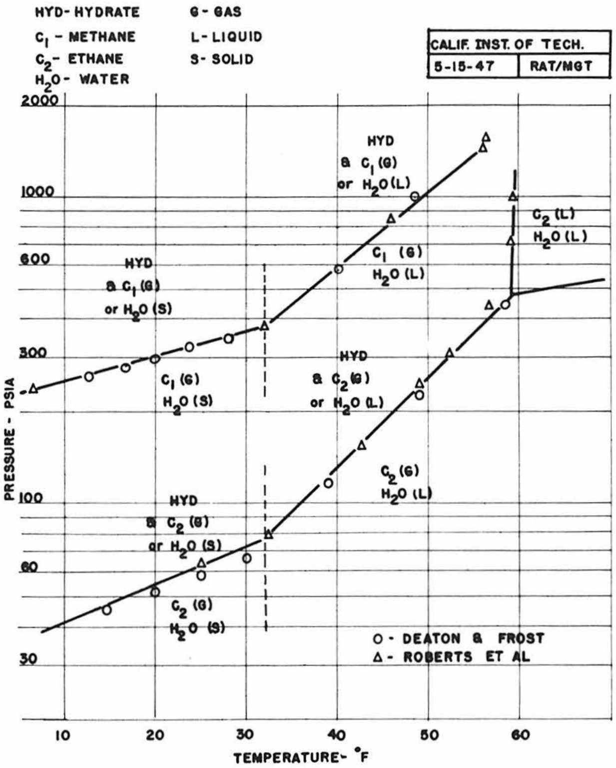


FIG. II

PROPANE - WATER SYSTEM

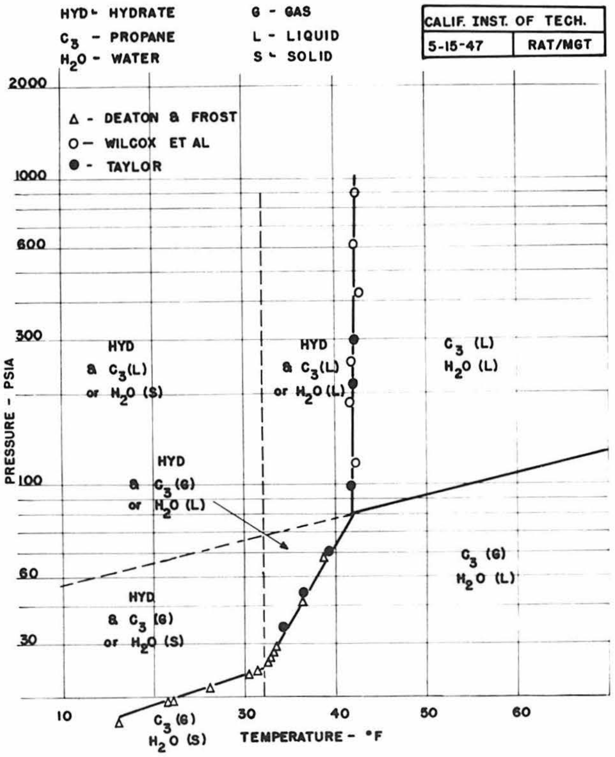


FIG. III

PROPENE - WATER SYSTEM

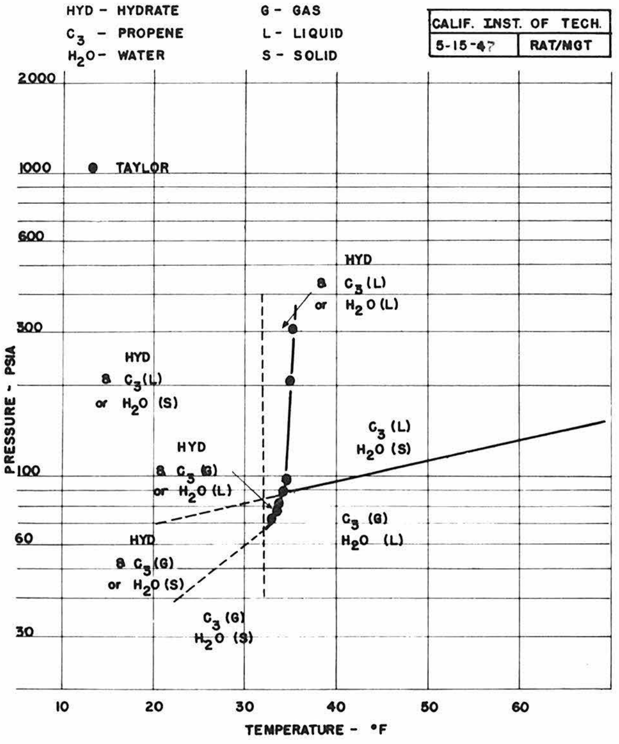
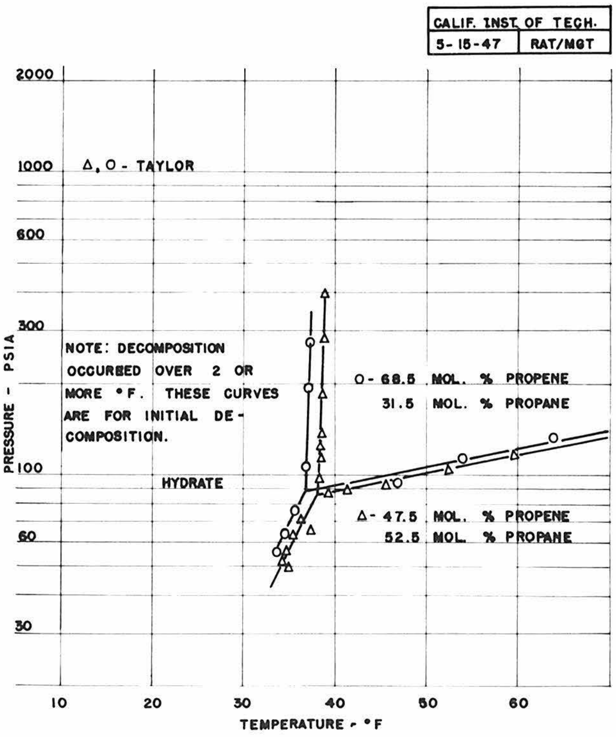


FIG. IV

PROPANE - PROPENE - WATER SYSTEM



Figs. I, II, III, IV. It can be seen that there is good agreement among the various investigators.

Several papers have been published summarizing past work and remedial measures available to industry, an example being that of Bechtold (14). And for completeness the work of Nikitin (15) should be mentioned although it was unavailable for study.

The purpose of this thesis is to extend the knowledge of the composition of propane and propene hydrates and mixtures of same, and to ascertain the difference in ratio of propene to propane between a hydrocarbon phase in equilibrium with a hydrate phase.

III. PROCEDURE

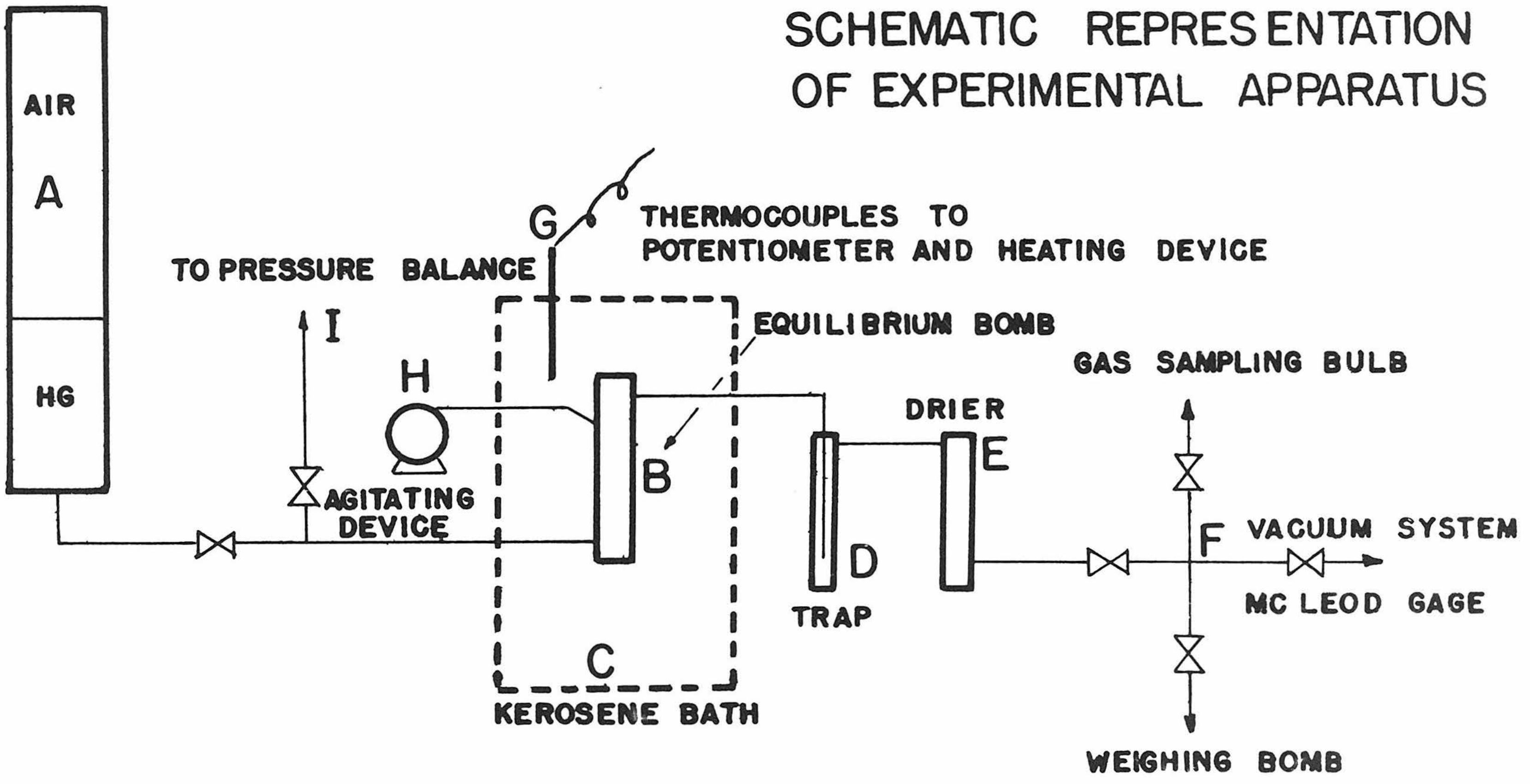
The experimental equipment is shown schematically in Fig. V. The essentials are a double ended equilibrium bomb (B) which may be agitated (H) while in a temperature controlled bath (C), (G). To increase the pressure in the bomb, mercury was added from the reservoir (A), and the resulting pressure measured by the pressure balance (I). For sampling, the equilibrium bomb was connected through a trap (D) and a drier (E) to a manifold (F) where connections were made to sampling bomb or sampling bulb or vacuum system.

The equilibrium bomb employed was made of H 17 hardened steel. Overall length was 13.5 inches with a valve on each end; the inside volume was 10 cubic inches (160 cc) being 6 inches long and 1.5 inches in diameter. A small filter plate was held in the upper end of the bomb by a steel spring. The valve stem in the upper end was fitted with a small probe to aid in sampling.

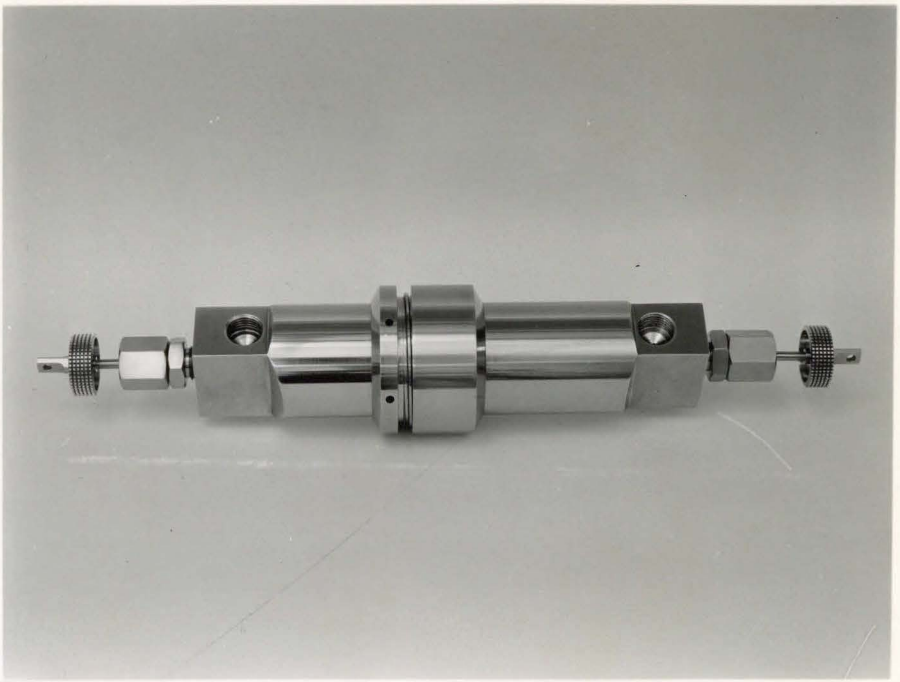
Propane, propene, and water were the chemicals required. The propane and propene were procured from Phillips Petroleum Company and were to be better than 99.0 mol percent pure. No further checks on purity were made. Distilled water was reheated to drive off gases before using. The mixture of hydrocarbon (50.0 weight percent propane, 50.0 weight percent propene) was made up by transferring by means of a weighing bomb quantities of both hydrocarbons to a large cylinder. Care was taken in the amount so made up in order that all the

FIG. V

SCHEMATIC REPRESENTATION OF EXPERIMENTAL APPARATUS



CALIF. INST. OF TECH.	
5-15-47	RAT/MGT



Equilibrium Bomb

hydrocarbons transferred to the cylinder would remain in the gas phase and hence be of uniform composition.

The amounts of the materials to be used were added to the equilibrium bomb in the following manner. After cleaning, assembling and pressure testing, the bomb was evacuated and weighed. Next water was added (the amount being estimated by a buret) with prior evacuation of the lines to eliminate air. Before making a weighing to determine the exact amount of water, the contents of the bomb were placed under a vacuum for three to five minutes. It was felt that this action constituted an additional precaution to the eliminating of gases dissolved in the water. Finally, the hydrocarbon was added. In all runs hydrocarbon was in excess of that required to combine with the water.

Pure propane or propene was condensed into the equilibrium bomb by an ice bath through an evacuated manifold. The hydrocarbon mixture described above was transferred by a pump operated by compressed air and using mercury as a confining fluid. This elaborate method was necessary to accomplish the need of having the same mixture for several runs and also being able to control the amount of hydrocarbon used for each experiment within ten percent. In the last seven runs, six pieces of 7 mm capillary tubing each 2 cm long were placed inside of the bomb before charging. Future use of these glass pieces in an effort to initiate hydrate formation is not advisable because it is felt that small grindings as a result of agitation did contribute to the difficulty of sampling these last runs.

After placing the equilibrium bomb in its holder, the pressure was increased to the desired value by the addition of mercury. The measurement of the pressure was made by a pressure balance of the type described by Sage and Lacey (16). The bomb and its contents were then cooled in the kerosene bath. The temperature of the bath was measured by a platinum resistance thermometer which had been compared with a L&N thermometer calibrated by the Bureau of Standards in the range 10 - 110° F. A copper resistance thermometer actuated a control circuit which balanced the heat supplied against the refrigeration. When the bath reached the proper temperature, agitation was begun. For horizontal agitation, the pressure and sampling lines (in coil form to prevent breaking) remained attached while the bomb in a horizontal position was shaken through an angle of 20 - 30 degrees at a rate of 250 - 300 times per minute. Vertical agitation was similar except that the bomb was in a vertical position. For end over end agitation after adjusting the pressure at the lowest operating temperature, the connecting lines were removed and the bomb rotated end over end at a rate of 60 revolutions per minute.

After agitating for the prescribed time, lines were reconnected if necessary and the contents of the bomb sampled through a previously evacuated manifold. Pressure was maintained in the bomb during sampling by the air reservoir while the mercury so admitted to the bomb was cooled by first passing through a coil located in the bath. The mercury forced the liquid contents of the bomb into the manifold where they flashed. During this operation henceforth termed displacement, the hydrate was held in the bomb by the filter located in the upper end. The displacement products first passed through a trap, then a drier filled with Drierite and finally to either an evacuated gas sampling bulb for analysis or to an evacuated weighing bomb cooled with liquid air. Displacement was continued until mercury came over into the trap. Then the equilibrium bomb was shut off. The gain in weight of the drier was reported as water, while the gain in weight of the sampling bulbs and weighing bomb as hydrocarbon. In the event that water was displaced into the trap, the water was washed out with acetone and the trap plus mercury dried under vacuum, the difference in weight being reported as water. The equilibrium bomb was allowed to stand overnight at room temperature to decompose the hydrate. Reopening the bomb valve allowed the hydrocarbon from the decomposition to pass through the drier and to a weighing bomb cooled in liquid air. The increase in weight of the drier was reported as water and the increase in weight of the bomb as hydrocarbon. Subsequently, the equilibrium bomb was placed in a thermostat at 200 - 210° F where the water remaining in the bomb was distilled into an evacuated condenser cooled to the ice point.

The hydrocarbon was analyzed for propene content by mixing a measured amount of sample with a measured amount of hydrogen. The mixture was passed over a nickel catalyst which caused the propene to be hydrogenated. The decrease in volume after hydrogenation was used to calculate the amount of propene in the sample. For a fuller description of method see (17).

IV. SUMMARIZED DATA AND CALCULATIONS

	OPERATING CONDITIONS					MATERIAL BALANCE										
Run No.	Pressure Psia	Temp. °F.	Time Hours Agitating	Type of Agitation	Hydrocarbon Charge	Hydrocarbon In Grams	Hydrocarbon Out Grams	Loss Grams	Water In Grams	Water Out Grams	Loss Grams	Mols Water per Mol Hydrocarbon In Charge	Mols Water per Mol Hydrocarbon In Hydrate	Mol Fract. Propene In Charge	Mol Fract. Propene In Excess Hydrocarbon	Mol Fract. Propene In Hydrate
9	400	33.0	3.0	H	Mixt.*	35.602	35.570	0.031	10.108	10.151	-0.043	0.679	9.99	0.512	0.516	0.508
10A	400	35.0	4.5[1]	V	Mixt.*	34.518	34.461	0.057	9.953	9.949	0.004	0.689	7.66	0.512	0.523	0.482
11	400	33.0	4.0	V	Mixt.*	35.012	35.071	-0.059	10.054	9.974	0.080	0.686	9.70	0.512	0.505	0.509
12	400	37.0	4.7[1]	V	Mixt.*	34.956	34.876	0.080	10.053	10.001	0.052	0.687	No Hydrate	0.512		
13	400	40-33	0.8	V	Mixt.*	35.022	35.016	0.006	10.052	9.900	0.152	0.686	No Hydrate	0.512		
		33	2.3													
		37.0	4.0													
14	400	40-33	0.5	V	Mixt.*	35.019	35.020	-0.002	10.030	9.976	0.053	0.685	9.19	0.512	0.501	0.496
		33	2.0													
		36.0	3.0													
15	400	40-36	0.3	V	Mixt.*	34.606	34.572	0.034	10.046	9.942	0.104	0.694	No Hydrate	0.512	0.505	
		36.0	2.3													
16	400	40-33	0.8	V	Mixt.*	34.474	34.428	0.047	9.915	9.975	-0.060	0.688	7.77	0.512	0.498	0.487
		33	2.0													
		36.0	15.5													
17	400	40-35	0.5	V	Mixt.*	20.927	20.810	0.117	47.163	46.699	0.464	5.387	No Hydrate	0.512	0.517	
		35.0	2.1													
18	400	33.0	3.1	V	Mixt.*	21.065	20.972	0.092	47.175	46.910	0.266	5.353	No Hydrate	0.512	0.510	
19	400	32.2	1.0	V	Mixt.*	37.427			2.217			Run Void Drier Defective		0.512		
		33.1	4.0													
20	400	32.2	1.0	V	Mixt.*	33.161	33.141	0.020	2.104	1.956	0.147	0.152	No Hydrate	0.512	0.513	
		33.0	4.0													
21	400	33.0	3.4	H	Mixt.*	34.541	34.534	0.007	9.884	9.860	0.024	0.684	No Hydrate	0.512	0.500	
22	400	31.2	0.5	V(G)	Propane	34.820	34.782	0.038	9.933	9.860	0.073	0.698	10.51			
		33.0	4.0													
23[2]	400	31.5	0.5	V(G)	Propane	16.997	16.875	0.122	46.701	46.761	-0.060	5.861	6.04			
		33.0	4.0													
24	400	31.3	0.5	V(G)	Propene	31.459	29.925	1.533	9.801	10.507	-0.706	0.728	5.40			
		33.0	4.0													
25	400	31.1	0.5	E(G)	Propane	21.397	21.286	0.112	45.005	44.728	0.277	5.148	11.44			
		33.0	48.0													
26	400	31.3	0.5	E(G)	Propene	21.714	21.512	0.201	44.819	45.503	-0.683	4.821	14.45			
		33.1	48.0													
27	400	31.5	0.5	E(G)	Mixt.*	34.196	34.149	0.047	9.964	10.180	-0.216	0.697	5.16	0.511	0.508	0.501
		33.1	47.0													
28[3]	400	31.5	0.5	E(G)	Mixt.*	28.417			18.684				No Hydrate	0.511		
		38.9	49.0													

IV. (Continued)

CODE

H - Horizontal

V - Vertical

(G) - Pieces of glass in equilibrium bomb

E - End over end

* - 50 weight percent propane, 50 weight percent propene

1 - Only one-half of time with agitation

2 - Three phases present at end of run; hydrocarbon, water, and hydrate.

3 - Run discontinued after displacement when apparent that no hydrate formed. Material balance not completed.

V. DISCUSSION OF RESULTS

Operating Conditions:- The pressure reported as 400 psia was not allowed to vary more than ± 5 psi for runs 9 - 24 even during displacement. In runs 25 - 28 it was necessary to disconnect the pressure lines during agitation. Therefore, no measurement of pressure could be made after agitation was begun. However, the displacement was also carried out at 400 ± 5 psia. The pressure balance could measure to 0.1 psi, but no effort was made to record the value closer than 0.5 psi. The bath temperature could be measured ± 0.003° F and controlled ± 0.1° F under most adverse conditions.

Procedure:- It is believed that the procedure in general is good. When using the normal amount of reactants, material balance closures of one percent or less were obtained. As an example, the experimental data of run No. 22 are tabulated below.

Amount added to equilibrium bomb		
Wt. of propane	34.820	gm
Wt. of water	9.933	"
Total	44.753	"
Initial Displacement		
Gain in wt. of drier (water)	0.042	gm
Gain in wt. of bomb (propane)	32.496	"
After allowing hydrate to decompose		
Gain in wt. of drier (water)	0.038	"
Gain in wt. of bomb (propane)	2.286	"
Gain in wt. of condenser (water)	9.781	"
Total	44.643	"
Losses		
Water	0.073	gm
Propane	0.038	"
	0.111	"

The features of this material balance are very small losses and the low gain in weight of drier during initial displacement indicating that the filter was effective in holding the hydrate within the equilibrium bomb. However, some difficulty was experienced in the operation of the analytical equipment for the determination of the mol fraction of propene, and therefore the values reported are not considered more accurate than 0.01 mol fraction.

Results of Runs:- The runs will be discussed chronologically for the decision what was to be done next depended on the previous runs. And, as often was the case, the results of the last runs caused some of the intermediate runs to seem unnecessary. For more complete data see section entitled Summarized Data and Calculations.

To begin with, the pressure of 400 psia was chosen arbitrarily in order that no gas phase would be present so that the sampling procedure would be simplified. A temperature of 33° F was chosen because at this pressure the decomposition point of propane hydrate is 42° F and of propene hydrate is 34° F. Run No. 9 gave an apparent hydrate composition of 1:9.99 mols of hydrocarbon to mols of water, henceforth referred to only by ratio, with no appreciable separation of propene from propane between excess hydrocarbon phase and hydrate phase, henceforth referred to only by the term separation. In run No. 10, temperature was increased by 2° F other conditions remaining the same. When the displacement was attempted, it was found that the lower valve had become clogged. Therefore, agitation was changed from horizontal to vertical and conditioning carried out once more. This run gave a value of 1:7.66 and a small amount of separation. However, difficulty with the analytical apparatus causes these figures to be doubtful. The purpose of run No. 11 was to see whether run No. 9 could be duplicated. A ratio of 1:9.70 with no appreciable separation versus 1:9.99 was obtained. It was concluded that the procedures employed were suitable. For run No. 12, the temperature was raised an additional 2° F to 37° F with no hydrate being formed. Since it is known that hydrate formation is difficult to initiate, it was thought that in run No. 12 failure might be because of a supersaturated condition. As a consequence, run No. 13 had a short period of agitation at 33° F followed by a longer period at 37° F. Still there was no hydrate. Run No. 14 was the same as run No. 13 except for a final temperature of 36° F. Hydrate was obtained of apparent composition 1:9.19 with no appreciable separation. Here arises as throughout this entire problem, the difficulty of obtaining equilibrium in a system containing solids. Since run No. 14 probably formed hydrate at 33° F although conditioned finally at 36° F, it was decided in run No. 15 to go directly to 36° F instead of starting formation at 33° F. However, again there was no hydrate. Run No. 16 was the same as No. 14 except that it was conditioned at 36° F for 15 hours instead of 3 hours. Apparent composition of hydrate was 1:7.77 with no appreciable separation. The value of 7.77 was closer to the value for 35° F of 7.66 than the value of run No. 14 which was 9.19. These runs seem to indicate that for this given set of conditions and mixture of hydrocarbon (50 weight percent propane, 50 weight percent propene), the combining amount of water decreased with increasing temperature and increasing time as equilibrium was approached. Run No. 17 was an effort to recheck the apparent composition at 35° F without going to 33° F. However, no hydrate formed. Run No. 18 carried the temperature down to 33° F with a change in the proportion of reactants. Again there was no hydrate. These repeated failures to form hydrate under conditions where it was known to exist demonstrated that it was necessary to employ more vigorous methods to insure hydrate formation. Carrying out each run demanded considerable time and effort, and it was undesirable to have any doubt as to whether hydrate formation was not effected because of supersaturation. Runs Nos. 19, 20, 21 represent efforts to develop a technique to insure hydrate formation without going below the ice point. But there was no success. The reason for these runs was that it was felt that if hydrate could be formed above the ice point, equilibrium values would be relatively easier to obtain. Nevertheless, it was necessary for run No. 22 and subsequent ones to cool the equilibrium bomb below 32° F for a short period with the idea of forming a few ice crystals, and then to condition at a specified temperature. In addition small pieces of glass were placed with the reactants. Runs Nos. 22, 23 gave a value for propane hydrate of 1: 10.51 and 1: 6.04 respectively. It should be noted that in run No. 23 there were three phases on displacement; liquid propane, liquid water, and hydrate. Run No. 24 gave a value of 1: 5.40 for propene hydrate although this value has less accuracy than others because of poor material balance. The last four runs had a conditioning period of 48 hours and a more vigorous end over end agitation. Apparent composition values so obtained were for propane 1: 11.44, for propene 1: 14.45 and for the mixture 1: 5.16. And finally run No. 28 represented one more effort to obtain separation of the propene from propane by conditioning at a temperature of 39° F which was chosen as being approximately in between the decomposition temperatures of propene hydrate and propane hydrate at this pressure. But once more there was no hydrate.

General Discussion:- It may be seen from the results described above that under the conditions of the experiments: 1) no appreciable separation was obtained between propane and propene in the excess hydrocarbon phase versus the hydrate phase, 2) the ratio of mols of water to the mols of hydrocarbon varied for propane from 6.04 to 11.44, for propene from 5.40 to 14.45 and for the 50-50 weight percent mixture of propane and propene from 5.16 to 9.99, and 3) the range of the values above is many times the experimental error as shown by material balances.

The range of apparent composition values is difficult to explain when considering the fact that several investigators have obtained sharp boundary data that agree remarkably well, Figs. I, II, III. While it is recognized that the data presented here may not be the exact values if equilibrium were attained, the conditioning time interval was as long as much of the boundary data conditioning period. No proofs can be offered for the causes of these effects, but merely the suggestions that occlusion, entrapment, or adsorption of the water or hydrocarbon within or upon the hydrate may have occurred.

These experiments indicate that there is much to be learned about the fundamental nature of and phase behavior of hydrates. The experience gained in this project indicate that a technique should be developed which will insure hydrate formation whenever environmental conditions are suitable and which will enable one to check, visual or otherwise, whether or not the hydrate formed. This is needed to answer the ever present question whether the hydrate just did not form or could not form for a given temperature and pressure. The determination of the time necessary to attain equilibrium remains to be done. It is recognized that systems containing solid phases may be difficult to bring to equilibrium, and for this reason, the time required for these systems may be much longer than the maximum time of 48 hours used here even though a knowledge of apparent composition versus time would be of considerable interest. With these factors under control, one could then begin to extend the composition, pressure, and temperature range studied.

In conclusion, no theoretical explanation is offered for the unusual results obtained. These data do show that there remains much to be learned about the fundamental nature of hydrates and factors affecting their formation.

VI. CONCLUSIONS

1. No appreciable difference in the ratio of propene to propane was found between the hydrate phase and the coexisting hydrocarbon phase for a 50 - 50 weight percent mixture at 400 psia and 33 - 36° F.

2. Variable apparent compositions, mols of water per mol of hydrocarbon, for the hydrate were obtained. The values ranged from 6.04 to 11.44 for propane, 5.04 to 14.45 for propene, and 5.16 to 9.99 for the 50 - 50 weight percent mixture.

3. No theoretical explanation is offered for the results summarized in 2. Whether the causes are non-equilibrium, occlusion or entrapment, intrinsic nature of hydrates, a defect in technique used or some other cause is not known.

VII. ACKNOWLEDGEMENT

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