

Gas Hydrates in Circulating Lines
By Kommenmacher, Ludwigshafen, June 30, 1942.
(with 3 Sketches)

From the data sent us by the hydrogenation works some rough calculations were made about the possibility of the formation of gas hydrates in the liquid and vapor phase circulating lines in hydrogenation and compared with the observations made by the individual works on the formation of gas hydrates. Since the given compositions of the circulating gases do not vary greatly from each other, it did not seem necessary to make separate calculations for each individual case, but only the most important cases were taken. The others may then be classified and arranged according to their own special conditions.

Tables 1 and 2 show the most important data submitted by the works on the liquid and vapor phase circulating lines as a basis for calculation. Some works did not give the percentage content of the various hydrocarbons in the circulating gas, but only the percentage of the total and the mean C of the hydrocarbons. Because the composition of the hydrocarbons was necessary for the calculation, it was estimated in these cases from Ludwigshafen data. As may be seen from the tables, water is injected into the circulating gas lines in all works except Merseburg (Leuna). The quantities vary between abt. 0.3 to 4.2 kg H₂O/100 m³ circulating gas or between 0.01 and 0.8 kg/m³ hydrocarbons. Hence, H₂O in liquid phase is surely present in the pipe lines between H₂O injection and H₂O separation, i.e. the formation of gas hydrates is possible at certain pressure-temperature relations. On the other hand, the quantities of water are not enough to prevent plugging by gas hydrates with assurance. Hammerschmidt mentions a case in American practice in which gas hydrates could not be removed with an injection of 0.5 kg H₂O/m³ gas. The diagrams of Fig. 1 were used to calculate the curves of initial gas hydrate formation in the pressure-temperature diagram, in the presence of H₂O in liquid phase. The phase diagrams of the hydrates of pure hydrocarbons, methane, ethane, propane, n-butane, are known from literature, compare Fig. 1, diag. 1. They were discussed in detail at the round table meeting of December 4, 1941. According to investigations by Beaton, Frost, and others, the gas hydrates of hydrocarbons behave like solutions of solids. Diagram 3 of Fig. 1 was taken from an article by Willard, Wilcox, Carson and Katz, in which the equilibriums of hydrocarbons forming mixed hydrates

$$k = \frac{\text{Mol \% in gas}}{\text{Mol \% in gas hydrate}}$$

are shown compared to the total pressure of the hydrocarbon mixture, on a logarithmic scale, for a temperature of 35°F = 1.7°C. The experimental data for the curves are still very meager. The curve for n-butane is particularly uncertain. Isobutane does not seem to form a mixed hydrate with the other hydrocarbons. If the Raoult law were valid for a system of gas mixture and gas hydrate, the curves of diagram 3 would be straight lines at an angle of 45°. This is shown by the following consideration:

If, at a given temperature, in diagram 3: P = total pressure of gas mixture, p_i = partial pressure of a component of the gas mixture, z_i = the mol fraction of the same component in vapor phase, x_i in the solid phase, and P_i = the decomposition pressure of the pure gas hydrates of the components

in question, then, according to the Dalton-Raoult law:

$$p_i = z_i \cdot P = x_i \cdot \bar{P}_i.$$

It follows that:

$$k = \frac{z_i}{x_i} = \frac{\bar{P}_i}{P}, \text{ or}$$

$$\log k = -\log P + \log \bar{P}_i,$$

i.e., if $\log k$ is plotted against $\log P$, we get a straight line at an angle of 45° . As may be seen in diagram 3, the values of $\log k$ drop at a greater angle than 45° against $\log P$. With n-butane the curve reverses itself at higher pressures, which corresponds to the behavior of the less volatile components of a gas-liquid system. The curves of the initial gas hydrate formation of 3 natural gases, diagram 2, are taken from the same article as diagram 3. A comparison of diagrams 1 and 2 shows that the sharp bend C has been replaced by a curve, which is all the flatter, the smaller the mean C of the gas mixture. In the first approximation the curves consist of 2 straight lines slightly inclined against each other. Now, while with the pure hydrocarbons, point C is determined by the intersection of the gas hydrate curve with the vapor pressure curve of the hydrocarbon in question, the position of the initial change of direction in hydrocarbon mixtures is approximately given by the intersection of the gas hydrate curve with the dew-point curve of the gas mixture, or with the straight dew-point curve projected beyond the critical point. In the case of curve B, the dew-point curve projected beyond the critical point is indicated. The critical point is probably in the neighborhood of 10°C . Average values of the equilibrium constants given in literature, partly calculated from the volatiles, partly experimentally determined in binary systems (CH_4 - C_2H_6 , CH_4 -n- C_4H_{10} , C_2H_6 -n- C_4H_{10}), were used in calculation. The values used are given in Table 3. Compare "Ind. & Eng. Chem." 24 (1932), 26 (1934), and 32 (1940).

No data are available in literature on the behavior of gas hydrate formers 1- C_4H_{10} , as well as CO_2 and H_2S in mixture with the gas hydrate formers methane, ethane, propane and n-butane, nor on the influence of H_2 -pressure on the formation of hydrates. These factors were neglected in the calculation. The pressure of the initial hydrate formation, as well as the approximate composition of the gas hydrates, was first calculated from diagram 3 at a temperature of 1.7°C . For gas mixtures with an average C to about 1.32 the further course of the curve was extrapolated with the aid of diagram 2. For gas mixtures with a higher mean C the course of the gas hydrate curve to its intersection with the dew-point curve, also calculated, was approximated from diagrams 1 and 2, and continued from there with a slightly greater slope than the curves of diagram 2. The limit of error of the calculation is approximately $\pm 5^\circ$ on the assumption that the diagrams of Fig. 1 are correct.

The method of calculation is more clearly illustrated by an example on the Welheim liquid phase circulating gas. The hydrocarbon gas mixture has the following composition, see Fig. 2, gas A:

Mol % CH_4	= 57.2
C_2H_6	= 22.9
C_3H_8	= 13.2
n- C_4H_{10}	= 4.6
i- C_4H_{10}	= 0.9
C_5H_{12}	= 1.2

1). Calculating the Pressure of the Initial Gas Hydrate Formation and the Composition of the Gas Hydrate at a Temperature of 1.7°C.

From the composition of the hydrocarbon gas mixture, the composition of the gas hydrate formers figures to be:

%	CH ₄	=	58.4
%	C ₂ H ₆	=	23.4
%	C ₃ H ₈	=	13.5
%	n-C ₄ H ₁₀	=	4.7

At the initial gas hydrate formation the mol fractions x_i of the individual components in the vapor phase are given by this composition, x_i being the mol fractions in the solid phase. Diagram 3 shows that at a pressure of 3.6 atm for the hydrate formers, $x_i = 1$. At this pressure, therefore, gas hydrate is formed of the following composition:

x_1	=	0.015	(CH ₄)
x_2	=	0.025	(C ₂ H ₆)
x_3	=	0.34	(C ₃ H ₈)
x_4	=	0.57	(n-C ₄ H ₁₀)

2). Calculating the Dew-Point Curve.

At initial condensation the mol fractions x_i of the individual components in the vapor phase are given by the composition of the hydrocarbon mixture (CH₄, C₂H₆, C₃H₈, C₄H₁₀, C₅H₁₂). Let x_i be the mol fractions in the liquid phase.

At a temperature of 0°C, the following may be calculated from the equilibrium constants x_i/x_i of Table 3 for a pressure of 7 atm:

$$\sum x_i = 0.82, \text{ or } \sum x_i = 1.35 \text{ for a pressure of 14 atm.}$$

By linear extrapolation we get a pressure of 9.4 atm for $\sum x_i = 1$.

At a temperature of 10°C, the following are calculated from the equilibrium constants x_i/x_i of Table 3 for a pressure of 14 atm:

$$\sum x_i = 1.02, \text{ or } \sum x_i = 1.29 \text{ for a pressure of 21 atm.}$$

By linear extrapolation we get a pressure of 13.5 atm for $\sum x_i = 1$. At 0°C, therefore, the dew-point pressure = 9.4 atm, at 10°C = 13.5 atm.

Now, in the first approximation the dew-point curve is given by a straight line through these points, within a narrow temperature range in a $\log p_1/T$ diagram. For a hydrocarbon mixture with a very low mean C, in which the critical range already lies within the temperature range of 5 to 15°C, the dew-point pressures were calculated for -12.2° and 0°C, and the dew-point curve was drawn through these points and extended beyond the critical range.

3) Estimating the Remaining Course of the Gas Hydrate Curve.

Since the gas mixture contains more propane and n-butane than the natural gases of diagram 2, Fig. 1, and the gas hydrate curves of pure propane and n-butane are steeper than those of pure methane and ethane, the gas hydrate curve to its intersection with the dew-point curve is also steeper than the gas hydrate curves of the natural gases. The slope was roughly estimated graphically as $t_g = 1.3$. The second part of the gas hydrate curve, beyond its intersection with the dew-point curve, was also assumed to be somewhat steeper than the curves for the natural gases.

As shown in Fig. 2 and 3, the observations satisfactorily agree with the calculation. In only one case, Kesseling liquid phase, was a gas hydrate observed at a temperature a few degrees outside of the calculated range of gas hydrate formation. It is possible that the discrepancy is due to neglecting the CO_2 and H_2S contents, comparatively high in this case.

The following can be said about the influence of H_2 -pressure on the formation of gas hydrates:

It is well known that a high H_2 partial pressure causes an increase in the vapor pressure of the hydrocarbons, hence a shifting of the dew-point curve towards higher temperatures and pressures. A similar effect can also be expected on the curve of the initial gas hydrate formation, though nothing can be said about the magnitude of this effect.

For more exact determination of the phase diagram of the gas hydrates, course at high pressure, as well as for the clarification of the influence of inert gases, the injection of oil, alcohol and other liquids, experiments are shortly to be made in high pressure operations with pure gases and mixtures of gases of compositions such as are found in liquid and vapor phase circulating systems. Until experimental results are available, the above calculations must be considered preliminary.

Data from Individual Works on the Liquid Phase Circulating System

Hydro-North	500 - 700		300		Scholven	Ms (Louna)	Ehler
	Politz	Gelsenberg	Welbela	Nesseling			
Press. atm	649	645	495	442	285	215	
Temp. at Suction Side	708	700	520	492	325	-	
Temp. at Press. Side	-	-	496	452	-	-	
Temp. at which gas hydr. were observed	-	-	-	-	-	-	
Temp. of Circul. Gas °C	48	50-70	25	35	44	abt. 40°	30-40°
Temp. side	59	45-55	28	42	54		
Temp. before cooler	36	50-60	165	46	55		40-70°
Temp. after	32	30-40	20	25	35		
at point gas hydr. were found	-	-	20-25	25	-	-	
Observation of Gas Hydrates	no	no	Yes, behind Gas Cooler	no	no	no	in severe cold in Gas Cooler
kg H ₂ O/100m ³ circ. gas behind cold catcher	0.5	4.16	3.9	H ₂ O in Liq. Phase present	0.75	-	0.35
kg H ₂ O/100m ³ circ. gas where gas hydrate was found	0.035	0.36	0.14	-	0.029	-	0.012
Composition of Circul. Gas	on succ. side	after circ. syst. cooler	behind gas cooler	on succ. side	before cooler	stall outlet	stall outlet
CO ₂ /cc	1.0/0.5	0.03/0.6	0.00/0.51	4.18/4.29	0.12/0.4	4.74/5.9%	0.41/2.9
H ₂ S	0.2	0.035	0.07	0.39	0.09	1.09	0.6
O ₂	0.0	-	0.00	0.0	0.00	0.00	0.00
H ₂	76.0	79	63.53	73.46	73.4	66.33	65.5
N ₂	6.9	9	5.54	3.25	7.1	5.87	4.8
CH ₄	11.1 (1)	8	17.31	11.7 (1)	14.5	12.85	21.5
C ₂ H ₆	2.5	2	6.96	1.6	2.3	1.46	2.7
C ₃ H ₈	0.8	0.7	4.00	0.7	1.8	0.96	1.1
i-C ₄ H ₁₀	0.05/0.25	0.07/0.43	0.28/1.39	0.04/0.21	0.07/0.35	0.04/0.24	0.06/0.34
n-C ₄ H ₁₀	0.2	0.2	0.36	0.15	0.08	0.15	0.1
Gas unsaturated	0.4	-	-	0.42	-	0.33	-
Gas H ₂ /m ³	0.007	0.01	0.21	0.006	0.02	-	-
Stall date	12	1-5	1.12.41	Jan. 42	March 42	March 42	17.12.40
	15.1.42			Winter 41			

(1) Estimated from S Hydro-Carbons, near C and Li Data.
(2) Common Liq. & Vap. Ph. Circulating System

TABLE 2

Data from Individual Runs on Vapor Phase Circulating System

Press. Range atm	300		300		300		300	
Hydro-Noxide	Pölite	Gelsenberg	Scholven	Wp (Lohns)				
Catalyst	6434	5058/6434	5058	6434	5058/6434			
Press. atm Suct. Side	290	285	285	285	215			
Press. Side	321	320	325	325	-			
where Gas Hydrates were found	300	-	-	-	-			
Temp. of Circul. Gas °C	19	15-30	33	23	25-30			
Suct. Side	27	35-45	47	47	-			
Press. Side	-	-	-	-	-			
at point Gas Hydr. was found	at times 10°							
Temp. of c.c.p. product °C	15-20°	15-30°	28°	27°	25-30°			
Observation of Gas Hydrates	no	no	no	no	no			
	Yes, in Prod. Cooler							
kg H ₂ O/100 m ³ Circ. Gas in system	?	2.5	1.8	3.6	-			
kg H ₂ O/m ³ Hydro-Carbons		0.23	0.10	0.78	-			
Composition								
CO ₂ /CO	on suct. side	on suct. side	suct. tank outlet	suct. tank outlet	stall outlet			
H ₂	0.0/0.6	0.0/0.0	0.02/0.19	0.15/0.0	0.00/0.28			
O ₂	0.0	0.0	0.005	0.01	0.22			
H ₂	0.0	0.0	0.0	0.0	86.94			
N ₂	21.0	24.2	81.1	95.3	5.46			
CH ₄	5.0	3.0	11.0	3.4	5.57			
C ₂ H ₆	2.9	2.8	5.9	0.11	0.21			
C ₃ H ₈			1.0	0.10	0.55			
10 ⁴ H ₂ O/m ³ H ₂ O	m. 2.21	m. 3.0	0.39	0.55	0.60			
C ₅ & higher			0.14/0.09	0.30/0.16	0.15			
% Unsaturated			0.05	0.08	0.02			
ET MH ₃ /m ³	0.004	0.007	0.06	0.03	-			
Stalls	3,4,5	4	11,12	9,10	-			
Date	15.1.42	18.1.41	1940-42	9,10	14.5.40			

TABLE 3. (For calculating Dew-Point Curves)

Approx. Values of Equilib. Constants $k = \frac{\text{Mol \% in Gas}}{\text{Mol \% in Liquid}}$ of Methane, Ethane, Propane, n-Butane, iso-Butane and Pentane Dependent on Total Pressure

Temperature °C	0°						10°						15.6°						21.1°					
	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	C ₅ H ₁₂	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	C ₅ H ₁₂	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	C ₅ H ₁₂	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	C ₅ H ₁₂
3.5	30	5.2	1.4	0.34	0.48	0.12	36	6.0	1.8	0.48	0.68	0.180	42	3.2	1.0	0.30	0.45	0.011	50	4.0	1.17	0.35	0.54	0.135
7	15	2.6	0.7	0.17	0.24	0.06	17.5	3.0	0.90	0.24	0.34	0.090	20	3.2	1.0	0.30	0.45	0.011	24.5	4.0	1.17	0.35	0.54	0.135
14	7.5	1.42	0.41	0.11	0.16	0.037	8.5	1.7	0.51	0.16	0.226	0.055	9.5	1.83	0.60	0.185	0.28	0.067	12.2	2.0	0.67	0.2	0.32	0.084
21	5.3	1.08	0.32	0.085	0.12	0.032	6.2	1.24	0.41	0.126	0.178	0.045	7.0	1.36	0.47	0.149	0.22	0.052	8.1	1.45	0.51	0.17	0.26	0.069
28	4.3	0.90	0.28	0.071	0.10	0.025	5.1	1.05	0.37	0.105	0.148	0.039	5.5	1.14	0.40	0.129	0.29	0.046	6.2	1.2	0.44	0.15	0.25	0.058
35	3.9	0.80	0.25	0.065	0.092	0.029	4.5	0.90	0.32	0.095	0.134	0.035	4.8	0.97	0.36	0.117	0.17	0.041	5.0	1.0	0.40	0.13	0.20	0.050
42							3.75	0.75	0.30	0.090	0.126	0.033							4.0		0.363	0.12		
49							3.2	0.64	0.28	0.085	0.120	0.035							3.4		0.375	0.116		
56							2.8												2.9		0.382	0.115		

Temperature °C	12.2°					
	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	C ₅ H ₁₂
Hydro-carbon	CH ₄	C ₂ H ₆	C ₃ H ₈	n-C ₄ H ₁₀	i-C ₄ H ₁₀	C ₅ H ₁₂
Press. atm	7	1.3	0.34	0.086	0.12	0.030
	5	1.0	0.26	0.07	0.10	0.024