Hydrates at High Pressures: Part III. Methane-Argon-Water, Argon-Nitrogen-Water System

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The experimental procedure for determining the initial hydrate formation conditions along the univariant gas-water rich liquid-hydrate locus through the measurement of equilibrium pressures and temperatures alone in a constant volume system has been successfully applied to several binary gas mixtures with water to pressures as high as 15,000 lb./sq. in.

The general hydrate theory of van der Waals and Platteeuw, after appropriate modifications, was found valid for the accurate prediction of the initial hydrate formation conditions for selected mixtures of argon-methane and argon-nitrogen.

The calculated methane-argon compositions in the hydrate phase are presented as a function of the methane-argon composition in the gas phase on a water-free basis but were not verified experimentally.

Van der Waals and Platteeuw developed a general theory of clathrate solutions (*16*) applicable to gas hydrates of both pure gases and mixtures below the ice point. Saito, Marshall, and Kobayashi made appropriate modifications to the theory and confirmed that the solid solution theory could be applied above the ice point to hydrates of pure gases quite well where the caged gas molecules were essentially spherical (*12*).

As determined by the X-ray studies of von Stackelberg and Muller (*13, 14*), all gas hydrates in binary systems (an essentially pure gas and water) crystallize in one of two frameworks, referred to as either *Structure I* or *Structure II.* However, in ternary systems the hydrate may crystallize in either Structure I or II, or in a mixture of the two (*16*).

The hydrates discussed in this paper crystallize as a solid solution of Structure I; hence, only those thermodynamic relations relating to Structure I are reviewed.

The general equation (*12*) correlating the thermodynamic properties of gas hydrates above the quadruple point is

$$\Delta\mu' = RT \sum_i \nu_i \ln\left(1 + \sum_J C_{Ji} f_J\right) + RT \ln x_w \qquad (1)$$

If it is assumed that the gases in equilibrium with the hydrate behave as ideal solutions, the general equation may be written for a ternary system as follows:

$$\Delta\mu'/RT = \nu_1 \ln\left[1 + \{C_{A1} f_A^\circ x + C_{B1}(1-x) f_B^\circ\}\right] + \nu_2 \ln\left[1 + \{C_{A2} f_A^\circ x + C_{B2}(1-x) f_B^\circ\}\right] + \ln x_w \qquad (2)$$

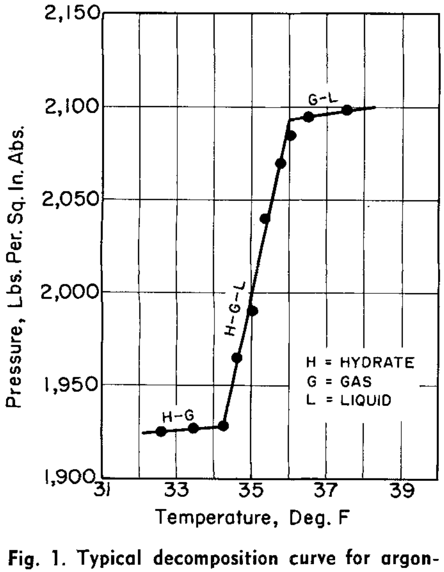

Fig. 1. Typical decomposition curve for argon-nitrogen hydrate (48.8 mole % argon).

TABLE 1. HYDRATE EQUILIBRIUM CURVE DATA FOR METHANE-ARGON MIXTURE

CH_4(75.0%)-A(25.0%)*

	T, °F.	P, lb./sq. in. abs.
1	44.0	950
2	49.2	1,320
3	55.5	1,838
4	58.2	2,208
5	61.5	2,726
6	67.2	4,098
7	72.9	6,310
8	76.8	8,120

CH_4(49.3%)-A(50.7%)*

	T, °F.	P, lb./sq. in. abs.
1	36.7	826
2	44.8	1,300
3	51.0	1,910
4	55.0	2,460
5	60.7	3,683
6	65.8	5,100
7	72.5	8,150
8	72.9	8,190

CH_4(26.2%)-A(73.8%)*

	T, °F.	P, lb./sq. in. abs.
1	39.1	1,277
2	50.0	2,422
3	57.5	4,040
4	64.0	6,544
5	67.8	8,200
6	78.4	16,500

* Equilibrium gas composition, mole percent on a water-free basis.

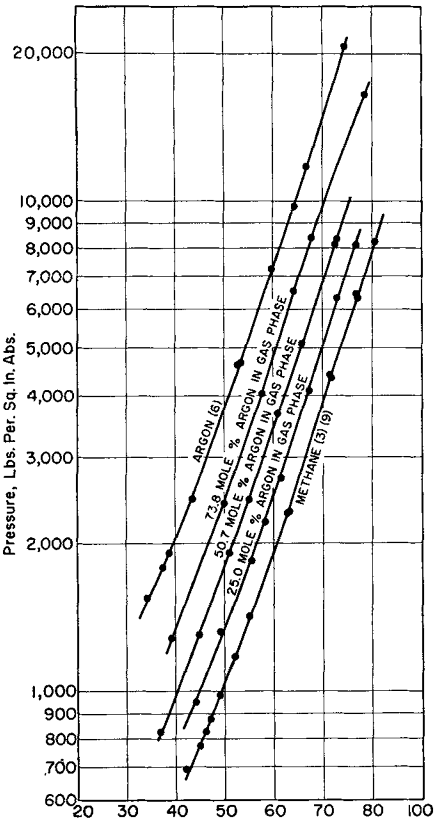

Fig. 2. Gas-liquid hydrate loci for argon-methane-water system.

The chemical potential difference at the same temperature for gases other than methane is calculable from the equation

$$\Delta\mu' = \Delta\mu'_{CH_4} + \Delta v' \, (P - P_{CH_4}) \qquad (3)$$

where $\Delta\mu'_{CH_4}$ and P_{CH_4} are the chemical potential difference and pressure of pure methane hydrate at the same temperature. The value of $\Delta v'$ is 4.5 cc./g.-mole (*16*). By utilizing Equations (2) and (3), the pressures at each gas composition and temperature can be predicted. The necessary values of $\Delta\mu_{CH_4}$ and P_{CH_4} for substitution in Equation (3) were determined in an earlier work and are obtainable from a previously published paper (*12*).

EXPERIMENTAL APPARATUS AND METHOD

The experimental apparatus and method were the same as those described in detail in a previous report (*10*). The method is based on the determination of the hydrate equilibrium curve through direct pressure and temperature measurements of a constant volume system. After evacuation, water was charged into the system, followed by the hydrate-forming gases whose composition had been previously analyzed by mass spectrometer. The change of gas composition was less than 0.2%, even at the conditions of highest solubility in water. Therefore, the correction for the change in gas composition during each run due to solubility was neglected. After the hydrate had formed, the system temperature was slowly increased. When the equilibrium conditions for three-phase gas-water-hydrate coexistence were reached, the hydrate began to break down rapidly. Thus, a small increase in temperature at this point was accompanied by an abrupt increase in pressure. In the following ternary studies, the movement of the gas from the hydrate to the gas phase produced a smaller pressure change than for the binary system. This is because the three-phase coexistence region no longer falls along a univariant locus on the P-T plane, and thus the concentration of the gas and the hydrate changes as one moves across the region as a result of the temperature change. The upper break was adopted as the initial hydrate formation point corresponding to the initial charged gas composition.

Table 2. Hydrate Equilibrium Curve Data for Argon-Nitrogen Mixture

A(48.8%)-N_2(51.2%)*

	T, °F.	*P*, lb./sq. in. abs.
1	36.0	2,090
2	40.3	2,790
3	46.0	3,895
4	50.9	5,385
5	56.0	7,290
6	59.4	9,120
7	60.9	8,900

* Equilibrium gas composition, mole percent on a water-free basis.

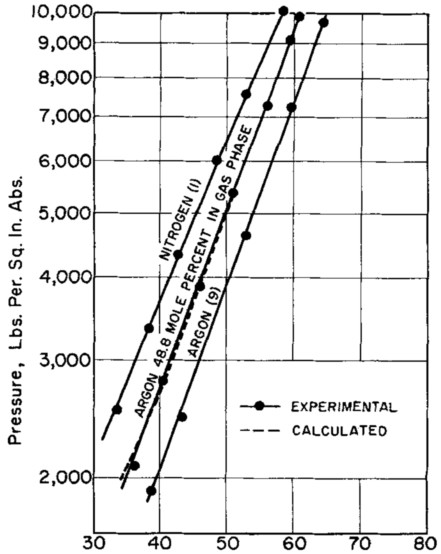

Fig. 3. Gas-liquid-hydrate loci showing comparison of experimental and calculated results: argon-nitrogen-water system.

The methane gas used in this study was found by mass spectrographic analysis to be 99.7 mole % methane, 0.2 mole % nitrogen, and 0.1 mole % other hydrocarbons, principally ethane.

The purities of the argon and nitrogen were 99.99 mole %.

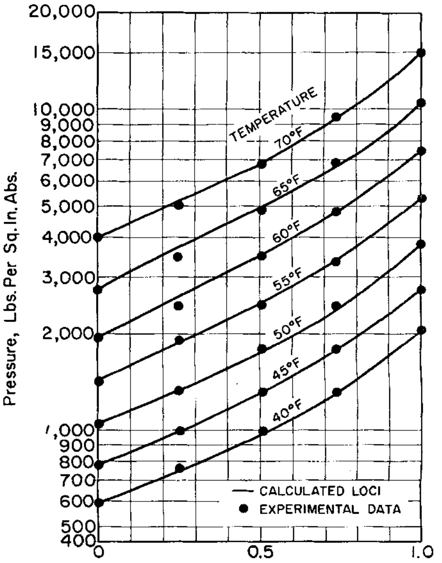

Fig. 4. Pressure vs. gas phase composition loci for initial hydrate formation: argon-methane-water system.

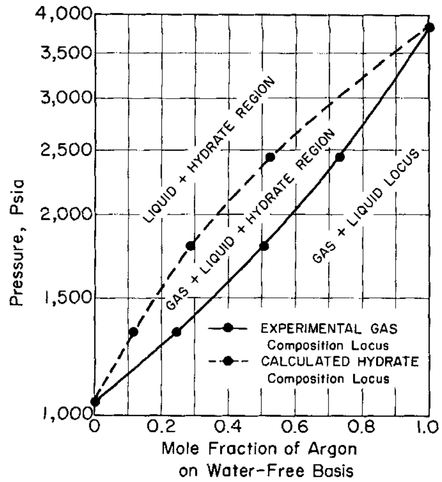

Fig. 5. Gas and hydrate phase envelope for argon-methane-water system at 50°F.

EXPERIMENTAL RESULTS

The following mixtures were prepared, analyzed by mass spectrometer, and studied by the experimental technique discussed in the previous section: 73.8, 50.7, and 25.0 mole % argon in methane; 48.8 mole % argon in nitrogen.

The initial hydrate formation conditions as interpreted from the experimental runs typified by Figure 1 are tabulated in Tables 1 and 2 and presented in Figures 2 and 3. The pure gas hydrate curves (1, 3, 10) over the range of interest are also shown on Figures 2 and 3. The average deviation of the experimental data from the graphically smoothed values is 0.2°F. The maximum deviation is 0.5°F.

THEORETICAL CALCULATIONS AND DISCUSSION

To study the consistency of the solid solution theory, the pressures at each gas composition and temperature were calculated from Equations (2) and (3). First, the temperature was fixed, and both equations were plotted as functions of pressure. From the graphical intersection one found that pressure in equilibrium with the gas phase of composition x. In the above calculations, the Langmuir constants were obtained from a previous paper (*12*); the fugacities were obtained from the thermodynamical tables of Din (*4, 5, 15*) and Sage and Lacy (*11*); and the mole fractions of water in the liquid phase were obtained from the data of Culberson and McKetta (*2*), Linke (*9*), and Krichevsky and Kasarnovsky (*7*).

For the argon-methane-water system, pressure vs. gas-phase composition loci for initial hydrate formation were calculated and compared with the experimental data at several temperatures. Figure 4 shows the closeness of the agreement between the values obtained from the two sources. The use of the Lennard-Jones and Devonshire model (*8*) for the calculation of the partition coefficients and hence the Langmuir constants for adsorptions appears to be fully justified for argon-methane mixtures.

The calculations were also carried out for the argon-nitrogen hydrates for which data were obtained in this study. The comparison between the experimental and calculated values are presented in Figure 3. It should be noted that the gas molecules involved are essentially spherical.

The pressure-composition envelope for the argon-methane system at 50°F. is presented in Figure 5, showing the various regions of phase coexistence. The argon composition in the gas phase vs. its calculated composition in the hydrate on a water-free basis at various temperature parameters is presented in Figure 6. These curves indicate that the volatility of argon in relation to methane in the hydrate is decreased somewhat by raising the temperature from 40° to 70°F.

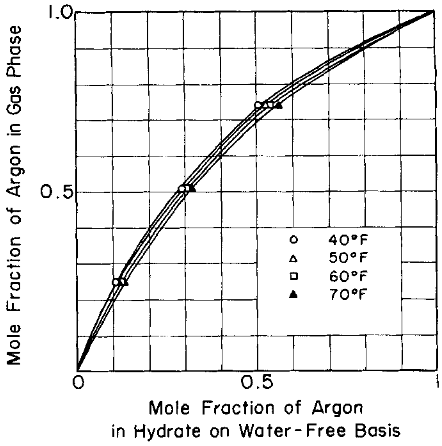

Fig. 6. Calculated compositional relation between gas and hydrate phases.

CONCLUSIONS

The nonvisual experimental procedure for determining the initial hydrate formation conditions for a binary gas-water system (*10*) has been successfully applied to determine the initial hydrate formation condition for selected argon-methane and argon-nitrogen mixtures with water. The van der Waals and Platteeuw theory for clathrates (*16*) as modified for application above 32°F. (*11*) has been shown to be applicable to the ternary systems methane-argon-water and the argon-nitrogen-water systems to pressures as high as 1,000 atm. pressure.

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NOTATION

C = Langmuir constant
C_{J_i} = Langmuir adsorption constant for gas J, n cavities of type i
f = fugacity
f_J = fugacity of J type of gas in equilibrium gas phase
f^o = fugacity of pure gas component at equilibrium temperature and pressure
G = gas
H = hydrate
L = liquid
P = pressure
R = gas constant
T = temperature
x_w = mole fraction of water in the water-rich liquid phase
x = mole fraction of A component in gas phase
ν_i = number of cavities of the type i per mole of water
$\Delta\mu'$ = chemical potential {See Equation (1) or Equation (22) [*12*].}
$\Delta v'$ = difference between molar volumes of β modification of the hydrate and pure liquid water

Subscripts

A and B = gas component
1 and 2 = type of cavity

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Stability Criteria for Miscible Displacement of Fluids from a Porous Medium

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Stability criteria are formulated for displacement of a fluid from an infinite porous medium by a second more dense fluid miscible with the fluid being displaced. Pure displacing fluid is separated from pure displaced fluid by a region of constant thickness in which the two fluids interpenetrate. The steady displacement process takes place at a constant velocity in the direction of gravity. It is shown that appreciable differences in pure-component densities, viscosity variation within the zone of interpenetration, and the displacement velocity can have a major effect on the stability criteria of such a flow.

Persons concerned with the production of petroleum crude from underground reservoirs have in recent years become greatly interested in so-called *secondary recovery processes.* Among these processes are techniques whereby the crude is displaced by a nonaqueous fluid (for example, liquefied petroleum gas) which is miscible with the crude. By driving the solvent fluid with a third relatively inexpensive material, it was hoped that the solvent would essentially dry clean the reservoir with the resultant recovery of virtually all of the oil in place plus the injected solvent. Such a scheme potentially offers great improvement over customary recovery techniques which obtain something less than 50% of the oil in place.

Ideally one envisions a pistonlike displacement of the crude by the solvent with some interpenetration of the two materials owing to diffusion. In practice this happy