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Hydrates in the Methane-Nitrogen System[1]

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The gas hydrate equilibrium curves for systems containing methane and nitrogen have been obtained in the temperature interval 32°F. to 72°F. and between pressures of 350 and 5100 lb./sq.in.abs. The composition of the equilibrium gas and hydrate phases was determined experimentally at 32°F. and 44°F. This information was used to calculate vapor-solid equilibrium ratios for both nitrogen and methane. A comparison is made between the equilibrium ratios in this system which crystallizes in Structure I and the ratios in systems reported earlier which crystallize in Structure II.

Les courbes d'équilibre de clathrates pour les systèmes contenant du méthane et de l'azote ont été obtenues entre les températures de 32° à 72°F. et les pressions de 350 à 5100 lbs/po². On a déterminé la composition à l'équilibre entre les phases gaz et clathrate à 32, 39.7 et 44°F. qui a été utilisée pour calculer le rapport vapeur-solide pour le méthane et l'azote. Ce rapport vapeur-solide est comparé avec un système antérieur qui cristallise différemment.

Gas hydrates belong to a common class of substances known as clathrates. A clathrate compound is formed by the complete enclosure of one or more species of molecules in a suitable structure formed by another species. The binding forces between the two sets of molecules in clathrates are of a physical nature. When the host species is water, the clathrate is called a hydrate. It is generally believed that hydrates crystallize in two structures, referred to as Structure I and Structure II. Details concerning the crystal lattice of these structures have been described(1, 2, 3) and a comprehensive survey of the thermodynamics of hydrate formation has been presented by van der Waals and Platteeuw(4).

In view of the recent discovery of the hydrates of nitrogen and oxygen by Van Cleeff and Diepen(5), it was decided to study the hydrate forming conditions in the ternary system containing nitrogen, methane and water. Apart from the scientific interest in this system, the information gained from the study would be of value in determining the hydrate forming conditions in methane rich natural gases containing nitrogen.

Theory

The solution theory of hydrate formation has been thoroughly summarized by Van der Waals and Platteeuw(4). One of the important relationships correlating the properties of gas hydrates with the molecular properties is as follows:

$$Y_{K_i} = \frac{C_{K_i} P_K}{1 + \sum\limits_{K=1}^{n} C_{K_i} P_K} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

In this equation, Y_{K_i} represents the probability of finding a K-type molecule in an i-type cavity in the hydrate lattice, P_K is the partial pressure of a K-type gas in the equilibrium gas phase, and the C_{K_i} values represent constants characteristic of each k-type molecule in an i-type cavity. The summation is taken over the total number of components present, n.

If the number of i-type cavities per molecule of water in the hydrate lattice is defined by ν_i, then the number of molecules of any K species in all the cavities per molecule of water will be given by

$$\sum_{i=1}^{m} \nu_i Y_{K_i} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

where m is the number of cavity types in the lattice. Thus, on a water free basis, the fraction of any particular K species in the hydrate will be

$$x_K = \frac{\sum\limits_{i=1}^{m} \nu_i Y_{K_i}}{\sum\limits_{K=1}^{n} \sum\limits_{i=1}^{m} \nu_i Y_{K_i}} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

This expression for the mole fraction of each species in the hydrate lattice can be directly related to the equilibrium ratios in gas-hydrate equilibrium as originally proposed by Carson and Katz(6). These ratios were defined as the ratio between the mole fraction of a particular component in the gas phase to that in the co-existing hydrate phase on a water-free basis and they have been used to predict hydrate forming conditions in multicomponent systems. The equilibrium ratio for each component is given by

$$K_K = \frac{y_K}{x_K} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

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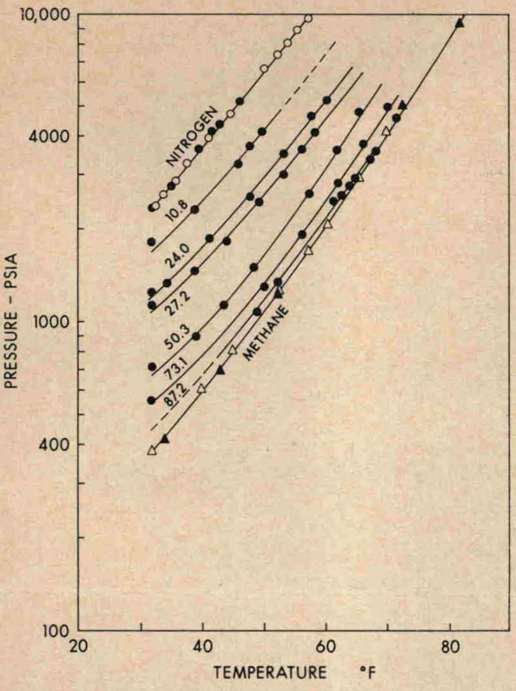

Figure 1—Initial hydrate forming conditions for the nitrogen-methane system.

● This work ○ Van Cleef and Diepen(5) ▲ Deaton and Frost(10) Kobaysahi and Katz(12) △ This work, methane. Numbers indicate mole % methane in the gas phase on a water free basis.

where y_K is the fraction of K in the equilibrium gas phase on a water free basis.

When equilibrium ratios are evaluated from experimental data for components in a system of two or more components, the ratios for the most volatile component are always greater than unity. The experimental values of the equilibrium ratios which have been reported for methane were all obtained for systems in which methane was the most volatile component and hence all the ratios are greater than unity. Furthermore, it is now known that all the systems which were studied formed hydrates in the Structure II crystal system.

One of the objects of this work was to experimentally determine equilibrium ratios for methane in a system where it was the less volatile of two components. In this way equilibrium ratios in the region less than unity would be obtained. Furthermore, with the system chosen, the hydrates would exist in the Structure I crystal system and the results would give an indication of the effect of structure on the equilibrium ratios.

It is apparent from Equations (1) and (3) that the Y_{K_i} values and hence the x_K values depend on the nature of the molecular constants and on the characteristics of the lattice cavities. Hence equilibrium ratios for Structure I systems would not be expected to agree with Structure II systems even for similar components.

Experimental Technique

The experimental equipment used in this investigation was similar to that used by earlier workers(7,8). The equilibrium cell was a liquid level gauge capable of withstanding 6000 p.s.i.a. at 250°F. with a test pressure of 9000 p.s.i.a. The cell was constructed of type 316 stainless steel with sight glasses on both sides for visual observation. The cell was enclosed in a lucite jacket to hold the coolant which controlled the temperature of the cell and its contents. The temperature of the equilibrium mixture was measured with a calibrated iron constant thermocouple and a Leeds-Northrup Model K-2 potentiometer. The pressures were indicated on 0-1000 and 0-5000 p.s.i. Heise bourdan tube gauges that had been calibrated in place with a Ruska dead weight tester. A rocker arm was provided for continuous agitation of the cell contents.

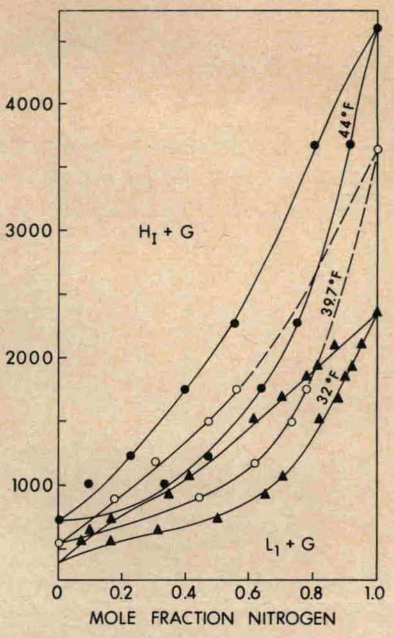

Figure 2—Pressure composition diagrams for the nitrogen-methane-water system.

The experimental technique employed for the determination of the initial hydrate forming conditions was similar to that described by Otto(9).

The determination of the pressure composition diagrams involves the analysis of the gas phase and the hydrate phase at a fixed pressure and the corresponding equilibrium temperature. A charge consisting of water and the desired gases was compressed to a pressure which was estimated to be about 25% greater than that needed for the initial hydrate forming conditions. The temperature was set at the desired value, and the cell was allowed to rock for four to six hours. During this period the pressure continued to fall due to the formation of hydrate. When the equilibrium between the phases was established no further drop in pressure was observed. It was recognized that this procedure involved the assumption that crystals of hydrate forming under transient conditions of pressure and gas phase composition would repeatedly decompose and reform gradually until they ultimately represented the equilibrium composition at the desired conditions. This assumption was thought to be reasonably valid in view of the time allowed and the fact that a liquid phase was always present.

The gas phase in equilibrium with the hydrate and water phase was analysed chromatographically. The gas from the equilibrium cell was isobarically transferred to an auxiliary cell, retaining the hydrate crystals at the top of the equilibrium cell. The pressure was then released and the hydrate crystals decomposed. The gas resulting from the decomposition of the hydrate was then analysed for nitrogen and methane.

*Experimental Results**

The initial hydrate forming conditions of pure nitrogen and pure methane and of six mixtures of nitrogen and methane were investigated up to 5100 p.s.i.a. The pressure-temperature data of pure nitrogen and methane agreed very well with the data

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*Tables 1, 2, 3 and 4 of this paper have been deposited with the National Depository of Unpublished Data, National Sciences Library, National Research Council, Ottawa 2, Ontario. Photo copies may be obtained on request.