Two-phase natural gas hydrate equilibrium

E. Dendy Sloan, Jr.

Chemical and Petroleum-Refining Engineering, Colorado School of Mines, Golden, Colorado 80401, USA

Equilibrium of hydrates with hydrocarbon vapours or liquids is of importance when free water is not present as a phase in the system. Such equilibria may infrequently be found in permafrost hydrocarbon reservoirs, but it is very common in gas-processing lines and dense-phase transport lines through regions of low temperatures.

A review is presented for two current experimental techniques available to measure the water content of hydrocarbon vapours and liquids in equilibrium with hydrates. The current predictive techniques are presented and their value is shown to be closely allied with the accuracy of experimental measurements.

Lorsqu'il n'y a pas de phase d'eau libre dans un système, l'équilibre entre les hydrates et les vapeurs ou liquides composés d'hydrocarbures joue un rôle important. Dans les réservoirs d'hydrocarbures situés dans le pergélisol, on rencontre de temps à autre ce type d'équilibre, mais on le retrouve très souvent dans les réseaux de traitement du gaz et dans les lignes de transport des phases gazeuses denses, dans l'ensemble des régions froides.

Dans cet article, on présente une étude de deux techniques expérimentales couramment utilisées pour mesurer le contenu en eau des vapeurs et liquides d'hydrocarbures en équilibre avec des hydrates. On y présente les techniques courantes de calcul, et l'on montre que leur valeur est étroitement liée à la précision des mesures expérimentales.

Introduction

Natural gas hydrates are non-stoichiometric, ice-like solids whose structure is determined by the inclusion of guest molecules. The hydrate structure contains a crystalline lattice, in which a single molecule occupies each of several cavities. The translational degree of freedom of the guest molecule is limited by the cavity size, but the smaller molecules have essentially the same degree of rotation and vibration as in the gas phase. An excellent review of the physio-chemical aspects of hydrates is given by Davidson (1973).

In situ hydrate deposits affect hydrocarbon drilling (Weaver and Stewart 1982). Kvenvolden and McMenamin (1980) presented a review of the geological occurrence of hydrates. Trofimuk *et al.* (1979) optimistically predicted that the ultimate hydrate reserve equals three times that of the other earth resources of combustible fuels!

While hydrocarbon–hydrate equilibria (without a free-water phase) is not thought to occur in reservoirs, such situations commonly occur in low-temperature, gas-processing and transport lines, such as dense-phase transport lines through Canada and the North Sea. Since only two phases are present, relative to normal gas–hydrate–water equilibria, another degree of freedom is necessary to describe the system. The final degree of freedom is expressed in terms of the concentration of water in the hydrocarbon phase. In other words, how wet must the hydrocarbon (vapour or liquid) phase be in order to exist in equilibrium with hydates? The answer to this question gives the gas processor a quantitative answer as to the procedure for drying the hydrocarbon to prevent hydrate formation which would plug transport lines, erode expanders, foul heat exchangers, etc.

Experimental Systems

In measurements of the water content of hydrocarbon phases in equilibrium with hydrates, most often water mole fractions of less than 0.001 occur. At these relatively small concentrations, a high degree of metastability occurs in the formation of hydrates. Consequently, one does not duplicate the gas-processing conditions in allowing the hydrates to form. Rather, the experimentalist places a free-water phase into an equilibrium cell, converts all of the water to hydrate, then measures the water concentration in the hydrocarbon phase.

The above description contains the three primary experimental difficulties, cited in increasing order: 1) the metastability of hydrate formation, 2) the conversion of all the free water to hydrate, and 3) the measurement of relatively low water concentrations. To date two methods, one for vapours and one for liquid hydrocarbons, have been used in hydrate apparatus for this purpose as described below.

Method of Hydrocarbon Phase Withdrawal

During the last seven years, Professor Kobayashi at Rice University has developed a method for measurement of the water content of hydrocarbon vapour in equilibrium with hydrate. While some modifications have been made, details of the major components of

the method were presented by Sloan *et al.* (1976). The experimental cell (Figure 1), into which the free water and gas are charged, rotates along the cylindrical axis, causing the stainless steel balls to grind the solid phase and prevent water occlusion as the hydrate forms. A special chromatograph was constructed to analyze the withdrawn hydrocarbon phase for water content. Although a sonic detector has recently been added, the remainder of the system is essentially as in Figure 2, for which details were presented by Ertl *et*
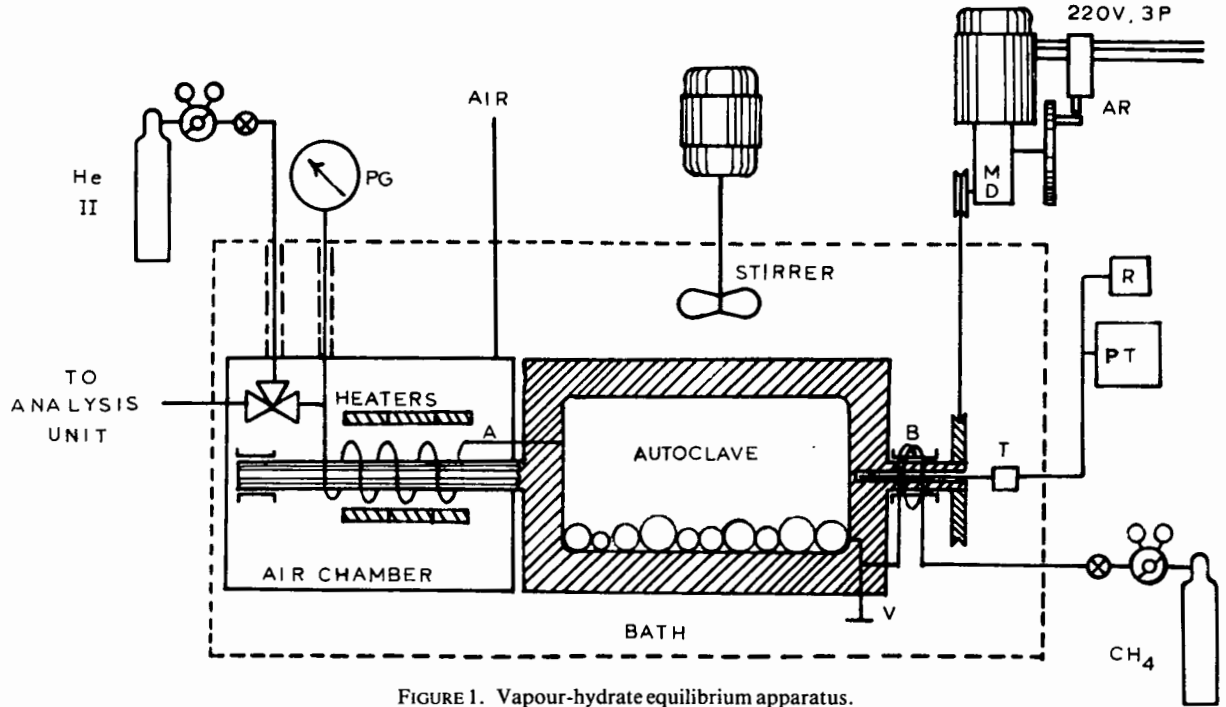

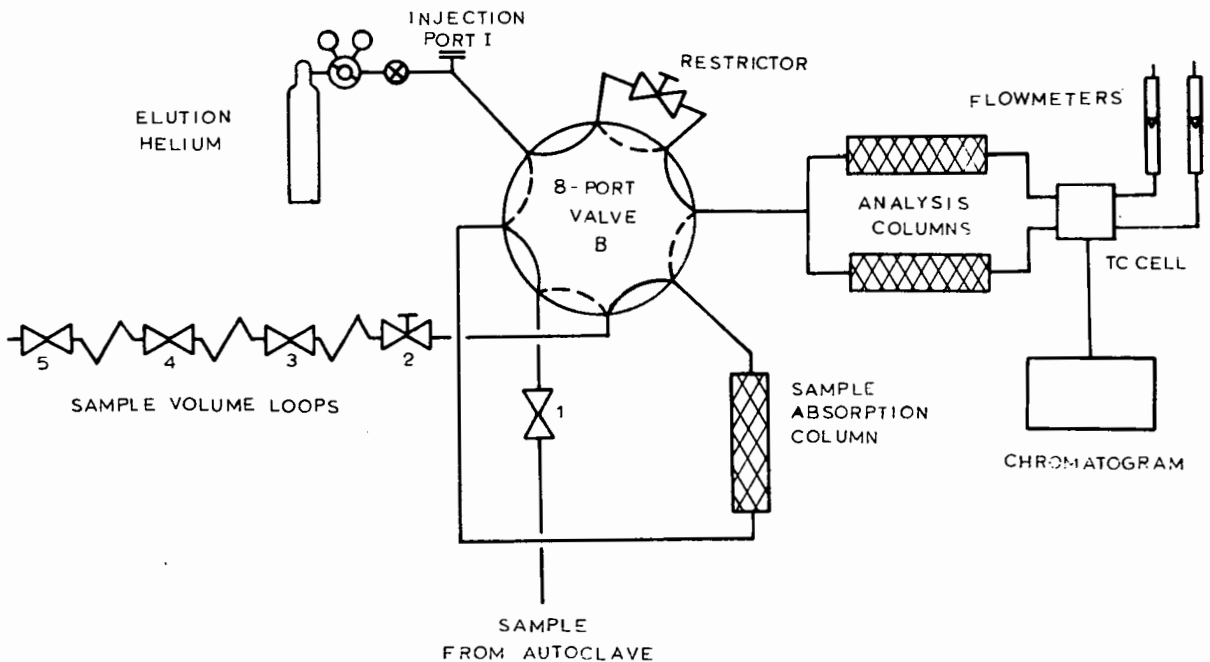FIGURE 1. Vapour-hydrate equilibrium apparatus.

FIGURE 2. Hydrocarbon withdrawal.

al. (1976). The water in the sample is absorbed on the lower column in the figure, and separated by differential glycerol loadings in each analysis column.

The advantages of the hydrocarbon withdrawal system is that the withdrawn hydrocarbon phase may be measured very accurately. Although the accuracy has never been explicitly cited, it is almost certainly within 10 ppm (mole basis). There are only a few disadvantages, the chief of which is that the method is very time consuming and relatively expensive. As with any rotating equilibrium cell, connecting line fatigue and rupture is a small problem. There may also be water drops on the ends of the cell cylinder, which are not ground by the balls to prevent occlusion. In spite of these small problems, the method is excellent, and remains the only apparatus available for the vapour–hydrate measurement. As an indication of accuracy of measurement, a neoprene diaphragm on the elution helium regulator (*see* Figure 2)

allowed a small amount of ambient water to diffuse through the diaphragm, ruining several samples before a stainless steel diaphragm was installed.

In Situ Water Measurement

Recently a new apparatus has been constructed in this laboratory for the measurement of the water content of hydrocarbon liquid in equilibrium with hydrate. While only preliminary measurements have been made to date, the initial indications are that the method is viable and rapid. The oscilliometric apparatus is shown to be a capacitance measurement of liquid above the hydrate phase (Figure 3). In fact, the apparatus is identical to the one described by Pan *et al.* (1975), but the application of the apparatus is new. The hydrates are formed in a free-water phase below the capacitance plates, where they remain, and the capacitance of the hydrocarbon liquid is meas-
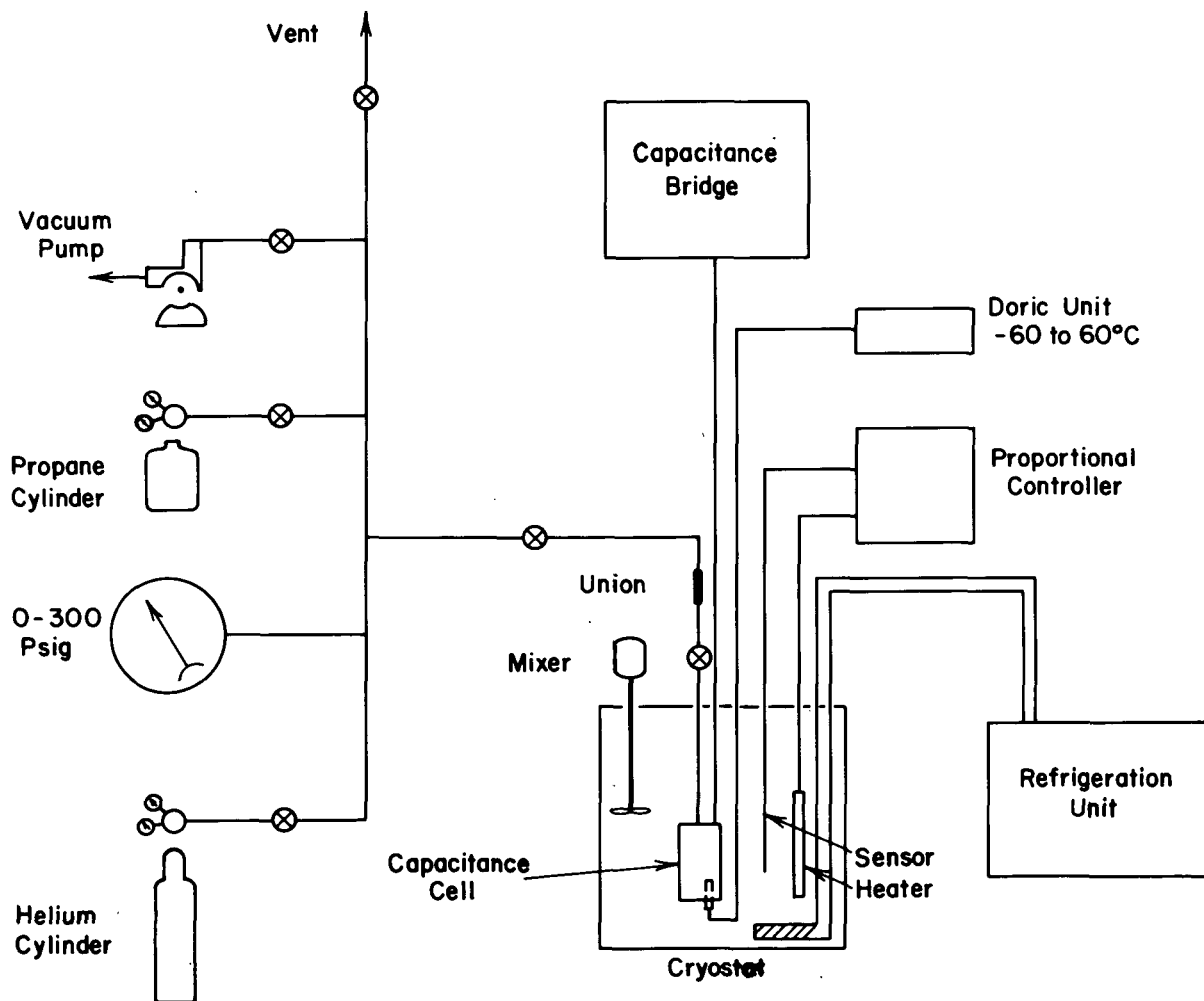

FIGURE 3. *In situ* hydrocarbon–hydrate apparatus.

ured. The instrument is calibrated by measuring the capacitance of known water concentrations in hydrocarbon. The single-phase calibration may be extended into the region of equilibrium with hydrates due to metastability.

This method has the advantage of measurement *in situ* without withdrawal, thus reducing cost and time of experiment. Also, it appears to be relatively rapid. The disadvantages of the method are: 1) that the inaccuracy is larger than the vapour–hydrate estimate described above, and 2) a modification of the apparatus has been proposed, but not used, to prevent occlusion of free water in the hydrate mass. An ultrasonic oscillator will be installed to inhibit occlusion.

Prediction Techniques

The determination of the molecular structure of hydrates during the early 1950's enabled van der Waals and Platteeuw (1959) to derive a statistical mechanics model for the chemical potential of water in hydrate as:

$$[1] \qquad \mu_w^H = \mu_w^{MT} + RT\Sigma_i \nu_i \ln(1 - \Sigma_j \theta_{ij})$$

The above equation is seen as a slight modification of Raoult's Law, with the term θ_{ij} to account for cavity filling, as related to fugacity by a Langmuir isotherm-type expression:

$$[2] \qquad \theta_{ij} = \frac{C_{ij} f_i}{1 + \Sigma_j C_{ij} f_i}$$

In equation 2, the values of C_{ij} are unique functions of temperature for each component in every cavity which it can occupy. Parrish and Prausnitz (1972), among others, have shown that values of C_{ij} may be obtained from fitting three-phase, pure-component, hydrate data and used successfully in mixture hydrate prediction without further correction.

Sloan *et al.* (1976) first showed that the difference in chemical potentials of equation may be related to the fugacity of water in the hydrate phase by the equation:

$$[3] \qquad f_w^H = f_w^{MT} \exp(-\Delta\mu_w/RT)$$

where f_w^{MT} is an experimentally determined parameter related to the hypothetical vapour pressure of the empty hydrate.

Ng and Robinson (1980) give expressions for f_w^{MT} in both structures, obtained by fitting the data of R. Kobayashi and co-workers (Aoyagi *et al.* 1978, 1979). Therefore their method may be considered a correlation of existing two-phase (vapour–hydrate) data.

Dharmawardhana (1980) used three-phase (vapour–hydrate–ice) equilibria data to equate the fugacities of water in ice and hydrate. In so doing, many data points were reduced to common values of empty hydrate vapour pressures as shown for Structure I in Figure 4. These values may be used in equation 3 to predict two-phase data, using none of the existing two-phase data in the prediction scheme.
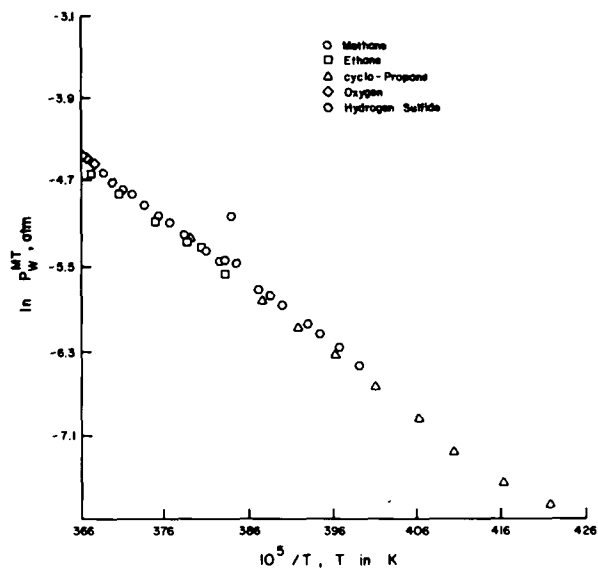

FIGURE 4. Structure I empty hydrate vapour pressure as a function of reciprocal temperature.

Parrish (*Pers. Commun.* 1980) suggested that ice be used as a reference, because the ice fugacity may be easily calculated. This is the second method available to predict two-phase hydrate data *a priori*.

In order to use any of these fugacities for the hydrate phase, it is necessary to equate them to the fugacity of water in the other phase (vapour or liquid) determined by the equation:

$$f_w = z\phi P$$

where z is the molar composition of water and ϕ is the fugacity coefficient of water in the fluid phase. In this work, the fugacity coefficient was determined using the equation of state suggested by Peng and Robinson (1976).

Calculations are presented for water in methane vapour in equilibrium with hydrate, using each of the above three methods to determine f_w^{MT} (Table 1). The correlated values of Ng and Robinson are seen to do significantly better than the *a priori* predicted values. Future two-phase data may help to discriminate between these methods.

The water content of liquid propane in equilibrium

TABLE 1. The prediction of the water content in the methane vapour phase in equilibrium with the hydrate phase

Temp.	Pressure	Water content in the vapour phase			
		Kobayashi and co-workers (Aoyagi et al. 1979) Exp. data	Correlated values by Ng and Robinson (1980)	Predicted values by equations Dharmawardhana (1980)	Parrish (Pers. Commun. 1980)
°F	psi	ppm (mole)	ppm	ppm	ppm
26.33	500.	178.09	176.89	144.99	150.38
26.33	1000.	94.43	95.28	77.11	82.42
26.33	1500.	64.22	65.48	57.44	63.28
8.33	500.	78.24	79.23	57.09	60.54
8.33	1000.	39.56	38.51	31.09	34.01
8.33	1500.	24.23	23.95	23.80	26.87
−9.67	500.	32.17	33.67	20.88	22.68
−9.67	1000.	15.45	14.83	11.71	13.14
−9.67	1500.	8.46	8.40	9.29	10.77
−27.67	500.	12.30	13.45	7.04	7.84
−27.67	1000.	5.60	5.42	4.10	4.72
−27.67	1500.	2.72	2.82	3.41	4.06
Note: Mean absolute deviation			1	9	7

System: Methane–water
Phase identification: Hydrate phase (methane hydrate) and vapour phase (methane and water)

[Ed. note: Data have not been converted to SI units]

with hydrate is predicted in Figure 5, using f_w^{MT} from a figure for Structure II like that in Figure 4. Unfortunately, there are no published data to confirm or deny these predictions. Such data are currently being obtained at the Colorado School of Mines.

Conclusions

Two-phase, hydrate equilibria data are necessary for the processing and transportation of natural gas. However, there is a paucity of data available. Such data are vital to enable the verification of several prediction and correlation schemes.

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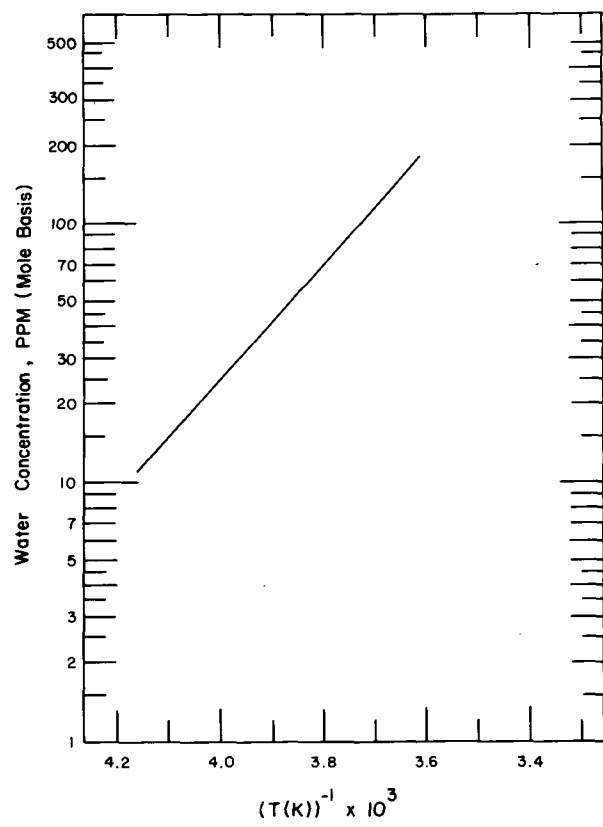
FIGURE 5. Water concentration of liquid propane in equilibrium with hydrates.

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