

Effects of the Driving Force on the Composition of Natural Gas Hydrates

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Fractionation data were obtained in the range 3.0 to 7.5 MPa and for driving forces (subcoolings) between 2 and 16 K. High pressure and large driving force were desirable to suppress fractionation. The equilibrium content of different gas components in the hydrate phase can be modeled using the van der Waals-Platteeuw model. In the present work van der Waals-Platteeuw expressions were expanded by adding exponential terms which include the driving force and a system dependent tuning parameter. The tuning parameter depends on the pressure and there is one parameter for each component. The expanded expressions rely on two assumptions. For the hypothetical case of hydrate formation at an infinite driving force, there is no fractionation. For the case of hydrate formation at equilibrium conditions, the extra term equals zero. After tuning, the normalized contents of different components in the hydrate phase were described with accuracies of about 1 %absolute which corresponded to about 10 %relative.

1 Introduction

The present work is related to the development of hydrate technology for storage and transport of natural gas. Storage of natural gas in the form of hydrate at elevated pressure was proposed in the 1940's (Berez and Balla-Achs 1983). Gudmundsson (1990) proposed storage at ambient pressure even for temperatures not far below 0 °C. The hydrate may be in the form of a powder (dry hydrate concept) or dispersed in condensate or crude to form a pumpable hydrate-in-oil slurry (hydrate slurry concept) (Gudmundsson et al. 1998).

Natural gas hydrate contains up to 182 Sm³ gas per m³ hydrate. It has been demonstrated that natural gas hydrate with ice can be stored for prolonged times at -15 °C at ambient pressure without a significant loss of gas. At these conditions of pressure and temperature the hydrate is thermodynamically unstable, but is regarded metastable for practical purposes (Gudmundsson et al. 1994).

Natural gas hydrate may be produced at 60-90 bar and 2-10 °C. The hydrate can then be cooled to for example -15 °C, while an elevated pressure is maintained. Next, the system is depressurized to ambient pressure while appreciable temperature increase is not allowed. The hydrate is then stored and transported under ambient pressure and about -15 °C. Upon heating above 0 °C, the hydrate readily dissociates to yield natural gas and water. Such hydrate technology has two important characteristics:

Ambient pressure. Storage and transport of natural gas in the form of hydrate is carried out at ambient pressure. This gives large savings, since pressure equipment has relatively high capital expenditures. Maintenance and operation of high pressure equipment are more involved and

the equipment is heavy, so the operation expenditures are high too, compared to unpressurized operation.

No active cooling. The hydrate is cooled down to the storage temperature in the hydrate production plant. During storage and transport it is not necessary to actively provide cooling. Passive insulation is sufficient. This permits cheap systems for storage and transport units.

When hydrate forms from gas mixtures the gas components partition between the hydrate and the gas. Different components partition differently. This is fractionation. Usually the heavy components concentrate in the hydrate phase, and light components tend to stay in the gas phase. But the opposite could also be the case, as in some systems with hydrogen sulfide. Fractionation was first reported by Hammerschmidt (1934). Fractionation is not desirable in the hydrate process. It is necessary to have more quantitative knowledge about how hydrate production conditions, especially how pressure and temperature, affect fractionation.

2 Apparatus

The assembly for hydrate production is shown in Figure 1. The reactor was a stirred batch reactor made of stainless steel. Inner diameter was 75 mm and inner length was 140 mm, yielding a volume of about 600 cm³. The stirrer was a plastic coated, magnetic bar. Two small bolts on the reactor bottom baffled the water. The magnetic bar was rotated by a magnetic stirrer placed under the reactor. The reactor had two ports with closing valves on the wall. One port was connected to an Alcatel vacuum pump. The other port was connected to a gas supply line. The top cap of the reactor could be removed to get access to the hydrate.

The reactor was placed in a water bath with good mixing. A cold sink which provided excess cooling ex-

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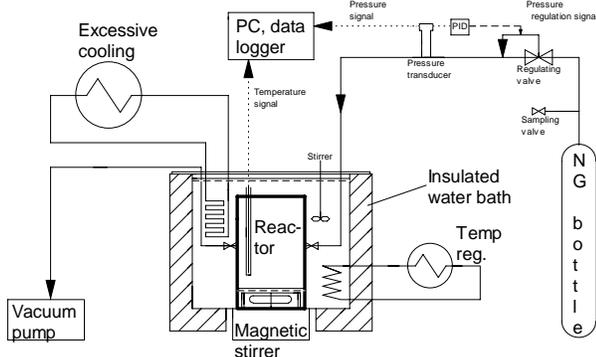


Figure 1: Laboratory for hydrate production.

changed heat with the water bath. Bath temperature was kept constant by a thermostatic heater, thus the reactor temperature was regulated indirectly. It was taken into account that during hydrate production the reactor temperature was typically 0.3 to 0.5 K above the cooling water temperature. The reactor temperature was read by a PT-100 sensor in a thermopocket and the cooling water temperature by a thermocouple. The pressure in the reactor was read by a pressure transducer. Via a PID regulator, the transducer gave a signal to a pressure regulating valve. The reactor was operated within ± 0.5 K of the temperature set point and within ± 0.2 MPa of the pressure set point. Reactor pressure and temperature as well as cooling bath temperature were logged by a computer.

An Intersmat IGC 120 DFL gas chromatograph with a loop (0.3 cm^3), a porapak N 80-100 column ($\approx 2 \text{ m}$) and a flame ionization detector was used to make quantitative analyses of methane, ethane and propane. The temperature program had three sequences; an isotherm (351 K, 1.5 min), a ramp (20 K/min) and a final isotherm (403 K) which lasted long enough for propane to elute. The gas in the loop was injected after a static period (6 s) to make the total molar amount of gas in the loop approximately equal in all injections. A Hewlett-Packard HP 3396 series II integrator was used to perform peak integration. Normalized concentrations were calculated from the measured chromatographic areas. Absolute concentrations were not needed.

The gas samples that were injected to the gas chromatograph were of three different categories; calibration gas, gas from the gas cap in the reactor at the end of the hydrate production period and gas from dissociated hydrate. Calibration gas was injected from the gas bottle. Reactor gas was injected directly from the reactor. Gas from dissociated hydrate was injected from a dissociation cell with a volume of about 80 cm^3 . The cell was made from tubular heavy-duty transparent plastic with threaded ends for the caps. It was possible to visually observe the hydrate sample as dissociation proceeded.

3 Methods

The experiments can be grouped in terms of driving force. 2, 4, 8, 12 and 16 K subcooling were used.

Experiments can also be grouped in terms of operating pressure. 3.0, 4.5, 6.0 and 7.5 MPa were used. With these sets of driving forces and operating pressures, a set of operating temperatures was implicitly defined.

To produce hydrate, distilled water (80 cm^3) was brought in contact with natural gas (5 %mol ethane and 3 %mol propane in methane). But before feeding the gas, the air in the reactor and air that was dissolved in the water was removed by evacuating the reactor ($\approx 5 \text{ Pa}$) for 20 minutes or more. Then the reactor was cooled to the operating temperature, while pressurized with the gas to somewhat below the hydrate equilibrium pressure for this temperature. The magnetic stirrer was started ($\approx 400 \text{ RPM}$). When the desired temperature was reached, the data logger was started and the reactor pressurized to the operating pressure. Pressurization could take up to a few minutes, depending on the operating pressure.

The reactor was operated for about four hours. Afterwards, a sample of the gas in the reactor was analysed by gas chromatography. The pressure decrease in the reactor due to gas sampling was insignificant. With the pressure still maintained the reactor was refrigerated (252 K) overnight.

The next day the reactor was quickly depressurized to ambient pressure. It took about half a minute or less, depending on the initial reactor pressure. The reactor was opened, and hydrate quickly scraped into the precooled dissociation cell. The cell was closed immediately. The sample transfer took place in the freezer at around 252 K. The closed dissociation cell with the sample was allowed to heat to room temperature which caused the hydrate to dissociate and associated ice to melt. One or more gas samples were then analysed by gas chromatography.

4 Results

Tables 1 to 4 give the results of all the gas chromatograph measurements. $C_{i,react}$ (%mol) is the normalized gas phase concentration of gas i in the reactor when the hydrate production was stopped after 4 hours operation. $C_{i,diss}$ (%mol) is the normalized concentration of gas component i in the gas from a completely dissociated sample.

5 General Model

A general fractionation model is proposed, which includes a van der Waals-Platteeuw equilibrium term and a term which accounts for the effect that the driving force has. The extra term includes the subcooling and a system dependent tuning parameter for different components. The model is based on three assumptions:

- A1** When operating with zero driving force (on the equilibrium line), the largest possible fractionation takes place.
- A2** When operating with infinite driving force, no fractionation takes place.
- A3** Between these extremes, the fractionation as function of the driving force changes exponentially.

Table 1: Composition of reactor gas and gas from dissociated samples. Hydrate production pressure: 7.5 MPa.

ΔT (K)	$C_{i,react}$ (%mol)			$C_{i,diss}$ (%mol)		
	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
2	93.4	4.6	2.0	76.6	10.1	13.2
2				76.0	9.6	14.4
4	94.5	4.1	1.4	85.6	6.9	7.6
4				84.8	7.4	7.8
4	93.2	4.5	2.3	75.6	9.3	15.1
8	92.5	4.8	2.7	85.1	7.5	7.4
16	92.2	5.0	2.9	88.9	6.0	5.1

Table 2: Composition of reactor gas and gas from dissociated samples. Hydrate production pressure: 6.0 MPa.

ΔT (K)	$C_{i,react}$ (%mol)			$C_{i,diss}$ (%mol)		
	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
2	92.4	4.9	2.8	83.5	6.8	9.7
4	93.1	4.5	2.4	76.8	10.7	12.5
8	92.7	4.8	2.6	84.6	7.8	7.6
8	92.6	4.8	2.7	84.3	7.9	7.7
8				84.0	8.0	8.0
12	92.2	5.0	2.8	88.4	5.9	5.6
12	92.1	5.0	2.9			
16	92.3	4.9	2.8	89.3	5.6	5.1
16				89.5	5.6	5.0

Table 3: Composition of reactor gas and gas from dissociated samples. Hydrate production pressure: 4.5 MPa.

ΔT (K)	$C_{i,react}$ (%mol)			$C_{i,diss}$ (%mol)		
	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
2	93.1	4.8	2.1	76.1	8.9	15.0
4	93.4	4.5	2.1	76.6	10.2	13.3
8	92.9	4.7	2.4	82.4	8.4	9.2
12	92.4	4.9	2.7	89.0	5.6	5.4
12				88.9	5.6	5.5

Table 4: Composition of reactor gas and gas from dissociated samples. Hydrate production pressure: 3.0 MPa.

ΔT (K)	$C_{i,react}$ (%mol)			$C_{i,diss}$ (%mol)		
	CH ₄	C ₂ H ₆	C ₃ H ₈	CH ₄	C ₂ H ₆	C ₃ H ₈
2	93.3	4.7	2.0	73.0	9.3	17.7
4	94.7	4.1	1.2	75.5	10.7	13.8
8	93.9	4.3	1.8	79.3	9.6	11.1

Hydrate equilibrium compositions can be calculated using van der Waals-Platteeuw's model. This is taken advantage of by introducing assumption A1.

It is impossible, indeed without any physical meaning, to do experiments with infinite driving force. For an equilibrium temperature T_{eq} , the highest practical driving force in the apparatus used is $\Delta T = T_{eq} - 273$. A larger driving force would bring the system below 273 K where the water freezes to ice. For an infinite driving force assumption A2 was made.

A3 must be consistent with A1 and A2. Thus, as the driving force approaches zero, the content of any component in the hydrate approaches the equilibrium value. For increasing driving forces the normalized content of any component in the hydrate approaches asymptotically that of the feed gas. An exponential term is assumed to describe this behavior.

Fractionation is known to be component dependent. It is believed to be system dependent too. Accordingly, the model contains a system dependent empirical constant, k_i , for all components i .

For a system with n guests, exponential expressions are deduced for $n - 1$ guests. The last equation is the mass balance which closes at 100 %mol. For the system in the present work with methane, ethane and propane as guests, the three assumptions can now be formulated in mathematical terms.

$$\text{A1: } C_{i,diss} = C_{i,eq} = \theta_{i,eq} \cdot 100$$

for $\Delta T = 0$ and P fixed.

$$\text{A2: } C_{i,diss} = C_{i,feed}$$

for $\Delta T = \infty$ and P fixed.

$$\text{A3-a: } C_{i,diss} = C_{i,eq} + (C_{i,feed} - C_{i,eq})e^{-k_i/\Delta T}$$

for $0 < \Delta T < \infty$, $i = C1, C3$ and P fixed.

$$\text{A3-b } C_{C2,diss} = 100 - (C_{C1,diss} + C_{C3,diss})$$

for $0 < \Delta T < \infty$ and P fixed.

$C_{i,diss}$ is the normalized concentration of component i in the gas from a dissociated hydrate sample. $C_{i,eq}$ is the normalized concentration of component i in the gas from a dissociated sample of hydrate which was formed at equilibrium conditions. $C_{i,feed}$ is the concentration of component i in the feed gas used to form hydrate (for the feed gas, the normalized concentrations are equal to the actual concentrations). $\theta_{i,eq}$ is the equilibrium fraction of occupied hydrate cavities that contain the i -type guest. k_i is a system dependent tuning parameter which depends on pressure and which includes effects that are not taken into account explicitly, for example effects of kinetics and mass transfer rates. ΔT is the driving force (subcooling). $C1$, $C2$ and $C3$ denotes methane, ethane and propane, respectively.

The most important equation is the one labeled A3-a. For a fixed pressure, it expresses how the normalized hydrate content of guest type i depends on the driving force and the content of guest i in the feed gas. This equation is consistent with A1 and A2; Equation A3-a yields $C_{i,eq}$ for $\Delta T = 0$, as in Equation A1. Equation A3-a yields $C_{i,feed}$ for $\Delta T = \infty$, as in Equation A2. Equation A3-a could be presented in a more out-written way, but that is not necessary for the present purpose. More details are presented elsewhere (Levik 2000).

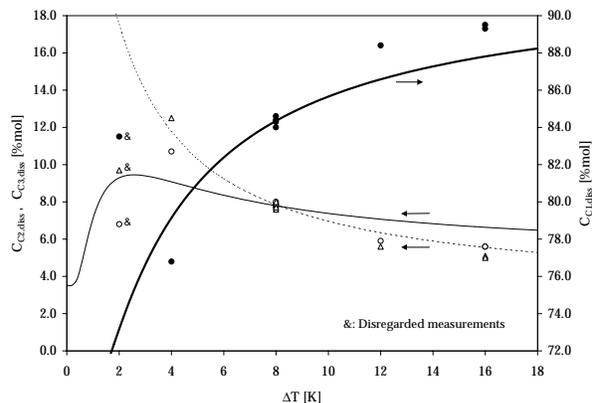


Figure 2: Simulations and measurements at 6.0 MPa. Methane: bold line, ●; ethane: thin line, ○; propane: dashed line, △.

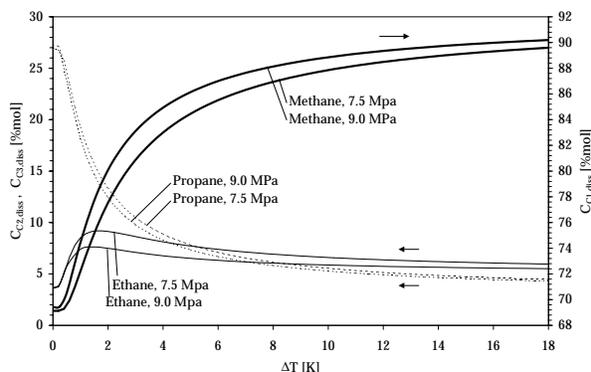


Figure 3: Extrapolation of the fractionation model to simulate fractionation at 9.0 MPa. The simulation at 7.5 MPa is shown for comparison.

6 Tuned Model

An example of how the tuned model compares to experimental measurements is given in Figure 2. The figure illustrates well the strong effect that the driving force has on fractionation. While the model is based on data in the pressure range 3.0 to 7.5 MPa, the model has been extrapolated to a pressure of 9.0 MPa in Figure 3 to give an impression of what one may expect regarding fractionation and hydrate composition. The figure also shows how fractionation is dependent on pressure.

The $\Delta T = 0$ endpoints of the curves were fixed at the normalized hydrate content of methane, ethane and propane that resulted from equilibrium simulations using the CSMHYD software. Estimates of the gas composition to be used as input for the different pressures were found by extrapolating the trend established in the experiments, which were carried out for a range of non-zero values of values of ΔT .

The $\Delta T = \infty$ limits of the curves approach the

Table 5: Representative differences between measurements and simulations using the tuned model.

i	$\Delta_{i,abs}$ (%mol)	$\Delta_{i,rel}$ (%)
CH ₄	±1.1	±1
C ₂ H ₆	±0.68	±9
C ₃ H ₈	±1.1	±14

feed gas values. The underlying assumption was that for infinite driving forces there is no fractionation.

Model tuning was carried out by using a least square method to minimize the average difference between the simulated values and the measured values.

7 Discussion

Since no experiments were carried out for $\Delta T = 0$ an extrapolation procedure mentioned above was used to estimate what the composition of the reactor gas at the end of experiments with $\Delta T = 0$ would have been. Such extrapolation can be argued against. But Figure 2 shows that the error introduced is not very large. Also refer to Table 5. Besides, in the context of the present work an error made for the lower ΔT region is of less concern, since the interest lies in fractionation suppression, and that directs the focus towards the higher ΔT values.

While the curves in Figure 3 are monotonous in ΔT for methane and propane, the ethane curve goes through a local maximum. The ethane curve pattern results from the mass balance in Equation A3-b. The fractionation tendency was strongest for methane and propane, being the lightest and the heaviest component, respectively. Accordingly, $|C_{diss} - C_{feed}|$ is generally smaller for ethane than for methane and propane.

Topics that were not studied in the present work include kinetics and transfer of mass and heat. Effects of varying parameters other than the pressure and the driving force (and hence the temperature) were not considered. Parameters that are likely to have effects on fractionation are for example the degree of water filling, the operation time, stirring rate, baffle and impeller characteristics.

A promising observation in an industry context is that fractionation can be significantly suppressed by operating at a high pressure and with a large driving force (meaning that the temperature is low). It seems that methane purge may still be necessary, depending on the feed gas composition. Gas recycling and using multiple reactor stages are ways to reduce purging, and can in principle make purging unnecessary. Future work needs to consider how fractionation affects hydrate plant engineering.

Several details have not been commented in the present paper, for example how the disregarded measurements in Figure 2 can be explained. The reader is referred to Levik (2000).

8 Conclusions

- The tuned model yields an absolute error of about ± 1 %mol compared to experimental data.
- The absolute errors convert into relative errors of about ± 1 % for methane, which is present in high concentrations. The relative errors are about ± 10 % for ethane and propane, which are present in lower concentrations.
- To suppress fractionation a large driving force should be used, operating at a high pressure.

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