**Mathematical Operator**

$$\gamma(a,x) = \int_o^x \exp(-x)x^{a-1}dx$$

### LITERATURE CITED

Abramowitz, M., and I. A. Stegum, eds., *Handbook of Mathematical Functions*, p. 255, Dover Publications, Inc., New York (1965).

Alfani, F., G. Iorio, G. Greco, Jr., M. Cantarella, M. H. Remy, and V. Scardi, "Kinetic Behavior of Immobilized Enzyme Membrane Reactors," *Chem. Eng. Sci.*, **34**, 1213 (1979).

Bean, C. P., "The Physics of Porous Membranes-Neutral Pores," *Membranes*, **1**, p. 1, G. Eisenman, ed., Marcel Dekker, Inc., New York (1972).

Butterworth, T. A., D. I. C. Wang, and A. J. Sinskey, "Application of Ultrafiltration for Enzyme Retention during Continuous Enzymatic Reaction," *Biotech. Bioeng.*, **12**, 615 (1970).

Chang, H. N., and I. H. Kim, "A Theoretical Analysis on the Performance of Membrane/Enzyme Reactor with Pressure Swing," *Proceedings of 2nd World Congress of Chemical Engineering*, Montreal, Canada, p. 256 (Oct. 4-9, 1981).

Cross, R. A., W. H. Tyson, Jr., and D. S. Cleveland, "Asymmetric Hollow Fiber Membranes for Dialysis," *Trans. Amer. Soc. Art. Int. Organs*, **17**, p. 279 (1971).

Furusaki, S., T. Kojima, and T. Miyauchi, "Reaction by the Enzyme Entrapped by UF Membrane with Acceleration of Mass Transfer by Pressure Swing," *J. Chem. Eng. Japan*, **10**, p. 233 (1977).

Ku, K., M. J. Kuo, J. Delente, B. S. Wildi, and J. Feder, "Development of a Hollow-Fiber System for Large-Scale Culture of Mammalian Cells," *Biotech. Bioeng.*, **23**, p. 79 (1981).

Michaels, A. S., "Membrane Technology and Biotechnology," *Desalination*, **35**, p. 329 (1980).

Rony, P. R., "Multiphase Catalysis II. Hollow Fiber Catalysis," *Biotech. Bioeng.*, **13**, p. 431 (1971).

Schmid, R. D., "Stabilized Soluble Enzymes," in *Adv. in Biochem. Eng.*, **12**, p. 41, T. K. Ghose, A. Fiechter, and N. Blakebrough, eds., Springer Verlag, Heidelberg (1979).

Waterland, L. R., A. S. Michaels, and C. R. Robertson, "A Theoretical Model for Enzymatic Catalysis Using Asymmetric Hollow Fiber Membranes," *AIChE J.*, **20**, p. 50 (1974).

*Manuscript received November 5, 1981; revision received May 25, and accepted June 18, 1982.*

# Occurrence of Methane Hydrate in Saturated and Unsaturated Solutions of Sodium Chloride and Water in Dependence of Temperature and Pressure

Experimental results of the formation of methane hydrate in dependence of temperature and pressure in unsaturated solutions of NaCl in water will be presented in a temperature range from 261.85 to 285.98 K and pressure up to 11.0 MPa. Furthermore the four-phase equilibrium $NaCl{\cdot}2H_2O_S$–$CH_4{\cdot}nH_2O_S$–$L$–$G$ has been calculated from the experimental results. Also the heats of transformation of several other equilibria in the ternary system $CH_4$–$H_2O$–NaCl are obtained.

**J. L. de ROO, C. J. PETERS,**
**R. N. LICHTENTHALER, and**
**G. A. M. DIEPEN**
**Department of Chemistry**
**Delft University of Technology**
**Delft, The Netherlands**

## SCOPE

At present there are several regions of industrial interest where gas hydrates play a role. Another possibility to apply gas hydrates, which can become of industrial interest, is the storage of natural gas as hydrates in salt holes in the crust of the earth. This application of gas hydrates requires knowledge of the conditions of hydrate formation. If we should store natural gas in salt holes as hydrates, the three components will be present: methane, water and sodium chloride. For this reason the phase behavior of the ternary system $CH_4$-$H_2O$-NaCl, especially in the region where the methane hydrate occurs, is investigated.

To achieve this, we measured temperature and pressure values at which methane hydrate just disappeared in the presence of an unsaturated solution of NaCl in water as the liquid phase and nearly pure methane as the vapor phase. From these measurements the $p,T$-projection of the invariant and the univariant equilibria in the ternary system $CH_4$-$H_2O$-NaCl will be derived. The measurements were carried out in a Cailletet equipment in a temperature region from 261.85 to 285.98 K and pressures up to 11.0 MPa.

## CONCLUSIONS AND SIGNIFICANCE

The measurements allowed us to calculate the invariant as well as the univariant equilibria of the ternary system $CH_4$-$H_2O$-NaCl. To obtain a higher accuracy, direct measurement of the univariant equilibria has to be preferred over the experimental and calculation procedures here. The accuracy will then largely depend on the possible accuracy of the experimental equipment. Nevertheless, we were able to derive the $p,T$-projection of the ternary system $CH_4$-$H_2O$-NaCl with reasonable accuracy. Furthermore, the composition of the methane hydrate was calculated.

---

Correspondence concerning this paper should be addressed to C. J. Peters

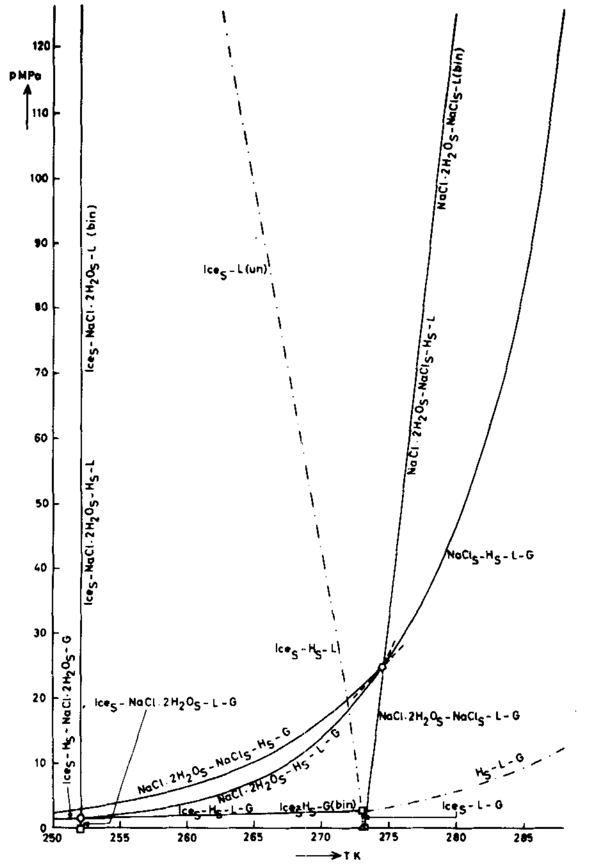

Figure 1. $p,T$-projection of the ternary system $CH_4$–$H_2O$–NaCl; △ = triple point; □ = quadruple point; ○ = quintuple point.

## INTRODUCTION

Since the discovery of the hydrate of chlorine in 1811 by Davy, numerous other gas hydrates have been found. An excellent review on this subject is given by Byk et al. (1968). After it was found by Hammerschmidt (1934) that natural gas hydrates instead of ice were responsible for the plugging of gas pipelines, the study of gas hydrates became of direct practical significance. It was necessary to obtain information about the conditions of the formation of gas hydrates; consequently, systematic research was carried out on the phase behavior of gas hydrates.

For example, the pioneer work of Deaton et al. (1946) must be mentioned. For industrial purposes, the study of the inhibition of hydrate formation in natural gas streams also became very important. As a recent result on this subject, the reader is referred to the work of Menten et al. (1981). With respect to gas hydrates, some other topics are of importance at present: (1) the desalination of seawater; (2) the separation of gas and liquid mixtures; and (3) the storage of gases as hydrates.

The research in this paper is related to the third application. It is known that liquefaction of natural gas is a frequently proposed method for storage. The storage of natural gas as a liquid has some serious disadvantages. For example, the presence of a large amount of liquid natural gas in densely populated areas is in general not very attractive. An alternative possibility to store natural gas is the utilizing of salt holes in the crust of the earth. To simplify the problem, the following components will then be present in these salt holes: methane, water and sodium chloride. With respect to this application it is important to determine the conditions of methane hydrate formation in this ternary system. In other words, the phase behavior of the ternary system $CH_4$–$H_2O$–NaCl, in the region where the methane hydrate occurs, must be obtained.

In literature, no information is available about this ternary system. The occurrence of methane hydrate in the binary system $CH_4$–$H_2O$ has been studied extensively. Methane hydrate was first obtained by Villard (1888) in the binary system $CH_4$–$H_2O$ and, as was already dealt with, further investigations were performed by Deaton et al. (1946). Additional measurements in this binary system are reported by Kobayashi et al. (1949), McLoad et al. (1961), and Marshall et al. (1964).

In this paper we will study the phase behavior of the ternary system $CH_4$-$H_2O$-NaCl in dependence of temperature and pressure.

## PHASE DIAGRAM OF $CH_4$-$H_2O$-NaCl

In this section the phase diagram of the ternary system $CH_4$–$H_2O$–NaCl will be discussed. Because of the fact that two solid compounds can occur in this system (the hydrates NaCl•$2H_2O$ and $CH_4$•$nH_2O$), the following phases can be present: NaCl$_S$, NaCl•$2H_2O_S$, Ice$_S$, $CH_4$•$nH_2O_S$($H_S$), liquid ($L$) and gas ($G$). Figure 1 shows the $p,T$-projection of the several invariant and univariant phase equilibria in the following region: temperatures from about 250 to 285 K and pressures up to 120 MPa.

In the region of interest (about the range of the four-phase line NaCl•$2H_2O_S$-$H_S$-$L$-$G$), some simplifications can be introduced in the phase diagram. If we consider the experimental data of the solubility of methane in water of Culberson et al. (1951), O'Sullivan et al. (1970) and Bonham (1978) as well as the experimental data of the solubility of methane in solutions of sodium chloride of Michels et al. (1936) and O'Sullivan et al. (1970), we can estimate a nearly saturated solution of sodium chloride in water at a temperature of 274.5 K and a pressure of 24.17 MPa. They are the conditions of the quintuple point NaCl•$2H_2O_S$–NaCl$_S$–$H_S$–$L$–$G$ and will contain a mole fraction of methane which will certainly not be higher than 0.0010. With respect to this very low solubility of methane in the liquid phase, we decided to ignore this solubility throughout this work. Another simplification is to neglect the vapor pressure of water in comparison with the applied experimental pressures in the temperature region of interest. This means that the vapor phase will be considered to be pure methane.

In the $p,T$-projection (Figure 1), two invariant quintuple points can be distinguished:

NaCl•$2H_2O_S$-NaCl$_S$-$H_S$-$L$-$G$ and

NaCl•$2H_2O_S$-Ice$_S$-$H_S$-$L$-$G$

Both suppositions, that the liquid phase does not contain methane and the gas phase always consists of pure methane, have some consequences for the arrangement of the four-phase equilibria around these quintuple points (Figure 1). On both ternary four-phase lines, NaCl•$2H_2O_S$–NaCl$_S$–$H_S$–$L$ and NaCl•$2H_2O_S$–NaCl$_S$–$L$–$G$, a phase transformation can only take place between the three phases NaCl•$2H_2O_S$, NaCl$_S$ and $L$. This means that both four-phase lines must coincide with the three-phase line NaCl•$2H_2O_S$–NaCl$_S$–$L$ of the binary system $H_2O$–NaCl; thus, the quintuple point NaCl•$2H_2O_S$–NaCl$_S$–$H_S$–$L$–$G$ must also be located on this binary three-phase line.

Further, it is obvious that on both ternary four-phase lines NaCl•$2H_2O_S$–Ice$_S$–$H_S$–$L$ and NaCl•$2H_2O_S$–Ice$_S$–$L$–$G$, a phase transformation can only occur between the three phases NaCl•$2H_2O_S$, Ice$_S$ and $L$. For this reason, both ternary four-phase lines will coincide with the binary eutectic three-phase line NaCl•$2H_2O_S$–Ice$_S$–$L$. Also the phase transformation on both ternary four phase lines Ice$_S$–$H_S$–$L$–$G$ and NaCl•$2H_2O_S$–Ice$_S$–$H_S$–$G$ is the same and takes place between the phases Ice$_S$, $H_S$ and G. Thus both ternary four-phase lines will coincide with the three-phase line Ice$_S$–$H_S$–$G$ of the binary system $CH_4$–$H_2O$. The quintuple point NaCl•$2H_2O_S$–Ice$_S$–$H_S$–$L$–$G$ can be obtained from the intersection of the eutectic line NaCl•$2H_2O_S$–Ice$_S$–$L$ of the binary system $H_2O$–NaCl and the three-phase line Ice$_S$–$H_S$–$G$ of the binary system $CH_4$–$H_2O$. Both discussed quintuple points are connected by the four-phase line NaCl•$2H_2O_S$–$H_S$–$L$–$G$ (Figure 1).

## EXPERIMENTAL STRATEGY

The objective of this research was to determine the four-phase line NaCl•$2H_2O_S$–$H_S$–$L$–$G$. Preliminary experiments showed that a direct

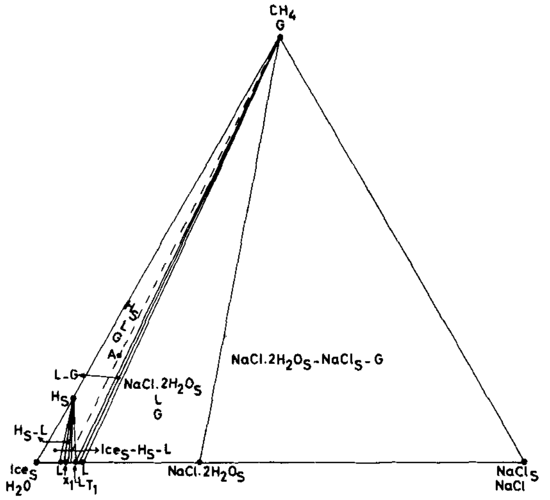

**Figure 2a. Phases present at experimental conditions.** ***A*** **= overall composition of the mixture, used for the measurements. At** $T_1$ **much methane hydrate** $H_S$ **is present.**

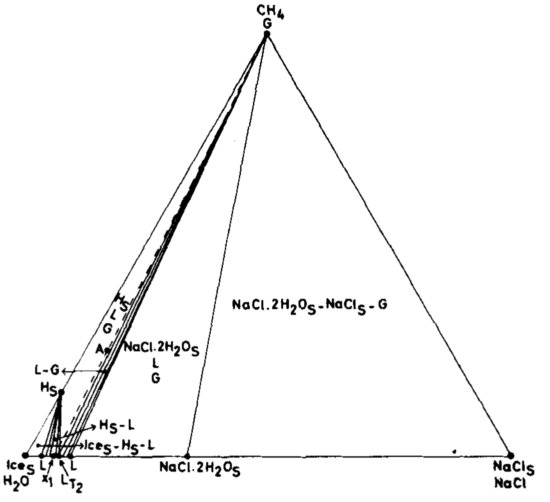

**Figure 2b. At** $T_2 > T_1$ **and the other experimental conditions identical with those of Figure 2a; the amount of phase** $H_S$ **has been decreased.**

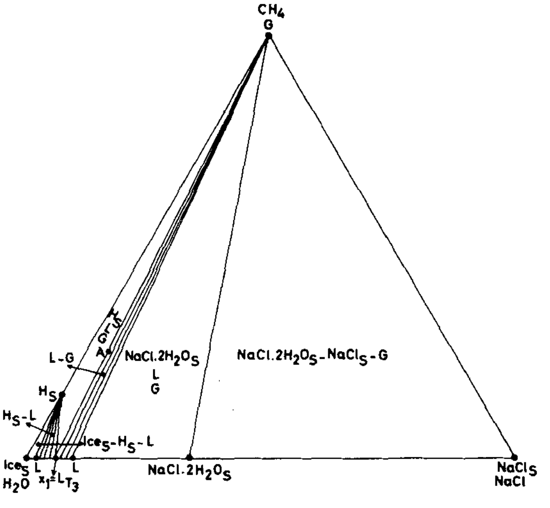

**Figure 2c. At** $T_3 > T_2 > T_1$ **and the other experimental conditions identical with those of Figures 2a and 2b; the phase** $H_S$ **has just been disappeared.**

measurement of this four-phase line cannot be easily performed. It is difficult to observe visually the presence of both solid phases $NaCl{\cdot}2H_2O_S$ and $H_S$ in the mixture of the four phases. Furthermore, a large amount of time was required to attain equilibrium between the four phases. We therefore decided to measure those temperatures and pressures where the hydrate of methane just disappeared in the presence of a liquid and a vapor phase for several ternary compositions.

Figure 2 shows how the measurements have been carried out. In a Cailletet tube, we have an unsaturated solution of NaCl of composition $x_1$ together with a certain amount of methane. This system has an overall composition represented by A in Figure 2a. The pressure $p$ and the temperature $T_1$ have been chosen so that the overall composition A lies in the triangle $H_S$-$L$-$G$ of Figure 2a. When equilibrium has been established, certain amounts of the three phases are present. Raising the temperature at constant pressure will cause the decomposition of the methane hydrate according to:

$$CH_4{\cdot}nH_2O_S \rightarrow CH_{4G} + nH_2O_L$$

For this reason the liquid phase of the $H_S$-$L$-$G$ equilibrium becomes richer in water at higher temperatures. At the same pressure and a temperature $T_2$, with $T_2 > T_1$, the phase equilibria are represented by Figure 2b. The amount of the solid phase $H_S$ has been decreased and the amounts of the liquid and vapor phases have been increased. If we continue to increase the temperature at constant pressure, we can finally reach a temperature $T_3$ at which the solid-phase $H_S$ just disappears and the liquid-phase $L_{T_3}$ has attained its original composition $x_1$ (Figure 2c). At the chosen pressure $p$ and the measured temperature $T_3$, this point lies on the saturation line of $H_S$ in an unsaturated solution of NaCl in water with composition $x_1$. It is obvious that, for the same composition $x_1$, another pressure can be chosen for which identical experiments can be performed. In this way several pressures and temperatures at constant composition have been determined for which the hydrate $H_S$ just disappears in the presence of a liquid and a vapor phase. These experiments are repeated for other compositions $x$.

From these measurements, isobaric $T,x$-projections can be derived and extrapolation of the isobars to the saturation curve of $NaCl{\cdot}2H_2O_S$ in water gives then the temperature, pressure and composition of the liquid phase of the four-phase line $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$.

## EXPERIMENTAL METHOD AND APPARATUS

The experiments have been carried out in a Cailletet equipment, which allowed us to apply temperatures from about 250 to 310 K and pressures up to 15 MPa. Temperature was kept constant within 0.05 K by means of a kryostat (Ultra Kryostat UK-40 DW, Lauda) and the temperature was measured within 0.05 K with a gauged thermometer. A pressure balance combined with a pneumatic hydraulic pump (Dreyer, Rosenkranz and Droop AG, Hannover) to maintain a constant pressure was used to measure pressures within a precision of 0.01 MPa. Details of the applied Cailletet equipment are given by Van der Kooi (1981).

Because methane can not be liquefied under the experimental filling conditions of the Cailletet-tube, this tube was provided with a reservoir (Figure 3). After certain amounts of water and sodium chloride were brought into the top of the Cailletet-tube and high vacuum was obtained, methane with a pressure lower than the atmospheric pressure was supplied. The components are confined in the top of the thick-walled tube by pressing mercury in it. In this way mercury acts as a sealing and pressure-transmitting fluid. After that, the experimental routine was exactly the same as the procedure usually needed for a Cailletet equipment and will therefore not be discussed here further.

Research-grade methane gas (Matheson, Research Purity, 99.9995%) was used for our experiments; the purity of the sodium chloride was better than 99.8%. The distilled water was degassed before use.

## EXPERIMENTAL RESULTS

For five different NaCl mole fractions (the mole fractions are given on a methane free basis) including a mole fraction zero, experimentally determined pressures and temperatures at which solid methane hydrate just

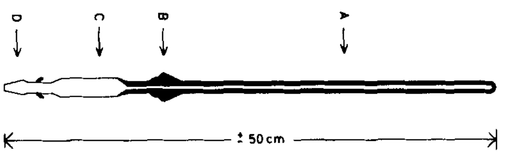

**Figure 3. Cailletet tube;** ***A*** **= thick walled glass tube;** ***B*** **= glass conus;** ***C*** **= reservoir to supply methane;** ***D*** **= glass joint to connect to high vacuum apparatus.**

TABLE 1. EXPERIMENTAL AND FITTED DATA TO EQ. 1 OF $H_S$-$L$-$G$ EQUILIBRIA IN THE TERNARY SYSTEM $CH_4$-$H_2O$-NaCl

| $x$ | $T$(K) | $p$(MPa)-exp. | $p$(MPa)-calc. | dev. (MPa) |
|---|---|---|---|---|
| 0.00000 | 273.30 | 2.69 | 2.62 | +0.07 |
| | 275.41 | 3.34 | 3.29 | +0.05 |
| | 275.95 | 3.34 | 3.49 | −0.15 |
| | 279.49 | 5.04 | 5.07 | −0.03 |
| | 281.29 | 6.04 | 6.11 | −0.07 |
| | 282.80 | 7.04 | 7.14 | −0.10 |
| | 283.98 | 8.05 | 8.04 | +0.01 |
| | 284.98 | 9.04 | 8.90 | +0.14 |
| | 285.98 | 10.04 | 9.84 | +0.20 |
| 0.03936 | 268.30 | 2.69 | 2.63 | +0.06 |
| | 271.05 | 3.53 | 3.58 | −0.05 |
| | 273.25 | 4.50 | 4.56 | −0.06 |
| | 274.75 | 5.29 | 5.36 | −0.07 |
| | 275.90 | 5.98 | 6.07 | −0.09 |
| | 278.05 | 7.55 | 7.63 | −0.08 |
| 0.05976 | 263.35 | 2.39 | 2.28 | +0.11 |
| | 265.75 | 3.13 | 3.01 | +0.12 |
| | 268.85 | 4.26 | 4.30 | −0.04 |
| | 271.95 | 6.12 | 6.07 | +0.05 |
| | 274.95 | 8.57 | 8.42 | +0.15 |
| 0.07785 | 261.85 | 2.94 | 3.03 | −0.09 |
| | 264.45 | 4.06 | 4.12 | −0.06 |
| | 266.45 | 5.05 | 5.19 | −0.14 |
| | 268.15 | 6.12 | 6.31 | −0.19 |
| | 269.45 | 7.05 | 7.30 | −0.25 |
| | 271.15 | 8.83 | 8.83 | +0.00 |
| | 272.85 | 11.00 | 10.65 | +0.35 |
| 0.08909 | 263.05 | 4.78 | 4.85 | −0.07 |
| | 264.55 | 5.78 | 5.79 | −0.01 |
| | 266.25 | 7.11 | 7.05 | +0.06 |
| | 267.55 | 8.36 | 8.18 | +0.18 |
| | 268.65 | 9.55 | 9.27 | +0.28 |

disappeared in the presence of a liquid and a vapor phase are collected in Table 1.

We found that the experimental data can be described very well by the empirical equation:

$$ln\left(\frac{p}{p^o}\right) = -\frac{8{,}160.43}{T} + 33.1103 - 128.65x + 40.28x^2 - 138.49\, ln(1-x) \quad (1)$$

The parameters of Eq. 1 were calculated by a standard least-squares computer program. Table 1 also gives the calculated pressures according to Eq. 1 as well as the deviations between the experimental and calculated data. Figure 4 represents the measurements and the predicted pressures as a function of temperature for each experimental mole fraction. For the mole fraction $x = 0.0$, the experimental data of Villard (1888) and Deaton et al. (1946) are also given in Figure 4.

## CALCULATION OF $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$

In the discussion of the experimental strategy, it was pointed out that from the experimental data isobaric $T,x$-projections can be derived and that extrapolation of an isobar up to the saturation line of $NaCl{\cdot}2H_2O_S$ in water yields a point of the four-phase line $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$ at the pressure of the isobar. To be able to perform this, we need information about the saturation surface of $NaCl{\cdot}2H_2O_S$ in dependence of temperature and pressure. Experimental data of the saturation line of $NaCl{\cdot}2H_2O_S$ in water are reported by Benzler (1955). These data are only measured at a pressure of 0.1 MPa in a temperature range from 252.05 to 273.25 K and include the eutectic point with $Ice_S$ and the transition point of $NaCl{\cdot}2H_2O_S$ into $NaCl_S$ and $L$. The experimental data of Benzler (1955) at a pressure of 0.1 MPa can be excellently summarized by:

$$ln\, x = \frac{1{,}003.73}{T} - 38.1736 + 5.7370\, ln\, T \quad (2)$$

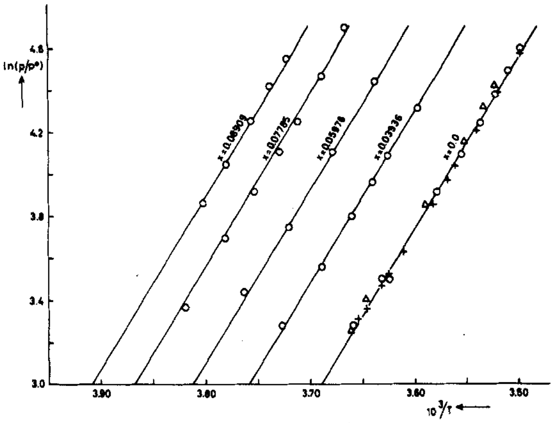

**Figure 4. Experimental and fitted data to Eq. 1 of $H_S$-$L$-$G$ equilibria in the ternary system $CH_4$-$H_2O$-NaCl: $x$ = mole fraction of NaCl on a methane free basis; $O$ = this work; + = Deaton et al. (1946); Δ = Villard (1888); full curves = fit according to Eq. 1.**

To calculate the mole fraction of NaCl at higher pressures, we made the supposition that this mole fraction will be influenced by pressure in the same way as that of the liquid phase of the binary three-phase line $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$L$. This means that at a particular temperature the solubility of $NaCl{\cdot}2H_2O_S$ will increase with pressure. However, from the experimental data of Adams et al. (1930) and Jänecke (1949) of this binary three-phase line, it can be concluded that in the region of interest (the range of the four phase line $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$) the mole fraction of NaCl in the liquid phase is not strongly influenced by pressure. We calculated that in the mole fraction of NaCl at the most a deviation of 0.05% can occur, and we therefore decided to apply Eq. 2 in the whole pressure range of interest (pressures up to 11.0 MPa).

Calculation of the point of intersection of both Eqs. 1 and 2 for a chosen pressure completes the numerical procedure to obtain a point of the four-phase line $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$. The simultaneous solution of both Eqs. 1 and 2 was performed with the nonlinear optimization method of Marquardt (1963). Chosing another pressure, it is obvious that additional points of the four-phase line can be calculated in the same way. For some chosen pressures in Table 2, the calculated points of intersection are given. The $T,x$-points of Table 2 can be very well represented by:

$$ln\, x = -\frac{503.98}{T} - 0.4730, \quad (3)$$

and the $p,T$-points of Table 2 by:

$$ln\left(\frac{p}{p^o}\right) = -\frac{9{,}594.42}{T} + 40.4265 \quad (4)$$

As was already pointed out, the quintuple point $NaCl{\cdot}2H_2O_S$-$Ice_S$-$H_S$-$L$-$G$ must be located on the eutectic line $NaCl{\cdot}2H_2O_S$-$Ice_S$-$L$. Because no information of the pressure dependence of this eutectic line is available, we supposed that this line is independent of the temperature and used 252.05 K, which is the temperature value of the eutectic point at 0.1 MPa, as is given by Benzler (1955). Substituting this temperature into Eq. 4 gives a pressure for the quintuple point of 1.074 MPa. The quintuple point $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$H_S$-$L$-$G$ lies on the three-phase line $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$L$. From the experimental data of Adams et al. (1930) and Jänecke (1949), we can derive the pressure dependence of the temperature for this three-phase line for pressures up to 200 MPa. This relationship can be considered linear and reads:

$$T = 273.20 + 0.05475\, p \quad (5)$$

If we calculate the point of intersection of both Eqs. 4 and 5, we obtained for this quintuple point a temperature of 274.50 K and a pressure of 24.166 MPa. The calculated results of this section are presented in Figure 5.

TABLE 2. CALCULATED TEMPERATURES AND LIQUID-PHASE COMPOSITION VALUES OF THE FOUR-PHASE LINE $NaCl\cdot 2H_2O$-$H_S$-$L$-$G$

| $p$ (MPa) | $T$(K) | $x$ |
|---|---|---|
| 2.0 | 256.19 | 0.08724 |
| 3.0 | 259.05 | 0.08904 |
| 4.0 | 261.09 | 0.09036 |
| 5.0 | 262.69 | 0.09143 |
| 6.0 | 264.01 | 0.09231 |
| 7.0 | 265.12 | 0.09307 |
| 8.0 | 266.09 | 0.09375 |
| 9.0 | 266.95 | 0.09435 |
| 10.0 | 267.72 | 0.09489 |
| 11.0 | 268.42 | 0.09539 |

## CALCULATION OF METHANE HYDRATE COMPOSITION

To calculate the composition of the methane hydrate in the quadruple point Ice$_S$-$H_S$-$L$-$G$, according to the method of Scheffer et al. (1919), knowledge of the heats of formation of the following reactions has to be available:

$$CH_{4G} + nH_2O_S \rightarrow CH_4{\cdot}nH_2O_S + \Delta H_1 \qquad (6)$$

$$CH_4G + nH_2O_L \rightarrow CH_4{\cdot}nH_2O_S + \Delta H_2 \qquad (7)$$

Subtraction of both equations gives the melting line of ice:

$$nH_2O_S \rightarrow nH_2O_L + n\overline{\Delta H}_m \qquad (8)$$

The hydrate number can then be calculated from:

$$n = \frac{\Delta H_1 - \Delta H_2}{\overline{\Delta H}_m} \qquad (9)$$

We already discussed that the four-phase line $NaCl{\cdot}2H_2O_S$-Ice$_S$-$H_S$-$G$ coincides with the three phase line Ice$_S$-$H_S$-$G$ of the binary system $CH_4$-$H_2O$. This means that in the $p,T$-projection the quadruple point Ice$_S$-$H_S$-$L$-$G$ as well as the quintuple point $NaCl{\cdot}2H_2O$-Ice$_S$-$H_S$-$L$-$G$ is located on the three-phase line Ice$_S$-$H_S$-$G$. The location of the quadruple point can be calculated from the intersection of the melting line of ice and the three-phase line $H_S$-$L$-$G$ of the binary system $CH_4$-$H_2O$. If we substitute $x = 0.0$ into Eq. 1, we obtain the equation of the three-phase line $H_S$-$L$-$G$:

$$ln\left(\frac{p}{p^o}\right) = -\frac{8,160.43}{T} + 33.1103 \qquad (10)$$

In the temperature range between the triple point of water and the quadruple point Ice$_S$-$H_S$-$L$-$G$ (Figure 1), the melting line of ice can be represented by the linear expression:

$$T = 273.16 - 0.0736\,p \qquad (11)$$

Experimental data of Tammann (1913) have been applied to obtain Eq. 11. Solving both Eqs. 10 and 11 simultaneously we find for the quadruple point a temperature of 272.95 K and a pressure of 2.523 MPa. From these values and the temperature and pressure values ($T$ = 252.05 K and $p$ = 1.074 MPa) of the quintuple point $NaCl{\cdot}2H_2O_S$-Ice$_S$-$H_S$-$L$-$G$, we calculated the following equation for the three-phase line Ice$_S$-$H_S$-$G$:

$$ln\left(\frac{p}{p^o}\right) = -\frac{2,811.18}{T} + 13.5141 \qquad (12)$$

From Eq. 12 we can derive the heat of formation $\Delta H_1$ of Eq. 6: $\Delta H_1 = -23{,}374.1$ J. In the same way $\Delta H_2$ was calculated from Eq. 10: $\Delta H_2 = -67{,}851.5$ J. Substitution of $\Delta H_1$, $\Delta H_2$ and the molar heat of fusion $\overline{\Delta H}_m$ (6,008.2 J·mol$^{-1}$) of ice into Eq. 9, results in a hydrate number $n$ at the conditions of the quadruple point Ice$_S$-$H_S$-$L$-$G$ of 7.4.

An alternative method to calculate the composition of methane hydrate, which is used in this work, is that of Miller and Strong (1946). In this method the binary $H_S$-$L$-$G$ equilibrium is compared with the ternary $H_S$-$L$-$G$ equilibrium at the same temperature and a known composition of the liquid phase. As the third component, a salt can be used. So we could use our experimental results of the $H_S$-$L$-$G$ equilibria for several mole fractions of NaCl in the liquid phase to calculate the hydrate number n from the following equation derived by Miller et al. (1946):

$$n = \frac{ln\,(f_2/f_1)}{ln\,(a_1/a_2)} \qquad (13)$$

This equation is solved at the temperature of the quadruple point Ice$_S$-$H_S$-$L$-$G$ (272.95 K) and for the mole fractions of NaCl for which the experiments were done. The activities of water needed in Eq. 13 were taken from Van Cleeff (1962). The pressure of the ternary $H_S$-$L$-$G$ equilibrium at a constant mole fraction of NaCl were calculated from Eq. 1. The fugacities of methane, needed in Eq. 13 at these pressure values, were obtained from an expression of the fugacity coefficient as a function of volume and temperature and was given by Angus et al. (1978). Hydrate numbers $n$ found in this way are collected in Table 3. The average value of the hydrate number is 6.3.

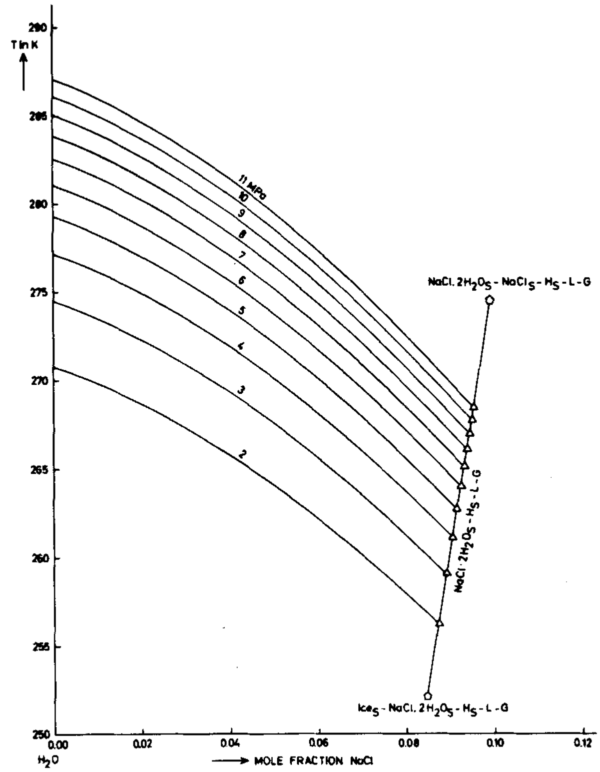

**Figure 5.** $T,x$-projection: $\Delta$ = calculated point of the four-phase equilibria $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$; $\bigcirc$ = calculated quintuple points; full curve between both quintuple points is the fit according to Eq. 3.

## CALCULATION OF $NaCl_S$-$H_S$-$L$-$G$ AND $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$H_S$-$G$

In the $p,T$-projection of Figure 1, the four-phase line $NaCl{\cdot}2H_2O_S$-$H_S$-$L$-$G$ can be described by Eq. 4. Both four-phase lines $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$L$-$G$ and $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$H_S$-$L$ coincide with the three-phase line $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$L$ of the binary system $H_2O$-NaCl and are represented in the $p,T$-projection by Eq. 5.

In this section both remaining four-phase lines, which also come together in the quintuple point $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$H_S$-$L$-$G$, will be evaluated. These four-phase lines are: $NaCl_S$-$H_S$-$L$-$G$ and $NaCl{\cdot}2H_2O_S$-$NaCl_S$-$H_S$-$G$. To calculate both four-phase lines, we have to decide what hydrate number will be applied. Saito et al. (1964) discussed that with increasing pressure, the limiting value of the hydrate number $n$ for methane hydrate is 5.75. Because the

TABLE 3. CALCULATED HYDRATE NUMBERS $n$ ACCORDING TO THE METHOD OF MILLER AND STRONG

$T = 272.95$ K

| $x$ | $p$ (MPa) | $f$ (MPa) | $a$ | $n$ |
|---|---|---|---|---|
| 0.00000 | 2.519 | 2.376 | 1.0000 | |
| 0.00893 | 2.774 | 2.601 | 0.9837 | 5.5 |
| 0.01069 | 2.833 | 2.653 | 0.9805 | 6.1 |
| 0.01245 | 2.896 | 2.707 | 0.9775 | 6.6 |
| 0.01421 | 2.962 | 2.765 | 0.9741 | 6.1 |
| 0.01595 | 3.031 | 2.824 | 0.9708 | 6.2 |
| 0.01770 | 3.104 | 2.888 | 0.9675 | 6.6 |
| 0.02116 | 3.259 | 3.020 | 0.9610 | 6.6 |
| 0.02631 | 3.523 | 3.245 | 0.9510 | 6.9 |

TABLE 4. COMPOSITION OF THE PHASES IN THE QUINTUPLE POINT $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$L$–$G$

| Phase | $x_{CH_4}$ | $x_{H_2O}$ | $x_{NaCl}$ |
|---|---|---|---|
| $NaCl{\cdot}2H_2O_S$ | 0.0000 | 0.6667 | 0.3333 |
| $NaCl_S$ | 0.0000 | 0.0000 | 1.0000 |
| $H_S$ | 0.1481 | 0.8519 | 0.0000 |
| $L$ | 0.0000 | 0.9005 | 0.0995 |
| $G$ | 1.0000 | 0.0000 | 0.0000 |

pressure of the quintuple point is 24.166 MPa, it seems reasonable to use this limiting value of the hydrate number in the calculation of the course of both four phase lines. The composition of one mole of each phase in the quintuple point $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$L$–$G$ is given in Table 4. At the temperature and pressure of the quintuple point ($T = 274.50$ K and $p = 24.166$ MPa) the composition of the liquid phase has been taken from the measurements of the three-phase line $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$L$ of Adams et al. (1930) and Jänecke (1949). The information of Table 4 allows us to give the phase transformation in the neighborhood of the quintuple point $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$L$–$G$:

$$1\ \text{mol}\ CH_4{\cdot}5.75\ H_2O_S + 0.3625\ \text{mol}\ NaCl{\cdot}2H_2O_S \rightarrow 1.2144\ \text{mol}\ L + 0.1481\ \text{mol}\ G - 79{,}775\ \text{J}. \quad (14)$$

Applying Clapeyron's equation to Eq. 4, the heat of transformation of Eq. 14 was calculated. The heat of transformation of the three-phase line $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$L$ is given by Adams et al. (1930):

$$1\ \text{mol}\ NaCl{\cdot}2H_2O_S \rightarrow 0.2596\ \text{mol}\ NaCl_S + 0.7404\ \text{mol}\ L - 13{,}601\ \text{J} \quad (15)$$

Elimination of $NaCl{\cdot}2H_2O_S$ from both Eqs. 14 and 15 enables us to calculate the heat of the phase transformation on the four-phase line $NaCl_S$–$H_S$–$L$–$G$:

$$1\ \text{mol}\ CH_4{\cdot}5.75\ H_2O_S + 0.0941\ \text{mol}\ NaCl_S \rightarrow 0.9460\ \text{mol}\ L + 0.1481\ \text{mol}\ G - 74{,}844\ \text{J} \quad (16)$$

Substituting the heat of transformation of Eq. 16 as well as the temperature and pressure of the quintuple point into Clapeyron's equation, we obtain the following equation for this four-phase equilibrium in the $p,T$-projection:

$$ln\left(\frac{p}{p^o}\right) = -\frac{9{,}001.4}{T} + 38.2664 \quad (17)$$

At the conditions of the quintuple point $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$L$–$G$, we also can calculate the heat of transformation on the four-phase line $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$G$. To obtain this heat of transformation, we now have to eliminate the liquid phase from both Eqs. 14 and 15 in a similar way as done before. This results in the following equation for the phase transformation:

$$1\ \text{mol}\ CH_4{\cdot}5.75\ H_2O_S + 0.4258\ \text{mol}\ NaCl_S \rightarrow 1.2777\ \text{mol}\ NaCl{\cdot}2H_2O_S + 0.1481\ \text{mol}\ G - 57{,}466\ \text{J} \quad (18)$$

Substitution of this heat of transformation and the conditions of the quintuple point into Clapeyron's equation results in the following expression of the four-phase line $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$G$:

$$ln\left(\frac{p}{p^o}\right) = -\frac{6{,}911.4}{T} + 30.6525 \quad (19)$$

## DISCUSSION

In spite of the fact that it was experimentally fairly difficult to measure the four-phase line $NaCl{\cdot}2H_2O_S$–$H_S$–$L$–$G$ directly for reasons already dealt with, the measurement of three-phase equilibria $H_S$–$L$–$G$ in unsaturated solutions of NaCl in water allowed us to determine this four-phase line indirectly. Nevertheless, it would be desirable to measure the four-phase line directly, because the experimental determination of the point where the methane hydrate just disappears has also some disadvantages. It was our experience that some hysteresis occurred in the appearance and disappearance of the hydrate. This hysteresis was the primary source of error in our measurements and it is obvious that, because of the univariance of the four-phase equilibrium, this source of error does not play a role in direct measurements of the four-phase line.

Another advantage of direct measurements is that no interpolation of experimental data of the solubility of $NaCl{\cdot}2H_2O_S$ in water, reported in literature, are necessary. Comparable experimental data of the three-phase equilibria $H_S$–$L$–$G$ in the ternary system $CH_4$–$H_2O$–NaCl are not known in literature. In the temperature range we are interested in, only experimental data of the three-phase line $H_S$–$L$–$G$ of the binary system $CH_4$–$H_2O$ are reported by Villard (1888) and Deaton et al. (1946).

From Figure 4 it can be concluded that these data are in good agreement with our corresponding experimental data at $x = 0.0$. Once the four-phase line $NaCl{\cdot}2H_2O_S$–$H_S$–$L$–$G$ has been calculated from the measurements, both four-phase lines $NaCl_S$–$H_S$–$L$–$G$ and $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$G$ could be obtained. Therefore, it was necessary to make a choice of the hydrate number of the methane hydrate. In the calculation of both four-phase lines, the high pressure limit of 5.75 of the hydrate number was used. Because this hydrate number is not exactly the right value, it is important to check the influence of another value of the hydrate number on the course of both four-phase lines. For that reason the calculation of both four-phase lines was repeated for the hydrate number $n = 7.4$; the highest value calculated in this work, which was found according to the method of Scheffer et al. (1919). Due to this higher value of the hydrate number we found that the parameters in Eqs. 17 and 19 deviated within a maximum value of 1.2% from those obtained before. In other words, the course of both four-phase lines is not very much influenced by the hydrate number. From the experimental and literature data, the course of the four-phase lines and the location of both quintuple points $NaCl{\cdot}2H_2O_S$–$Ice_S$–$H_S$–$L$–$G$ and $NaCl{\cdot}2H_2O_S$–$NaCl_S$–$H_S$–$L$–$G$ was calculated. We are then able to construct the $p,T$-projection of the ternary system $CH_4$–$H_2O$–NaCl as given in Figure 1.

In principle we can compare our calculated hydrate number in the quadruple point $Ice_S$–$H_S$–$L$–$G$ ($T = 272.95$K and $p = 2.523$ MPa) with those of Saito et al. (1964) and Byk et al. (1978). However this comparison must be made with prudence, because different kinds of models are used for the calculation of the hydrate number. Saito et al. (1964) applied the statistical thermodynamical model developed by van der Waals et al. (1959) using the Lennard-Jones (12,6) pair potential. These authors calculated the potential parameters from experimental data of Deaton et al. (1946). Byk et al. (1978) used the same model, but now the Langmuir constants in the model were adopted from Parrish et al. (1972), who used the Kihara potential with spherical core. The calculated hydrate numbers by Saito et al. (1964) and Byk et al. (1978), at the same experimental conditions, are 6.9 and 6.1 respectively.

Furthermore, we have to take into account that in our work the hydrate number can be influenced by the presence of NaCl, which makes also a comparison of our hydrate numbers with literature values less reliable. Our calculated hydrate numbers according to the method of Miller et al. (1946) show some scattering. Much of this scattering is inherent to this method; for example, a deviation of 1% in the activity can already cause a scattering of this magnitude.

There is a significant difference between the hydrate number as found according to the method of Scheffer et al. (1919) (7.4) and the averaged value according to the method of Miller et al. (1946) (6.3). From the work of Aaldijk (1971), it can be concluded that already at moderate concentrations of NaCl the method of Miller et al. (1946) can lead to wrong results. It was also pointed out by Van Cleeff (1952) that it is desirable to apply his modified method of Miller et al. (1946), whereby the hydrate number depends on pressure.

In this work we prefer the hydrate number of 7.4. This means physically that only the large cavities in the hydrate lattice are occupied with methane molecules which should be in agreement with the expected value of $7\frac{2}{3}$.

## ACKNOWLEDGMENTS

The authors are grateful to H. J. van der Kooi for the helpful discussions and comments on the manuscript.

## NOTATION

$a$ = activity
$f$ = fugacity
$G$ = vapor phase
$H$ = methane hydrate
$L$ = liquid phase
$n$ = hydrate number
$p$ = pressure, MPa
$p^o$ = 0.101325 MPa
$S$ = solid phase
$T$ = temperature, K
$x$ = mole fraction NaCl in the liquid phase
$\underline{\Delta H}$ = heat of transformation
$\underline{\Delta H}_m$ = molar heat of fusion of ice

## LITERATURE CITED

Aaldijk, L., "Monovariante gashydraatevenwichten in het stelsel xenon-water," Thesis, Delft (1971).

Adams, L. H., and R. E. Gibson, "The melting curve of sodium chloride dihydrate. An experimental study of an incongruent melting at pressures up to twelve thousand atmospheres," *J. Am. Chem. Soc.*, **52**, p. 4252 (1930).

Angus, S., B. Armstrong, and K. M. de Reuck, "International Thermodynamic Tables of the Fluid State—5, Methane," Pergamon Press, Oxford (1978).

Benzler, H., "Kälteerzeugung durch Auflösen von Eis in Sole," *Kältetechnik*, **7**, p. 66 (1955).

Bonham, L. C., "Solubility of methane in water at elevated temperatures and pressures," *Am. Assoc. Pet. Geol. Bull.*, **62**, p. 2478 (1978).

Byk, S. Sh., and V. I. Fomina, "Gas Hydrates," *Russ. Chem. Rev.*, **37**, p. 469 (1968).

Byk, S. Sh., and V. I. Fomina, "Water content of hydrates of gases at different temperature," *Russ. J. Phys. Chem.*, **52**, p. 748 (1978).

Cleeff, A. van, "Gashydraten van stikstof en zuurstof," Thesis, Delft (1962).

Culberson, O. L., and J. J. McKetta, Jr., "Phase equilibria in hydrocarbon-water systems," *Pet. Trans. AIME*, **189**, p. 319 (1950).

Deaton, W. M., and E. M. Frost, Jr., "Gashydrates and their relation to the operation of natural gas pipelines," U.S. Department of the Interior, Bureau of Mines, *Monograph 8* (1946).

Hammerschmidt, E. G., "Formation of gas hydrates in natural gas transmission lines," *Ind. Eng. Chem.*, **26**, p. 851 (1934).

Jänecke, E., "Über das inkongruente Schmelzen von Salzhydraten bis zum Aufreten von Eis VI, inbesondere von $NaCl{\cdot}2H_2O$," *Z. Elektrochem.*, **53**, p. 251 (1949).

Kobayashi, R., and D. L. Katz, "Methane hydrate at high pressure," *Pet. Trans. AIME*, **186**, p. 66 (1949).

Kooi, H. J. van der, "Metingen en berekeningen aan het systeem methaan-n-eicosaan," Thesis, Delft (1981).

Marshall, D. R., S. Saito, and R. Kobayashi, "Hydrates at high pressures," *AIChE J.*, **10**, p. 202 (1964).

Marquardt, D. W., "An algorithm for least squares estimation of nonlinear parameters," *SIAM J.*, **11**, p. 431 (1963).

McLoad, H. O., and J. M. Campbell, "Natural gas hydrates at pressures to 10,000 psia," *J. Pet. Techn.*, p. 590 (1961).

Menten, P. D., W. R. Parrish, and E. Dendy Sloan, "Effect of inhibitors on hydrate formation," *Ind. Eng. Chem. Process Des. Dev.*, **20**, p. 399 (1981).

Michels, A., J. Gerver, and A. Bijl, "The influence of pressure on the solubility of gases," *Physica*, **3**, p. 797 (1936).

Miller, B., and E. K. Strong, "Possibilities of storing natural gas in the form of a solid hydrate," *Am. Gas Assoc. Monthly*, **28**, p. 63 (1946).

O'Sullivan, Th. D., and N. O. Smith, "The solubility and partial molar volume of nitrogen and methane in water and in aqueous sodium chloride from 50 to 125° and 100 to 600 atm," *J. Phys. Chem.*, **74**, p. 1460 (1970).

Parrish, W. R., and J. M. Prausnitz, "Dissociation pressures of gas hydrates formed by gas mixtures," *Ind. Eng. Chem. Process Des. Dev.*, **11**, p. 26 (1972).

Saito, S., D. R. Marshall, and R. Kobayashi, "Hydrates at high pressures," *AIChE J.*, **10**, p. 734 (1964).

Scheffer, F. E. C., and G. Meijer, "Over een indirecte analyse van gashydraten langs thermodynamischen weg en de toepassing daarvan op het hydraat van zwavel-waterstof, I en II," *Proc. Acad. Sci. Amsterdam*, **21**, 1204, p. 1338 (1919).

Tammann, G., "Über das Zustandsdiagramm des Wassers," *Z. physik Chem.*, **84**, p. 257 (1913)

Villard, M., "Sur les hydrates de méthane et d'éthylène," *Compt. Rend.*, **107**, p. 395 (1888).

Waals, J. H. van der, and J. C. Platteeuw, "Clathrate solutions," *I. Prigogine: Advances in chemical physics II*, New York (1959).

*Manuscript received January 29, 1982; revision received June 23, and accepted July 20, 1982.*