



Improvements in clathrate modelling: I. The H₂O–CO₂ system with various salts

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Abstract—The formation of clathrates in fluid inclusions during microthermometric measurements is typical for most natural fluid systems which include a mixture of H₂O, gases, and electrolytes. A general model is proposed which gives a complete description of the CO₂ clathrate stability field between 253–293 K and 0–200 MPa, and which can be applied to NaCl, KCl, and CaCl₂ bearing systems. The basic concept of the model is the equality of the chemical potential of H₂O in coexisting phases, after classical clathrate modelling. None of the original clathrate models had used a complete set of the most accurate values for the many parameters involved. The lack of well-defined standard conditions and of a thorough error analysis resulted in inaccurate estimation of clathrate stability conditions. According to our modifications which include the use of the most accurate parameters available, the semi-empirical model for the binary H₂O–CO₂ system is improved by the estimation of numerically optimised Kihara parameters $\sigma = 365.9$ pm and $\epsilon/k = 174.44$ K at low pressures, and $\sigma = 363.92$ pm and $\epsilon/k = 174.46$ K at high pressures. Including the error indications of individual parameters involved in clathrate modelling, a range of 365.08–366.52 pm and 171.3–177.8 K allows a 2% accuracy in the modelled CO₂ clathrate formation pressure at selected temperatures below Q₂ conditions. A combination of the osmotic coefficient for binary salt–H₂O systems and Henry's constant for gas–H₂O systems is sufficiently accurate to estimate the activity of H₂O in aqueous solutions and the stability conditions of clathrate in electrolyte-bearing systems. The available data on salt-bearing systems is inconsistent, but our improved clathrate stability model is able to reproduce average values. The proposed modifications in clathrate modelling can be used to perform more accurate estimations of bulk density and composition of individual fluid inclusions from clathrate melting temperatures. Our model is included in several computer programs which can be applied to fluid inclusion studies.

1. INTRODUCTION

Behaviour of H₂O–gas–salt-rich fluids close to the freezing point of water is of interest both in natural gas industry and in fluid inclusion research in order to obtain characteristics about fluids circulating in the rock during entrapment. In addition, desalination processes for brackish and seawater rely upon phase transitions in H₂O–gas–salt-rich systems at relative low temperatures. The formation of a gas hydrate (or clathrate) seems to complicate phase relations in the H₂O–gas-rich fluid system. Close to the freezing point of pure water, molecules of H₂O form a metastable framework with various types of cavities, which is stabilised by the presence of gas molecules in part of these cavities (e.g., Powell, 1948; Stackelberg and Müller, 1954; Waals and Platteeuw, 1959; Sloan, 1990). In nature, clathrates are often present in sediments, which contain both natural gas and water. The clathrates are pervasive in permafrost regions and in the thermodynamically stable regions of the ocean, and are, therefore, important gas reserves (e.g., Makogon, 1981; Sloan, 1990).

The appearance of clathrates in fluid inclusions was firstly described by Roedder (1963). Neglecting the presence of a clathrate during fluid analysis in inclusions may result in erroneous conclusions on salinity, composition, and density (e.g., Hollister and Burruss, 1976; Collins, 1979; Seitz et al., 1987; Dubessy et al., 1992; Diamond, 1992, 1994a; Yerokhin, 1993). For example, the exclusion of salts from the clathrate phase will increase the salinity of the other phases present in fluid inclusions. In contrast, the absorption of

gases in the clathrate decreases the density of the remaining non-aqueous phase. Therefore, prediction of phase relations and stability conditions of clathrates are necessary to improve characterisation of individual fluid inclusions.

A first approach in modelling consisted of representing clathrate stability conditions by smoothed values, by non-specified best-fit curves, and by purely empirical polynomial functions (e.g., Deaton and Frost, 1946). Relatively simple empirical relations are still used for mathematical comfort, e.g., Parrish and Prausnitz (1972) for reference clathrates, Bozzo et al. (1975), Adisasmato et al. (1991), Yerokhin (1993), Barton and Chou (1993), and Dholabhai et al. (1993), although this approach gives erroneous results for conditions and fluid systems other than those used to prepare them. For encaged gas species, whose critical temperature exceeds clathrate stability conditions, no universal model existed because thermodynamic modelling of liquid-like and vapour-like fluids in the established clathrate studies appears to be substantially different. Modifications of classical adsorption statistical mechanics (see Appendix) were the first substantial approach to fundamental modelling of clathrates in equilibrium with vapour-like and super-critical fluids (Waals and Platteeuw, 1959). Characteristic aspects of the model were improved or adjusted by McKoy and Sinanoglu (1963), Parrish and Prausnitz (1972), Ng and Robinson (1976), Holder et al. (1980), Dwarmawardhama et al. (1980), John et al. (1985), Munck et al. (1988), and Dubessy et al. (1992). Only Ng and Robinson (1977) attempted to model the stability of clathrates in equilibrium with liquid-

like fluids. The fundamental concepts of these classical clathrate models are briefly outlined in the Appendix.

1.1. Systematic Error

None of the previously mentioned publications on clathrate modelling have used a complete set of most accurate values for the physical and chemical parameters involved, and none of them gave a thorough error analysis. Waals and Platteuw (1959) reconstructed a purely empirical clathrate stability model into a semi-empirical model, based on statistical thermodynamics. Consequently, the empirical reference was transferred to each parameter in this model, which include P - T - V properties of H_2O and gases, Henry's constants, molecular potentials, and heat capacity coefficients. Unfortunately, some of these empirical relations have to be extrapolated to P - T conditions relevant to clathrate dissociation. For example, parameters which were originally fitted to temperatures above 273.15 K have to be extrapolated to lower temperatures in ionic aqueous solutions due to the freezing point depression effect. The accuracy and assumptions of this clathrate model were improved by the determination of more suitable parameters of intermolecular potentials, according to the method of Saito et al. (1964) and Parrish and Prausnitz (1972). Unknown Kihara parameters (Kihara, 1953) between a water and a gas molecule in the clathrate structure were estimated with the least-square method, which compares experimental data points of clathrate dissociation conditions to calculated values. This method was partly adopted by Dubessy et al. (1992), and they illustrated the presence of systematic errors between calculated and observed clathrate stability conditions. A systematic deviation is present in electrolyte-free fluid systems near the higher quadruple point Q_2 of the clathrate stability field (see Fig. 2 in Dubessy et al., 1992). Furthermore, according to the clathrate model modifications used by Dubessy et al. (1992) the systematic error increases over the total P - T range between the quadruple points Q_1 and Q_2 for solutions with higher salinities (see Fig. 4 in Dubessy et al., 1992).

In this study, further improvements are proposed to increase the accuracy of the method and to eliminate some systematic errors in established clathrate models. The interpretation of the fluid density and composition in inclusions from microthermometric measurements including clathrate melting temperatures will be more accurate according to our adjustments which is of importance to any fluid inclusion study.

1.2. Topology of the H_2O - CO_2 System

A purely qualitative P - T diagram of the binary H_2O - CO_2 system (Fig. 1) illustrates schematically phase relations involving the formation of a clathrate. Univariant lines illustrate three-phase associations which are labelled according to the abbreviations in Fig. 1. These lines intersect at invariant quadruple points Q_1 and Q_2 , which represent equilibria between four phases, i.e., clathrate + ice + H_2O -rich liquid + CO_2 -rich vapour, and clathrate + H_2O -rich liquid + CO_2 -rich liquid + CO_2 -rich vapour, respectively. The topology is described in more detail by, e.g., Bakker and Thiery

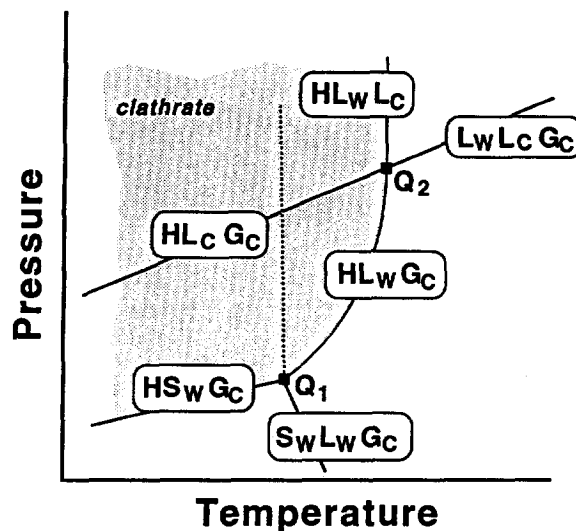


FIG. 1. P - T diagram with schematically indicated phase relations in the H_2O - CO_2 system. H , S , L , and G stand for clathrate, solid, liquid, and vapour phase, respectively. The subscripts W and C denote water-rich and carbon dioxide-rich, respectively. The dashed area indicates the stability field of clathrate. The quadruple points Q_1 and Q_2 represent four-phase equilibria $HS_wL_wG_c$ and $HL_wL_cG_c$, respectively. The HS_wL_w three-phase curve is dashed, because experimental data are not available.

(1994) and Diamond (1994b). In this study, the notation method from Fig. 1 is used to identify specific equilibria involving clathrate.

2. MODEL MODIFICATIONS FOR SALT-FREE SYSTEMS, AS EXEMPLIFIED BY THE H_2O - CO_2 SYSTEM

2.1 Composition of Clathrates

Clathrates are nonstoichiometric compounds. If all cages are occupied, the ideal composition of structure-I and structure-II clathrates are $M \cdot 5\frac{3}{4}H_2O$ and $M \cdot 5\frac{1}{2}H_2O$, respectively, where M denotes a gas molecule. The composition of structure-I and structure-II clathrates are $M \cdot 7\frac{2}{3}H_2O$ and $M \cdot 17H_2O$, respectively, if only the larger cavities are filled.

Hydration numbers used to be obtained indirectly using the Clapeyron equation to the clathrate stability curve at Q_1 conditions (e.g., Sortland and Robinson, 1964). This method is not precise because it calculates the average hydration number within a temperature interval of 4° on either side of 273.15 K, and because the thermodynamic properties of clathrates are not precise.

Filling of the clathrate structures can be theoretically obtained with the sophisticated theoretical treatment from Waals and Platteuw (1959). The hydration number is obtained from the inverse product of the probability of finding a gas molecule in a type of cavity (Eqn. A4) and the amount of cavities. CO_2 -clathrate composition calculations according to the model of Parrish and Prausnitz (1972) and Dubessy et al. (1992) are compared in Fig. 2. Although both models use the Kihara molecular potential to calculate Langmuir constants (Eqn. A4), hydration numbers may differ up to 2% at Q_1 conditions. This small discrepancy is a

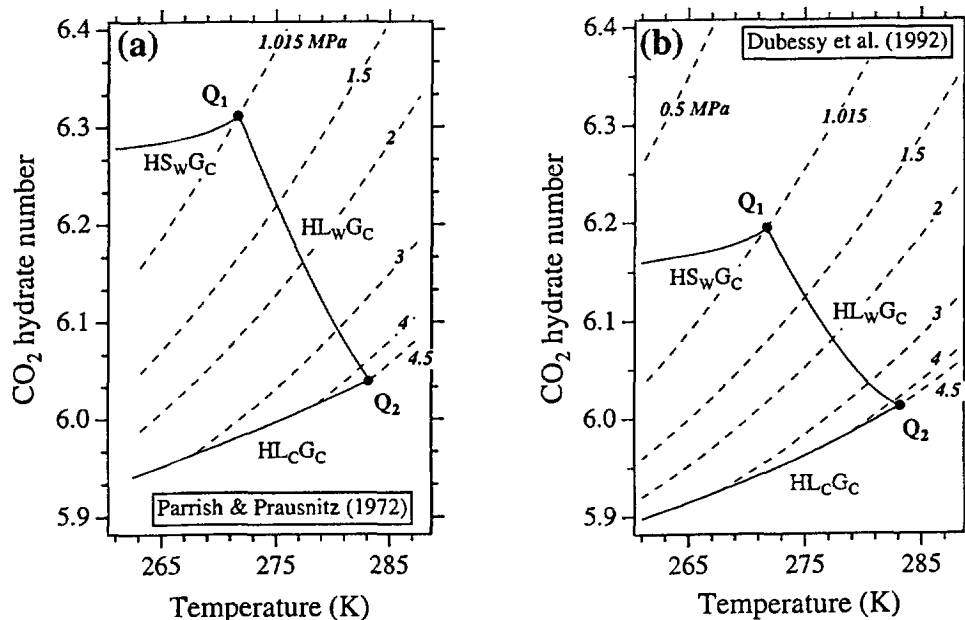


FIG. 2. Theoretical hydration numbers for the CO₂-clathrate as a function of temperature and pressure, according to the model of (a) Parrish and Prausnitz (1972), and (b) Dubessy et al. (1992). Dashed lines indicate several selected isobars (0.5, 1.015, 1.5, 2, 3, 4, and 4.5 MPa). The boundary of clathrate stability is indicated with lines HL_wG_C , HL_CG_C , and HS_wG_C . The dots Q_1 and Q_2 represent the invariant quadruple points.

result of the selected Kihara parameters and gas fugacity coefficients. It is important to note that clathrates have the highest hydration number at Q_1 conditions (Fig. 2).

Determination of the composition of clathrates with any direct chemical analysis seems to be problematic. The accuracy of many direct methods is affected by the variable stoichiometry, and by the occlusion of pure H₂O in clathrates (e.g., Dharmawardhana et al., 1980), which may result in a considerable compositional variation. However, several analytical procedures were developed with high precision. First, Dharmawardhana et al. (1980) determined the amount of enclathrated cyclo-propane by volumetric measurements, and the amount of H₂O consumed by specific conductivity increase in a KCl solution, from which the clathrate was formed. As a consequence of the relatively large size of cyclo-propane molecules, only larger cavities may be occupied in both types of clathrate structures. Due to nonstoichiometry, hydration numbers may only be higher than the ideal composition, in which all the larger cavities are occupied. Consequently, the hydration number of cyclo-propane must exceed 7.67 in structure I clathrate and 17.0 in structure II clathrate. These theoretical considerations and the calculated composition according to Hafemann and Miller (1969) are not consistent with the experimental data of Dharmawardhana et al. (1980) for the structure-II clathrate stability field below 274.61 K (Fig. 3). Furthermore, Dharmawardhana et al. (1980) did not describe the abrupt change in clathrate composition near the transition of clathrate structures I and II (Fig. 3), which is evident from their experimental data. Therefore, according to these data cyclo-propane molecules in clathrates formed below 274.61 K may also occupy small cavities, or cyclo-propane does not form a structure-II clathrate, which is seriously challenging the

fundamental concepts of the model proposed by Parrish and Prausnitz (1972). Second, Cady (1983) developed a procedure to measure directly the weight of a clathrate, that was formed from a known amount of pure H₂O. At 273.15 K and various pressures, the isothermal composition of several clathrates appears to correspond to the theoretical predictions of the model of Waals and Platteuw (1959). Third, nuclear magnetic resonance spectra of guest species in clathrates is a direct, nondestructive technique for the determination of cage occupancy and hydration numbers (e.g., Ripmeester and Ratcliffe, 1988; Collins et al., 1990).

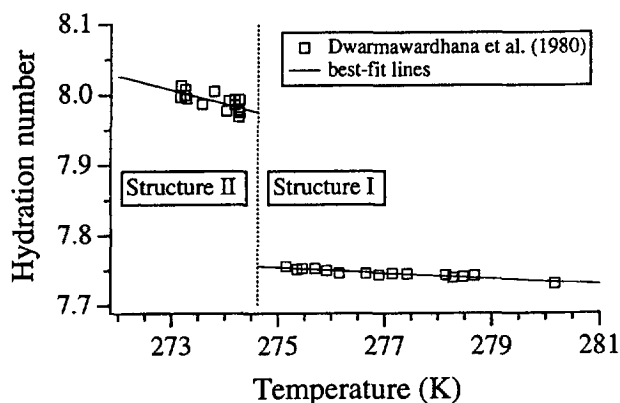


FIG. 3. Experimental hydration numbers for cyclo-propane clathrate from Dharmawardhana et al. (1980) as a function of temperature. The vertical dotted line is the phase boundary between structure-I and structure-II clathrate (Hafemann and Miller, 1969). The ideal hydration number for cyclo-propane in structure I and structure II clathrate are 7.67 and 17.0, respectively, which is assumed to occupy only the larger cavities.

Data are not available on direct measurements of the composition of CO₂ clathrates, but it is assumed that the theoretical predictions are sufficiently accurate, in agreement to the considerations of Cady (1983).

2.2. Chemical Potential Difference $\Delta\mu^*$: Standard Properties and Temperature and Pressure Dependence

The expression in Eqn. A9 for the chemical potential difference between pure H₂O and a hypothetical empty clathrate is derived from the total differential of the quotient of $\Delta\mu^*$ and the temperature multiplied by the gas-constant R . This expression can be simplified, for the chemical potential difference $\Delta\mu^*$ may be directly derived from its total differential equation towards temperature and pressure (Eqn. 1), using simple straight forward thermodynamics.

$$\Delta\mu^*(T, P)$$

$$= \Delta\mu_0^* - \int_{T_0}^T \Delta s^*(T) dT + \int_{P_0}^P \Delta v^*(P) dP \quad (1a)$$

$$\Delta s^*(T) = \Delta s_0^* + \int_{T_0}^T \left(\frac{\Delta cp^*}{T} \right) dT \quad (1b)$$

$$\Delta\mu_0^* = \Delta h_0^* - T_0 \Delta s_0^* \quad (1c)$$

where Δs^* , Δh^* , Δcp^* , and Δv^* are entropy difference, enthalpy difference, heat capacity difference, and molar volume difference, respectively. Equation A9 and 1 are equivalent.

In general, standard values for $\Delta\mu_0^*$ were calculated from indirectly obtained compositions of clathrates at Q₁ conditions using the Clapeyron equation. For example, Sortland and Robinson (1964) estimated $\Delta\mu_0^* = 883$ J/mol at Q₁ conditions (273.15 K and 0.081 MPa) from the composition of the SF₆ structure-II clathrate. They indicated that only small errors in the estimation of the heat of clathrate formation will be greatly magnified in the calculations of $\Delta\mu_0^*$. Davidson (1973) concluded from widely scattered data, all of doubtful precision at Q₁ conditions, that $\Delta\mu_0^*$ lies between 523 and 1109 J/mol for structure-II clathrates in which only the large cavities may be occupied. Davidson (1973) considered a $\Delta\mu_0^*$ of 1109 ± 63 J/mol for structure-I clathrates. For apparent convenience, all gas-clathrate systems were compared at their quadruple point Q₁, which was proposed to be the standard condition at 273.15 K and an undefined pressure. However, this definition of standard condition is very awkward because Q₁ conditions are distinct for most systems, mainly in pressure.

Parrish and Prausnitz (1972) adopted the $\Delta\mu_0^*$ value from Sortland and Robinson (1964) for the standard temperature of 273.15 K for all gas clathrate systems. Unlike the original value given by Sortland and Robinson (1964), the standard pressure was defined at 0 MPa. Although a zero absolute pressure appears to be close to actual Q₁ conditions and may introduce some mathematical comfort, this value is very awkward because it has no physical significance. Parrish and Prausnitz (1972) developed a method in which four independent variables, the Kihara parameters (ϵ and σ),

Δh_0^* and $\Delta\mu_0^*$, are numerically optimised and related to purely empirical equations for dissociation conditions of reference clathrates. They estimate optimum Kihara parameters for cyclo-propane structure-II clathrates, which is assumed to form either clathrate structures I or II (Hafemann and Miller, 1969). Subsequently, they calculated a numerically optimised $\Delta\mu_0^*$ for structure-I clathrates with these optimum Kihara parameters. The reliability of this method is problematical, because a set of wrong Kihara parameters and wrong thermodynamic constants may occasionally lead to right clathrate dissociation pressures (John et al., 1985). Increasing the mystification of standard conditions, Munck et al. (1988) defined P_0 as the vapour pressure at 273.15 K and used an approximate value of 0 MPa for the same set of thermodynamic constants given by Parrish and Prausnitz (1972).

Direct methods for determining the composition of clathrates (Dwarmawardhama et al., 1980; Cady, 1983) should give more accurate values of $\Delta\mu_0^*$ and Δh_0^* at any chosen standard conditions. That is, the composition is the only property of clathrates which can be used to estimate the chemical potential difference $\Delta\mu^*(T, P)$ in Eqn. A8 without recourse to theoretically obtained Langmuir-constants (Eqn. A4), according to the model of Waals and Platteeuw (1959) and Parrish and Prausnitz (1972). Unfortunately, Dwarmawardhama et al. (1980) used the complex trial-and-error method of Parrish and Prausnitz (1972) to estimate extrapolated $\Delta\mu_0^*$ and Δh_0^* values at 0 MPa and 273.15 K, and Cady (1983) preferred to use the $\Delta\mu_0^*$ value given by Davidson (1973).

Several thermodynamic arguments are available to introduce 0.1 MPa as a standard pressure. First, as previously mentioned, 0 MPa has no physical significance. Second, the equations for heat capacity are usually defined at 0.1 MPa. Third, at a zero absolute pressure, which is the lower integration limit in Eqn. 1, the volumetric properties of H₂O are theoretically unidentified. Consequently, the molar volume difference between H₂O and an empty clathrate are not defined at these conditions, and Eqn. 1 can not be solved. Furthermore, below H₂O saturation pressures the molar volume difference will differ seriously from the constant value of 18 cm³/mol, which is generally used in clathrate modelling. Therefore, the most convenient, and the less obscure standard conditions defined at $T_0 = 273.15$ K and $P_0 = 0.1$ MPa are chosen in this study. As a first approximation, the $\Delta\mu_0^*$ and Δh_0^* values of Dwarmawardhama et al. (1980) are adopted as the new standard value at 273.15 K and 0.1 MPa (Eqn. 2):

$$\Delta\mu_0^* = 1297 \pm 33 \text{ J/mol} \quad (2a)$$

$$\Delta h_0^* = -4622 \pm 33 \text{ J/mol.} \quad (2b)$$

The error values are given by Dwarmawardhama et al. (1980). Consequently, the entropy difference between pure H₂O and an empty clathrate at standard conditions is equal to 21.67 J/mol (from Eqn. 1c). This value is very similar to the entropy of melting of pure H₂O (22.01 J/mol).

Stackelberg and Müller (1954) estimated the molar volume of the clathrate structure I (=22.6 cm³/mol) from a detailed X-ray crystallographical study of the clathrate lat-

tice. The hypothetical empty clathrate was assumed to have a similar molar volume. The molar volume of ice was assumed to be constant at 19.6 cm³/mol. In this study, a pressure dependent molar volume equation (Eqn. 3) is introduced for both clathrate and ice to take into account the compressibility of both solid phases.

$$V_{H_2O} = V_0 \cdot \exp\{-K(P - P_0)\}, \quad (3)$$

where V_0 is the molar volume of either ice or clathrate at standard condition P_0 (0.1 MPa) and K is the isothermal compressibility, which is assumed to be equal for both ice and clathrate, i.e., 10⁻⁴ MPa⁻¹.

The molar volume of liquid H₂O was assumed to be constant (18.0 cm³/mol) due the small range of variations in temperature and pressure of clathrate stability conditions, which has been generally accepted in clathrate modelling. However, significant errors are introduced at higher pressures and temperatures for the difference between liquid H₂O and empty clathrate. An accurate equation of state for liquid H₂O at relative low temperatures and pressures is appropriate to reduce these erroneous estimations. The molar volume of pure liquid H₂O is calculated from the equation of state as proposed by Kell and Whalley (1965) and Kell (1967), which is valid between 273–423 K and 0.1–100 MPa (Eqn. 4).

$$V_{H_2O}^{liquid} = V_0 \left[\frac{1 + a_1(P - P_0) + a_2(P - P_0)^2}{1 + b(P - P_0)} \right], \quad (4)$$

where V_0 is the molar volume of liquid H₂O at 1 atmosphere between 273 and 423 K according to Kell (1967), P_0 is 1 atmosphere (0.101325 MPa), and a_1 , a_2 , and b are only temperature dependent. The molar volume of liquid H₂O below 273.15 K is required in specific circumstances to calculate clathrate stability conditions. Molar volume calculated at 273.15 K from Eqn. 4 was selected for lower temperatures, because data are not available in this temperature range.

At CO₂-clathrate stability conditions between quadruple point Q₁ and Q₂ the calculated Δv^* that is obtained from Eqns. 3 and 4 differs to an extent of 0.5% from the constant value of Stackelberg and Müller (1954). However, the deviation has increased to about 20% at 100 MPa.

The heat capacity of empty clathrate was assumed to be similar to that of ice due to corresponding lattice structures (Stackelberg, 1954; Handa and Tse, 1986). Sortland and Robinson (1964) used a constant value for the heat capacity of clathrates, defined by the outdated Kopp's rule (Kopp, 1866) and data from Gambill (1957). Parrish and Prausnitz (1972) introduced a temperature dependent factor, using tabulated heat capacity data of water and ice from Tables D174 and D175 in Weast (1968) to calculate the difference between empty clathrate and pure H₂O. Consequently, the experimental data on ice must have been extrapolated to temperatures above 273.15 K to calculate the clathrate stability field. Munck et al. (1988) and Dubessy et al. (1992) simplified the calculations by assuming again a constant value for Δcp^* , independent of temperature. In this study, the difference in heat capacity between empty clathrate and liquid pure H₂O was assumed to be equal to the difference between ice (Giauque and Stout, 1936) and liquid H₂O (Os-

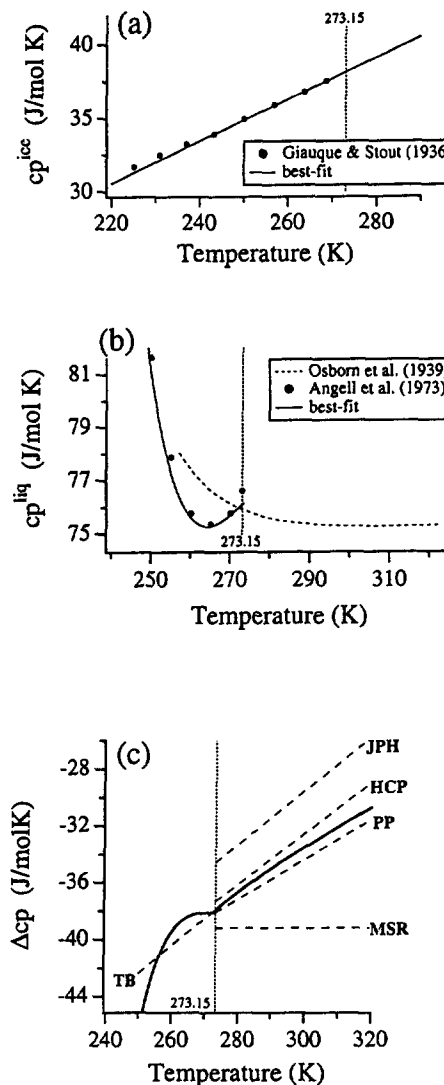


FIG. 4. (a) Heat capacity of pure ice as a function of temperature. Data are obtained from Giauque and Stout (1936). (b) Heat capacity of liquid pure H₂O. Data below 273.15 K are obtained from Angell et al. (1973). Above 273.15 K, the equation given by Osborn et al. (1939) is used to calculate heat capacities. (c) Δcp -temperature diagram for the models MSR (Munck et al., 1988), PP (Parrish and Prausnitz, 1972), HCP (Holder et al. (1980), JCP (John et al., 1985), TB (Thurmond and Brass, 1988), and this study (solid line).

borne et al., 1939; Angell et al., 1973). The heat capacity data on pure ice from Giauque and Stout (1936) are fitted to a linear function between 240 and 270 K (Eqn. 5 and Fig. 4a).

$$cp_{H_2O}^{ice}(\pm 0.1\%) = -0.3840 + 0.1406T_K, \quad (5)$$

where T_K is temperature in Kelvin. The uncertainty after extrapolation of Eqn. 5 to 293.15 K has increased to 0.2%. The heat capacity for liquid H₂O above 273.15 K (Fig. 4b) is obtained from the equation given by Osborn et al. (1939) (Eqn. 6a). A polynomial function in temperature fit through the data of Angell et al. (1973) is estimated to represent

accurately the heat capacity for liquid H₂O below 273.15 K (Eqn. 6b and Fig. 4b).

$T_C > 0^\circ\text{C}$:

$$cp_{\text{H}_2\text{O}}^{\text{liquid}} = 75.4030 \left[0.996185 + 2.874 \cdot 10^{-4} \left(\frac{T_C + 100}{100} \right)^{5.26} + 0.01116 \cdot 10^{(-0.0367T_C)} \right] \quad (6a)$$

$T_K < 273.15 \text{ K}$:

$$cp_{\text{H}_2\text{O}}^{\text{liquid}} = \exp(202.96 - 2.1947 \cdot T_K + 0.0080767 \cdot T_K^2 - 9.8997 \cdot 10^{-6} \cdot T_K^3), \quad (6b)$$

where T_C is temperature in Celsius. Holder et al. (1980) estimated a difference in heat capacity between ice and empty clathrate from experimental data of reference hydrates. John et al. (1985) claimed to have used the values of Holder et al. (1980); however, their specified values appear to have been adjusted. Theoretically, both solids have differences in structure and composition and should have distinctive heat capacities. However, these differences remain undetectable due to the relative large error in $\Delta\mu_0^*$. For example, a hypothetical error of 100% in the estimated Δcp^* value results in an absolute error of about 7 J/mol for $\Delta\mu^*$ at 283 K, which is much less than the previously mentioned error in $\Delta\mu_0^*$ of 33 J/mol by Dwarmawardhana et al. (1980).

Figure 4c indicates the differences between Δcp^* values given in literature and Eqns. 5 and 6. Above 273.15 K, this study is very similar to that of Holder et al. (1980) and Parrish and Prausnitz (1972). The Δcp^* values given by Munck et al. (1988) are clearly underestimations over the whole temperature range of the clathrate stability field. The assumption of $\Delta cp^* = 0$ below 273.15 K (e.g., Munck et al., 1988; Dubessy et al., 1992) results in erroneous calculations of the chemical potential difference $\Delta\mu^*$ near Q_1 and in fluid systems containing dissolved electrolytes. The equation from Thurmond and Brass (1988) increasingly overestimates the heat capacity towards lower temperatures.

A numerical integration method (Gaussian ten-point) is used to solve Eqn. 1, because of the complex equation for heat capacity (Eqn. 6). Figure 5 indicates the differences in $\Delta\mu^*$ between Eqn. 1 and the models proposed by John et al. (1985) and Munck et al. (1988). The equations for heat capacity in both models above T_0 (273.15 K) have to be extrapolated to lower temperatures, because these models do not include the effect of any additional inhibitors. The large deviation of the model of John et al. (1985) is mainly caused by the selected value for $\Delta\mu_0^*$. The differences in calculated $\Delta\mu^*$ may account for some part of the systematic deviation between calculated and observed clathrate stability pressures in electrolyte-free fluid systems, as illustrated by Dubessy et al. (1992).

2.3. Fugacity Coefficients in Fluids

An accurate estimation of the fugacity coefficients of nearly pure gases and gas mixtures at conditions relevant to

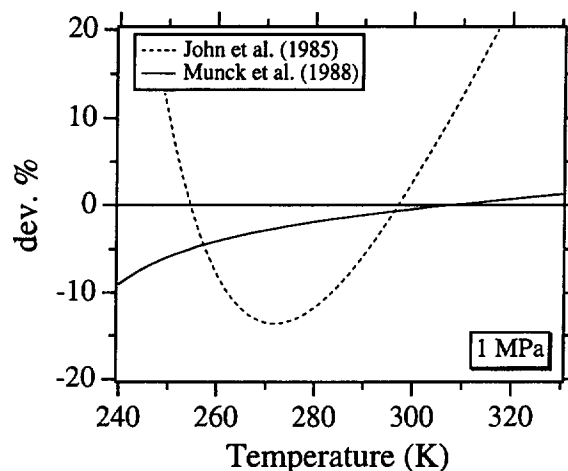


FIG. 5. The difference in $\Delta\mu^*$ between our model and the models according to Munck et al. (1988), and John et al. (1985) as a function of temperature at 1 MPa. The deviation is defined as $100\% \times (\Delta\mu^* - \Delta\mu_{\text{this study}}^*) / \Delta\mu_{\text{this study}}^*$.

the clathrate stability field is essential for the calculation of the probability of finding a gas molecule in cavities (Eqn. A4) and the calculation of the activity of H₂O in the liquid solution (Eqn. A7).

The fugacity coefficients of mixtures and pure gases in Eqns. A4 and A7 were calculated from semi-empirical modified Redlich-Kwong equations of state in established clathrate stability models, e.g., Parrish and Prausnitz (1972) or Dubessy et al. (1992). This type of equation seems to give a good prediction of P - T - V properties of vapour-like fluids at relative low pressures.

The equation of state for pure CO₂ defined by Redlich and Kwong (1949), Chueh and Prausnitz (1967), Soave (1972), Peng and Robinson (1976), and Duan et al. (1992a,b) are compared with P - T - V properties of pure CO₂ defined by IUPAC (Angus et al., 1976). For a vapour-like CO₂-rich fluid phase at relative low pressures along the clathrate stability curve (Fig. 6a), most equations of state remain within 1% accuracy of IUPAC values for fugacity coefficients. The most accurate equation is the Chueh-Prausnitz equation, which remains within 0.2% accuracy. The Soave equation appears to be a second-best equation of state in Fig. 6a, and has a similar accuracy as the Duan-Møller-Weare equation. At higher pressures, for a liquid-like CO₂-rich fluid phase, most modified Redlich-Kwong equations of state appear to result in highly erroneous fugacity coefficient calculations (Fig. 6b), which may differ up to 30% from IUPAC values. The most accurate equation is the Duan-Møller-Weare equation of state, which remains within 1.5% accuracy along the clathrate stability field. The Peng-Robinson equation of state has a similar accuracy up to 20 MPa, but is increasingly in error at higher pressures.

Specific P - T conditions are indicated in Fig. 7 for each equation of state that is the most accurate. Clathrate stability conditions are projected to mark the most appropriate equation of state to calculate fugacity coefficients in the clathrate model, and to facilitate the choice of the best equation for

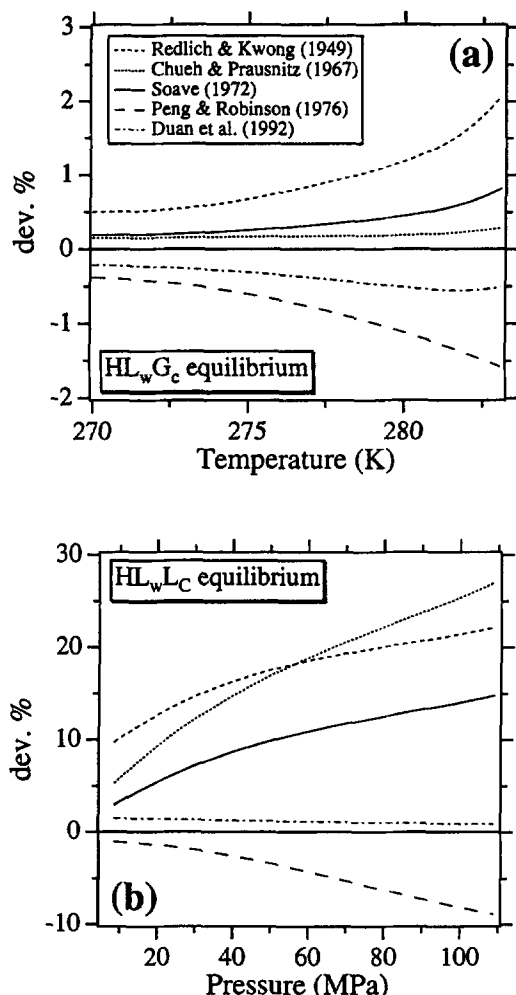


FIG. 6. Comparison of several modified Redlich-Kwong equations of states with the equation reported by IUPAC (Angus et al., 1976) along the clathrate stability curve below Q_2 conditions (a) and above Q_2 conditions (b). The deviation is defined as $100\% \times (P_{\text{eos}} - P_{\text{IUPAC}}) / P_{\text{IUPAC}}$.

calculations of a shifted clathrate stability field as a consequence of the presence of inhibitors.

In this study, the equation of state according to Chueh and Prausnitz (1967) and Duan et al. (1992a,b) are used for modelling $HL_w G_c$ equilibrium and $HL_w L_c$ equilibrium, respectively.

2.4. Henry's Constant

The solubility of gases can be theoretically predicted with an equation of state that accurately describes both coexisting liquid and vapour phases (e.g., Lundgaard and Møllerup, 1991). However, the Henry's law appears to represent more accurately the low solubility data for gases in H₂O, and it has been used to test the accuracy of the other methods. The Henry's law approach of liquid-vapour equilibria for the CO₂-H₂O fluid system is preferred in this study because it describes sufficiently accurately the available solubility data of both CO₂ in a H₂O-rich liquid phase, and H₂O in a CO₂-

rich vapour phase within the temperature and pressure limits of the clathrate stability field. Solubility data in liquid H₂O is usually only available for temperatures above 273.15 K. Henry's law states that at equilibrium conditions the fugacity of a gas above a solution is proportional to the mole fraction of the gas in the liquid phase:

$$x_M^{\text{liq}} \cdot H_{M,\text{water}} = f_M^{\text{vap}}(T, P), \quad (7)$$

where f_M^{vap} is the fugacity (in MPa) of component M in the vapour phase, x_M^{liq} is the mole fraction of component M in the liquid phase, and $H_{M,\text{water}}$ is Henry's constant (in MPa). Equation 7 is derived from the equivalence of the chemical potential of gas M in the vapour and liquid phase (after Eqn. A2). In traditional clathrate modelling, the amount of H₂O in the vapour phase was neglected (e.g., Parrish and Prausnitz, 1972; Munck et al., 1988; Dubessy et al., 1992). Munck et al. (1988) and Dubessy et al. (1992) used the CO₂ solubility equation from Wilhelm et al. (1977), which is defined at 1 atmosphere CO₂-partial pressure. However, the proposed clathrate model does not take into account a defined partial pressure of CO₂, but considers the total pressure of a gas mixture since the amount of H₂O does not exceed 0.1 mol% in the CO₂-rich vapour phase. Carroll et al. (1991) included the effect of H₂O in the vapour phase and gave a complete description of the molar properties of both liquid and vapour phase in the H₂O-CO₂ system. In order to solve Eqn. 7, Henry's law was extended with the requirement of equilibrium between the H₂O component in the liquid and in the vapour phase (Eqn. 8), which is also extracted from Eqn. A2.

$$x_{\text{H}_2\text{O}}^{\text{liq}} \cdot P_s = f_{\text{H}_2\text{O}}^{\text{vap}}(T, P, n_{\text{H}_2\text{O}}, n_M), \quad (8)$$

where P_s is the saturation pressure of pure H₂O and n_i is

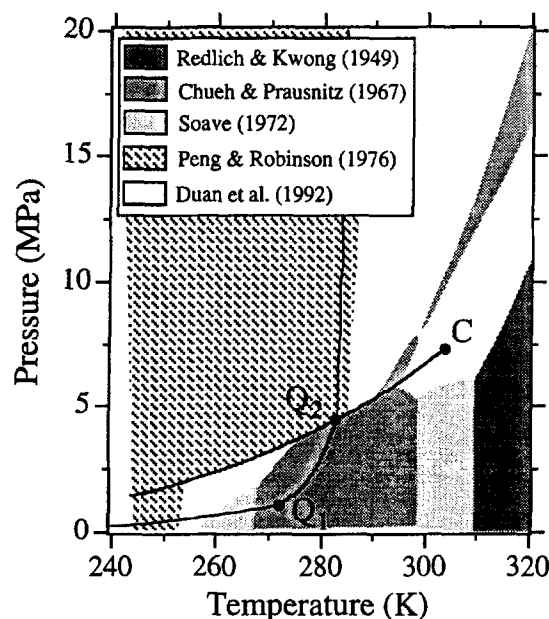


FIG. 7. P - T domains for several equations of state that give the best reproduction of fugacity values for pure CO₂, compared to IUPAC.

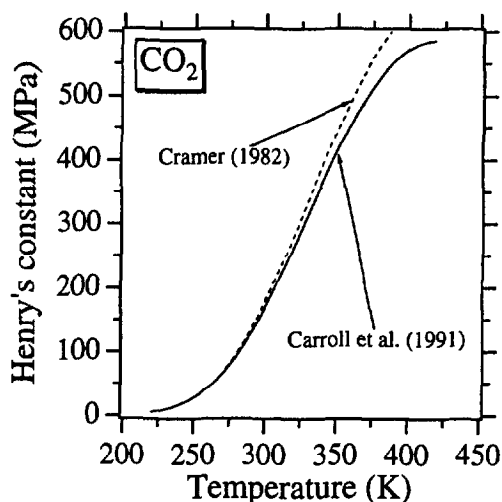


FIG. 8. The Henry's constant (in MPa) for CO₂ in aqueous solutions as a function of temperature, according to Cramer (1982) and Carroll et al. (1991).

the amount of component i in the vapour phase. Equations 7 and 8 were simultaneously iterative solved to estimate Henry's constant from a large database of CO₂ solubility in water. Henry's constant (Carroll et al., 1991) was best represented by an empirical polynomial function in reciprocal temperature (Eqn. 9 and Fig. 8). This equation has an uncertainty of about 5% and is valid between 273.15 and 433.15 K:

$$\ln(H_{\text{CO}_2, \text{water}}) = -6.8346 + \frac{1.2817 \cdot 10^4}{T} - \frac{3.7668 \cdot 10^6}{T^2} + \frac{2.997 \cdot 10^8}{T^3} \quad (9)$$

The Henry's constant according to Cramer (1982) is very similar to this equation, but is increasingly overestimated at higher temperatures (Fig. 8). Benson and Kraus (1976) related a equation similar to Eqn. 9 to other thermodynamic properties and molecular parameters of gases and demonstrated the predictability of this type of equation beyond the experimental limits of their data. It should be noted that the fugacity coefficient which was originally used to calculate the Henry's constant should be used again to obtain the initially measured solubility (mole fraction). Carroll et al. (1991) and Carroll and Mather (1992) used the original Redlich-Kwong equation of state for pure gases (Redlich and Kwong, 1949) to calculate fugacity coefficients of gaseous H₂O-CO₂ mixtures. However, it is theoretically not possible to calculate a fugacity coefficients of pure substances in the vapour-like phase, at pressures above the saturation pressure. Consequently, fugacity coefficients for the liquid phase are accidentally calculated instead, which differ seriously from those calculated for the vapour phase. As previously mentioned, a Redlich-Kwong-like equation of state is extremely inaccurate for liquid-like fluids. Nevertheless, we have adopted the method of Carroll et al. (1991) to estimate the solubility of CO₂ in aqueous solutions at

clathrate stability conditions. The equation of state from Chueh and Prausnitz (1967) and combining rules as defined by Redlich and Kwong (1949) are used to calculate fugacity coefficients of small amounts of gaseous H₂O in CO₂-rich vapour phases. At clathrate stability conditions, the accuracy of the calculated fugacity coefficient for CO₂ is not significantly affected by the presence of any H₂O, because its amount in the CO₂-rich vapour phase does not exceed 0.1 mol% (Carroll et al., 1991).

The effect of pressure on Henry's constant can be expressed according the equation given by Krichevsky and Kasarnowsky (1935):

$$\ln(H_{M, \text{water}})^{T, P} = \ln(H_{M, \text{water}})^{T, P_{\text{ref}}} + \int_{P_{\text{ref}}}^P \left(\frac{v_M^\infty}{RT} \right) dP, \quad (10)$$

where v_M^∞ is the partial molar volume of gas i at infinite dilution, which was assumed to be independent of pressure. Carroll and Mather (1992) estimated a temperature dependence for $v_{\text{CO}_2}^\infty$ values and pointed out that this value is theoretically always positive. We have estimated a linear best-fit between 298.15 and 373.15 K (Eqn. 11) through these scarce data (Fig. 9), which is proposed to represent $v_{\text{CO}_2}^\infty$ values:

$$v_{\text{CO}_2}^\infty (\pm 3.4\%) = 58.9 - 0.08T. \quad (11)$$

The uncertainty after extrapolation of this equation to 253.15 K has increased to 8%. Carroll and Mather (1992) demonstrated that the Krichevsky-Kasarnowsky model can be applied to the CO₂-H₂O fluid system below 373 K and up to 100 MPa.

Equations 9–11 have been applied to calculate the activity of H₂O in the liquid phase, according to Eqn. A7. In Fig. 10, the calculated activity of H₂O is shown as a function of temperature for several isobars. This activity is equal to the H₂O mole fraction for the activity coefficient is assumed to

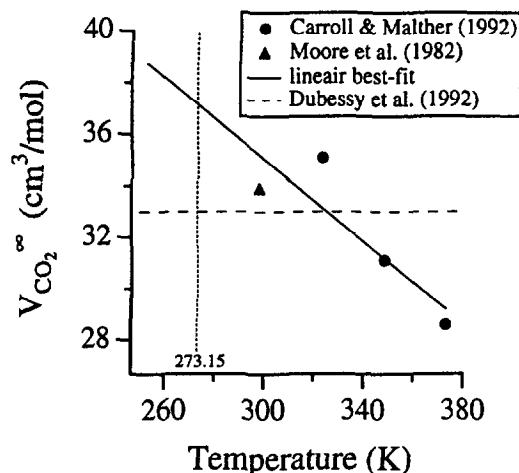


FIG. 9. The partial volume of CO₂ at infinite dilution as a function of temperature. Data are from Carroll and Mather (1992) and Moore et al. (1982). The dashed line indicates the constant value that was used by Dubessy et al. (1992).

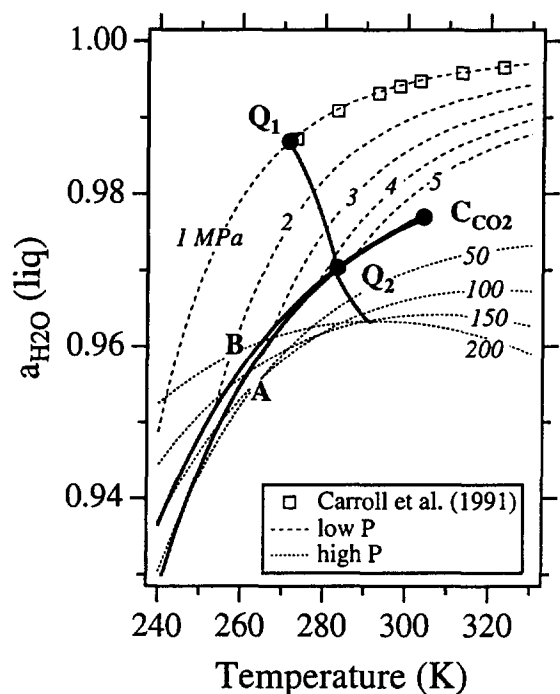


FIG. 10. Activity of H₂O in the binary H₂O-CO₂ liquid phase according to Eqn. A7. Dashed lines indicate several selected isobars at low pressures (1, 2, 3, 4, and 5 MPa), dotted lines indicate high pressure isobars (50, 100, 150, and 200 MPa). The quadruple points Q₁ and Q₂ are indicated with solid circles. C_{CO2} is the critical point of CO₂. Lines A and B are the activity estimates according to a liquid-like CO₂ fugacity calculation and a vapour-like CO₂ fugacity calculation along the boiling curve of CO₂. Solid lines indicate similar phase transitions as in Fig. 1.

be 1.0. Both a temperature decrease and a pressure increase are lowering the H₂O activity in this system (Fig. 10). The clathrate stability conditions are projected to illustrate the activity along the stability curve. According to thermodynamic equilibrium considerations the activity of H₂O should be equal along the saturation curve of CO₂ for both a liquid-like CO₂ (A in Fig. 10) and a vapour-like CO₂ (B in Fig. 10). However, Fig. 10 shows a split curve, which is the direct consequence of the inability of a modified Redlich-Kwong equation of state to predict liquid-vapour equilibria in this system. The activity calculations according to the model presented by Dubessy et al. (1992) are very similar to our model and may differ up to 2% at lower temperatures. The main causes for the differences are the neglect of small amounts of H₂O in the vapour phase and the selected equation of state to calculate fugacity coefficients.

Henry's law describes an equilibrium between the vapour phase and the liquid phase, and does not take into account any additional chemical equilibrium between solute and solvent. The weak acid H₂CO₃ is formed in CO₂ solutions, which may dissociate into HCO₃⁻ ions to a small extent. At Q₂ conditions the solution reaches a pH of about 3.8, which is derived from equilibrium calculations according to Monnin and Schott (1984). The concentration of HCO₃⁻ and H⁺ ions is about 3 orders of magnitude lower than that of CO₂,

and is, therefore, neglected in further modelling of clathrate stability conditions.

2.5. Molecular Potential

The Langmuir-constant (Eqn. A5) can be calculated with a simple empirical equation (e.g., Table A-II in Parrish and Prausnitz, 1972; Munck et al. 1988), which may correspond to a square-well molecular cell potential. Likewise, the Kihara-potential (Kihara, 1953) can be used to calculate the molecular cell potential $w(r)$, which considers the size and shape of interacting molecules. This potential seems to give better predictions of clathrate dissociation pressures (McKoy and Sinanoglu, 1963) than the Lennard-Jones 12-6 potential (Jones, 1924), as originally used by Waals and Platteeuw (1959).

Unfortunately, various notations are available for the Kihara-potential, which is used to describe the interaction between unlike molecules in the clathrate structure. Most equations use different standards for the distance between molecules (Fig. 11) as well within one formula. The most universal version is the equation originally proposed by Kihara (1953):

$$\Gamma(\rho) = \epsilon_0 \left\{ \left(\frac{\rho_0}{\rho} \right)^{12} - 2 \cdot \left(\frac{\rho_0}{\rho} \right)^6 \right\}, \quad (12)$$

where ρ is the shortest distance between two impenetrable molecular cores of any size and shape, and at distance ρ_0 the minimum potential energy is designated ϵ_0 . The core of rodlike molecules was defined as the line segment between nuclei (e.g., N₂ and CO₂), while CH₄ was represented by a tetrahedral core formed by the midpoints of C-H bonds. A simplified version of Eqn. 12 was used by McKoy and Sinanoglu (1963) for spherical cores with radius a :

$$\Gamma(r) = \epsilon_0 \left\{ \left(\frac{\rho_0}{r - 2a} \right)^{12} - 2 \cdot \left(\frac{\rho_0}{r - 2a} \right)^6 \right\}, \quad (13)$$

where r is the distance between the centre of molecules, and ρ_0 is the distance between the molecule cores at the minimum energy ϵ_0 . Obviously, two different standards are used for distance in Eqn. 13 (Fig. 11). The notation method of Tee et al. (1966) gives all molecular parameters relative to the centre of molecules (Eqn. 14), and is, therefore, clearer and more direct than Eqn. 13:

$$\Gamma(r) = 4\epsilon_{ij} \left\{ \left(\frac{\sigma_{ij} - 2a_{ij}}{r - 2a_{ij}} \right)^{12} - \left(\frac{\sigma_{ij} - 2a_{ij}}{r - 2a_{ij}} \right)^6 \right\}, \quad (14)$$

where σ_{ij} is the collision diameter (by definition the distance between the centres of molecules when $\Gamma(r) = 0$), which is equal to $2^{-1/6} \cdot \rho_0 + 2a_{ij}$. Increasing the diversity of notation methods, Parrish and Prausnitz (1972) defined the collision diameter as $\sigma + 2a$. The spherical form of the Kihara potential (Tee et al., 1966) was solely used in later studies in clathrate modelling. Consequently, all types of molecules are assumed to be represented by a spherical core. Tee et al. (1966) give Kihara parameters for many individual gas species, which can be adsorbed in clathrates. A generalised corresponding state correlation was estimated by Tee et al. (1966) to calculate Kihara parameters for any type of gas

species. Although, the original specific values for gases like CO₂, N₂, and CH₄ are available (Tee et al., 1966), the generalised corresponding state correlation is used to calculate Kihara parameters in clathrate modelling (e.g., Parrish and Prausnitz, 1972; Holder et al., 1980), which is obviously less accurate. Furthermore, the parameters of Kihara (1953) solely based on the second virial coefficient were preferred, although, Tee et al. (1966) indicate that additional viscosity data improve the physical relevance of the parameters. In this study, the core size parameter a for CO₂ (68.05 pm) from Tee et al. (1966) is chosen to perform the clathrate stability calculations. The core radius of a H₂O molecule is assumed to be 0 (McKoy and Sinanoglu, 1963). The core size parameter is typically uncertain to the extent of about 10%. According to the hard-sphere mixing rule, the core radius for an interacting H₂O and CO₂ molecule is 34.025 pm.

2.6. Molecular Potential in Clathrate Cavities

Equation 14 is transformed to a spherically symmetrical cell potential $w(r)$ (Eqn. 15), similar to the model of McKoy and Sinanoglu (1963):

$$w(r) = 2Z\epsilon_{ij} \left\{ \frac{(\sigma_{ij} - 2a_{ij})^{12}}{rR^{11}} \left(\delta^{10} + \frac{2a_{ij}}{R} \delta^{11} \right) - \frac{(\sigma_{ij} - 2a_{ij})^6}{rR^5} \left(\delta^4 + \frac{2a_{ij}}{R} \delta^5 \right) \right\} \quad (15a)$$

$$\delta^n = \frac{1}{n} \left\{ \left(1 - \frac{r}{R} - \frac{2a_{ij}}{R} \right)^{-n} - \left(1 + \frac{r}{R} - \frac{2a_{ij}}{R} \right)^{-n} \right\}, \quad (15b)$$

where Z and R are the coordination number, and the cell radius of a type of cavity, respectively, r is the distance from the centre of the cavity. The subscript ij indicate the

interaction between an encaged gas molecule and a water molecule in the cavity wall. Several restrictions must be applied to Eqn. 15 because the integration limits in Eqn. A5 give rise to mathematical difficulties. At $r = 0$, the quotient of δ^n and r should be replaced by the limit of the equation:

$$\lim_{r \rightarrow 0} \left(\frac{\delta^n}{r} \right) = \frac{2R^n}{(R - 2a_{ij})^{n+1}}. \quad (16)$$

The infinite upper limit of integration (Eqn. A5) should be replaced by a value close to the cell radius, because it was assumed that the encaged gas molecule has no interaction with molecules outside its cages.

In classical clathrate modelling, the cell dimension of clathrate cavities is independent of temperature and pressure, and remains constant. As pointed out by Lundgaard and Møllerup (1992), a small variation of 0.25% in cavity diameter is seriously influencing stability conditions for structure I and II clathrates. Therefore, the compressibility of clathrates has been taken into account in this study to describe the variation of R as function of total pressure:

$$R = R_0 \cdot \sqrt[3]{\exp[-K \cdot (P - P_0)]}, \quad (17)$$

where R_0 is the cell radius at standard pressure P_0 (0.1 MPa), and K is the isothermal compressibility of clathrate, similar to Eqn. 3.

2.7. Determination of Kihara Parameters in Clathrates

Waals and Platteeuw (1959) estimated theoretically a value of ρ_{H_2O} (0.28 nm), which was obtained from the van der Waals radius of covalently bound oxygen atoms (Pauling, 1945). The minimum energy ϵ_0 for H₂O ($\epsilon_0/k = 167$ K) was derived from numerical iterative procedure, which minimises the difference between calculated and experimental values of the dissociation of argon clathrate (Waals and Platteeuw, 1959). The Lennard-Jones parameters for pure gases were obtained from Whalley and Schneider (1955) and Hirschfelder et al. (1954). Subsequently, the interaction parameters between an encaged gas molecule and a H₂O molecule in the clathrate lattice were then obtained from classical combining rules, the arithmetic mean (hard-sphere) and geometric mean approximations. For a Kihara potential, the core parameters for pure gases were obtained from the second virial coefficients reported in Tee et al. (1966), and the same combining rules were applied to obtain Kihara parameters for gas-water interactions. This method was successfully applied to small gases (CH₄, Ar, Kr) in electrolyte-free solutions (e.g., Holder et al., 1980), which are most likely to adhere to the assumptions of the statistical model of Waals and Platteeuw (1959).

Alternatively, the Kihara parameters between H₂O and gas molecules in the clathrate structure can be directly obtained from computations using the least squares criterion on minimising the deviation between experimental and calculated dissociation pressure of clathrates (e.g., Saito et al., 1964; Parrish and Prausnitz, 1972; Dubessy et al., 1992). This method avoids uncertainties in classical combining rules. Only the core size parameter of gas-water interaction was calculated with the hard-sphere combining rule. It is obvious

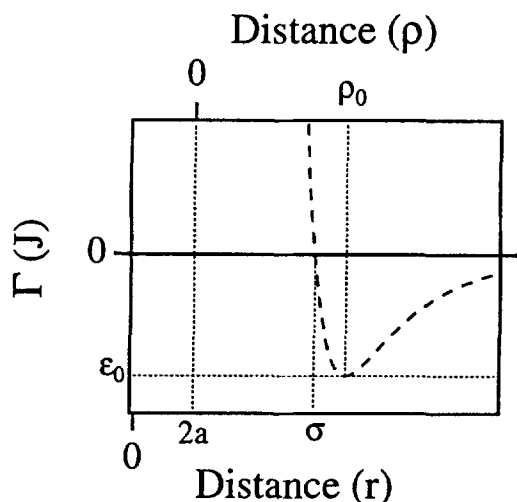


FIG. 11. Schematic diagram of potential energy (Γ) as a function of intermolecular distance, to indicate the difference between several notation methods for the Kihara potential.

Table 1. Published values of the Kihara-parameters σ and ϵ/k obtained from HL_wG_C and HS_wG_C equilibria in the CO₂-H₂O fluid system. n is the amount of experimental data which was used in these studies.

	σ (pm)	ϵ/k (K)	n
Parrish & Prausnitz (1972)	368.81	169.09	24
Anderson & Prausnitz (1986)	367.61	169.44	8 (?)
Ng & Robinson (1977)	367.58	169.52	(?)
Sloan (1990)	366.23	168.77	70
Lundgaard & Møllerup (1991)	335.43	162.37	15(?)
Avlonitis (1994)	365.7	172.0	3 (?)

(?) no clear indication of the used experimental data

from the clathrate equilibrium equation (Eqns. A2–A4) that a unique set of Kihara parameters ϵ and σ cannot be obtained from a single experimental data point; therefore, at least two points are necessary to estimate a solution. The best solution should be obtained from the use of a large amount of experimental data. It is important to use as many independently obtained experimental data as possible, because a solution based on a single set of data may differ considerably from other sets. Most studies have included only a small part of the available data (Table 1), and, all the more, some publications appear to have used maximally three data points (e.g., Avlonitis, 1994). A thorough error analysis of the accuracy of these Kihara parameters was never revealed, and, therefore, no conclusive interpretation could have been given. Unfortunately, these Kihara parameters for binary H₂O-CO₂ interactions cannot be related those of pure H₂O and CO₂ according to the simple classical combining rules, which were used by Waals and Platteeuw (1959). John et al. (1985) noticed this discrepancy, and they increase the complexity of the clathrate model by incorporating more molecular interactions and by accounting for the asymmetry in such interactions.

In this study, we have adopted the method of Saito et al. (1964) to use a least squares fit with all available data on CO₂ clathrates. The molecular characteristics for the cage forming H₂O lattice are assumed to be similar to those given by McKoy and Sinanoglu (1963) including our modifications described in the previous paragraph (Eqns. 15–17).

2.8. Optimum Kihara Parameters in the H₂O–CO₂ System

Unsmoothed data on HL_wG_C clathrate phase equilibria for the fluid system H₂O–CO₂ from Deaton and Frost (1946), Uhrh and Katz (1949), Larson (1955), Robinson and Mehta (1971), Dholabhai et al. (1993), and Englezos and Hall (1994) are used to determine optimal Kihara parameters ϵ and σ between an encaged gas molecule and a cage forming water molecule. The experimental data of Bozzo et al.

(1975) seemed to be only represented by a best-fit equation, which is, therefore, not used in our calculations.

An average error of 1.42% in calculated clathrate dissociation pressures for eighty-two experimental data points is obtained from $\sigma = 365.9$ pm and $\epsilon/k = 174.44$ K (Fig. 12a). The range of σ and ϵ/k values is 363.7–367.5 pm and 174.1–174.9 K, respectively, if an average error of 2% is accepted (Fig. 12a). The previous mentioned 10% variation in core radius a and the 33 J/mol error in $\Delta\mu_0^*$ mainly affect the best solution for ϵ/k values (Fig. 12b). The 5% error in Henry's constant has only a minor effect on the estimation

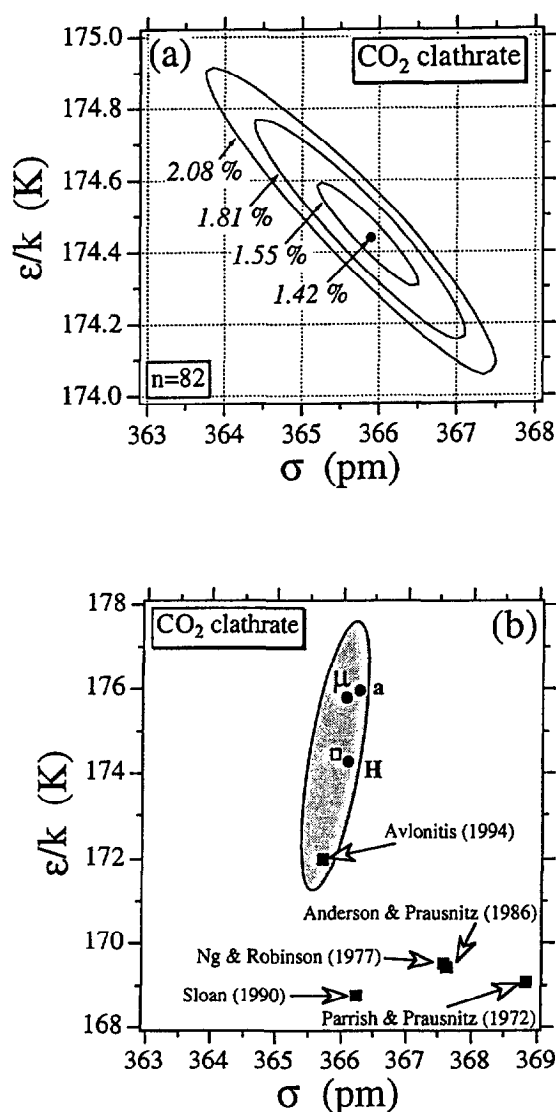


FIG. 12. (a) Contours of equal average deviation of experimental data ($n = 82$) from our modified model (1.42, 1.55, 1.81, and 2.05%) in a ϵ/k - σ diagram. The best solutions for σ and ϵ/k are 365.9 pm and 174.44 K, respectively. (b) The shaded area indicate the range of best solution for σ and ϵ/k with an average deviation of less than 1.42%, as a function of error indications in Kihara core parameter (**a**), chemical potential difference (μ) and Henry's constant (**H**). The open square represents our best values for σ and ϵ/k from (a). The optimum Kihara parameters from Parrish and Prausnitz (1972), Ng and Robinson (1977), Anderson and Prausnitz (1986), Sloan (1990), and Avlonitis (1994) are shown for comparison.

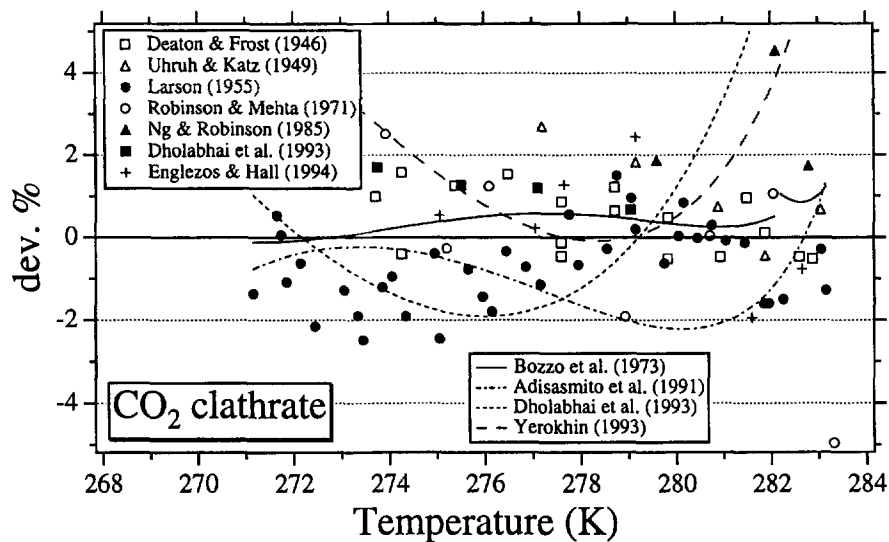


FIG. 13. Relative deviation of individual experimental data points of HL_wG_C stability conditions from our model. Additionally, several purely empirical equations are compared to our calculated clathrate stability field. The deviation is defined as $100\% \times (P_{exp} - P_{model})/P_{model}$.

of optimum values for σ and ϵ/k (Fig. 12b). Likewise, a hypothetical error of 5% in fugacity coefficient calculations result in a minor shift of the best solution ($\sigma = 365.6$ pm and $\epsilon/k = 173.9$ K). Simultaneous evaluation of these error indications resulted in a range of best values for ϵ/k between 171.3 and 177.8 K. The variation for σ is much smaller, i.e., 365.08–366.52 pm. The reported values from other studies (Parrish and Prausnitz, 1972; Ng and Robinson, 1977; Anderson and Prausnitz, 1986; Sloan, 1990; Avlonitis, 1994) are very similar and close to our optimum Kihara parameters (Fig. 12b), but only the values from Avlonitis (1994) fall within our range of best solutions. Lundgaard and Møllerup (1991) obtained optimum Kihara parameters from experimental data on HS_wG_C equilibrium, which differ significantly from our solution.

Most individual experimental data points are accurate within 2% to the clathrate model (Fig. 13), which demonstrates the quality and relevance of the proposed modifications. Apparently, the systematic error, as observed by Dubessy et al. (1992) resulted from a wrong choice of parameters, obtained from less accurate thermodynamic constants and fugacity estimations. Although, error indications for individual measurements are not available for the data from Uhrh and Katz (1949), Larson (1955), and Robinson and Mehta (1971), it is assumed that the error in measured clathrate dissociation pressures is defined by the accuracy of the used apparatus, which must be similar to the value given by Deaton and Frost (1946) of 2 psi ($=0.0138$ MPa). This error in the measurements result in a 1.5% error bar at temperatures near Q_1 conditions, and a 0.5% error bar near Q_2 conditions in Fig. 13. The empirical equation given by Bozzo et al. (1975), which is projected in Fig. 13, agrees very well with our model. Two recently defined purely empirical equations (Yerokhin, 1993; Dholabhai et al., 1993) are both very inaccurate at temperatures near Q_2 conditions. The empirical equation from Adisasmito et al. (1991), which

can also be applied to CO_2 - CH_4 mixtures, remains within 2% accuracy to our model. Some characteristics of clathrate stability according to our model are presented in Table 2. The quadruple points Q_1 and Q_2 conditions are estimated at 271.65 K and 1.036 MPa and 282.98 K and 4.49 MPa (Table 2), respectively, which are obtained from the intersection of the modelled clathrate stability conditions for the HL_wG_C , HL_CG_C , and HS_wG_C equilibrium curve. Table 2 can be used to obtain instantaneously P - T properties of this system corresponding to measured clathrate melting temperatures at heating-freezing stages, without recourse to the complex calculation method of the clathrate stability model presented in this study.

At higher pressures for HL_wL_C clathrate stability equilib-

Table 2. Temperature-pressure relation of HL_wG_C and HL_wL_C equilibria.

	T (K) P (MPa)		T (K) P (MPa)
Q_1	271.65 1.036	Q_2	282.98 4.49
HL_wG_C	272 1.08	HL_wL_C	283.5 9.09
	273 1.21		284.0 13.98
	274 1.36		284.5 19.28
	275 1.52		285.0 24.96
	276 1.72		285.5 31.02
	277 1.94		286.0 37.47
	278 2.19		286.5 44.31
	279 2.49		287.0 51.56
	280 2.84		287.5 59.26
	281 3.26		288.0 67.43
	282 3.78		288.5 76.43
			289.0 85.41
			289.5 95.34
			290.0 106.04
			290.5 117.62
			291.0 130.26
			291.5 144.23
			292.0 159.90
			292.5 177.91

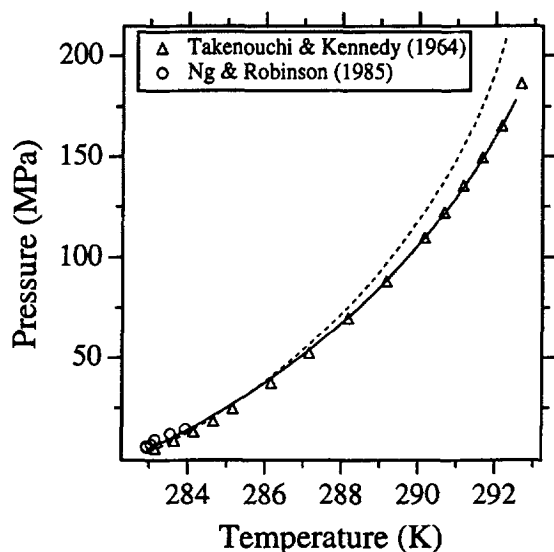


Fig. 14. Clathrate stability conditions for the HL_wLC equilibrium. The solid line is based on optimum Kihara parameters obtained from experimental data from Takenouchi and Kennedy (1965) and Ng and Robinson (1985). The dashed line indicates model predictions from the low pressure set of Kihara parameters.

rium calculations, the model of Ng and Robinson (1977) predicts a straight, nearly pressure independent vertical line in a P - T diagram. This model is based on the properties of clathrates at Q_2 conditions, which were assumed to remain fixed at higher pressures. The experimental data of Takenouchi and Kennedy (1965) were not included, and, consequently, this model seemed to be unable to reproduce or even approach the stability conditions of CO₂ clathrate in the temperature-pressure range for which it was designed. The use of the previous estimated set of optimum Kihara parameters results in an overestimation of clathrate stability pressures (dashed line in Fig. 14). Therefore, the experimental data of Ng and Robinson (1977) and Takenouchi and Kennedy (1965) are used to obtain a separate set of optimum Kihara parameters on minimising the deviation between experimental and calculated dissociation temperature of clathrates at selected pressures. The best solution is obtained from the Kihara parameters $\sigma = 363.92$ pm and $\epsilon/k = 174.46$ K. Table 2 list a set of stability conditions for HL_wLC equilibrium according to our model.

2.9. Discussion

Theoretically, both sets of optimum Kihara parameters, which are based on different experimental datasets should be equal, because they are independent variables in the clathrate stability model. The ϵ/k values are similar and they are within the range of the error indication. However, the σ value for high pressure data is considerably smaller than the value for low pressures. These results may indicate that the distance σ in clathrates may be pressure dependent.

The selected parameters for molecular potentials in clathrate modelling have important consequences for the filling of cavities. It is evident from Eqn. A4 that large cavities are

more likely to be completely occupied than small cavities. Neglecting any inter-molecular forces, small cavities in structure-I clathrates may contain molecules with diameter less than 530 pm (Stackelberg and Müller, 1954; Davidson, 1973), like CO₂ (Fig. 15). The cell potential $w(r)$ indicate that CO₂ molecules will experience only repulsive forces at a distance greater than ± 60 and ± 110 pm from the centre of small cavities, according to Kihara and Lennard-Jones potentials, respectively. Therefore, CO₂ molecules will have no difficulty entering small cavities according to the Lennard-Jones potential (Fig. 15a), which allows molecules to interpenetrate to separations smaller than the collision diameter σ . For the Kihara potential (Fig. 15b and c), a CO₂ molecule with a rod-like (McKoy and Sinanoglu, 1963) and a spherical core (Parrish and Prausnitz, 1972) are both unable to enter or form a small clathrate cavity, because both impenetrable cores will experience only repulsive forces with the cavity wall. In other words, the stick and the ball in the molecules are too large. According to our model, the $w(r)$ is 0 at a distance of 55 pm from the centre of a small cavity, which is, again, smaller than the radius of the impenetrable core of a CO₂ molecule (68.05 pm). Therefore, it must be concluded that small cavities in a CO₂-clathrate structure are either empty or deformed. John et al. (1985) replaced the smoothed-cell approach (Waals and Platteeuw, 1959) with an angular dependence cell potential in regular cavities, and Rodger (1990) considered an anisotropic molecular potential within a spherical cavity. However, according to our theoretical considerations (Fig. 15) the cell potential will be represented by a different equation, which is not spherically symmetrical, and which depends on the irregular shape of the cavity. These considerations have far-reaching consequences to the estimation of optimum Kihara parameters.

The diversity in CO₂ clathrate structures is reinforced by laser Raman spectroscopy (Seitz et al., 1987), from which only one CO₂ peak for a mixed CO₂-CH₄ clathrate could be detected, suggesting the presence of CO₂ in only one type of cavity in structure-I clathrates. FT-IR spectroscopy (Fleyfel and Devlin, 1991) indicated the existence of an epitaxial grown structure-II CO₂ clathrate.

In addition, an important concept of the Langmuir adsorption theory (Langmuir, 1918), which is easily forgotten in clathrate modelling, is that it is describing the adsorption of a gas at a certain solid surface at very low pressures, which is substantially different from the actual processes involved in clathrate formation. Nonetheless, the proposed modifications of the classical clathrate model are able to give very accurate predictions on clathrate stability conditions.

3. MODEL MODIFICATIONS FOR ELECTROLYTE-BEARING SYSTEMS

Until recently, the effect of inhibitors on clathrate formation was only represented by inaccurate purely empirical relations (e.g., Hammerschmidt, 1939) and undefined curves (e.g., Ng and Robinson, 1985). Hammerschmidt (1939) established one single general equation for any type of inhibitor, which was modified by Makogon (1981) for NaCl solution. The empirical equations defined by Yerokhin (1993) appear to be inconsistent with those he defined for salt-free

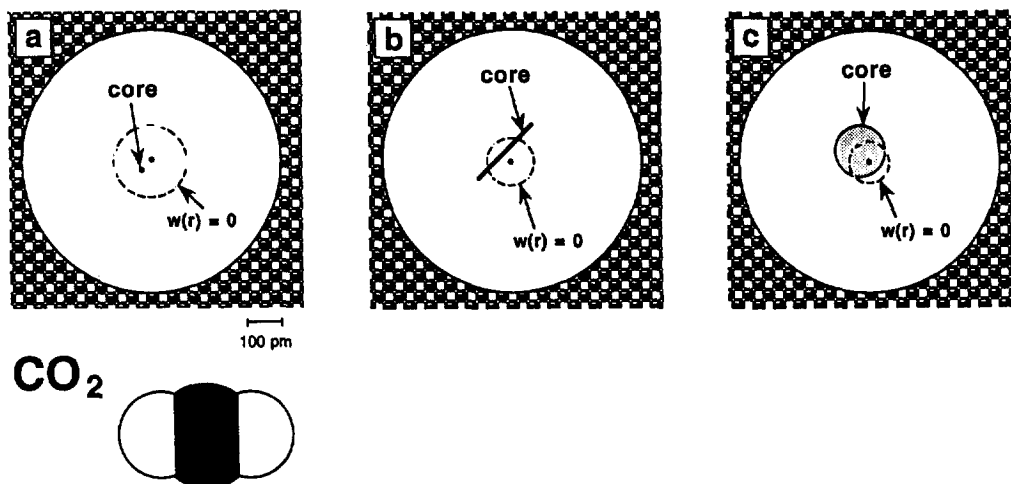


FIG. 15. The dimension of a small cavity in structure-I CO₂ clathrate according to the spherically symmetrical cell potential, compared to the dimension of a CO₂ molecule (Pauling, 1945). The dashed lines indicate the position of $w(r) = 0$ within the cavities. The model of (a) Waals and Platteuw (1959), (b) McKoy and Sinanoglu (1963), and (c) Parrish and Prausnitz (1972) are compared. See text for further details.

fluid systems. Dholabhai et al. (1993) introduced several purely empirical equations for electrolyte solutions with selected mixtures of NaCl, KCl, and CaCl₂. The disadvantage of this approach is that the equations can not be used for compositions and salinities that are different from those examined.

Salts are assumed to be entirely excluded from the clathrate phase, and to have neglectable concentrations in the vapour phase (e.g., Menten et al., 1981). The primary effect of the inhibitor is on the liquid structure of the aqueous solution (e.g., Sloan, 1990). The temperature depression of clathrate stability is comparable to the freezing point depression in binary H₂O-salt systems. Therefore, the activity estimation of H₂O along the freezing point depression curve was used to obtain clathrate stability conditions at various salinities. For example, Menten et al. (1981) used the tabulated values of concentrative properties of aqueous solutions (Table D227-D276 in Weast, 1968) to calculate the reduced activity of H₂O in electrolyte bearing solutions. Barton and Chou (1993) used the Van't Hoff equation for dilute solutions, in which the heat capacity difference between ice and liquid H₂O was assumed to be constant. Englezos and Bishnoi (1988) and Dubessy et al. (1992) introduced the model of Pitzer (1973, 1992) to calculate the activity of H₂O in aqueous solutions from the osmotic coefficient at various temperatures and pressures. This method has been chosen in combination with Henry's law for gas solubilities in this study, because displacement of the clathrate stability field in ternary H₂O-CO₂-salt systems occurs at P - T conditions that are different from freezing point depression in binary systems.

3.1. Osmotic Coefficient

Dissolved electrolytes affect the activity of H₂O in aqueous solutions, as characterised by the model of Debye and

Hückel (1923). This model was modified by Helgeson and Kirkham (1974) and Pitzer (1973, 1992) based on statistical treatment. The activity of H₂O is determined by the product of the osmotic coefficient (Φ) and the amount of dissolved ions:

$$a_{\text{H}_2\text{O}} = \exp \left[-\Phi^*(m_{\text{C}} + m_{\text{A}}) \times \frac{MW_{\text{H}_2\text{O}}}{1000} \right] \quad (18a)$$

$$\Phi = 1 + |z_{\text{C}}z_{\text{A}}|f_{\Phi} + m_{\text{CA}} \left(\frac{2\nu_{\text{C}}\nu_{\text{A}}}{\nu_{\text{C}} + \nu_{\text{A}}} \right) B_{\Phi} + m_{\text{CA}}^2 \left(\frac{2(\nu_{\text{C}}\nu_{\text{A}})^{1.5}}{\nu_{\text{C}} + \nu_{\text{A}}} \right) C_{\Phi}, \quad (18b)$$

where f_{Φ} is the Debye-Hückel term, $MW_{\text{H}_2\text{O}}$ is the molecular weight of H₂O, and m is the salt concentration in molality. The subscripts C, A, and CA refer to cation, anion, and the electrolyte itself, respectively. The electrolyte has ν_{C} positive ions of charge z_{C} and ν_{A} negative ions of charge z_{A} . The binary and ternary ion interaction parameters B_{Φ} and C_{Φ} , respectively, are obtained from complicated empirical best-fit curves. The constant A_{Φ} (Eqn. 19) within the Debye-Hückel term (f_{Φ}) in Eqn. 18b indicates the limiting value for the osmotic coefficient at very low ionic strength:

$$A_{\Phi}(T, P) = \frac{1}{3} \sqrt{\rho_{\text{H}_2\text{O}}(T, P) 2\pi N_{\text{A}}} \left(\frac{e^2}{\epsilon_{\text{H}_2\text{O}}(T, P) 4\pi \epsilon_0^* kT} \right)^{2/3}, \quad (19)$$

where the constants e , ϵ_0^* , N_{A} , and k are the elementary charge, vacuum permittivity, Avogadro's constant, and Boltzmann's constant, respectively. The variables $\rho_{\text{H}_2\text{O}}^*$ and $\epsilon_{\text{H}_2\text{O}}^*$ are the density of pure H₂O (in kg/m³) and the dielectric constant of pure H₂O, respectively. The dielectric constant defined by Bradley and Pitzer (1983) and the density defined by Kell (1967) (Eqn. 4) are chosen to calculate A_{Φ} in this

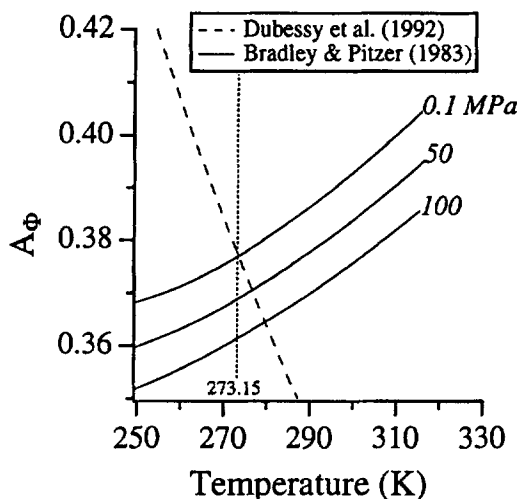


FIG. 16. Debye-Hückel limiting constant A_ϕ , according to the model of Bradley and Pitzer (1983) and Dubessy et al. (1992).

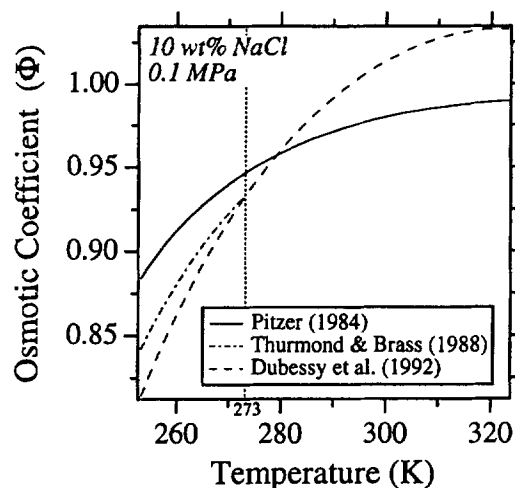


FIG. 18. Comparison of the osmotic coefficient for a 10 wt% NaCl solution between the model from Pitzer (1984), Thurmond and Brass (1988) and Dubessy et al. (1992) at 0.1 MPa.

study. Below 273.15 K, both dielectric constant and density estimations result from extrapolations. Using the selected constant value for $\epsilon_{\text{H}_2\text{O}}^*$ and $\rho_{\text{H}_2\text{O}}^*$ by Dubessy et al. (1992) results in an erroneous estimation of the Debye-Hückel limiting constant A_ϕ (Fig. 16).

Pitzer (1992) gives a theoretical treatment of the calculation method of the osmotic coefficient in liquid solutions with mixed electrolytes. This method can be used to estimate the activity of H₂O in, for example, mixed NaCl-KCl-CaCl₂ solutions.

3.2 Freezing Point Depression and Osmotic Coefficients

The accuracy of the osmotic coefficient was tested using freezing point depression data in binary H₂O-salt systems according to the method of Thurmond and Brass (1988). In the binary H₂O-NaCl system (Fig. 17a), the equation for

the osmotic coefficient by Pitzer et al. (1984) is originally fitted to temperatures above 273.15 K, although, it seems to be more accurate in predicting freezing point depression (e.g., Bodnar, 1993) than the calculations of Thurmond and Brass (1988), who originally estimated the osmotic coefficient for temperatures between 233.15 and 273.15 K. A comparison between several models for the osmotic coefficient (Fig. 18) indicate that the erroneous calculated osmotic coefficient by Dubessy et al. (1992) deviate up to 7% from the model of Pitzer et al. (1984) in 10 wt% NaCl solutions at 0.1 MPa total pressure.

The osmotic coefficient of KCl was determined by Holmes and Mesmer (1983) as a function of temperature (from 273.15 to 523.15 K) and molality (up to about 6 M). This equation is able to predict the freezing point depression in the binary H₂O-KCl system at high salinities (Fig. 17b), which may be represented by Eqn. 20. However, the calcu-

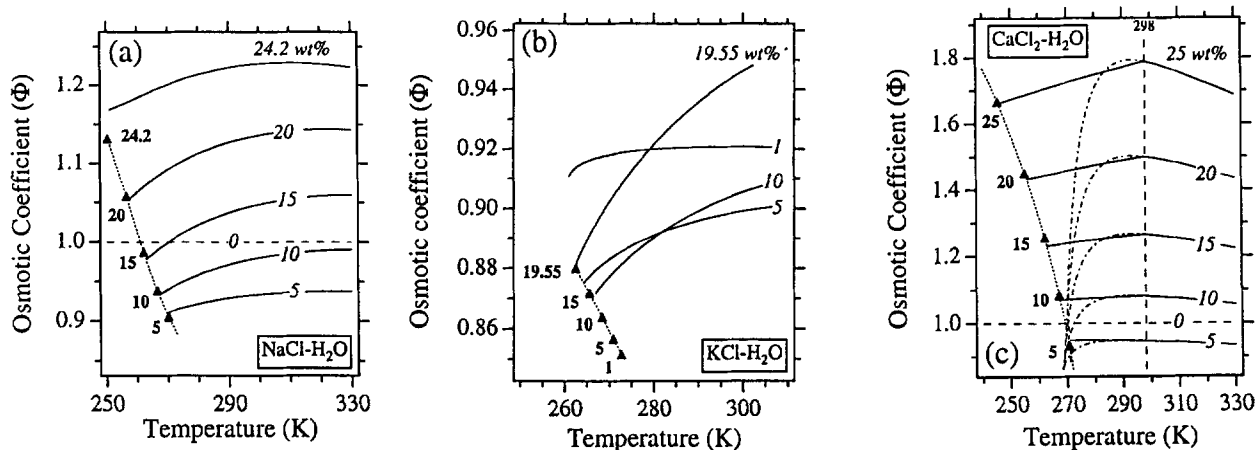


FIG. 17. Comparison between calculated osmotic coefficients at the freezing point depression (triangles) and extrapolated values (a) from Pitzer et al. (1984) for NaCl, (b) from Holmes and Mesmer (1983) for KCl and (c) from Møller (1988) for CaCl₂. The dash-dot lines in (c) indicate the extrapolation of the equation according to Møller (1988) to temperatures below 298 K.

lated osmotic coefficient according to the method of Thurmond and Brass (1988) is increasingly different at lower salinities:

$$T = 273.15 - 3.2936 \cdot m_{\text{KCl}} + 0.047578 \cdot m_{\text{KCl}}^2. \quad (20)$$

The osmotic coefficient for CaCl_2 solutions is estimated by Møller (1988) at temperatures above 298.15 K. Calculations of the osmotic coefficient (Fig. 17c) can not be extrapolated to temperatures below 263.15 K due to mathematical restrictions. Furthermore, this equation is unable to predict the freezing point depression in the binary $\text{H}_2\text{O}-\text{CaCl}_2$ system (Weast, 1968), which may be represented by Eqn. 21:

$$T = 273.15 - 4.4362 \cdot m_{\text{CaCl}_2} - 1.5929 \cdot m_{\text{CaCl}_2}^2. \quad (21)$$

Therefore, for temperatures below 298.15 K both B_ϕ and C_ϕ are defined as constant values calculated at 298.15 K according to the model of Møller (1988), which are then corrected (Eqn. 22) to be able to interpolate between the effect of freezing point depression and the limit of the osmotic coefficient equation:

$$T < 298.15 \text{ K}$$

$$\phi_{\text{cor}} = \frac{m_{\text{CaCl}_2}}{1000} (T - 298.15). \quad (22)$$

This correction term is designed to approach zero towards 298.15 K and neglectable salinities. The correction term does not effect the Debye-Hückel limiting law, and does not, therefore, reduce the physical significance of the liquid solution model.

3.3. Activity of H_2O in Liquid Solutions

The activity of H_2O in aqueous solutions is determined by the amount of dissolved electrolytes and gases, as previously described in Eqns. A7 and 18. These equations do not take into account the effects of both simultaneously occurring processes. A sound model is not available which include all molecular interactions in aqueous solutions at conditions relevant to clathrate stability, i.e., $\text{H}_2\text{O}-\text{H}_2\text{O}$, CO_2-CO_2 , salt-salt, $\text{CO}_2-\text{H}_2\text{O}$, H_2O -salt, and CO_2 -salt interactions. The activity coefficient for H_2O ($\gamma_{\text{H}_2\text{O}}$ in Eqn. 23) in binary H_2O -salt systems is obtained from the quotient of $a_{\text{H}_2\text{O}}$ and $x_{\text{H}_2\text{O}}$ from Eqn. 18a:

$$(\gamma_{\text{H}_2\text{O}})_{\text{binary}} = \frac{a_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}}} = \left(1 + \sum_i m_i \frac{MW_{\text{H}_2\text{O}}}{1000} \right) \exp \left(-\Phi \sum_i m_i \frac{MW_{\text{H}_2\text{O}}}{1000} \right). \quad (23)$$

According to Henry's law in electrolyte-free systems, $\gamma_{\text{H}_2\text{O}}$ is not affected by the presence of any dissolved gas. The effect of dissolved gases in electrolyte-bearing solutions (i.e., CO_2 -salt interactions) is even smaller, because gas solubility's are reduced according to the salting-out effect (Setschenow, 1889). Cramer (1982) demonstrated a variable salting-out coefficient (Eqn. 24) for CO_2 in NaCl solutions between 273.15 and 573.15 K, which was computed

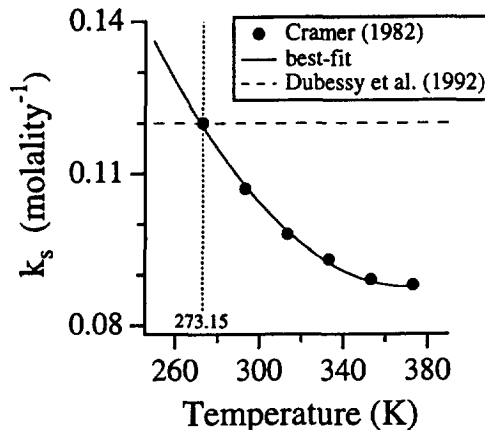


FIG. 19. Salting-out coefficient k_s as a function of temperature, according to Cramer (1982) and Dubessy et al. (1992).

by least squares fit to smoothed values of Henry's constants. A third order polynomial function in temperature (Eqn. 24b) is fit through his data between 273.15 and 373.15 K (Fig. 19) to be able to calculate k_s values at conditions relevant to clathrate formation:

$$\ln \left(\frac{H_{(M-\text{ionic solution})}}{H_{(M-\text{pure water})}} \right) = k_s m_i \quad (24a)$$

$$k_s = 0.5456 - 0.00247 \cdot T + 3.334 \cdot 10^{-6} \cdot T^2 \quad (24b)$$

where k_s is the salting-out coefficient. Below 273.15 K, the extrapolation of Eqn. 24 is approximately linear, which may adequately calculate values for k_s . This equation, is not effective above 373.15 K. As a first approximation this k_s is assumed to be similar for different types of electrolytes.

The mass balance of the solution is transformed to Eqn. 25, which considers the presence of both electrolytes and dissolved gases:

$$\frac{1}{(x_{\text{H}_2\text{O}})_{\text{ternary}}} = 1 + \left(\frac{x_{\text{CO}_2}}{1 - x_{\text{CO}_2}} \right) + (m_c + m_a) \frac{MW_{\text{H}_2\text{O}}}{1000} \quad (25a)$$

$$(a_{\text{H}_2\text{O}})_{\text{ternary}} = (\gamma_{\text{H}_2\text{O}})_{\text{binary}} \cdot (x_{\text{H}_2\text{O}})_{\text{ternary}}, \quad (25b)$$

where x_{CO_2} is the reduced gas solubility, and *binary* refers to $\text{NaCl}-\text{H}_2\text{O}$ interactions. The diversity in methods of activity calculation is illustrated by several studies. The activity of H_2O is obtained from the product of Eqns. A7 and 18 according to the method of Dubessy et al. (1992). Their model may calculate activities which differ up to 1% from Eqn. 25 at higher pressures, temperatures, and salinities. The method of Barton and Chou (1993) assumes that the contributions of dissolved NaCl and CO_2 in lowering the activity of H_2O are additive, i.e., the sum of Eqns. A7 and 18, which is only valid if $\gamma_{\text{H}_2\text{O}}$ in Eqn. 23 is equal to 1. Englezos (1992) calculated the fugacity coefficient of H_2O from salt-free liquid-vapour equilibrium using an equation of state. Subsequently, this coefficient is corrected according

to the Debye-Hückel term (Eqns. 18 and 19). This model excludes the effect of salts on the equation of state for H₂O-rich fluids.

4. PREDICTABILITY IN NaCl-KCl-CaCl₂-BEARING FLUID SYSTEM

4.1. $HL_W G_C$ Equilibria

As salts do not enter the clathrate structure, application of osmotic coefficient to activity calculations and our modified clathrate stability model for $HL_W G_C$ equilibrium should predict clathrate dissociation pressure in electrolyte-bearing systems within the accuracy of the electrolyte-free system ($\approx 2\%$ in Fig. 13).

There are only a few studies reported on clathrate stability conditions between Q_1 and Q_2 conditions in salt solutions.

Most data in these systems are represented in M.S. thesis and Ph.D. dissertations (e.g., Larson, 1955; Chen, 1972a) and are, therefore, not readily available. Part of these data were reproduced by Sloan (1990), Darling (1991), and Englezos (1992). Although, many experimental data seem to exist, Bozzo et al. (1975) preferred to smooth their results with the controversial model of Miller and Strong (1945). Barton and Chou (1993) indicated that several assumptions for this model seemed to be incorrect and may result in significant errors in calculated clathrate stability conditions.

The experimental data for $HL_W G_C$ equilibria in the H₂O-CO₂ system containing NaCl, KCl, CaCl₂, and mixed salts from Larson (1955), Vlahakis et al. (1972), Dholabhai et al. (1993), and Englezos and Hall (1994) are compared to the predictions of our modified model for clathrate stability conditions (Fig. 20). Apparently, these datasets are not con-

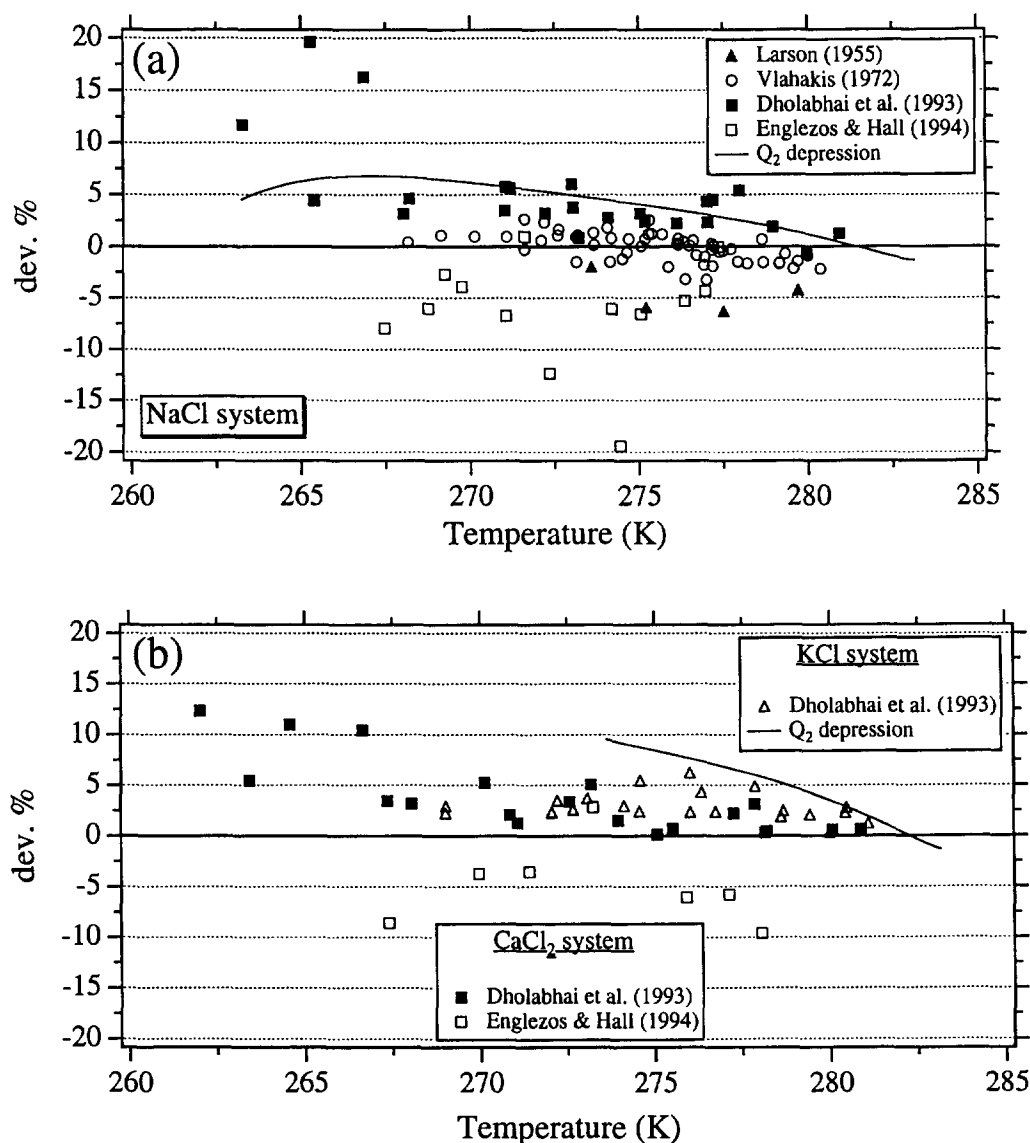


FIG. 20. Deviation of experimental data for $HL_W G_C$ equilibria from our model calculations in NaCl-bearing system (a) and KCl-CaCl₂-bearing system (b). The deviation is defined as $100\% \times (P_{\text{exp}} - P_{\text{model}})/P_{\text{model}}$. The solid lines indicate Q_2 depression for NaCl (Chen, 1972b) and KCl (Diamond, 1992).

Table 3. Model comparison between Englezos and Hall (1994) and this study. *n* is the amount of experimental data.

Salt	wt%	n	Average deviation (%) experimental data	
			Englezos & Hall	this study
-	0	6	2.4	1.2
NaCl	10	8	6.2	4.8
NaCl	15.2	5	12.2	9.2
CaCl ₂	10.57	7	8	5.7

sistent and show a wide scatter compared to modelled dissociation pressures. Our clathrate model is able to reproduce the experimental data of Vlahakis et al. (1972) within 3% accuracy (Fig. 20a). The data from Larson (1955) and Englezos and Hall (1994) are consistently lower than predicted values, and deviate increasingly for higher salinities (maximally -20%). In contradiction, the data from Dholabhai et al. (1993) is always higher than model prediction, with a similar trend of increasing deviations towards higher salinities (maximally +20%). Both individual datasets are indicating a systematic error as a function of salinity, however,

in the opposite sense. Independently from the accuracy of our clathrate stability model, the rather large differences between these data indicate a major difficulty in the analysis of clathrate stability conditions in salt-bearing systems. The clathrate stability model used by Englezos and Hall (1994) appears to be less accurate than our theoretical considerations (Fig. 20 and Table 3). Shmulovich and Plyasunova (1993) used activity calculations for the freezing point depression in the binary H₂O-CaCl₂ system to obtain theoretical clathrate stability conditions in the ternary H₂O-CO₂-CaCl₂ system. Experimental data was not used to verify to predictability of their model, and, consequently, their model may differ up to 0.8 MPa from the model presented in this study.

In general, the fit between the experimental data and our calculated clathrate melting pressures in *HL_wG_C* equilibria is good. Our model represents an acceptable compromise between the available experimental data. These results reinforce the justifications of the modifications that we have used for clathrate stability calculations. Tables 4-6 reveal a series of calculated clathrate stability pressures at selected temperature and salinities for *HL_wG_C* equilibria in NaCl, KCl, and CaCl₂ bearing fluid systems. Similar to Table 2, Tables 4-6 can be used to obtain instantaneously *P-T* properties of these systems corresponding to measured clathrate melting temperatures at heating-freezing stages. In addition, clathrate

Table 4. Temperature-pressure conditions for *HL_wG_C*, *HL_wL_C*, *Q₁*, and *Q₂* equilibria at selected NaCl salinities (in wt% and molality). The italic numbers for *Q₂* temperatures are obtained from Chen (1972b).

NaCl		5 wt% (0.901 m)	10 wt% (1.901 m)	15 wt% (3.020 m)	20 wt% (4.278 m)	24.2 wt% (5.463 m)
Q ₁	HL _w G _C	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)
		268.71 0.932	265.3 0.823	261.07 0.702	255.43 0.565	248.45 0.426
					256 0.604	249 0.454
				262 0.782	257 0.678	250 0.508
		269 0.963	266 0.892	263 0.878	258 0.762	251 0.569
		270 1.080	267 1.000	264 0.987	259 0.857	252 0.638
		271 1.211	268 1.122	265 1.109	260 0.965	253 0.716
		272 1.360	269 1.261	266 1.249	261 1.086	254 0.804
		273 1.530	270 1.419	267 1.407	262 1.225	255 0.904
		274 1.724	271 1.598	268 1.588	263 1.383	256 1.017
		275 1.947	272 1.805	269 1.797	264 1.564	257 1.146
		276 2.204	273 2.043	270 2.038	265 1.773	258 1.293
		277 2.505	274 2.320	271 2.319	266 2.015	259 1.461
		278 2.861	275 2.645	272 2.652	267 2.299	260 1.655
		279 3.289	276 3.034	273 3.051	268 2.636	261 1.880
		280 3.818	277 3.509	274 3.544	269 3.045	262 2.144
						263 2.456
Q ₂		280.63 4.227 (280.58)	277.72 3.926 (277.52)	274.04 3.566 (273.69)	269.19 3.133 (268.66)	263.63 2.685 (263.23)
	HL _w L _C	281.0 8.06	278.0 6.683	274.5 7.697	269.5 4.904	264.0 3.648
		281.5 12.98	278.5 11.702	275.0 13.158	270.0 10.551	264.5 9.414
		282.0 18.31	279.0 17.152	275.5 19.071	270.5 16.694	265.0 15.663
		282.5 24.029	279.5 23.012	276.0 25.425	271.0 23.321	265.5 22.388
		283.0 30.133	280.0 29.277	276.5 32.227	271.5 30.437	266.0 29.594
		283.5 36.628	280.5 35.956	277.0 39.493	272.0 38.062	266.5 37.302
		284.0 43.526	281.0 43.064	277.5 47.251	272.5 46.229	267.0 45.54
		284.5 50.85	281.5 50.628	278.0 55.538	273.0 54.983	267.5 54.348
		285.0 58.63	282.0 58.684	278.5 64.408	273.5 64.37	268.0 63.778
		285.5 66.903	282.5 67.276	279.0 73.929	274.0 74.498	268.5 73.896
		286.0 75.721	283.0 76.464	279.5 84.19	274.5 85.464	269.0 84.789
		286.5 85.148	283.5 86.328	280.0 95.313	275.0 97.414	269.5 96.567
		287.0 95.267	284.0 96.969	280.5 107.465	275.5 110.553	270.0 109.377
		287.5 106.187	284.5 108.525	281.0 120.882	276.0 125.178	270.5 123.416
		288.0 118.056	285.0 121.188	281.5 135.919	276.5 141.75	271.0 138.958
		288.5 131.08	285.5 135.236	282.0 153.153	277.0 161.048	271.5 156.405
		289.0 145.559	286.0 151.096	282.5 173.634	277.5 184.596	272.0 176.376
		289.5 161.962	286.5 169.492	283.0 199.715		272.5 199.921
		290.0 181.094	287.0 191.836			

Table 5. Temperature-pressure conditions for HL_wG_C, HL_wL_C, Q₁, Q₂ equilibria at selected KCl salinities (in wt% and molality). The italic numbers for Q₂ temperatures are obtained from Diamond (1992).

KCl	5 wt% (0.706 m)	10 wt% (1.49 m)	15 wt% (2.337 m)	19.55 wt% (3.26 m)
	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)
Q ₁	269.42 0.956	266.97 0.876	264.24 0.792	261.38 0.711
HL _w G _C	270 1.022 271 1.145 272 1.285 273 1.444 274 1.625 275 1.833 276 2.072 277 2.35 278 2.676 279 3.064 280 3.536 281 4.131	267 0.877 268 0.982 269 1.102 270 1.236 271 1.389 272 1.564 273 1.763 274 1.993 275 2.259 276 2.571 277 2.941 278 3.388 279 3.948	265 0.863 266 0.968 267 1.086 268 1.22 269 1.372 270 1.545 271 1.744 272 1.972 273 2.238 274 2.549 275 2.918 276 3.367	262 0.764 263 0.858 264 0.963 265 1.082 266 1.217 267 1.371 268 1.546 269 1.746 270 1.978 271 2.247 272 2.563 273 2.941 274 3.402
Q ₂	281.73 4.293 (281.10)	279.19 4.072 (278.84)	276.86 3.842 (276.30)	274.37 3.601
HL _w L _C	282.0 12.038 282.5 17.245 283.0 22.838 283.5 28.812 284.0 35.168 284.5 41.919 285.0 49.083 285.5 56.687 286.0 64.765 286.5 73.365 287.0 82.542 287.5 92.373 288.0 102.953 288.5 114.414 289.0 126.931 289.5 140.758 290.0 156.277 290.5 174.113 291.0 195.425	279.5 7.136 280.0 12.016 280.5 17.306 281.0 22.984 281.5 29.046 282.0 35.498 282.5 42.353 283.0 49.634 283.5 57.371 284.0 65.603 284.5 74.381 285.0 83.77 285.5 93.854 286.0 104.744 286.5 116.592 287.0 129.606 287.5 144.095 288.0 160.541 288.5 179.781	277.0 5.156 277.5 9.976 278.0 15.219 278.5 20.859 279.0 26.889 279.5 33.316 280.0 40.153 280.5 47.424 281.0 55.159 281.5 63.399 282.0 72.199 282.5 81.626 283.0 91.769 283.5 102.749 284.0 114.725 284.5 127.928 285.0 142.696 285.5 159.577 286.0 179.548	274.5 4.466 275.0 9.366 275.5 14.693 276.0 20.422 276.5 26.552 277.0 33.09 277.5 40.053 278.0 47.468 278.5 55.372 279.0 63.81 279.5 72.845 280.0 82.556 280.5 93.048 281.0 104.462 281.5 116.996 282.0 130.936 282.5 146.729 283.0 165.135 283.5 187.672

stability conditions for several salinities are shown in Fig. 21. The tabulated values from Bozzo et al. (1975) seems to fit perfectly the calculated clathrate stability curve (Fig. 21a). The large scatter of experimental data for 15 wt% NaCl solutions (Fig. 21a) indicate the previously described controversy.

4.2. Q₂ and HL_wL_C Equilibria

Modelling of clathrate stability at Q₂ conditions is proposed to be done according to HL_wG_C equilibria, because fugacity calculations are more accurate for a vapour-like than a liquid-like CO₂ phase. The depression of the invariant quadruple point Q₂ seems to occur along the HL_CG_C equilibrium curve (Chen, 1972a; Bozzo et al., 1975), which coincides with the boiling curve of pure CO₂. Darling (1991) reported the empirical equation from Chen (1972b) for the relation between the temperature of Q₂ depression and salinity. This empirical equation deviates maximally 6.8% from our model predictions at higher salinities (Fig. 20a).

Diamond (1992) investigated the temperature displacement of Q₂ in several selected KCl-NaCl solutions, and defined a relation between this displacement and salinities based on pure KCl solutions. His empirical equation seems

to deviate up to 9.5% at eutectic compositions from our model (Fig. 20b), and exceeds values obtained for HL_wG_C equilibria from Dholabhai et al. (1993). As mentioned before, the underestimated osmotic coefficient may introduce a systematic error in the activity calculations, which may cause the relative large deviation in clathrate stability calculations.

Zhang and Frantz (1989) provide the sole dataset of the depression of the clathrate stability field at apparent Q₂ conditions in the H₂O-CO₂-CaCl₂ system. However, the authors do not clearly indicate that the clathrate melted in the presence of both a CO₂-rich vapour and liquid phase. An empirical equation was provided for the relation between salinity and temperatures of Q₂ depression, which is only valid between 270 and 283 K, and cannot be extrapolated to lower temperatures due to mathematical restrictions. The experimental data close to Q₂ conditions from Dholabhai et al. (1993) and our calculated intersection between HL_wG_C and HL_CG_C equilibria disagrees with their equation (Fig. 21c). At 273.15 K, the empirical equation of Zhang and Frantz (1989) exceeds about 20% the molality estimation from our model predictions. The freezing point depression of Q₂ in CaCl₂-bearing systems should be represented by Eqn. 26, which emphasise the differences between both models:

Table 6. Temperature-pressure conditions for $HLwG_C$, $HLwL_C$, Q_1 , and Q_2 equilibria at selected $CaCl_2$ salinities (in wt% and molality). The italic numbers for Q_2 temperatures are obtained from Zhang and Frantz (1989).

$CaCl_2$	5 wt% (0.474 m)	10 wt% (1.001 m)	15 wt% (1.590 m)	20 wt% (2.252 m)	25 wt% (3.003 m)	30.2 wt% (3.898 m)
	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)	T (K) P (MPa)
Q_1	268.28 0.952	265.98 0.844	261.12 0.705	254.19 0.538	244.31 0.358	229.12 0.180
$HLwG_C$						230 0.198
						231 0.222
						232 0.248
					245 0.388	233 0.278
				255 0.59	246 0.436	234 0.312
		266 0.846	262 0.776	256 0.662	247 0.49	235 0.35
	270 1.033	267 0.948	263 0.87	257 0.744	248 0.551	236 0.394
	271 1.158	268 1.063	264 0.976	258 0.836	249 0.62	237 0.443
	272 1.299	269 1.192	265 1.096	259 0.94	250 0.698	238 0.5
	273 1.46	270 1.34	266 1.233	260 1.058	251 0.786	239 0.564
	274 1.644	271 1.508	267 1.388	261 1.192	252 0.887	240 0.637
	275 1.855	272 1.7	268 1.566	262 1.346	253 1.002	241 0.72
	276 2.098	273 1.921	269 1.77	263 1.522	254 1.134	242 0.816
	277 2.38	274 2.177	270 2.007	264 1.726	255 1.286	243 0.927
	278 2.713	275 2.477	271 2.283	265 1.964	256 1.461	244 1.055
	279 3.109	276 2.833	272 2.61	266 2.243	257 1.666	245 1.204
	280 3.594	277 3.261	273 3.002	267 2.575	258 1.906	246 1.379
	281 4.209	278 3.794	274 3.485	268 2.979	259 2.191	247 1.586
Q_2	281.09 4.273 (281.37)	278.30 3.983 (279.07)	274.17 3.580 (276.26)	268.15 3.047 (272.22)	259.60 2.390	247.20 1.632
$HLwL_C$	281.5 8.478	278.5 6.007	274.5 6.367	268.5 5.057	260.0 2.714	248.0 1.603
	282.0 13.406	279.0 10.851	275.0 11.466	269.0 10.342	260.5 8.15	248.5 7.106
	282.5 18.739	279.5 16.116	275.5 16.979	269.5 16.043	261.0 13.999	249.0 12.998
	283.0 24.459	280.0 21.777	276.0 22.893	270.0 22.156	261.5 20.269	249.5 19.306
	283.5 30.561	280.5 27.828	276.5 29.211	270.5 28.69	262.0 26.978	250.0 26.066
	284.0 37.051	281.0 34.274	277.0 35.944	271.0 35.665	262.5 34.159	250.5 33.325
	284.5 43.944	281.5 41.13	277.5 43.115	271.5 43.113	263.0 41.854	251.0 41.144
	285.0 51.261	282.0 48.416	278.0 50.753	272.0 51.074	263.5 50.12	251.5 49.604
	285.5 59.031	282.5 56.165	278.5 58.901	272.5 59.603	264.0 59.03	252.0 58.807
	286.0 67.293	283.0 64.416	279.0 67.612	273.0 68.771	264.5 68.683	252.5 68.894
	286.5 76.097	283.5 73.221	279.5 76.953	273.5 78.65	265.0 79.209	253.0 80.06
	287.0 85.507	284.0 82.648	280.0 87.017	274.0 89.403	265.5 90.791	253.5 92.591
	287.5 95.604	284.5 92.784	280.5 97.922	274.5 101.182	266.0 103.692	254.0 106.93
	288.0 106.498	285.0 103.743	281.0 109.833	275.0 114.233	266.5 118.316	254.5 123.837
	288.5 118.335	285.5 115.682	281.5 122.981	275.5 128.923	267.0 135.336	255.0 144.829
	289.0 131.315	286.0 128.822	282.0 137.714	276.0 145.858	267.5 156.052	255.5 173.986
	289.5 145.734	286.5 143.485	282.5 154.59	276.5 166.155	268.0 183.7	
	290.0 162.048	287.0 160.186	283.0 174.618	277.0 192.405	268.5 237.489	
	290.5 181.037	287.5 179.83	283.5 200.024			
	291.0 204.247	288.0 204.321				

$$m_{CaCl_2} = \exp[5.5522 - 0.65038 \cdot T_C + 0.023984 \cdot T_C^2 - 5.7015 \cdot 10^{-4} \cdot T_C^3], \quad (26)$$

where T_C is temperature in Celsius, and m_{CaCl_2} is the molality of $CaCl_2$. This equation is valid up to the eutectic composition.

Experimental data is not available for $HLwL_C$ equilibria, but the reliability of our model predictions is assumed to be much better than the method proposed by Ng and Robinson (1977). As previously mentioned, their model is only based on the properties of a system at Q_2 conditions, and they did not include the available high pressure data from Takenouchi and Kennedy (1965). Figure 22 and Table 4–6 reveal a series of $HLwL_C$ clathrate stability conditions for selected salinities in NaCl, KCl, and $CaCl_2$ -bearing systems.

4.3. Q_1 equilibria

The temperature displacement of the invariant quadruple point Q_1 can be related to specific salinities in NaCl, KCl, and $CaCl_2$ bearing systems, similar to the previously described depression of Q_2 . Unfortunately, experimental data are not available. Q_1 temperature is usually measured during micro-

thermometric analysis of inclusions containing electrolyte solutions as the final melting temperature of ice in the presence of clathrate. However, the presence of two solid phases, i.e., clathrate and ice which are not clearly separated in distinct single crystals, may camouflage true melting temperatures of the individual solid phases. Nevertheless, expressions have been estimated for the depression of Q_1 conditions in pure NaCl, KCl, and $CaCl_2$ solutions from the intersection of $HLwG_C$ and $HSwG_C$ equilibria at selected salinities:

$$m_{NaCl} = -[0.53241 + 0.34211 \cdot T_C + 4.0025 \cdot 10^{-3} \cdot T_C^2] \quad (27a)$$

$$m_{KCl} = -[0.50308 + 0.3272 \cdot T_C + 5.9252 \cdot 10^{-4} \cdot T_C^2] \quad (27b)$$

$$m_{CaCl_2} = -[0.061971 + 0.14879 \cdot T_C + 1.3947 \cdot 10^{-3} \cdot T_C^2]. \quad (27c)$$

These equations can be used to obtain the salinity of fluid inclusions at the final melting temperature of ice, which only represent true salinities if the clathrate phase is melting at

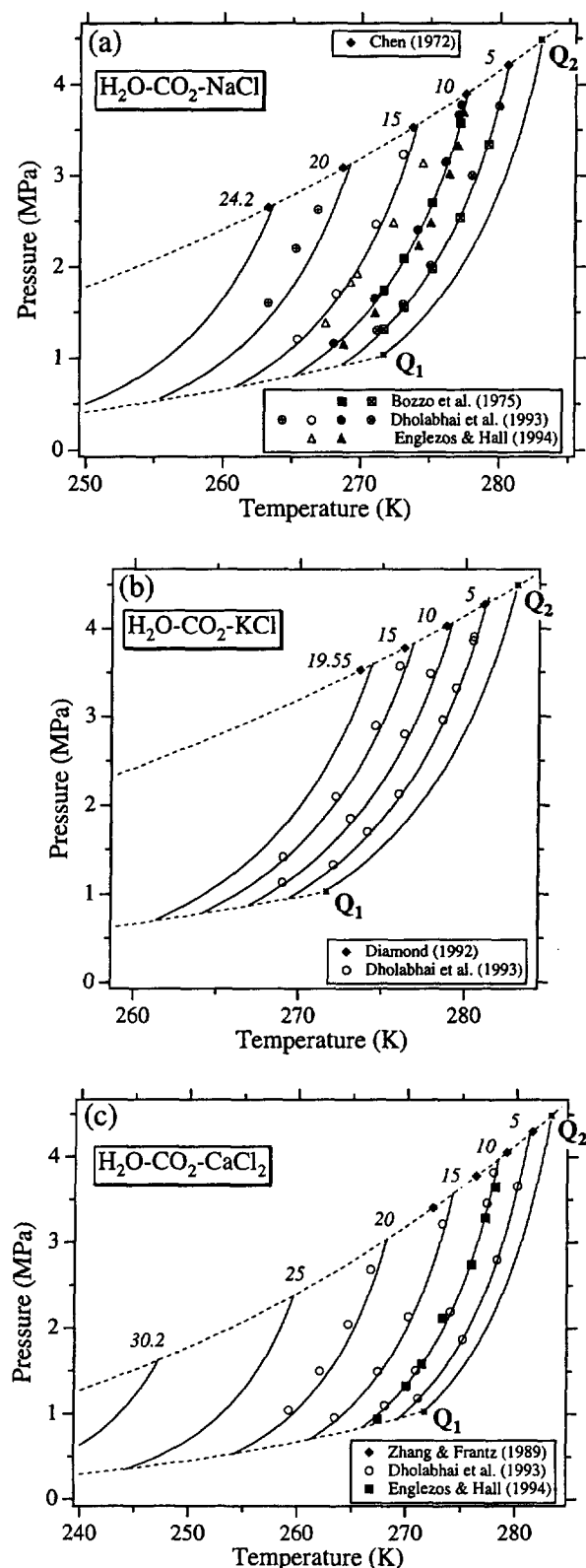


FIG. 21. P - T diagrams with the stability conditions of clathrate between quadruple point Q_1 and Q_2 in ternary systems H₂O-CO₂-salt: (a) NaCl; (b) KCl; (c) CaCl₂. The numbers indicate salinity values. The open and solid symbols in (a) represent experimental data of ≈ 15 wt% and ≈ 10 wt%, respectively. Symbols filled with a diagonal and horizontal cross in (a) represent experimental data of ≈ 5 wt% and ≈ 20 wt%, respectively.

similar conditions. The error estimation in these purely theoretical equations is uncertain because experimental data are not available. However, $HL_W G_C$ data near Q_1 conditions seem to agree sufficiently with model predictions (see Fig. 21). Dubessy et al. (1992) incorrectly used equations for freezing point depression in binary H₂O-salt systems to estimate the salinity at ice melting temperatures. To illustrate an example of erroneously estimated salinity of fluid inclusions, a final melting temperature of ice at 263 K corresponds to a salinity of 14.1 wt% in the binary H₂O-NaCl system (Bodnar, 1993). However, in the ternary H₂O-CO₂-NaCl system the salinity of the aqueous solution in the inclusion would be 12.9 wt% at the final ice melting point (Eqn. 27a).

5. COMPUTER PROGRAM IN C++ FOR FLUID INCLUSION STUDIES

The calculation of clathrate stability conditions according to our modifications are rather complex and a time consuming process. Therefore, a computer program in C++ language has been developed to handle the complex calculation method, which includes several numerical approximations. For fluid inclusion studies, several computer programs have been made available to calculate stability conditions of CO₂-clathrate in the binary H₂O-CO₂ system and in various salt solutions. These programs are able to calculate bulk fluid inclusion salinities and densities obtained from clathrate melting temperatures (Bakker, 1995).

6. CONCLUSIONS

After extensive revision of various models for clathrate stability in H₂O-CO₂-salt systems, a new model has been developed that is valid between 253–293 K and 0–200 MPa, and that can be extrapolated to lower temperatures. This model is a general solution of the equality of chemical potentials of H₂O in the liquid solution and in the clathrate phase according to the theoretical considerations of Waals and Platteeuw (1959).

General standard conditions, which are essential to any reproducible thermodynamic calculation, seem to be lacking in the established clathrate models. Furthermore, several physical and chemical parameters used in the model are undefined at the previously chosen standard conditions. Consequently, new standard conditions (0.1 MPa and 273.15 K) had to be defined to perform the clathrate stability calculations consistently.

The molecular cell potential of cavities in clathrate structures according to McKoy and Sinanoglu (1963) is redefined to increase the comprehension of the formula, and to get rid of the double standard that is used in Kihara molecular potentials. The variation of the cell dimension with pressure is described according to the compressibility of clathrates.

Using the most accurate valuables which are available for thermodynamic constants of clathrate, water, and ice (heat capacity and volumetric properties), for the solubility of CO₂ in water (Henry's constant), and for the volumetric properties of the vapour-rich phase, Kihara parameters σ and ϵ/k between a CO₂ molecule and a cage forming H₂O molecule are numerically optimised at 362.9 pm and 174.44 K, respectively, for $HL_W G_C$ equilibria. Including the error

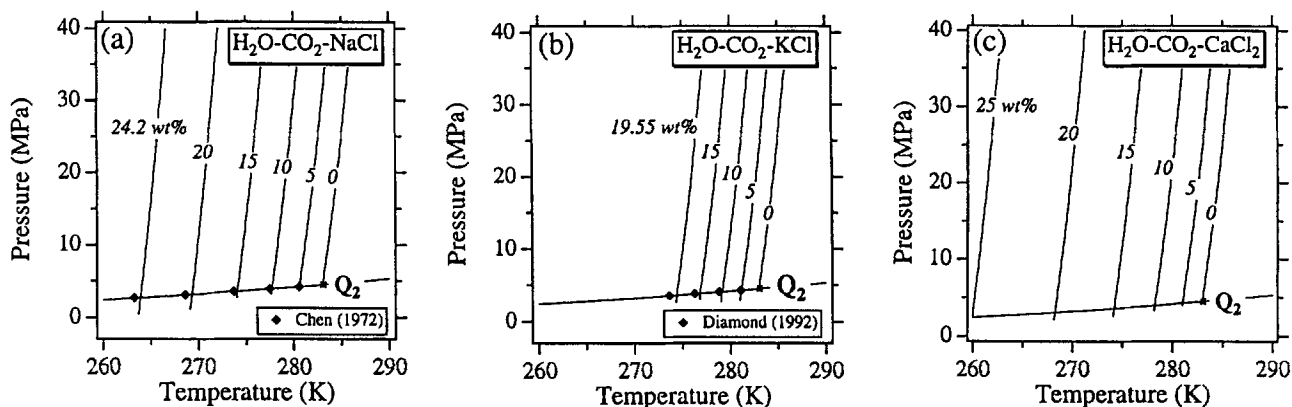


FIG. 22. P - T diagrams with the stability conditions of clathrate at pressures above quadruple point Q_2 in ternary systems H_2O - CO_2 -salt: (a) NaCl; (b) KCl; (c) $CaCl_2$.

indications for the individual parameters involved in clathrate modelling, a range of 365.08–366.52 pm and 171.4–177.8 K for optimised Kihara parameters allow a 2% accuracy in calculated clathrate formation pressures at selected temperatures between Q_1 and Q_2 conditions. At high pressures, the optimum Kihara parameters σ and ϵ/k are estimated at 363.92 pm and 174.46 K, respectively, from different sets of experimental data.

The lack of a thorough error analysis in clathrate stability models in previous studies have resulted in some erroneous conclusions. For example, the difference in heat capacity between H_2O and clathrate, as estimated by, e.g., Holder et al. (1980) cannot be detected due to the relative large error in $\Delta\mu_0^*$ values.

According to the method of Englezos and Bishnoi (1988) and Dubessy et al. (1992), the osmotic coefficient is sufficiently successful applied to quantify the effect of electrolytes (NaCl, KCl, and $CaCl_2$) on lowering the activity of H_2O in aqueous solutions at P - T conditions relevant to clathrate formation. Unfortunately, the available experimental data is inconsistent and our model appears to represent average values.

New equations are defined for the depression of the quadruple point Q_1 in NaCl, KCl, $CaCl_2$ bearing solutions. The depression of Q_2 in $CaCl_2$ solutions is not corresponding to the values given by Zhang and Frantz (1989), therefore, a new equation is defined according to the intersection of $HL_W G_C$ and $HL_C G_C$ equilibria.

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REFERENCES

- Adisasmatto S., Frank R. J., III, and Sloan E. D., Jr. (1991) Hydrates of carbon dioxide and methane mixtures. *J. Chem. Eng. Data* **36**, 68–71.
- Anderson F. E. and Prausnitz J. M. (1986) Inhibition of gas hydrates by methanol. *AIChE J.* **32**, 1321–1333.
- Angell C. A., Shuppert J., and Tucker J. C. (1973) Anomalous properties of supercooled water. Heat capacity, expansivity, and proton magnetic resonance chemical shift from 0 to -38° . *J. Phys. Chem.* **77**, 3092–3099.
- Angus S., Armstrong B., and Reuck K. M. (1976) *International Thermodynamic Tables of the Fluid State: Carbon Dioxide*, Vol. 3, pp. 385. Pergamon Press.
- Avlonitis D. (1994) The determination of Kihara potential parameters from gas hydrate data. *Chem. Engng. Sci.* **49**, 1161–1173.
- Bakker R. J. (1995) The application of a computerised and optimised clathrate stability model to fluid inclusion studies. *Bol. Soc. Esp. Mineral.* **18-1**, 15–17 (abstr.).
- Bakker R. J. and Thiery R. (1994) Application of clathrates to fluid inclusion studies. In *Fluid Inclusions in Minerals: Methods and Applications, Short Course IMA* (ed. B. de Vivo and M. L. Frezzotti), pp. 191–208.
- Barton P. B. and Chou I.-M. (1993) Calculation of the vapor-saturated liquidus for the NaCl- CO_2 - H_2O system. *Geochim. Cosmochim. Acta* **57**, 2715–2723.
- Benson B. B. and Kraus D., Jr. (1976) Empirical laws for dilute aqueous solutions of nonpolar gases. *J. Chem. Phys.* **64**, 689–709.
- Bodnar R. J. (1993) Revised equation and table for determining the freezing point depression of H_2O -NaCl solutions. *Geochim. Cosmochim. Acta* **57**, 683–684.
- Bozzo A. T., Chen H.-S., Kass J. R., and Barduhn A. J. (1975) The properties of the hydrates of chlorine and carbon dioxide. *Desalination* **16**, 303–320.
- Bradley D. J. and Pitzer K. S. (1983) Thermodynamics of electrolytes. 12. Dielectric properties of water and Debye-Hückel parameters to $350^\circ C$ and 1 kbar. *J. Phys. Chem.* **87**, 1599–1603.
- Cady G. H. (1983) Composition of clathrate gas hydrates of H_2S , Xe, SO_2 , Cl_2 , CH_3Cl , CH_3Br , $CHClF_2$, CCl_2F_2 , and C_3H_8 . *J. Phys. Chem.* **87**, 4437–4441.
- Carroll J. J. and Mather A. E. (1992) The system carbon dioxide-water and the Krichevsky-Kasarnovsky equation. *J. Soln. Chem.* **21**, 607–621.
- Carroll J. J., Slupsky J. D., and Mather A. E. (1991) The solubility of carbon dioxide in water at low pressure. *J. Phys. Chem. Ref. Data* **20**, 1201–1209.
- Chen H.-S. (1972a) The thermodynamics and composition of carbon dioxide hydrate. M.S. thesis, Syracuse Univ.
- Chen H.-S. (1972b) The properties of carbon dioxide hydrate. In *Office of Saline Water, Research and Development Progress Report No. 830, November 1972*, 1–55.
- Chueh P. L. and Prausnitz J. M. (1967) Vapor-liquid equilibria at high pressures. Vapor-phase fugacity coefficients in nonpolar and quantum-gas mixtures. *Ind. Eng. Chem. Fundam.* **6**, 492–498.
- Collins M. J., Ratcliffe C. I., and Ripmeester J. A. (1990) Nuclear

- Magnetic Resonance studies of guest species in clathrate hydrates: line-shape anisotropies, chemical shifts, and the determination of cage occupancy ratios and hydration numbers. *J. Phys. Chem.* **94**, 157–162.
- Collins P. L. F. (1979) Gas hydrates in CO₂-bearing fluid inclusions and the use of freezing data for estimation of salinity. *Econ. Geol.* **74**, 1435–1444.
- Cramer S. D. (1982) The solubility of methane, carbon dioxide, and oxygen in brines from 0° to 300°C. *Rep. U.S. Bur. Mines* **8706**, 1–14.
- Davidson D. W. (1973) Clathrate hydrates. In *Water in Crystalline Hydrates; Aqueous Solutions of Simple Nonelectrolytes* (ed. F. Franks), Vol. 2, pp. 155–234. Plenum Press.
- Darling R. S. (1991) An extended equation to calculate NaCl contents from final clathrate melting temperatures in H₂O-CO₂-NaCl fluid inclusions: Implications for P-T isochore location. *Geochim. Cosmochim. Acta* **55**, 3869–3871.
- Deaton W. M. and Frost E. M., Jr. (1946) Gas hydrates and their relation to operation of natural-gas pipe lines. *U.S. Bureau of Mines Monograph* **8**, 1–108.
- Debye P. and Hückel E. (1923) Zur Theorie der Electrolyte I: Gefrierpunktniedrigung und verwandte Erscheinungen. *Phys. Z.* **24**, 185–206.
- Dharmawardhana P. B., Parrish W. R., and Sloan E. D., Jr. (1980) Experimental thermodynamic parameters for the prediction of natural gas hydrate dissociation conditions. *Ind. Eng. Chem. Fundam.* **19**, 410–414.
- Dholabhai P. D., Kalogerakis N., and Bishnoi P. R. (1993) Equilibrium conditions for carbon dioxide hydrate formation in aqueous electrolyte solutions. *J. Chem. Eng. Data* **38**, 650–654.
- Diamond L. W. (1992) Stability of CO₂ clathrate hydrate + CO₂ liquid + CO₂ vapour + aqueous KCl-NaCl solutions: Experimental determination and application to salinity estimates of fluid inclusions. *Geochim. Cosmochim. Acta* **56**, 19–41.
- Diamond L. W. (1994a) Salinity of multivolatile fluid inclusions determined from clathrate hydrate stability. *Geochim. Cosmochim. Acta* **58**, 19–41.
- Diamond L. W. (1994b) Introduction to phase relations of CO₂-H₂O fluid inclusions. In *Fluid Inclusions in Minerals: Methods and Applications, Short Course IMA* (ed. B. de Vivo and M. L. Frezzotti), pp. 131–158.
- Duan Z., Møller N., and Weare J. H. (1992a) An equation of state for the CH₄-CO₂-H₂O system: I. Pure systems from 0 to 1000°C and 0 to 8000 bar. *Geochim. Cosmochim. Acta* **56**, 2605–2617.
- Duan Z., Møller N., and Weare J. H. (1992b) An equation of state for the CH₄-CO₂-H₂O system: II. Mixtures from 50 to 1000°C and 0 to 1000 bar. *Geochim. Cosmochim. Acta* **56**, 2619–2631.
- Dubessy J., Thiery R., and Canals M. (1992) Modelling of phase equilibria involving mixed gas clathrates: application to the determination of molar volume of the vapour phase and salinity of aqueous solution in fluid inclusions. *European J. Mineral.* **4**, 873–884.
- Englezos P. (1992) Computation of the incipient equilibrium carbon dioxide hydrate formation conditions in aqueous electrolyte solutions. *Ind. Eng. Chem. Res.* **31**, 2232–2237.
- Englezos P. and Bishnoi P. R. (1988) Prediction of gas hydrate formation conditions in aqueous electrolyte solutions. *AIChE J.* **34**, 1718–1721.
- Englezos P. and Hall S. (1994) Phase equilibrium data on carbon dioxide hydrate in the presence of electrolytes, water soluble polymers and montmorillonite. *Canadian J. Chem. Eng.* **72**, 887–893.
- Fleyfel F. and Devlin J. P. (1991) Carbon dioxide clathrate hydrate epitaxial growth: spectroscopic evidence for formation of the simple type-II CO₂ hydrate. *J. Phys. Chem.* **95**, 3811–3815.
- Gambill W. R. (1957) You can predict heat capacities. *Chem. Eng.* **64**, 243–248.
- Giauque W. F. and Stout J. W. (1936) The entropy of water and the third law of thermodynamics. Heat capacity of ice from 15 to 273°K. *J. Amer. Chem. Soc.* **58**, 1144–1150.
- Hafemann D. R. and Miller S. L. (1969) The clathrate hydrates of cyclopropane. *J. Phys. Chem.* **73**, 1392–1397.
- Hammerschmidt E. G. (1939) Preventing and removing gas hydrate formations in natural gas pipe lines. *Oil Gas J., May 1939*, 66–72.
- Handa Y. P. and Tse J. S. (1986) Thermodynamic properties of empty lattices structure I and structure II clathrate hydrates. *J. Phys. Chem.* **90**, 5917–5921.
- Helgeson H. C. and Kirkham D. H. (1974) Theoretical prediction of the thermodynamic behavior of the aqueous electrolytes at high pressure and temperatures: I. Summary of the thermodynamic/electrostatic properties of the solvent. *Amer. J. Sci.* **274**, 1089–1198.
- Hirschfelder J. O., Curtiss C. F., and Bird R. B. (1954) *Molecular Theory of Gases and Liquids*, pp. 1110–1111. Wiley.
- Holder G. D., Corbin G., and Papadopoulos K. D. (1980) Thermodynamic and molecular properties of gas hydrates from mixtures containing methane, argon, and krypton. *Ind. Eng. Chem. Fundam.* **19**, 282–286.
- Hollister L. S. and Burruss R. C. (1976) Phase equilibria in fluid inclusions from the Khtada Lake metamorphic complex. *Geochim. Cosmochim. Acta* **40**, 163–175.
- Holmes H. F. and Mesmer R. E. (1983) Thermodynamic properties of aqueous solutions of the alkali metal chlorides to 250°C. *J. Phys. Chem.* **87**, 1242–1255.
- John V. T., Papadopoulos K. D., and Holder G. D. (1985) A generalized model for predicting equilibrium conditions for gas hydrates. *Am. I. Chem. Eng. J.* **31**, 252–259.
- Jones J. E. (1924) On the determination of molecular fields II: From the equation of state of a gas. *Proc. Roy. Soc. A* **106**, 463–477.
- Kell G. S. (1967) Precise representation of volume properties of water at one atmosphere. *J. Chem. Eng. Data* **12**, 66–69.
- Kell G. S. and Whalley E. (1965) The PVT properties of water I. Liquid water in the temperature range 0 to 150°C and at pressures up to 1 kb. *Phil. Trans. Royal Soc.* **258A**, 565–614.
- Kihara T. (1953) Virial coefficients and models of molecules in gases. *Rev. Modern Phys.* **25**, 831–843.
- Kopp H. (1866) Investigations of the specific heat of solid bodies. *J. Chem. Soc.* **4**, 154–234.
- Krichevsky I. R. and Kasarnowsky J. S. (1935) Thermodynamical calculations of solubilities of nitrogen and hydrogen in water at high pressures. *J. Amer. Chem. Soc.* **57**, 2168–2172.
- Langmuir I. (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Amer. Chem. Soc.* **40**, 1361–1403.
- Larson S. D. (1955) Phase studies of the two-component carbon dioxide-water system involving the carbon dioxide hydrate. Ph.D. dissertation, Univ. Michigan.
- Lundgaard L. and Møllerup J. (1991) The influence of gas phase fugacity and solubility on correlation of gas-hydrate formation pressure. *Fluid Phase Eq.* **70**, 199–213.
- Lundgaard L. and Møllerup J. (1992) Calculation of phase diagrams of gas-hydrates. *Fluid Phase Eq.* **76**, 141–149.
- Makogon Y. F. (1981) *Hydrates of Natural Gas*. Translated from the Russian by W. J. Cieslesicz Pennwell Books, Tulsa, Oklahoma.
- Menten P. D., Parrish W. R., and Sloan E. D. (1981) Effect of inhibitors on hydrate formation. *Ind. Eng. Chem. Process Des. Dev.* **20**, 399–401.
- McKoy V. and Sinanoglu O. (1963) Theory of dissociation pressures of some gas hydrates. *J. Chem. Phys.* **38**, 2946–2956.
- Miller B. and Strong E. R., Jr. (1945) Possibilities of storing natural gas in the form of a solid hydrate. *Amer. Gas. Assn.*, 80–94.
- Møller N. (1988) The prediction of mineral solubilities in natural waters: A chemical equilibrium model for the Na-Ca-Cl-SO₄-H₂O system, to high temperature and concentration. *Geochim. Cosmochim. Acta* **52**, 821–837.
- Monnin C. and Schott J. (1984) Determination of the solubility products of sodium carbonate minerals and an application to trona deposition in Lake Magadi, Kenya. *Geochim. Cosmochim. Acta* **48**, 571–581.
- Moore J. C., Battino R., Rettich T. R., Handa Y. P., and Wilhelm E. (1982) Partial molar volumes of “gases” at infinite dilution in water at 298.15 K. *J. Chem. Eng. Data* **27**, 22–24.
- Munck J., Skjold-Jørgensen S., and Rasmussen P. (1988) Computations of the formation of gas hydrates. *Chem. Eng. Sci.* **43**, 2661–2672.
- Ng H.-J. and Robinson D. B. (1976) The measurement and predic-

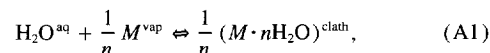
- tion of hydrate formation in liquid hydrocarbon-water systems. *Ind. Eng. Chem. Fundam.* **15**, 293–298.
- Ng H.-J. and Robinson D. B. (1977) The prediction of hydrate formation in condensed systems. *AIChE J.* **23**, 477–482.
- Ng H.-J. and Robinson D. B. (1985) Hydrate formation in systems containing methane, ethane, propane, carbon dioxide or hydrogen sulfide in the presence of methanol. *Fluid Phase Eq.* **21**, 145–155.
- Osborne N. S., Stimson H. F., and Ginnings D. C. (1939) Measurements of heat capacity and heat of vaporization of water in the range 0° to 100°C. *J. Res. Natl. Bur. Std.* **23**, 197–260.
- Parrish W. R. and Prausnitz J. M. (1972) Dissociation pressure of gas hydrates formed by gas mixtures. *Ind. Eng. Chem. Proc. Des. Dev.* **11**, 26–35.
- Pauling L. (1945) *The Nature of the Chemical Bond*. Cornell Univ. Press.
- Peng D.-Y. and Robinson D. B. (1976) A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **15**, 59–64.
- Pitzer K. S. (1973) Thermodynamics of electrolytes. I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268–277.
- Pitzer K. S. (1992) Ion interaction approach: theory and data correlation. In *Activity Coefficient in Electrolyte Solutions* (ed. K. S. Pitzer), pp. 76–153. CRC Press.
- Pitzer K. S., Peiper J. C., and Busey R. H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **13**, 1–102.
- Powell H. J. M. (1948) The structure of molecular compounds. Part IV. Clathrate Compounds. *J. Chem. Soc.*, 61–73.
- Redlich O. and Kwong J. N. S. (1949) On the thermodynamics of solutions V: an equation of state. Fugacities of gaseous solutions. *Chem. Rev.* **44**, 233–244.
- Ripmeester J. A. and Ratcliffe C. I. (1988) Low-temperature cross-polarization/magic angle spinning ¹³C NMR of solid methane hydrates: structure, cage occupancy, and hydration number. *J. Phys. Chem.* **92**, 337–339.
- Robinson D. B. and Mehta B. R. (1971) Hydrates in the propane-carbon dioxide-water system. *J. Canadian Petrol. Tech.* **10**, 33–35.
- Rodger P. M. (1990) Stability of gas hydrates. *J. Phys. Chem.* **94**, 6080–6089.
- Roedder E. (1963) Studies of fluid inclusions II: Freezing data and their interpretation. *Econ. Geol.* **58**, 167–211.
- Saito S., Marshall D. R., and Kobayashi R. (1964) Hydrates at high pressures: part II. Application of statistical mechanics to the study of the hydrates of methane, argon, and nitrogen. *Amer. J. Chem. Eng. J.* **10**, 734–740.
- Seitz J. C., Pasteris J. D., and Wopenka B. (1987) Characterization of CO₂-CH₄-H₂O fluid inclusions by microthermometry and laser Raman microprobe spectroscopy: Inferences for clathrate and fluid equilibria. *Geochim Cosmochim. Acta* **51**, 1651–1664.
- Setschenow J. (1889) Über die Konstitution der Salzlösungen auf grund ihres Verhaltens zu Kohlensäure. *Z. Phys. Chem.*, 117–125.
- Shmulovoch K. I. and Plyasunova N. V. (1993) Phase equilibria in ternary systems formed by H₂O, and CO₂ with CaCl₂ or NaCl at high T and P. *Geochem. Intl.* **30**, 53–71.
- Sloan E. D., Jr. (1990) *Clathrate Hydrates of Natural Gases*; *Chemical Industries* **39**. Marcel Dekker Inc.
- Soave G. (1972) Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **27**, 1197–1203.
- Sortland L. D. and Robinson D. B. (1964) The hydrates of methane and sulphur hexafluoride. *Canadian J. Chem. Eng.* **42**, 38–42.
- Takenouchi S. and Kennedy G. C. (1965) Dissociation of the phase CO₂-5.75H₂O. *J. Geol.* **73**, 383–390.
- Tee L. S., Gotoh S., and Steward W. E. (1966) Molecular parameters for normal fluids, Kihara potential with spherical core. *Ind. Eng. Chem. Fundam.* **5**, 363–367.
- Thurmond V. L. and Brass G. W. (1988) Activity and osmotic coefficients of NaCl in concentrated solutions from 0 to –40°C. *J. Chem. Eng. Data* **33**, 411–414.
- Unruh C. H. and Katz D. L. (1949) Gas hydrates of carbon dioxide-methane mixtures. *J. Petrol. Tech.* **1**, 83–86.
- van der Waals J. H. and Platteeuw J. C. (1959) Clathrate solutions. *Adv. Chem. Phys.* **2**, 1–57.

- Vlahakis J. G., Chen H.-S., Suwandi M. S., and Barduhn A. J. (1972) The growth rate of ice crystals: properties of carbon dioxide hydrate, a review of properties of 51 gas hydrates. *Syracuse University Research and Development Report*, 830.
- von Stackelberg M. (1954) Feste Gashydrate V: die Bindungsenergien. *Z. Electrochem.* **58**, 104–109.
- von Stackelberg M. and Müller H. R. (1954) Feste Gashydrate II: Struktur und Raumchemie. *Z. Electrochem.* **58**, 25–39.
- Weast R. C. (1968) *Handbook of Chemistry and Physics*. CRC Press.
- Whalley E. and Schneider W. G. (1955) Intermolecular potentials of argon, krypton, and xenon. *J. Chem. Phys.* **23**, 1644–1650.
- Wilhelm E., Battino R., and Wilcock R. J. (1977) Low pressure solubility of gases in liquid water. *Chem. Rev.* **77**, 219–262.
- Yerokhin A. M. (1993) A new method of determining CO₂ density and solution concentration in H₂O-CO₂-NaCl inclusions from the gas-hydrate melting point. *Geochem. Intl.* **30**, 107–129.
- Zhang Y.-G. and Frantz J. D. (1989) Experimental determination of the compositional limits of immiscibility in the system CaCl₂-H₂O-CO₂ at high temperatures and pressures using synthetic fluid inclusions. *Chem. Geol.* **74**, 289–308.

APPENDIX

A1. Equilibrium Between Clathrates and Vapour-Like Fluids (HL_wGC)

The formation (or dissociation) of clathrate can be represented by an equilibrium reaction (Eqn. A1) between three phases:



where M is a type of gas that is encaged and n is the amount of moles H₂O per mole of encaged gas. The vapour phase may be a mixture of gases, and the aqueous solution may contain several electrolytes besides dissolved gases. The chemical potential of each component (μ_i) must be equal for every phase in which that component is present at equilibrium conditions:

$$\mu_i^{\text{aq}} = \mu_i^{\text{vap}} = \mu_i^{\text{clath}}. \quad (\text{A2})$$

Only the chemical potential of H₂O in aqueous solutions and in clathrates are considered in clathrate modelling. Waals and Platteeuw (1959) used the partition function to express the chemical potential of a clathrate as a function of the distribution of gas molecules over all cavities. The clathrate behaves as an ideally dilute solution and fractional filling of the cavities reduces the chemical potential of H₂O (Eqn. A3) in the clathrate, thereby making it more stable.

$$\mu_{\text{H}_2\text{O}}^{\text{clath}} = \mu_{\text{H}_2\text{O}}^{\text{empty}} + RT \sum_i \nu_i \ln \left(1 - \sum_M y_{Mi} \right), \quad (\text{A3})$$

where $\mu_{\text{H}_2\text{O}}^{\text{empty}}$ is the chemical potential of a hypothetical empty clathrate, ν_i is the number of cavities of type i per cage forming H₂O molecule, and y_{Mi} is the probability of finding a gas molecule M in a cavity of type i .

A2. Langmuir Adsorption

Waals and Platteeuw (1959) established a relation between y_{Mi} and the Langmuir constant:

$$y_{Mi}(T, P) = \frac{C_{Mi} f_M}{1 + \sum_K (C_{Ki} f_K)}, \quad (\text{A4})$$

where C_{Mi} is the Langmuir constant for gas M in a cavity of type i and f_M is the fugacity of gas M . Equation A4 is a generalised notation for mixed hydrates, which contain more than one type of encaged gas species (M and K). The adsorption theory of Langmuir (1918) was transformed into a three dimensional generalisation of ideal localised adsorption, which assumes that the encaged gas molecules are not distorting the host lattice, which implies a small molecular size, that no mutual interactions exist between gas molecules, and that a cavity may contain maximally one gas molecule. Subse-

quently, the Langmuir constant was defined by molecular cell potentials within cavities:

$$C_{Mi}(T) = \frac{4\pi}{kT} \int_0^\infty \exp\left(\frac{-w(r)}{kT}\right) r^2 dr, \quad (\text{A5})$$

where r is the distance to the centre of the cage and $w(r)$ is the spherically symmetrical potential function describing the intermolecular potential between a gas molecule at the centre of the cage and a H₂O molecule of the cavity wall, which is averaged over all neighbouring H₂O molecules. The Lennard-Jones potential (Jones, 1924) was used as an approximation of the molecular potential.

A3. Thermodynamics of H₂O in Aqueous Solutions

The chemical potential of H₂O in aqueous solutions is defined by

$$\mu_{\text{H}_2\text{O}}^{\text{aq}}(T, P) = \mu_{\text{H}_2\text{O}}^{\text{pure}}(T, P) + RT \ln(a_{\text{H}_2\text{O}}), \quad (\text{A6})$$

where $a_{\text{H}_2\text{O}}$ is the activity of H₂O, which is by definition the product of the activity coefficient ($\gamma_{\text{H}_2\text{O}}$) and mole fraction ($x_{\text{H}_2\text{O}}$). The activity of H₂O in aqueous solutions is affected by dissolved substances. In electrolyte-free systems, dissolved gases appears to behave ideally due to low solubility's. Consequently, γ_i is unity for all components in the aqueous solution, and the solubility of gases is represented by Henry's Law (e.g., Wilhelm et al., 1977). The activity of H₂O in the aqueous solution (Eqn. A7) is defined by a combination of this law and the unity value of the sum of all mole fractions (x_i):

$$a_{\text{H}_2\text{O}}(T, P) = x_{\text{H}_2\text{O}} = 1 - \sum_M \left(\frac{f_M}{H_M} \right), \quad (\text{A7})$$

where f_M and H_M are the fugacity and Henry's constant of gas species M , respectively. Generally, relatively highly soluble gases like CO₂ significantly affect $a_{\text{H}_2\text{O}}$, and solubility of gases like CH₄ and N₂ can be neglected.

A4. Chemical Potential Difference $\Delta\mu$

An arbitrarily defined chemical potential difference $\Delta\mu$ (Eqn. A8) is obtained after substitution of Eqn. A3 in Eqn. A2:

$$\Delta\mu(T, P) \approx \mu_{\text{H}_2\text{O}}^{\text{empty}} - \mu_{\text{H}_2\text{O}}^{\text{aq}} = -RT \sum_i \nu_i \ln(1 - \sum_M y_{Mi}). \quad (\text{A8})$$

The chemical potential difference between H₂O in a hypothetical empty clathrate and pure liquid H₂O ($\Delta\mu^*$) is obtained after subtraction

of the $RT \ln(a_{\text{H}_2\text{O}})$ term from Eqn. A8. In order to determine $\Delta\mu^*$, Saito et al. (1964) described its temperature and pressure dependence with classical thermodynamics:

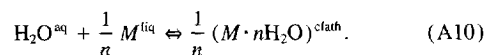
$$\frac{\Delta\mu^*}{RT}(T, P) = \frac{\Delta\mu_0^*}{RT_0} \int_{T_0}^T \left(\frac{\Delta h}{RT^2} \right) dT + \int_{P_0}^P \left(\frac{\Delta v}{RT} \right) dP \quad (\text{A9a})$$

$$\Delta h(T) = \Delta h_0 + \int_{T_0}^T (\Delta c_p) dT, \quad (\text{A9b})$$

where Δh , Δs , Δv , and Δc_p are the enthalpy difference, entropy difference, molar volume difference, and heat capacity difference between an empty clathrate and pure liquid H₂O, respectively. $\Delta\mu_0^*$ and Δh_0 are the chemical potential difference and the enthalpy difference at standard conditions. Integrated equations similar to Eqn. A9a are presented by, e.g., Parrish and Prausnitz (1972) and Holder et al. (1980). $\Delta\mu^*$ is considered a standard value for a given general hydrate structure, because it is not related to the type of encaged gas molecule or dissolved substances in the aqueous solution.

A5. Equilibrium Between Clathrates and Liquid-Like Fluids (HL_wLC)

The model of Ng and Robinson (1977) includes the prediction of the stability of clathrates in the presence of liquid-like fluid mixtures and is completely dependent on the estimation of the bubble point in multiple gas systems (Ng and Robinson, 1976) or the estimation of quadruple point Q₂ in single gas systems. The clathrate formation may be represented by a reaction (Eqn. A10) similar to Eqn. A1:



Ng and Robinson (1977) concluded from graphical analysis that the equilibrium curve was essentially linear, and could be reproduced by the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}, \quad (\text{A11})$$

where ΔV and ΔH are the molar volume change and the enthalpy change, respectively, that occur at the bubble point or at Q₂ conditions. ΔV is assumed to be constant along the equilibrium curve. Ng and Robinson (1977) obtained a relatively constant value for ΔH per mole clathrate former (65400 ± 2100 J/mol).