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# Modelling of phase equilibria involving mixed gas clathrates: Application to the determination of molar volume of the vapour phase and salinity of the aqueous solution in fluid inclusions

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**Abstract:** Modelling of clathrate stability in single component gases ($CO_2$, $CH_4$, $N_2$, $H_2S$ and $C_2H_6$) and of mixtures in systems with or without NaCl is described, and then applied to fluid inclusions in which the dissociation of clathrate occurs in the presence of a vapour phase. The chemical potential of the water component in clathrate is calculated from a combination of the models of Parrish & Prausnitz (1972) and of Munck *et al.* (1988). The Langmuir constants have been recalculated to obtain the best fit of the available experimental data on single gas systems. The dependence of the activity of water on the salt concentration in the aqueous solution is described by the model of Pitzer. Pressure is calculated with an uncertainty of less than 10 % along the dissolution curve of clathrate for single component gas systems and gas mixtures. The bulk salinity, expressed in equivalent NaCl concentration, can be derived from the melting temperature of ice in presence of the assemblage clathrate + vapour phase + aqueous solution, but is shown to be a function of the volume fraction of the vapour phase. The fugacity coefficient of the gas components and the molar volume of the vapour phase are computed from the Soave equation of state.

**Key-words:** clathrate stability, thermodynamic properties, fluid inclusions, molar volume, salinity.

## 1. Introduction

To a first approximation, fluid inclusions are constant volume and mass systems, determination of their V–X properties is the first step in any quantitative interpretation of paleo-fluid circulation based on fluid inclusion studies. A combination of microthermometric and micro-Raman measurements allows fairly accurate estimations of the V–X properties of the non-aqueous volatile portions of fluid inclusions, except if a gas clathrate is present at the homogenization temperature of the volatile phase (Ramboz *et al.*, 1985; Seitz *et al.*, 1987; Dubessy *et al.*, 1989). Recently, experimental data (Diamond, 1992) and a combination of experimental data and modelling by Diamond (submitted) have been carried out in order to achieve a better quantification of the salinity of fluid inclusions in the case of the homogenization of the carbonic phase in the presence of clathrate. However, the dissolution of clathrate in the presence of a vapour phase is often the only phase equilibrium which can yield information on the density of the vapour phase. Available experimental data on clathrate equilibria does not cover the whole range of compositions of natural fluid inclusions. Therefore, appropriate development of thermodynamic modelling of the stability of mixed gas clathrates ($CO_2$–$CH_4$–$N_2$–$C_2H_6$–$H_2S$) is essential (Seitz & Pasteris, 1990). The aim of this paper is to present the chosen model, to compare the model predictions with the experimental data and to discuss its application to fluid inclusions.

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## 2. Symbols and constant values

$a^{\phi}$: activity of component i in phase $\phi$
aq: aqueous solution
Cla: clathrate
e: charge of the electron = $1.60219 \cdot 10^{-19}$ C
g: vapour phase
H: enthalpy
k: Boltzmann constant = $1.38066 \cdot 10^{-23}$ (Joule $K^{-1}$)
ln: natural logarithm
log: decimal logarithm
$Mw_{H_2O}$: molecular weight of $H_2O$ = 18 $g \cdot mol^{-1}$
$Mw_{NaCl}$: molecular weight of NaCl = 58.5 $g \cdot mol^{-1}$
$m_{NaCl}$: NaCl molality
Na: Avogadro number = $6.022 \cdot 10^{23}$
P: pressure in bar
$P_{c,i}$ and $T_{c,i}$: critical pressure (bar) and temperature (°K) of gas component i
$P_{r,i}$: reduced pressure ($P/P_{c,i}$) of gas component i
R: perfect gas constant = 8.31441 (Joule $°K^{-1} \cdot mol^{-1}$)
T: temperature in ° Kelvin
$T_{r,i}$: reduced temperature ($T/T_{c,i}$) of gas component i
$V_{\phi}$: volume fraction of phase $\phi$
$\upsilon_{\phi}$: molar volume ($cm^{-3} \cdot mol^{-1}$) of phase $\phi$
$\upsilon^{\infty}$: partial molar volume of gas i at infinite dilution in aqueous solution
$X_i^{\phi}$: mole fraction of component i in phase $\phi$
$y_i$: mole fraction of gas i in the vapour phase g
Z: compressibility factor of the vapour phase g; $Z = P \cdot \upsilon_g/(RT)$
$\varepsilon_o$: vacuum permittivity = $8.854188 \cdot 10^{-12}$ ($Joule^{-1}\ C^2\ m^{-1}$)
$\varepsilon_r$: dielectric constant of pure water at 0 °C and 1 bar = 87.74
$\Phi$: practical osmotic coefficient
$\rho°aq$: density of pure water at 1 bar and 0 °C = 1000 $kg \cdot m^{-3}$
$\rho_{\phi}$: density ($g \cdot cm^{-3}$) of phase $\phi$
$\mu_{H_2O\phi}(P,T)$: chemical potential of $H_2O$ in phase $\phi$ at T and P
$\mu°_{H_2O\phi}$: chemical potential of $H_2O$ in phase $\phi$ at the reference state (P° = 1 bar and T° = 273.15 °K)
$\gamma_i$: fugacity coefficient of gas species i
$\gamma_{sc}$*: Setchenow coefficient

## 3. Thermodynamic models for clathrates

The aqueous solution – clathrate – vapour phase assemblage at equilibrium is described by the following equation:

$$\mu^{Cla}_{H_2O}(P,T) = \mu^{aq}_{H_2O} \quad (1)$$

Therefore, the problem is reduced to the modelling of two chemical potentials. The chemical potential of water in the aqueous solution (section 3.1) is calculated as a function of the salinity, in terms of the NaCl molality, and of solubility of gases. This calculation is carried out by a combination of the model of Pitzer, to account for the NaCl content, and of Raoult's Law to account for the concentration of the dissolved gas in the aqueous solution. Calculation of the chemical potential of water in clathrate is based on a statistical thermodynamic model based on the pioneering work of Van der Waals & Platteuw (1959). The model is briefly outlined in section 3.2 with all the equations necessary for its practical use. However, readers are referred to Sloan (1990) for a comprehensive description of the theory.

### 3.1. Chemical potential of $H_2O$ in aqueous solution

The chemical potential of water in aqueous solution, $\mu^{aq}_{H_2O}(P,T)$, is calculated from the activity of water. In salt-free aqueous solution, the activity of water is calculated from Raoult's Law taking into account the solubility of gases i using Henry's Law. Only $CO_2$ and $H_2S$ will be considered here, since they are the most soluble gaseous species in water that lower the activity of water in the aqueous solution suficiently enough to be measurable at the precision of microthermometric measurements.

$$a^{aq}_{H_2O} = 1 - [X^{aq}_{CO_2} + X^{aq}_{H_2S}] \quad (2)$$

$$X^{aq}_i = f(G)/K_{H,i}(P,T,0) \quad (3)$$

where $K_{H,i}(P, T, 0)$ is the Henry constant for the solubility of the gaseous species i in aqueous solution, at pressure P and temperature T, with a zero $m_{NaCl}$ molality, and f(i) is the gas fugacity calculated by the equation of state described below.

### 3.1.1. *Henry constant*

The equation of the Henry constant $K_{H,i}(1, T, 0)$ as a function of temperature is taken from Munck *et al.* (1988) based on the data and compilations of Wilhelm & Battino (1973) and Wilhelm *et al.* (1977):

$$\ln K_{H,i}(1, T, 0) = Ka + Kb/T + Kc \ln(T) + Kd\, T \quad (4)$$

where Ka = 162.39 (bar); Kb = –8880.6 (bar·K); Kc = –22.014 (bar/ln K); Kd = $1.1201 \cdot 10^{-4}$ (bar·$K^{-1}$) for $CO_2$
and Ka = 151.52; Kb = –8335.5; Kc = –20.499; KD = $-1.311 \cdot 10^{-3}$ for $H_2S$.

Theoretically, the Henry constant depends on pressure according to the following equation:

$$\ln K_{H,i}(P, T, 0) = \ln K_{H,i}(1, T, 0) + \upsilon_g^{\infty} (P-1) / (RT) \quad (5)$$

where $\upsilon_g^{\infty}$ is the partial molar volume of the dissolved gas at infinite dilution in the aqueous phase. For $CO_2$, $\upsilon_g^{\infty}$ = 33 $cm^3 \cdot mol^{-1}$ at 25 °C. For a maximum pressure of 50 bar, the second term of the right-hand-side of equation (5) is smaller than 0.05, resulting in negligible solubility variation. Therefore, the following approximation

$$\ln K_{H,CO_2}(P, T, 0) = \ln K_{H,CO_2}(1, T, 0) \quad (6)$$

is justified, as already used by several authors.

The dependence of the Henry constant on salinity is described by the empirical equation of Setchenow (Gerrard, 1980):

$$\ln \gamma_{sc}^{*} = \ln [K_{H,CO_2}(P, T, m_{NaCl}) / K_{H,CO_2}(P, T, 0)] = k_s \cdot m_{NaCl} \quad (7a)$$

where $k_s$ is the salting out coefficient. As the temperature interval of interest is rather small in these calculations, the $k_s$ value is considered to be constant and equal to its value at 0 °C for $CO_2$: 0.12 $molal^{-1}$ (Cramer, 1982).

For $H_2S$, the only available data are for temperatures higher than 25 °C (Drummond, 1981). The solubility data of Drummond (1981) in salt-free solution differs slightly from those of Wilhelm *et al.* (1977). Therefore, we have used the data of Drummond (1981) only for the calculation of the salt effect:

$$\ln [K_{H,H_2S}(P, T, m_{NaCl}) / K_{H,H_2S}(1, T, 0)] = 0.294 \cdot m_{NaCl} - 0.0001595 \cdot m_{NaCl} \cdot T - 46.81 \cdot m_{NaCl} / T - (.578+0.0018\, T) \cdot m_{NaCl} / [m_{NaCl} + 1] \quad (7b)$$

### 3.1.2. *Water activity in salt-bearing aqueous solutions*

For salt-bearing solutions, the model of Pitzer (1973) is used with fitted parameters between 0 and –40 °C (Thurmond & Brass, 1988), first to calculate the activity of water without gas. It is then multiplied by $\{1-[X^{aq}_{CO_2} + X^{aq}_{H_2S}]\}$.

The water activity is calculated from the following equations:

$$\ln a^{aq}_{H_2O} = -\Phi\, Mw_{H_2O} (m_{Na}+m_{Cl})/1000 = -\phi\, Mw_{H_2O} (2\, m_{NaCl})/1000 \quad (8)$$

where $\Phi$ is the practical osmotic coefficient calculated from equation (9)

$$\Phi - 1 = -A_\Phi\, m_{NaCl}^{1/2} / (1+1.2\, m_{NaCl}^{1/2}) + m_{NaCl}\, B_\Phi + m_{NaCl}^2\, C_\Phi \quad (9)$$

Detailed equations are given in Appendix 7.1 and values of all parameters (Thurmond & Brass, 1988) in Table 1.

### 3.1.3. *Molar volume and fugacity coefficients of gas components*

Four equations of state were checked on the P–υ–T–X properties of $CO_2$ and $CH_4$: Soave (1972), Peng & Robinson (1976), Heyen (1982), Heyen *et al.* (1982) and Patel & Teja (1982). The sources of thermodynamic data are the IUPAC tables ($CO_2$: Angus *et al.*, 1976; $CH_4$: Angus *et al.*, 1978). The pressure and temperature ranges used to assess the quality of these equations is the following: P (from 1 to 50 bar for $CO_2$ and 1 to 400 bar for $CH_4$) and T (from 270 to 300 °K). The relative deviations of the calculated molar volume, at given P and T in the single phase field with respect to experimental data, show that the Soave as well as the Patel and Teja equations are the most accurate. The Soave equation was therefore chosen for all the present calculations. The formula of the Soave equation of state is the following:

$$P = \{RT / (\upsilon_g - b)\} - a(T) / \{\upsilon_g(\upsilon_g + b)\} \quad (10)$$

Table 1. Coefficients for the calculation of the osmotic coefficient from the model of Pitzer and the values of Thurmond & Brass (1988).

| | | | | | |
|---|---|---|---|---|---|
| $x_1$ | 7.66249 | $x_2$ | $-1.00472 \cdot 10^{3}$ | $x_3$ | $-1.79001 \cdot 10^{-3}$ |
| $x_4$ | $1.15601 \cdot 10^{-5}$ | $x_5$ | $-1.90346 \cdot 10^{-8}$ | $x_6$ | $2.57468 \cdot 10$ |
| $x_7$ | $-3.25771 \cdot 10^{3}$ | $x_8$ | $-6.58529 \cdot 10^{-3}$ | $x_9$ | $4.49459 \cdot 10^{-5}$ |
| $x_{10}$ | $-7.86640 \cdot 10^{-8}$ | $x_{11}$ | $-5.34139 \cdot 10^{-1}$ | $x_{12}$ | $7.13101 \cdot 10$ |
| $x_{13}$ | $1.22262 \cdot 10^{-4}$ | $x_{14}$ | $-7.80262 \cdot 10^{-7}$ | $x_{15}$ | $1.27174 \cdot 10^{-9}$ |

Mixing rules are:

$$b_m = \sum y_i b_i \quad \text{and}$$

$$a_m(T) = \sum_i \sum_j y_i y_j a_{ij} \qquad (11a)$$

$$\text{with } a_{ii} = a_i \text{ and } a_{ij} = (1-\delta_{ij})(a_i a_j)^{1/2} \qquad (11b)$$

where is $\delta_{ij}$ an interaction parameter (Soave, 1972). All the equations required for the calculations are given in Appendix 7.2.

## 3.2. Chemical potential of $H_2O$ in clathrate

The chemical potential of water in clathrate, $\mu^{Cla}_{H_2O}$ (P,T), is calculated using the model of Van der Waals & Platteuw (1959), established from statistical thermodynamics:

$$\mu^{Cla}_{H_2O}(P,T) = \mu\beta(P,T) + RT \sum_i \nu_i \ln(1-\sum_j \Theta_{j,i}) \qquad (12)$$

where $\beta$ refers to a hypothetical empty hydrate state, $\nu_i$ is the number of cavities of type i, $\Theta_{j,i}$ is the fraction of type i cavity occupied by gas component j. All the clathrates of $CO_2$–$CH_4$–$H_2S$–$C_2H_6$ are of structure I and contain two small cavities and 6 large cavities for 46 $H_2O$ molecules per unit cell (Davidson, 1973). Recent crystallographic data have demonstrated that the structure of the $N_2$ clathrate is of type-II (Davidson *et al.*, 1986). As the adjustments for a structure of type-I are valid for the pure $N_2$ system and the different gas mixtures, this structure was the only one considered, which simplifies the calculations. $\Theta_{j,i}$ depends on the fugacity of each gas component according to the equation established by the Langmuir adsorption theory:

$$\Theta_{j,i} = C_{j,i} \cdot f_j / (1+\sum_k C_{k,i} \cdot f_k) \qquad (13)$$

where $C_{j,i}$ is the Langmuir constant which accounts for the interaction between gas j and $H_2O$ molecules in the different cavities, and $f_j$ is the fugacity of gas comonent j. Therefore, the calculation of the chemical potential of water requires an estimation of the Langmuir constants and $\mu^{\beta}(P,T)$ which is the chemical potential of the hypothetical empty clathrate lattice at P and T.

### 3.2.1. *Calculation of* $\mu^{\beta}(P,T)$

Munck *et al.* (1988) calculated $\mu^{\beta}(P,T)$ from the difference $\mu^{\beta}(P,T) - \mu^{aq}_{H_2O}(P,T)$ by integrating over P and T and using the corresponding differences in enthalpy, molar volume and constant pressure heat capacity at the reference state ($P^\circ$ = 1 bar and $T^\circ$ = 273.15) given in Table 2.

Table 2. Thermodynamic constants used for the calculation of $\mu_{\beta}(P,T) - \mu_{H_2O_l}(P,T)$ from Munck *et al.* (1988).

| Property | Unit | Value |
|---|---|---|
| $\mu^\circ_\beta - \mu^\circ_{aq}$ | $J \cdot mol^{-1}$ | 1264 |
| $H^\circ_\beta - H^\circ_{H_2O_l}$ | $J \cdot mol^{-1}$ | –4858 |
| $v^\circ_\beta - v^\circ_{H_2O_l}$ | $cm^3 \cdot mol^{-1}$ | 4.6 |
| $Cp^\circ_\beta - Cp^\circ_{H_2O_l}$ | $J \cdot mol^{-1} \cdot K^{-1}$ | –39.16 |

### 3.2.2. *Calculation of the Langmuir constants*

The model of Parrish & Prausnitz (1972) is satisfactory for single gas clathrates but rather poor for some gas mixtures (Peng & Robinson, 1976). The model of Munck *et al.* (1988) is quite realistic for single gas systems and mixtures with $X(CO_2) < 0.5$: for pure $CO_2$ fluids, and a fixed pressure, the dissolution temperature of clathrate was shifted by 0.5 °C towards lower temperature values. The poor agreement of the model of Munck *et al.* (1988) for $CO_2$-rich fluids is probably due to their estimation of the Langmuir constants from the experimental data given by Berecz & Balla-Achs (1983). The experimental data of Deaton & Frost (1940), Unruh & Katz (1949), Robinson & Mehta (1971) and Bozzo *et al.* (1976) are mutually consistent but signifi-

cantly different from those of Berecz & Balla-Achs (1983). Therefore, we used the set of consistent experimental data to calculate the parameters of the Langmuir constant. The Langmuir constants are calculated from the following equation:

$$C_{j,i}(T) = 4\pi/kT \int \exp(-\omega_{j,i}(r)/kT) \cdot r^2 dr \qquad (14)$$

where $\omega_{j,i}(r)$ is the cell potential of gas j in cavity i.

The cell potential can be calculated in two ways: (1) from the McKoy & Simanoglu (1963) formula, which assumes a Kihara potential $\Gamma_{j,i}(r)$ with a spherical core between water and gas molecules (appendix (3); Parrish & Prausnitz, 1972); or (2) assuming a square well potential $\Gamma(r)$ which simplifies the calculation of the integral in equation (14), thereby reducing equation (14) as follows:

$$C(T) = (A/T) \cdot \exp(B/T) \qquad (15)$$

The first model was chosen because only three parameters (a, $\sigma$ and $\varepsilon$) characteristic of the Kihara potential need to be determined and because the Langmuir constant is insensitive to variations of the a parameter. Values of the a, $\sigma$ and $\varepsilon$ parameters were obtained from a best-fit regression of the available experimental data (Table 3).

Table 3. a, $\sigma$ and $\varepsilon$ parameters of the Kihara potential used for the calculation of the Langmuir constants (appendix 7.3) and references of the experimental data.

| | a(pm) | $\sigma$(pm) | $\varepsilon$/k(K) | References |
|---|---|---|---|---|
| $CO_2$ | 70.3 | 295.8 | 170.00 | (a), (b), (d) |
| $CH_4$ | 30.0 | 327.0 | 152.00 | (b), (c), (d) |
| $N_2$ | 35.0 | 328.0 | 126.25 | (c), (e) |
| $C_2H_6$ | 40.0 | 344.0 | 175.0 | (b) |
| $H_2S$ | 35.0 | 325 | 197.0 | (f) |

(a): Bozzo *et al.* (1975); (b): Deaton & Frost (1946); (c) Marshall *et al.* (1964); (d): Robinson & Mehta (1971); (e): van Cleeff & Diepen (1960); Selleck *et al.* (1952).

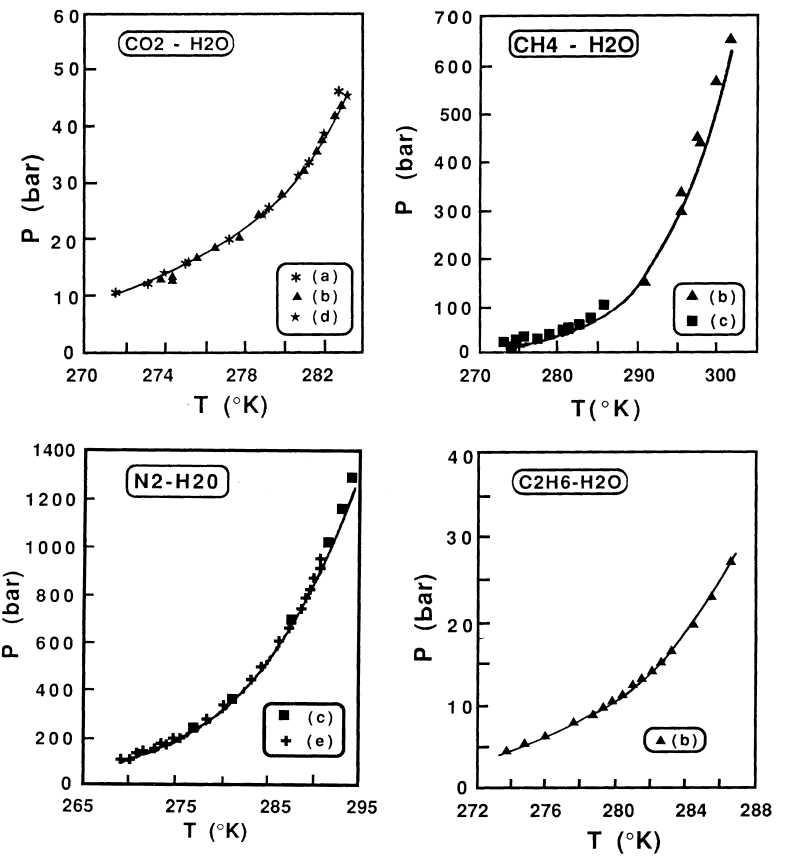


Fig. 1. Experimental and calculated pressure of pure gas clathrates versus temperature. References of experimental data are the same as those given in Table 3.

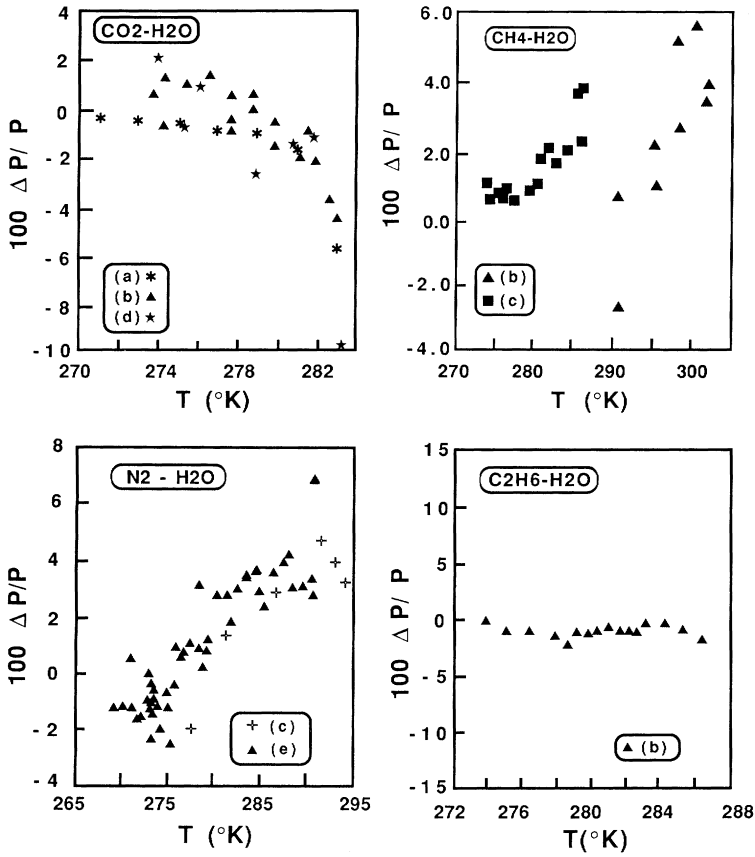


Fig. 2. Relative error {100 (Pexp–Pcalc)/(Pcalc} versus temperature for pure gas clathrate systems. Pexp: experimental pressure; Pcalc: calculated pressure from the model.

## 4. Results

### 4.1. Salt-free systems

Comparisons between experimental determinations of clathrate-gas-aqueous solution equilibria and the predictions of the present model are given in Figures 1 and 2. The relative deviation between experimental and calculated pressure at given temperature is always better than 6 %, which demonstrates the quality of the model and the adjusted parameters. Most of the calculated values show a smaller deviation. The relative deviation on pressure shows a trend with temperature except for $CH_4$. Indeed, the experimental data of the $CH_4$ clathrate were obtained by three groups of experimentalists on different P–T interval ranges, and thus show some inconsistencies. Usually, authors check the validity of their clathrate models using the relative deviation of the dissociation temperature at a given pressure, although temperature is a less sensitive parameter. The deviation in temperature is less than 0.3 K even for $CO_2$.

The model has also been also checked for several binary mixtures: $CH_4$–$CO_2$ (Fig. 3); $CH_4$–$C_2H_6$; $CH_4$–$N_2$. The relative deviation of pressure is slightly greater than for the pure end-members and can reach 10 % on individual sets of experimental data. Even if the uncertainties in pressure are rather high, the model predictions are of the same quality as the model of John *et al.* (1985) and Munck *et al.* (1988).

### 4.2. The $CO_2$–$H_2O$–NaCl system

The only available experimental data on a NaCl-bearing system are given by Bozzo *et al.* (1975). The relative uncertainty of the model predictions increases with the NaCl concentration, but remains always less than 10 % (Fig. 4).

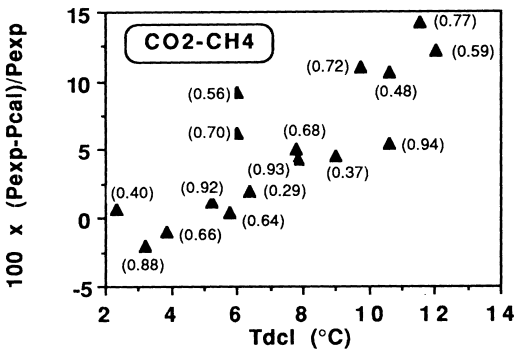


Fig. 3. Relative error {100 (Pexp–Pcalc)/Pexp} versus temperature for the binary $CO_2$–$CH_4$ system. The mole fraction of $CH_4$ is given in parentheses. The experimental pressures are those of Unruh & Katz (1949).

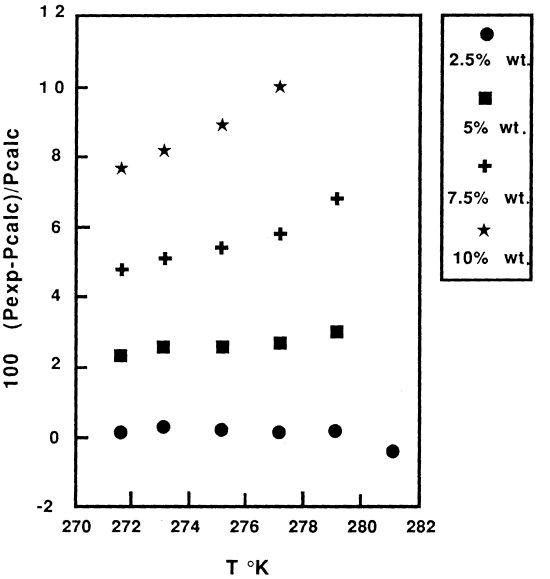


Fig. 4. Relative error {100 (Pexp–Pcalc)/Pcalc} versus temperature for the $CO_2$–$H_2O$–NaCl system. The numbers indicate the NaCl concentration in weight %.

## 5. Application to fluid inclusions

### 5.1. Variance analysis

For the application of the clathrate model to fluid inclusions, the composition of the vapour phase is assumed to be known from Raman microspectrometric analysis. The water salinity, referred to the $H_2O$–NaCl system, and the pressure of the vapour phase are the two unknowns which have to be determined from microthermometric measurements and the modelling of clathrate stability. At the melting temperature of ice, the phase assemblage is the following: ice – liquid water – clathrate – vapour phase. Since the temperature is known, the variance of the system is v = c+1–4 = c–3 where c is the number of independent components. For a fluid inclusion with only one gas component, c = 3 ($H_2O$–NaCl-Gas) and v = 0. Therefore, the composition of each phase is fixed. This implies that the salinity of the aqueous phase can be determined. If the system contains n gases, the variance of the system is increased by n–1 but, as analysis of the vapour phase yields n–1 mole fractions, the number of unknown variables remains zero. From the temperature of ice melting (TmIce) to the temperature of clathrate dissolution (TdCla), the clathrate releases water which lowers the salinity of the aqueous phase compared to its salinity at TmIce. Thus, the salinity of the aqueous phase and the pressure of the vapour phase at TdCla would be overestimated if the salinity were directly derived from TmIce without taking into account the trapping of water molecules by clathrate.

Cases are known to fractionate differently between the vapour phase and clathrate. Therefore, the composition of the vapour phase at TmIce is not strictly equal to its composition at TdCla. This point is addressed separately after the problem of salinity estimation.

### 5.2. Salinity calculation from TmIce

The number of moles $N_{i(t)}$ of component i at TmIce (t=1) and TdCla (t=2) are given by the following equations:

For $H_2O$:

$$n_{H_2O(1)} = \rho_{aq(1)} \cdot V_{aq(1)} / \{Mw_{H_2O}(1000+Mw_{NaCl} \cdot m_{NaCl(1)})\} + X^{Cla}_{H_2O(1)} \cdot V_{Cla(1)}/\upsilon_{Cla} \quad (16a)$$

where $X^{Cla}_{H_2O(1)}$ is the mole fraction of water molecules in clathrate at TmIce.

$$n_{H_2O(2)} = \rho_{aq(2)} \cdot V_{aq(2)} / Mw_{H_2O}(1000+Mw_{NaCl} \cdot m_{NaCl(2)}) \quad (16b)$$

$\rho_{aq(1)}$ and $\rho_{aq(2)}$ are calculated from the model of Potter & Brown (1977).

For NaCl:

$$n_{NaCl(1)} = \rho_{aq(1)} \cdot m_{NaCl(1)} \cdot V_{aq(1)} / (1000 + Mw_{NaCl} \cdot m_{NaCl(1)}) \quad (17a)$$

$$n_{NaCl(2)} = \rho_{aq(2)} \cdot m_{NaCl(2)} \cdot V_{aq(2)} / (1000 + Mw_{NaCl} \cdot m_{NaCl(2)}) \quad (17b)$$

For a gas component i, the mass balance equation involves the volume fraction of the vapour phase at TmIce and TdCla, which are respectively $V_{g(1)}$ and $V_{g(2)}$:

$$n_{i(1)} = V_{g(1)} / \upsilon_{g(1)} + X^{Cla}_{i(1)} \cdot V_{Cla(1)} / \upsilon_{Cla} + X^{aq}_{i(1)} \cdot (n_{H_2O(1)} + n_{NaCl(1)}) \quad (18a)$$

$$n_{i(2)} = V_{g(2)} / \upsilon_{g(2)} + X^{aq}_{i(2)} \cdot (n_{H_2O(2)} + n_{NaCl(2)}) \quad (18b)$$

where $X^{Cla}_{i(1)}$ is the mole fraction of gas component i in the clathrate at TmIce and $X^{aq}_{i(1)}$ is the mole fraction of gas i in the aqueous solution at temperature (t).

The three equations of mass conservation of the type $n_{i(1)} = n_{i(2)}$ are written using equations (16a) to (18b). The unknowns are $n_{H_2O(2)}$, $n_{NaCl(2)}$ and $n_{i(2)}$. Other unknowns are $V_{g(1)}$, $V_{Cla(1)}$ and $m_{NaCl(2)}$. $V_{g(2)}$ is estimated optically under the microscope. $m_{NaCl(1)}$ is calculated from the melting ice temperature from the Pitzer model. $V_{g(1)}$,

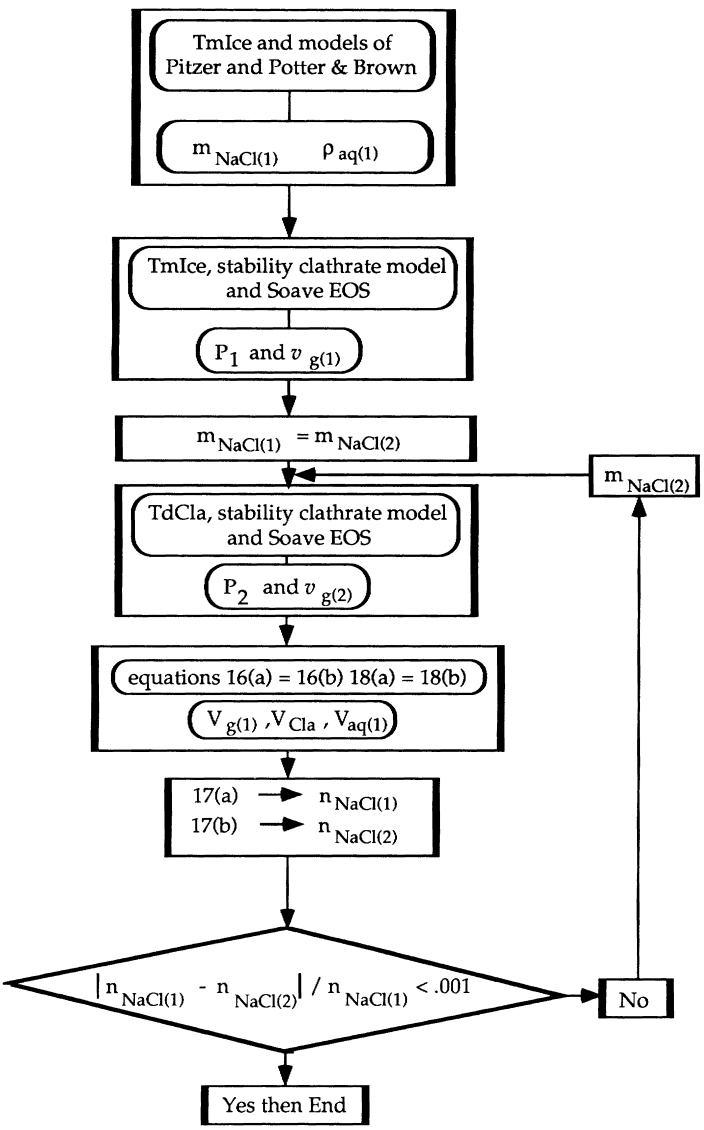


Fig. 5. Algorithm for the calculation of salinity from TmIce, TdCla and $V_{g(2)}$. EOS: equation of state.

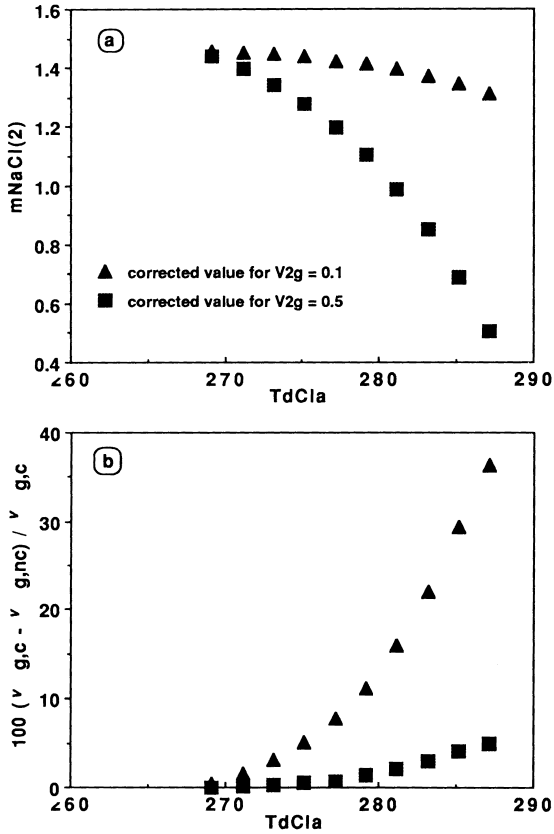


Fig. 6. Influence of the volume fraction of the vapour phase on the estimation of the correct salinity of the aqueous solution and the molar volume of the vapour phase. The vapour phase is assumed to contain only $CH_4$. TmIce = –5 °C. – a: variation of the NaCl molality of the aqueous solution versus TdCla for two volume fractions of the vapour phase at TdCla. b: relative error made on the molar volume of the vapour phase versus TdCla if the salinity of the aqueous solution was directly derived from TmIce. $\upsilon_{g,c}$: correct molar volume of the gas phase calculated at TdCla for a salinity calculated iteratively by the procedure described in Figure 6; $\upsilon_{g,nc}$: uncorrected molar volume of the vapour phase if the salinity is derived from TmIce and used for the calculation of the vapour pressure at TdCla.

$V_{Cla(1)}$ and $m_{NaCl(2)}$ are calculated by trial and error, the molar volume of the vapour phase at TdCla is calculated by the model from the pressure $P_I$ at TmIce. The algorithm of this calculation is described in Apendix 7.4 and in Figure 5. Numerical results are strongly dependent on the amount of vapour phase ($V_{g(2)}$) (Fig. 6a and 6b). For instance, $m_{NaCl(2)}$ is half of $m_{NaCl(1)}$ for $V_{g(2)}$ = 0.5. Obviously, the greater is the difference TdCla-TmIce, the greater is $m_{NaCl(2)} - m_{NaCl(1)}$. In addition, the molar volume of the vapour phase is underestimated if the salinity at TdCla is considered to be equal to $m_{NaCl(1)}$ instead of $m_{NaCl(2)}$ as calculated by the computer program. These calculations indicate that both the salinity and the vapour phase molar volume cannot be derived directly from TmIce: $V_{g(2)}$ and TdCla must be taken into account.

### 5.3. Influence of gas fractionation on salinity determination

The fractionation of the different gases between clathrate and vapour phase can be taken into account in the mass balance equations. The mass balance equations for $H_2O$ and NaCl remain identical to equations (16) and (17). The modifications concerning the gas components i are:

$$n_{i(1)}=y_{i(1)} \cdot V_{g(1)}/\upsilon_{\gamma(1)} + X^{Cla}_{i(1)} \cdot V_{Cla(1)}/\upsilon_{X\lambda\alpha} \quad X^{aq}_{i(1)} \cdot (n_{H_2O(1)} + n_{NaCl(1)}) \qquad (19a)$$

$$n_{i(2)} = y_{i(2)} \cdot V_{g(2)} / \upsilon_{g(2)} \quad X^{aq}_{i(2)} \cdot (n_{H_2O(2)}) + n_{NaCl(2)}) \qquad (19b)$$

Calculations show that there is a negligible influence of gas fractionation between TmIce and TdCla on the estimation of salinity. Indeed, the molar volume $5120_{g(1)}$ and $m_{NaCl(1)}$ are the only parameters affected by this effect. However, $m_{NaCl(1)}$ can be considered as constant since the variation of the activity coefficient of water does not vary significantly with pressure over an interval smaller than 10 bar, water being considered an incompressible fluid in the P–T interval of interest.

## 6. Conclusion

The model proposed in this paper predicts, with a satisfactory accuracy, the pressure of the vapour phase at the dissolution temperature of the gas clathrate in single component gas systems. The slightly larger uncertainty for gas mixtures is probably related to erratic variations in the quality of the experimental data. However, this model provides a good estimation of the molar volume of the vapour phase and salinity of the aqueous

solution using gas compositions determined by micro-Raman analysis and the microthermometry of phase equilibria involving gas clathrates. This resolves the problem of the determination of both the aqueous solution salinity and the vapour phase density in gas-bearing fluid inclusions, a difficult problem already pointed out by Ramboz *et al.* (1985) and Thomas & Spooner (1988). Such a model could also be used to derive the salinity of the aqueous solution in the case where clathrate dissolves in the presence of the $CO_2$-rich vapour and liquid phases, but this requires further research. Finally, this model may also be used to predict the behaviour of clathrates in natural environments, such as in permafrosts in continental environments or in sediments (Mako-gon *et al.*, 1972; Kvenvolden, 1988; Sloan, 1990).

## 7. Appendices

### 7.1. Equations for the calculation of the osmotic coefficient (equation 9)

$$A\Theta = (2\Pi\, Na\, \rho^{\circ}_{aq})^{1/2} \{e^2/(4\pi\varepsilon_0\varepsilon_r kT)\}^{1.5}$$

$$B\Theta = \beta^{(0)} + \beta^{(1)} \exp(-2 \cdot (m_{NaCl})^{1/2}$$

where $\beta^{(0)} = 2x_1 + 2x_2/T + x_3 T^2/6 + x_4T^3/12 + x_5T^4/20$

$\beta^{(1)} = 2x_6 + 2x_7/T + x_8T^2/6 + x_9T^3/12 + x_{10}T^4/20$

$C\Theta/2 = 2x_{11} + 2x_{12}/T + x_{13}T^2/6 + x_{14}T^3/12 + x_{15}T^4/20$

Values of $x_i$ parameters are given in Table 1.

### 7.2. Equations related to the Soave equation of state (equations 10, and 11)

The $a_i(T)$ and $b_i$ parameters for a gas i are calculated from the following equations:

$a_i(T) = \{0.42747\ (R\ T_{c,i})^2 / Pc,i\}\ \alpha_i(T)$

with $\{\alpha_i(T)\}^{0.5} = 1 + F_i\ (1-T_{r,i}^{0.5})$

and $F_i = 0.480 + 1.574\ \omega_i - 0.176\ \omega_i^2$

where $\omega_i$ is the acentric factor of gas species i calculated from the equation: $-1-\omega_i = \log (P_{r,i})$ for $T_{r,i} = 0.7$ along the saturation curve.

$b_i = 0.08664\ R\ T_{c,i}/P_{c,i}$

The fugacity $\gamma_i$ coefficient of a pure component is calculated from the equation:

$$\ln(\gamma_i) = Z-1-\ln(Z-B_i) - A_i/B_i \ln\{(Z+B_i)/B_i\}$$

where $A_i = \alpha_i(T)P/(RT)^2 = 0.42747\ \alpha_i(T)\ P_{r,i}/\{T_{r,i}\}^2$

and $B_i = b_iP/RT = 0.08664\ P_{r,i}/T_{r,i}$

The fugacity coefficient of the gas species i in a mixture is calculated from the equation:

$$\ln(\gamma_i) = (b_i/b_m)(Z-1) - \ln(Z-B_m) - A_m/B_m\ \{2(a_i/a_m)^{0.5} - (b/b_m)\}\ln(1+B_m/Z)$$

where $A_m = 0.42747\ P/T^2\{\Sigma\ y_i\ T_{c,i}\ a_i^{0.5}/P_{c,i}^{0.5}\}^2$

and $B_m = 0.08664\ P/T\{\Sigma\ y_i\ T_{c,i}/P_{c,i}\}$

### 7.3. Derivation of the spherically symmetric cell potential $\omega(r)$ for equation (14)

The Kihara potential used by Parrish & Prausnitz (1972) and in this work, describes the interaction between the gas molecule inside its cavity and an $H_2O$ molecule of the wall. It is defined by the following equations:

$\Gamma(r) = \infty, r \le 2a$

$\Gamma(r) = 4\ \varepsilon\ \{[\sigma/(r-2a)]^{12} - [\sigma/(r-2a)]^6\}$

where $\varepsilon$ is the characteristic energy, a is the core radius and $\sigma$+2 the collision parameter.

Summing over all the gas-$H_2O$ interactions in the cell, Parrish & Prausnitz (1972) give the cell potential $\omega(r)$ (McKoy & Simanoglu, 1963):

$$\omega(r) = 2z\varepsilon\{\sigma^{12}\ (\delta^{10} + a/[R\delta^{11}])\ /\ R^{11}r - \sigma^6\ (\delta^4 + a/[R\delta^5])\ /\ R^5r\}$$

where $\delta^N = \{(1 - r/R - a/R)^{-N} - (1 + r/R - a/R)^{-N}\}/N$

with z, the coordination number in cavities (20 and 24), 2R, the cell diameter (7.95 and 8.60 Å)

### 7.4. Algorithm for the calculation of salinity as a function of TmIce, Td Cl, $V_{2,g}$

Step 1: the salinity of the aqueous solution at TmIce is calculated from the model of Pitzer; the density of the aqueous solution is calculated from the equation of Potter & Brown (1977). Step 2: $\upsilon_{g(1)}$ is calculated at TmIce from the pressure $P_1$ calculated by the model. Step 3: calculation of pressure $P_2$ and $\upsilon_{g(2)}$ at TdCla. Step (4): calculation of $V_{g(1)}$, $V_{Cla(1)}$ and $V_{aq(1)}$ from mass balance equations on water and gas. Step (5): $n_{NaCl(1)}$ and $n_{NaCl(2)}$ are derived from equations (17a) and

(17b). Step 6: the convergence of the calculation is checked.

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