



CLATHRATES: COMPUTER PROGRAMS TO CALCULATE FLUID INCLUSION V - X PROPERTIES USING CLATHRATE MELTING TEMPERATURES

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(Received 26 March 1996; revised 1 August 1996)

Abstract—Knowledge of final clathrate melting temperatures is essential for estimates of salinity, bulk composition and density in H_2O -gas-rich fluid inclusions by nondestructive methods. The salinities calculated strongly depend on the thermodynamic model used, which involves many independent intensive properties and related parameters, such as osmotic coefficients, fugacity coefficients, gas solubilities. Four programs have been developed (*DENSITY*, *ICE*, *Q2*, and *NOSALT*) using Turbo C++ version 3.0 to handle clathrate melting temperatures with several initiation procedures. These programs allow the calculation of bulk densities and compositions (V - X properties) for H_2O - CO_2 - CH_4 - N_2 - $NaCl$ - KCl - $CaCl_2$ -rich fluid inclusions using the clathrate melting temperature in combination with liquid-vapour equilibria, data from Raman spectroscopic analysis of the nonaqueous phases, and volume fraction estimates of the phases present. Calculations are restricted to fluid compositions less than eutectic salinities. If volume estimates are not provided, the programs calculate only the properties of the individual phases present in fluid inclusions during clathrate melting, including the salinity. Errors in measured parameters and in volume fraction estimates, which may be relatively large, are also handled by the programs. © 1997 Elsevier Science Ltd. All rights reserved

Key Words: Clathrate, Fluid inclusions, Liquid-vapour equilibria, Salinity, C++.

INTRODUCTION

Salinity, bulk composition and density (V - X properties) of fluid inclusions may be determined from stability conditions of coexisting phases. The clathrate phase occurs frequently in fluid inclusions containing H_2O , gases such as CO_2 , CH_4 , N_2 , and salts such as $NaCl$, KCl , $CaCl_2$. These components appear to represent most natural fluid systems found in inclusions (e.g. Roedder, 1984). Depending on its V - X properties several successions of phase transitions may take place in such fluid inclusions, involving liquid-vapour equilibria of nonaqueous phases and clathrate dissolution in the presence of aqueous-rich and gas-rich phases. The aim of this study is to provide computer programs, which are able to handle both clathrate stability conditions and liquid-vapour equilibria of nonaqueous phases. The programs allow interpretation of clathrate melting temperatures so that fluid inclusionists can obtain bulk V - X properties of inclusions, such as salinity, composition, and density. These programs are written in Turbo C++, version 3.0 (Borland, 1992), and were presented at the ECROFI XIII

meeting (Bakker, 1995a) and the V.M. Goldschmidt Conference (Bakker and others, 1996). Clathrate stability conditions are estimated according to the model of Bakker (1995b) and Bakker, Dubessy, and Cathelineau (1996) for the fluid system H_2O - CO_2 - CH_4 - N_2 - $NaCl$ - KCl - $CaCl_2$. Liquid-vapour equilibria of the CO_2 - CH_4 - N_2 -rich phases are obtained from a modified Soave equation of state according to Thiéry, Kerkhof, and Dubessy (1994), and a combination of a modified Benedict-Webb-Rubin equation of state and Pitzer correlations from Lee and Kesler (1975). The term carbonic phase is used throughout this paper to refer to a fluid mixture of CO_2 , CH_4 , and N_2 , either liquid or vapour. In addition, the term eutectic is used for first melting conditions of the aqueous phase.

Clathrate melting in fluid inclusion studies

Smith (1953) noted that data on clathrate phase stability were never used in fluid inclusions studies although clathrates were expected to occur in many inclusions. Roedder (1963) was the first to describe the presence of both visible and invisible clathrates in H_2O - CO_2 -rich fluid inclusions, and he used three examples to illustrate the problems involved in the optical observation of clathrate melting in the presence of aqueous liquid, CO_2 -rich liquid, and a vapour phase (quadruple point Q_2). Hollister and

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Burruss (1976) noticed the opposite effect of CH_4 and NaCl on the clathrate melting temperature at Q_2 conditions in $\text{H}_2\text{O}-\text{CO}_2$ -rich fluid inclusions. They combined several phase transitions, i.e. melting of solid CO_2 in the presence of a CO_2 - CH_4 -rich vapour, and melting of clathrate to estimate limits in bulk fluid composition and salinity. Because of the lack of additional advanced techniques and applied thermodynamic models to analyse inclusions they questioned the usefulness of clathrate melting temperatures for fluid inclusion studies. They realised that determination of the inclusion composition based solely on clathrate melting temperatures was invalid due to the large range of solid solutions possible in the clathrate phase. It should be noted that this opposite effect is only valid at pressures greater than 4.5 MPa, both CH_4 and salts have a similar effect on the stability conditions of a CO_2 clathrate at lower pressures. In many fluid inclusion studies clathrate melting temperatures were used only qualitatively to confirm the presence of a gas other than H_2O .

The first quantitative use of clathrate melting temperatures to fluid inclusion studies was introduced by Collins (1979). He used experimental data of clathrate melting at Q_2 conditions from Chen (1972) to calculate the salinity of $\text{H}_2\text{O}-\text{CO}_2$ - NaCl -rich fluid inclusions. This fluid system was extended to include CaCl_2 by Zhang and Frantz (1989) and KCl by Diamond (1992). Unfortunately, the data on Q_2 depression as a function of CaCl_2 salinity by Zhang and Frantz (1989) deviate seriously from the experimental data of Dholabhai, Kalogerakis, and Bishnoi (1993) and modelled clathrate stability conditions according to Bakker, Dubessy, and Cathelineau (1996), who defined a new empirical equation for CaCl_2 -bearing solutions, up to eutectic compositions. Diamond (1992) provided some purely empirical equations for the calculation of salinity in $\text{H}_2\text{O}-\text{CO}_2$ - NaCl - KCl -rich fluid inclusion from clathrate melting in the presence of either a CO_2 -rich vapour or liquid phase. This method relies on the estimation of the density of the CO_2 -rich phase in the metastable absence of clathrate.

Clathrate stability models, based on statistical thermodynamics (Waals and Platteeuw, 1959), have only recently been used to estimate salinity in multivolatile fluid inclusions (Diamond, 1990, 1994a; Dubessy, Thiéry, and Canals, 1992; Bakker, 1995b; Bakker and others, 1996; Bakker, Dubessy, and Cathelineau, 1996). Dubessy, Thiéry, and Canals (1992) provided a new method to estimate the salinity of H_2O -rich fluid inclusions from both clathrate melting and ice melting temperatures in addition to a volume fraction estimate of the non-aqueous phase. A prerequisite for these calculations is the quantitative Raman spectroscopic analysis of a homogeneous nonaqueous phase. Diamond (1994a) tested the applicability of theoretical models for clathrate stability conditions against new exper-

imental data from synthetic fluid inclusions, and concluded that the models are eminently useful in geochemical applications, although the predictions are not always perfect. The established clathrate stability models (e.g. Waals and Platteeuw, 1959; Parrish and Prausnitz, 1972; Ng and Robinson, 1976; John, Papadopoulos, and Holder, 1985) have been scrutinised and modified for the fluid system $\text{H}_2\text{O}-\text{CO}_2$ - CH_4 - N_2 - NaCl - KCl - CaCl_2 by Bakker (1995b), Bakker and others (1996), and Bakker, Dubessy, and Cathelineau (1996) to obtain more accurate predictions over a wider range of conditions and compositions.

Accuracy of the model

Bakker, Dubessy, and Cathelineau (1996) have evaluated an accuracy of 2% in the modelled clathrate formation pressure at selected temperatures for the $\text{H}_2\text{O}-\text{CO}_2$ fluid system. In salt-bearing systems (NaCl - KCl - CaCl_2), their improved clathrate stability model appears to reproduce average values; however, it should be noted that the available experimental data are inconsistent. Bakker (1995b) and Bakker and others (1996) presented a similar accuracy for clathrate melting in the $\text{H}_2\text{O}-\text{CH}_4$ and the $\text{H}_2\text{O}-\text{N}_2$ fluid systems, and demonstrated that an additional excess free energy is necessary to obtain a good fit to experimental data of mixed-gas clathrates, i.e. CO_2 - CH_4 - N_2 . The excess free energy is a result of mixing the binary end-members to form the solid clathrate solution. The excess thermodynamic functions are asymmetric modifications of the Margules model (Thompson, 1967). Figure 1A and 1B illustrate the accuracy of the clathrate stability model for CO_2 - CH_4 clathrates (Adisasmito, Frank, and Sloan, 1991) and CH_4 - N_2 clathrates (Jhaveri and Robinson, 1965), respectively. For CO_2 - N_2 clathrates (Fig. 1C), the excess free energy function is based on the small experimental data set from Diamond (1994a), which is obtained from synthetic fluid inclusions (Table 1). Diamond (1994a) measured clathrate melting temperatures and homogenisation temperatures in synthetic fluid inclusions with known compositions. The density of the homogeneous carbonic phase is obtained from homogenisation temperatures, using a modified Soave equation of state (Soave, 1972; Thiéry, Kerkhof, and Dubessy, 1994) and a modified BWR equation of state (Benedict, Webb, and Rubin, 1949; Lee and Kesler, 1975). The isochores in Figure 1C are constructed with the equation of state according to Lee and Kesler (1975), which allows estimates of the pressure at the observed clathrate melting temperatures (Table 1). The three pseudo binary excess free energy functions are averaged in terms of mole fractions for three component (CO_2 - CH_4 - N_2) mixed-gas clathrates. Figure 1 demonstrates the quality of the proposed modifications in clathrate modelling, and its ability to cal-

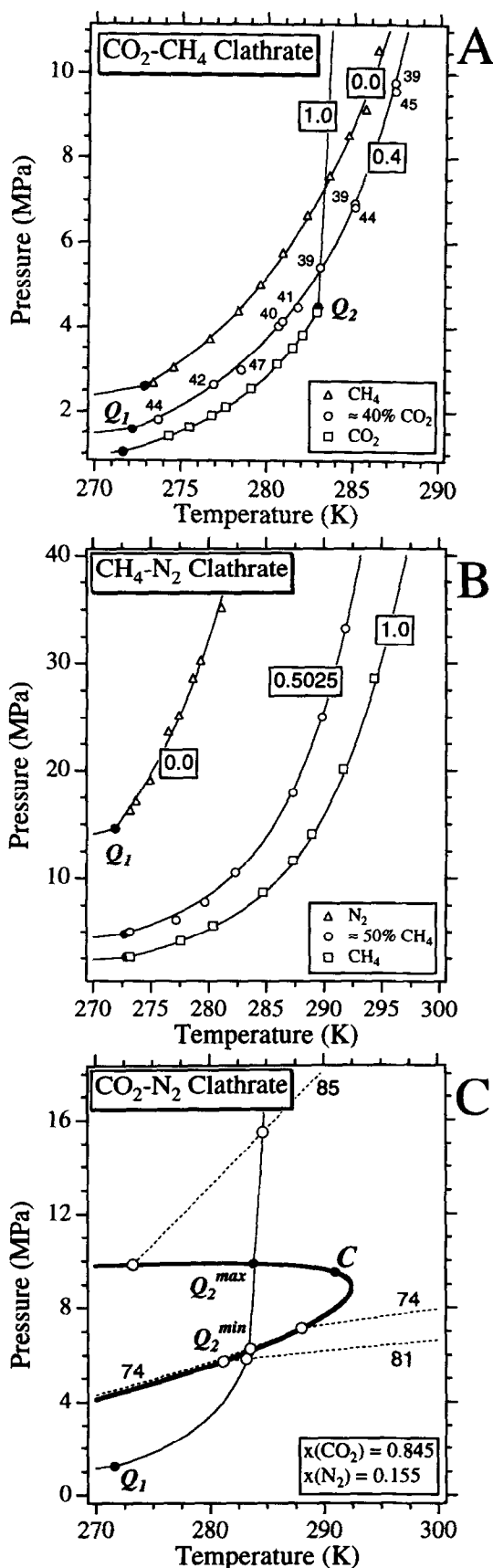


Table 1. Calculated clathrate stability conditions for CO₂-N₂ clathrate in equilibrium with an 84.5 mol.% CO₂ and 15.5 mol.% N₂ gas mixture, which are obtained from the experiments of Diamond (1994a).

Sample	<i>T</i> (°C)	<i>P</i> (MPa)
81 (vap)	10.0	5.84
74 (Q ₂)	10.4	6.27
85 (liq)	11.5	15.48

Note: phase (liquid or vapour) of carbonic part of each sample is indicated in parentheses. Q₂ indicates presence of both liquid and vapour carbonic phases during final clathrate melting.

calculate accurately clathrate stability conditions for both pure-gas clathrates and mixed-gas clathrates.

THE MAIN PROGRAMS

The *P-T-V-X* topology of phase elements in several fluid systems including salts was extensively described by Diamond (1994b) and Bakker and Thiéry (1994). A qualitative understanding of phase relations involving a clathrate phase is indispensable for the interpretation of clathrate melting temperatures in multicomponent fluid inclusions. These topologies form the basis for the design of the four main programs in this study (*DENSITY*, *ICE*, *Q2*, and *NOSALT*). Melting of a clathrate may occur in several configurations within fluid inclusions. Clathrate may melt in the presence of two other phases, i.e. aqueous solution (or ice) and a homogeneous carbonic phase (either liquid-like or vapour-like), in the presence of three other phases, i.e. the quadruple points Q₁ (aqueous solution, ice, and a vapour-like carbonic phase) and Q₂ (aqueous solution and two carbonic phases), or in the presence of four other phases at eutectic conditions in electrolyte-bearing systems (aqueous solution, ice, vapour-like carbonic phase, and salt-hydrate).

The clathrate stability model in a multicomponent system of H₂O, CO₂, CH₄, N₂, NaCl, KCl, and CaCl₂ involves many independent intensive properties and related parameters. Many iterative numerical calculations are involved due to the com-

Figure 1. *T-P* diagrams with stability curves of pure-gas and mixed-gas clathrates; (A) CO₂-CH₄ clathrate, numbers within small squares are mole fractions of CO₂ in gas mixture. Experimental data are obtained from Adisasmito, Frank, and Sloan (1991). Q₁ and Q₂ represent quadruple points; (B) CH₄-N₂ clathrate, numbers within small squares are mole fraction of CH₄ in gas mixture. Experimental data are obtained from Jhaveri and Robinson (1965). Quadruple points Q₂ are not present in this fluid system; (C) CO₂-N₂ clathrate for specific gas mixture of 84.5 mol.% CO₂ and 15.5 mol.% N₂. Isochores for samples from Diamond (1994a) are dashed lines. Note that isochore of sample 74 within immiscibility field nearly coincides with boundary of miscibility gap. Q₂^{max} and Q₂^{min} are maximum and minimum quadruple points Q₂ for this specific gas mixture. Point C represents critical point.

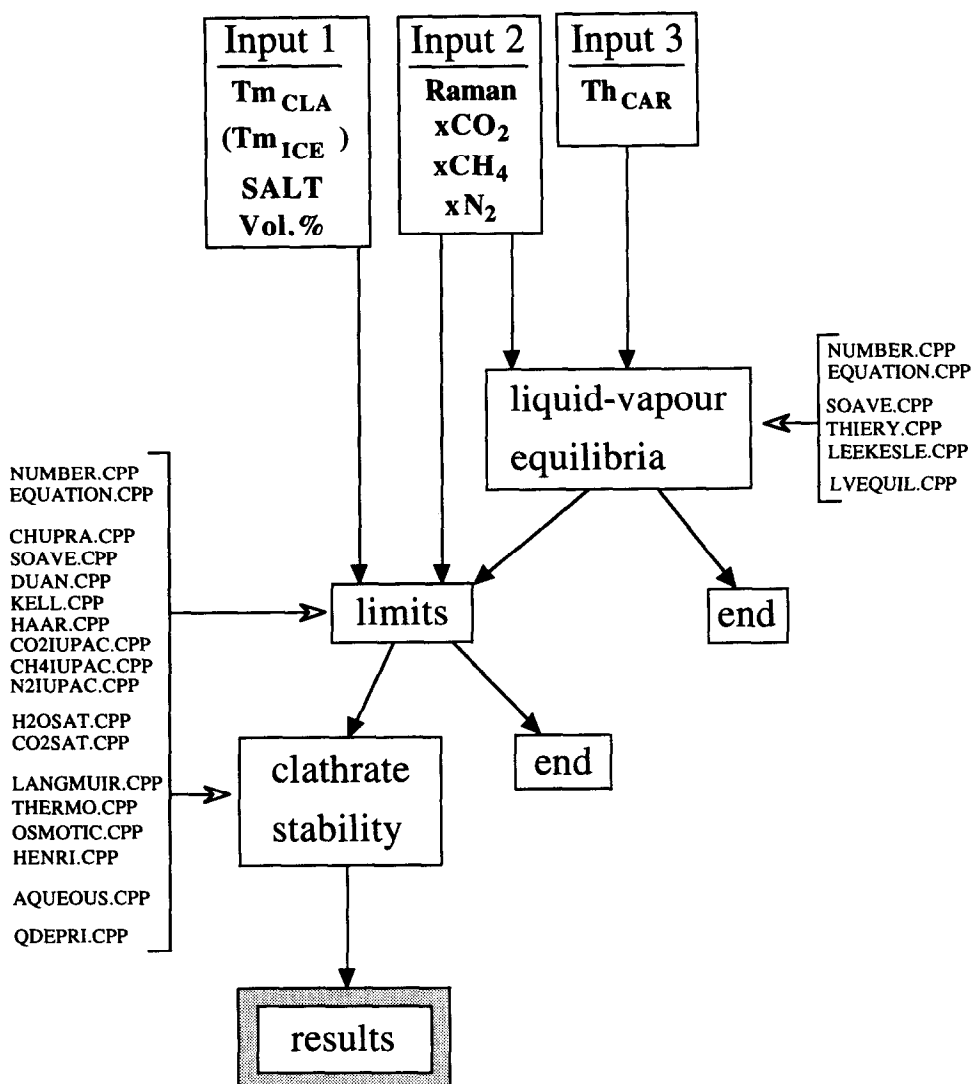


Figure 2. Schematic diagram illustrating general algorithm of main programs. Raman spectroscopic analysis of carbonic phase (x_{CO_2} , x_{CH_4} , x_{N_2}) and homogenisation temperature of carbonic phase (Th_{CAR}) are used as input for liquid-vapour equilibria calculations. Raman analysis, final clathrate melting temperature (T_{m_CLA}), final ice melting temperature (T_{m_ICE}), type of salt (NaCl, KCl, $CaCl_2$), and volume fraction estimations are used to estimate limits of clathrate stability model (limits), and to calculate finally VX properties of specified fluid inclusion. CPP files illustrate individual parameter calculations which are further explained in Appendix A.

plexity of the equations. In order to simplify the program structure, each parameter involved is assigned an individual routine, marked as CPP files in Figure 2. The routine descriptions provided in Appendix A give a concise outline of the theoretical models as developed by Dubessy, Thiéry, and Canals (1992), Thiéry, Kerkhof, and Dubessy (1994), Bakker (1995b), Bakker and others (1996) and Bakker, Dubessy, and Cathelineau (1996). Figure 2 illustrates the general algorithm used in the main programs. Liquid-vapour equilibria for the carbonic phase are not used in the program *ICE* because this program is designed for clathrate melting in the presence of a homogeneous

vapour-like carbonic phase. Program calculations may be ended as a consequence of no convergence during liquid-vapour equilibrium calculations. The transformation of homogenisation temperature to density in the CO_2 - CH_4 - N_2 -rich phase may be problematic. It is obvious that temperatures should not exceed a maximum value characteristic for the immiscibility gap of specific carbonic mixtures. The critical point of these mixtures does not coincide with this maximum temperature, and a measured temperature of homogenisation to the vapour phase may imply two possible solutions. In this context, it is important to know the pressure of homogenisation. Figure 3 illustrates the immiscibility field for

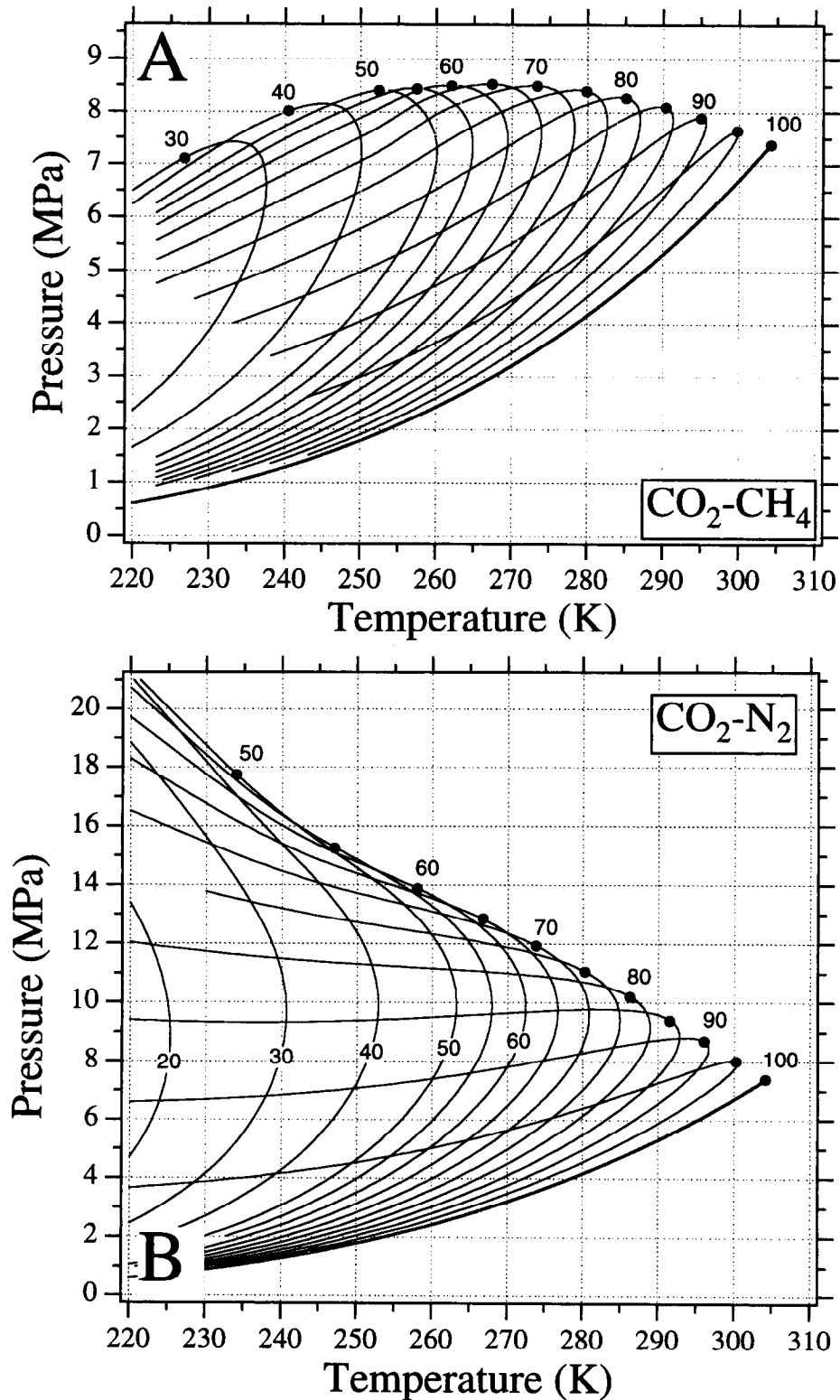


Figure 3. T - P diagrams illustrating immiscibility field for CO_2 - CH_4 gas mixtures (A), and CO_2 - N_2 gas mixtures (B) according to model of Thiéry, Kerkhof, and Dubessy (1994). Numbers refer to mole percentages of CO_2 . Solid dots represent critical conditions of selected compositions.

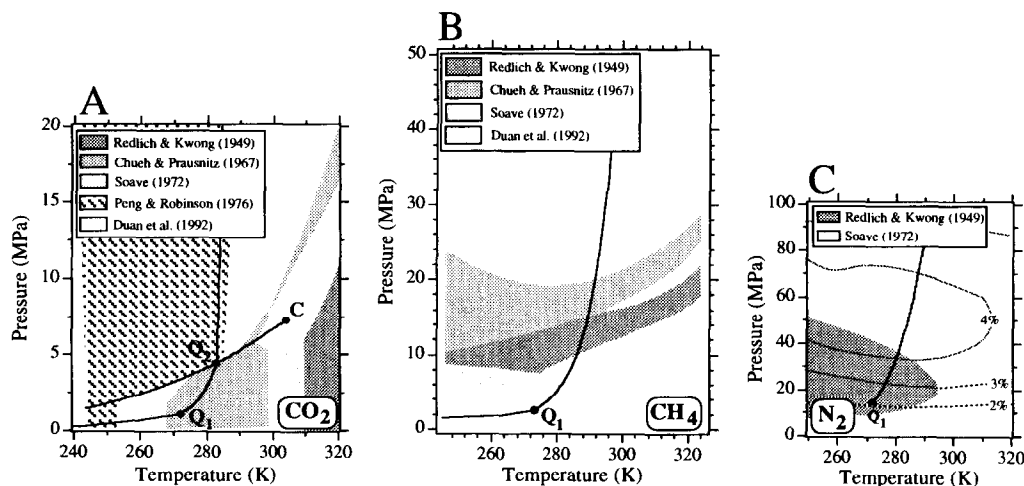


Figure 4. T - P diagrams indicating regions for which equations of state according to Redlich and Kwong (1949), Chueh and Prausnitz (1967), Soave (1972), Peng and Robinson (1976), and Duan, Møller, and Weare (1992a,b) best approach IUPAC values of pure CO_2 (A), CH_4 (B), and N_2 (C) (Angus, Armstrong, and Reuck, 1976, 1978; Angus, Reuck, and Armstrong, 1979). Clathrate stability curves for salt-free fluid systems are projected as solid lines. Q_1 and Q_2 represent quadruple points, C is critical point of pure CO_2 . Dashed lines in (C) represent constant deviation for N_2 system, which appears to be relatively high, indicating that none of these equations of state is able to reproduce accurately IUPAC values.

binary CO_2 - CH_4 and CO_2 - N_2 mixtures according to Thiéry, Kerkhof, and Dubessy (1994) which may emphasise the previously described conversion problem of the programs. For example, the vapour phase of a fluid inclusion contains 85 mol.% CO_2 and 15 mol.% CH_4 according to Raman spectroscopic analysis, and a homogenisation temperature of 20°C (293.15 K) is measured. The inconsistency of these experiment data can be directly inferred from Figure 3A. For inclusions that homogenise at 17°C with a similar vapour composition, the liquid-vapour equilibria procedures are initiated with a first estimate of the homogenisation pressure, which can be directly obtained from Figure 3A. The clathrate stability conditions modelled according to Bakker, Dubessy, and Cathelineau (1996) are limited to pressures below 200 MPa. Most individual parameters involved in clathrate modelling are poorly defined at higher pressures. Furthermore, clathrate melting temperatures at selected pressures should not exceed values obtained for salt-free fluid systems, as a consequence of the freezing-point depression effect. Each program has specific limit calculations for clathrate stability conditions which are further explained in the next paragraphs.

In principle, the final clathrate melting temperature, Raman spectroscopic analysis of the carbonic phase, and identification of the type of salt are prerequisites in the main programs (Input 1 and 2 in Fig. 2). An estimate of the volume fraction of the phases in fluid inclusions after final clathrate melting is optional in most programs, but it is a prerequisite to calculate bulk properties of fluid inclusions. Without the volumetric estimates the

programs are able to calculate only the V - X properties of the individual phases present in fluid inclusions. Uncertainties in volume fraction estimates may introduce large errors in the results of the calculations. The relative error in final bulk density as a direct consequence of a 10% error in volume fraction estimate is much larger at lower densities but approaches zero for higher densities. Fluid inclusions with a relative small vapour bubble are in general of high density, and consequently, the relative error in bulk density calculation will be much smaller than the 10% value calculated by default for the uncertainty in volume fraction estimate. However, the error may exceed this value extensively in inclusions with larger vapour bubbles. Therefore, a volumetric error estimate is included in the algorithms of our programs to calculate simultaneously fluid properties within these error indications.

The fugacity of gas mixtures involved in the formation of clathrates may be calculated according to several equations of state (Chueh and Prausnitz, 1967; Soave, 1972; Duan, Møller, and Weare, 1992a,b; Thiéry, Kerkhof, and Dubessy, 1994). In the past, equations of state were designed for either liquid-like fluids or vapour-like fluids. For example, the equations of state according to Redlich and Kwong (1949), Chueh and Prausnitz (1967), Soave (1972), and Peng and Robinson (1976) were designed for vapour-like fluids and are unable to predict accurately fugacities of liquid-like fluids. Recently, several equations of state have been published which described accurately the properties of both type of fluids (e.g. Duan, Møller, and Weare,

1992a,b). Figure 4 illustrates *T*–*P* domains in which these equations of state give the most accurate fugacity estimations of the pure gases CO₂, CH₄ and N₂, compared to IUPAC tables (Angus, Armstrong, and Reuck, 1976, 1978; Angus, Reuck, and Armstrong, 1979). Clathrate stability conditions are projected in Figure 4 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 calculations of a shifted clathrate stability field as a consequence of the presence of electrolytes in the aqueous solution.

The previously mentioned fugacity calculations are applied to a homogeneous carbonic phase. Fugacity calculations are also involved in liquid–vapour equilibria of the carbonic phases within the immiscibility field, according to the model of Thiéry, Kerkhof, and Dubessy (1994). Both fugacity calculations are completely independent in the programs. The modified Soave equation of state according to the model of Thiéry, Kerkhof, and Dubessy (1994) is designed for an accurate determination of the position of the immiscibility field for carbonic fluids in *P*–*T*–*X* space. These modifications are not applicable to a homogeneous carbonic phase outside the immiscibility field. Furthermore, their modified Soave equation of state is unable to accurately calculate densities of coexisting liquid and vapour phases; therefore, the equation of state according to Lee and Kesler (1975) is used to define the molar volume of this fluid.

Several examples are used to illustrate the use of each program (Table 2). The output files (Appendix B) of the program examples, which are described in the next paragraphs, give a complete report of most calculated parameters which are involved in clathrate modelling. These reports give the possibility to check whether the estimated values of individual parameters are realistic, and, consequently, this report indicates the significance of the results. The most stable clathrate structure is indicated in each report, because N₂ forms a different clathrate structure than CH₄ and CO₂ (Davidson and others, 1987). Chemical potentials of both clathrate structure 1 and 2 are compared to estimated the more stable configuration.

Program DENSITY

Final clathrate melting occurs in the presence of a salt-bearing aqueous solution and a homogeneous carbonic phase which is either liquid-like or vapour-like. The prerequisites of this program are the final clathrate melting temperature, the mole fractions of CO₂, CH₄, and N₂ in the homogeneous carbonic phase, which are usually obtained from Raman spectroscopic analysis, and the type of salt (either NaCl, KCl, or CaCl₂). Only one type of salt can be used in a given calculation. In addition, the density of the carbonic phase constrains the stab-

Table 2. Input values of examples of programs DENSITY, ICE, Q2, and NOSALT.

Example	Raman analysis of non-aqueous phase	Equation of state	Salt	Tm _{ICE}	Microthermometry (°C)		Volume percentage non-aqueous phase
DENSITY	95 mol.% CO ₂ 5 mol.% CH ₄	Duan, Møller, and Weare (1992a,b)	KCl		Tm _{CLA} 8 ± 0.1	Th _{CAR} 5 ± 0.1 (liq)	40 ± 4 vol%
ICE	82 mol.% CO ₂ 14 mol.% CH ₄ 4 mol.% N ₂	Chueh and Prausnitz (1967)	NaCl	–4.1	8.7		60 vol%
Q2	90 mol.% CO ₂ 10 mol.% CH ₄	Duan, Møller, and Weare (1992a,b)	CaCl ₂		7.1	19.8 (liq)	50 ± 5 vol%
NOSALT	70 mol.% CO ₂ 29 mol.% CH ₄ 1 mol.% N ₂	Soave (1972)	–		12 ± 0.2		80 ± 5 vol%

Notes: Tm_{ICE}, Tm_{CLA}, Th_{CAR} are final ice melting temperature, final clathrate melting temperature, and homogenisation temperature of carbonic phases, respectively. Mode of homogenisation (to liquid or vapour) is indicated in parentheses.

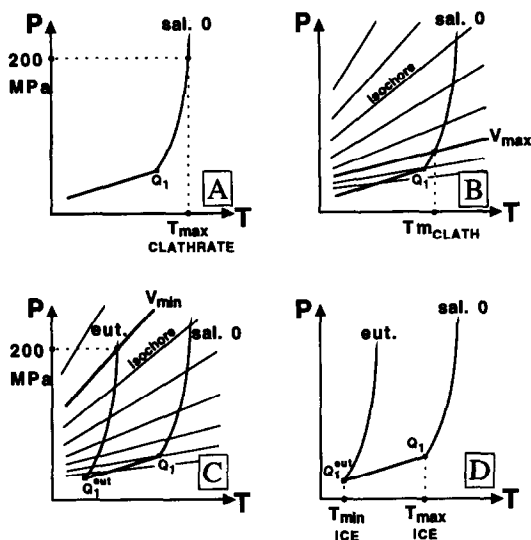


Figure 5. Schematic T - P diagrams indicating limit estimates for clathrate stability conditions. eut. and sal.0 represent clathrate stability curves for eutectic salinities and salt-free fluid systems, respectively. See text for further details.

ility conditions of the fluid system at final clathrate melting, because the intersection of the corresponding isochore and the final clathrate melting temperature defines the clathrate melting pressure. This density can be directly introduced in the program or may be obtained from the homogenisation temperature of the carbonic phases in the metastable absence of the clathrate phase (Diamond, 1992). This homogenisation temperature may not exceed final clathrate melting temperatures for the use of this program. Subsequently, these melting conditions are unique for a defined salinity of the aqueous phase. Limit calculations in the program consist of the calculation of a maximum clathrate melting temperature in salt-free fluid systems at 200 MPa (Fig. 5A), the calculation of a maximum molar volume (or minimum density) in salt-free fluid systems at the clathrate melting temperature (Fig. 5B), and the calculation of a minimum molar volume in fluid systems with eutectic salinities at 200 MPa (Fig. 5C).

The use of this program is best illustrated with an example (Table 2, Fig. 6A, and Appendix B). First, in the metastable absence of a clathrate phase, the fluid system follows the *isochore 2* (Fig. 6A) during cooling. The carbonic phase will dissociate into a liquid and vapour phase on entering the two phase region LV (Fig. 6A). After the homogenisation temperature (Th_{CAR} in Fig. 6A) is measured during heating of the inclusion in metastable absence of the clathrate, the inclusion is further cooled to temperatures below the nucleation limits of the clathrate phase. The formation of the clathrate phase causes an increase of the salinity of a remaining aqueous solution and a decrease of the

density of carbonic phases. At lower temperatures, salt-hydrate crystals will nucleate below eutectic conditions. During the heating procedure on the microthermometric stage, the pressure inside the fluid inclusion will initially follow *isochore 1* (Fig. 6A) until the clathrate phase begins to melt at the eutectic conditions (T_{mCLATH} in Fig. 6A). During further heating, the clathrate releases carbonic gases and the density of the nonaqueous portion will progressively increase, i.e. the fluid system is constantly moving to a higher density isochore (towards *isochore 2* in Fig. 6A). The salinity of the aqueous solution will progressively decrease as a result of H_2O release from the melting clathrate. Before the final melting temperature of the clathrate phase at T_{mCLATH} is reached, the carbonic phases homogenise at a lower density (Th_{CAR}^* in Fig. 6A) than the originally estimated density in the metastable absence of a clathrate (Th_{CAR}). Figure 6A illustrates the development of phases in fluid inclusions whose total composition is relatively enriched in carbonic gases compared to clathrates. Consequently, nearly all H_2O will be consumed in the clathrate phase and the remaining space will be occupied by two carbonic phases. The phase behaviour of fluid inclusions that are richer in H_2O than the clathrate phase is somewhat different and illustrated in Figure 7. The density of the carbonic phase will decrease drastically because the clathrate phase consumes most of the carbonic gases. Consequently, a second homogenisation ($Th_{CAR}^{\#}$ in Fig. 7) of the carbonic phases to the vapour phase occurs on lowering the temperature. At lower temperatures, ice is formed at Q_1 conditions, and salt-hydrate is formed below eutectic Q_1 conditions (Fig. 7). This ice melting temperature will only reflect momentary salinities, and cannot be used for fluid inclusion bulk salinity estimations.

The volumetric and compositional properties of each phase that occurs at the specified temperatures are indicated in the output file (Appendix B). The encircled data illustrate the original input of the program. Three columns are revealed in Appendix B of which the first shows the average calculated values, and the other two columns reveal the error analysis of this example. Salinity can be expressed according to many different definitions. Therefore, the output file of this program gives several calculated salinities and their definitions, including the summation of the mole fraction of dissociated ions in the aqueous solution, molality and weight% of the associated salt in the aqueous solution, weight% of the total fluid inclusion taking into account all components that are present, and molality of the total fluid inclusion based on the relative amounts of salt and H_2O .

Diamond (1992) introduced two purely empirical equations to calculate the salinity of the aqueous solution in fluid inclusions as a function of clathrate melting temperature and a known density of only a

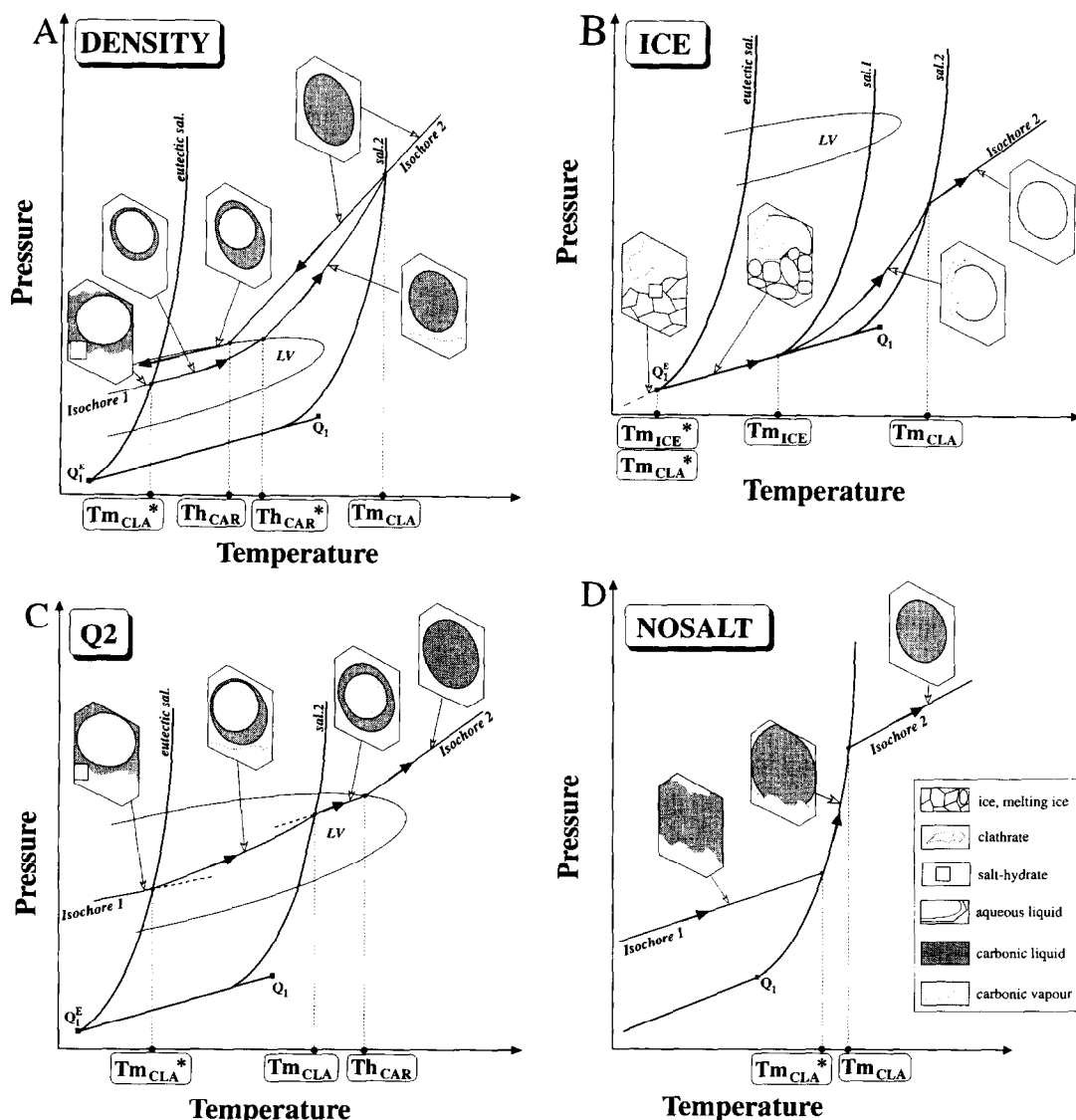


Figure 6. Schematic phase transitions in fluid inclusions that are used in programs *DENSITY* (A), *ICE* (B), *Q2* (C), and *NOSALT* (D). Tm_{CLA} , Th_{CAR} , and Tm_{ICE} are final clathrate melting temperature, homogenisation temperature of nonaqueous phase, and final ice melting temperature, respectively. Tm_{ICE}^* and Tm_{CLA}^* are initial melting temperature of ice and clathrate, respectively. Th_{CAR} is homogenisation temperature in presence of clathrate phase. See text for further details.

pure CO_2 phase. A comparison in estimated salinities in H_2O-CO_2-NaCl -rich fluid inclusions between these empirical equations and values calculated with the program reveals only minor differences. In general, both models are very similar and differ to a maximum of 0.6 wt.%, although they are based on different clathrate stability models. Diamond (1992) has used the clathrate model according to Ng and Robinson (1976, 1977) to prepare his empirical equations, which is increasingly in error at pressures exceeding Q_2 conditions (Bakker, Dubessy, and Cathelineau, 1996).

Consequently, the maximum difference between both models occurs at high pressures.

Program ICE

Similar to the previously described program *DENSITY*, final clathrate melting occurs in the presence of a salt-bearing aqueous solution and a homogeneous carbonic phase, which is vapour-like in this particular melting configuration. On many occasions, the homogenisation conditions of the carbonic phase cannot be measured, and, therefore, the program *DENSITY* cannot be used. The program *ICE* provides a possible solution to this problem.

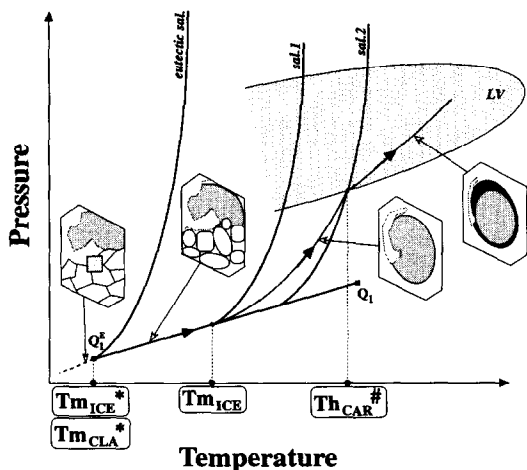


Figure 7. Schematic phase transitions at low temperatures for inclusions that are relatively rich in H_2O , compared with clathrate composition.

blem. The prerequisite data for the program *ICE* are the final clathrate melting temperature, the mole fractions of CO_2 , CH_4 , and N_2 in the carbonic phase, and one type of salt (either NaCl , KCl , or CaCl_2). Additionally, the final ice melting temperature, which is usually available for these H_2O -rich

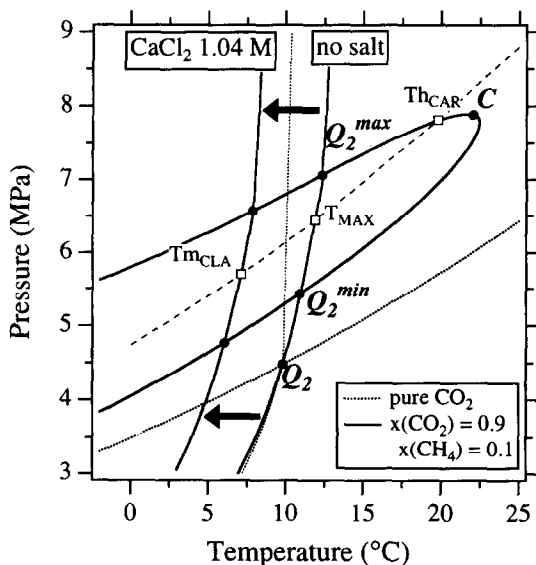


Figure 8. T - P diagram for clathrate stability conditions for Raman analysis of 90 mol.% CO_2 and 10 mol.% CH_4 (see Table 2). Carbonic two phase (liquid-vapour) field with its critical point C, and clathrate stability curves (at 0 and 1.04 M CaCl_2) are indicated with thick solid lines. Dashed line represents isochore for this example. $T_{\text{H_CAR}}$ and $T_{\text{m_CLA}}$ are measured homogenisation temperature and final clathrate melting temperature, respectively. T_{MAX} indicates maximum possible clathrate melting temperature in salt-free fluid systems. Q_2^{max} and Q_2^{min} represent maximum and minimum quadruple points Q_2 for this specific fluid system. Clathrate stability field for pure CO_2 fluid system (dotted line) is projected for comparison. Q_2 is its quadruple point.

fluid inclusions, and volume fraction estimates of the phases present in the inclusions after final clathrate melting allow bulk fluid property calculations, similar to the method described by Dubessy, Thiéry, and Canals (1992). Unlike the program *DENSITY*, volume fraction estimates after final clathrate melting are prerequisites to perform any calculation at all. The algorithm of program *ICE* is based on the conservation of mass at final ice melting temperature and final clathrate melting temperature. Limit calculations in this program consist of the calculation of a maximum clathrate melting temperature in salt-free fluid systems at 200 MPa (Fig. 5A), the calculation of a maximum ice melting temperature (Q_1) in salt-free fluid systems (Fig. 5D), and the calculation of a minimum ice melting temperature (Q_1^{min}) at eutectic conditions (Fig. 5D).

An example (Table 2, Fig. 6B, and Appendix B) is used to illustrate the application of this program. At temperatures less than the eutectic, the inclusion contains three solid phases, i.e. ice, clathrate, and salt-hydrate, and a vapour-like carbonic phase. At eutectic Q_1 conditions, both ice and clathrate start to melt ($T_{\text{m_ICE}}$ and $T_{\text{m_CLA}}$ in Fig. 6B) and the salt-hydrate crystal disappears immediately after a small temperature increment. The salinity of the aqueous solution will decrease progressively during further heating and the pressure in the inclusion evolves according to the displacement of Q_1 at decreasing salinities, as long as the four phases remain present, i.e. ice, clathrate, vapour-like carbonic phase, and liquid H_2O . The final ice melting temperature ($T_{\text{m_ICE}}$ in Fig. 6B) defines an initial salinity estimation (*sal.1* in Fig. 6B), which must exceed the final salinity estimation as the amount of H_2O released by the clathrate phase during melting will further decrease the salinity. At temperatures above the final clathrate melting temperature ($T_{\text{m_CLA}}$) the pressure in the inclusion which now contains only an aqueous solution and a carbonic vapour phase will follow the *isochore 2* (Fig. 6B).

Appendix B shows the complete output file of the example for program *ICE*, this includes the properties of the individual phases present at the final ice melting temperature, including initial salinity and volume fractions estimates of each phase. Again the original input is encircled, and three columns are indicated to illustrate the error analysis. Only the average values are calculated in this example because an error analysis was optionally excluded. The salinity of the aqueous solution at final ice melting temperature (0.841 mol per kg H_2O) appears to be about 2.3 times larger than the salinity of the solution after final clathrate melting (0.359 mol per kg H_2O). After final ice melting, the fluid inclusion contains 32 vol.% clathrate, 17 vol.% aqueous solution, and 51 vol.% vapour-like carbonic phase.

This program uses an algorithm similar to that of Dubessy, Thiéry, and Canals (1992). The adjust-

ments of individual parameters involved in clathrate modelling according to Bakker (1995b), Bakker and others (1996) and Bakker, Dubessy, and Cathelineau (1996) have improved the reliability and predictability of these phase equilibria. In addition, their algorithm has been adjusted to eliminate several unjustified simplifications. The improved salinity estimates differ seriously from those values calculated from the original algorithm according to Dubessy, Thiéry, and Canals (1992); however, bulk densities and compositions are less affected. The salinity estimates according to Dubessy, Thiéry, and Canals (1992) appear to exceed the new model predictions by maximally 5 wt.%. Yerokhin (1993) used a calculation method similar to that of Dubessy, Thiéry, and Canals (1992) and introduced a third temperature to avoid relatively inaccurate volume fraction estimates. He has claimed to observe an initial clathrate melting temperature in between the final ice melting temperature and final clathrate melting temperature. As illustrated in Figure 6B, both ice and clathrate start to melt at eutectic conditions, and apparent differences may occur due to observational difficulties (Roedder, 1963).

Program Q2

The previously described programs *DENSITY* and *ICE* are designed for final clathrate melting in the presence of a homogeneous carbonic phase. However, often the carbonic phase is separated in coexisting liquid–vapour phases at the temperature of final clathrate melting. Clathrate melting in the presence of an aqueous solution, a carbonic vapour and a carbonic liquid phase, i.e. at Q_2 conditions, regularly occurs in fluid inclusions whose carbonic phase is rich in CO_2 . The appearance of Q_2 melting is a result of the intersection of the carbonic immiscibility field (liquid–vapour equilibria) and the clathrate stability curve. Several purely empirical equations for the depression of Q_2 as a function of salinity are available for the H_2O – CO_2 –salt fluid system (Darling, 1991; Diamond, 1992; Zhang and Frantz, 1989; Bakker, Dubessy, and Cathelineau, 1996), and other gases such as CH_4 and N_2 are not included. Therefore, program *Q2* is designed to handle these specific melting conditions for an extended fluid system. The prerequisite data for the program *Q2* are the final clathrate melting temperature, the mole fractions of CO_2 , CH_4 , and N_2 in a homogeneous carbonic phase, and one type of salt (either NaCl , KCl , or CaCl_2). In addition, the homogenisation temperature of the carbonic phases, which must exceed the final clathrate melting temperature (unlike the program *DENSITY*), is a prerequisite for this program. At clathrate melting conditions, the composition of coexisting carbonic liquid and vapour phase are estimated numerically, according to a modified Soave equation of state (Thiéry, Kerkhof, and Dubessy, 1994) and a modi-

fied Benedict–Webb–Rubin equation of state (Lee and Kesler, 1975). Both coexisting carbonic liquid and vapour with specific compositions are in equilibrium with the clathrate phase. Subsequently, only the composition of the carbonic vapour phase is used in our algorithm to calculate the fluid properties in inclusions at final clathrate melting conditions. Calculations of the model limits in the program consist of calculating a maximum clathrate melting temperature in salt-free fluid systems within the immiscibility gap of the carbonic phases.

An example is used to illustrate the use of this program (Table 2, Fig. 6C, Appendix B). First, the density of the nonaqueous phase is estimated at the homogenisation temperature ($T_{\text{H-CAR}}$ in Fig. 6C), which is defined by the intersection of *isochore* 2 and the carbonic two-phase liquid/vapour field. As previously mentioned, this temperature must exceed the final clathrate melting temperature ($T_{\text{M-CLA}}$ in Fig. 6C) for the use of the program *Q2*. Figure 6C illustrates the phase changes occurring in fluid inclusions that are relatively enriched in carbonic gases compared to the composition of clathrate. At eutectic temperatures, the clathrate phase starts to melt ($T_{\text{M-CLA}}^*$ in Fig. 6C) and salt-hydrate crystals disappear. The pressure of the fluid system will shift towards a higher density isochore of the carbonic phases, and the salinity decreases continuously. The composition of the carbonic vapour phase becomes progressively enriched in CO_2 at the expense of its coexisting liquid phase. At the final clathrate melting temperature ($T_{\text{M-CLA}}$ in Fig. 6C) the salinity of the fluid system (*sal.2* in Fig. 6C) is defined by the intersection of continuation of *isochore* 2 within the immiscibility field and the clathrate stability field. Similar to phase occurrences in the program *DENSITY*, different types of phase changes may occur as a consequence of the relative amounts of gases and H_2O in the inclusions. Fluid inclusions that are relatively enriched in H_2O , compared to clathrate compositions, will reveal phase behaviour as illustrated in Figure 7.

The results of the example from Table 2 are illustrated in Appendix B and Figure 8. This program includes only the error analysis of fluid inclusion bulk properties, as a direct consequence of the error in volume fraction estimates. Therefore, the output file (Appendix B) only reveals three columns for the error analysis of the total fluid inclusion properties. In addition, the fluid properties at both the homogenisation temperature of the carbonic phases and at the final clathrate melting temperature are shown in the output file. At the final clathrate melting temperature, this fluid inclusion appears to have 31 vol.% carbonic vapour and 69 vol.% carbonic liquid within the estimated volume fraction of the carbonic phases. Figure 8 reveals small discontinuities in the clathrate stability curve on entering the two-phase field. This is a direct consequence of the use of an equation of state (Duan, Møller, and

Weare, 1992a,b) to calculate the clathrate stability curve, which differs slightly from those used to obtain carbonic liquid-vapour equilibria (Thiery, Kerkhof, and Dubessy, 1994; Lee and Kesler, 1975). Figure 8 emphasises the estimation of the maximum clathrate melting in a hypothetical salt-free fluid system (T_{MAX}), and the freezing point depression of the stability curve due to the presence of salts.

Program NOSALT

A large part of the calculations in the previously mentioned programs consists of limit estimations. Occasionally, the programs *DENSITY*, *ICE*, and *Q2* may not arrive at a solution due to the fact that these limits of the thermodynamic model are exceeded, or the manual input is inconsistent. For example, the final clathrate melting temperature may not exceed certain values depending on the composition of the fluid system. The presence of salts depresses the final clathrate melting temperatures and the ice melting temperatures in fluid systems less than eutectic compositions. Consequently, a salt-free fluid system may illustrate maximum melting conditions. Therefore, the program *NOSALT* has been developed to obtain clathrate stability conditions in salt-free fluid systems, which can be used as a limiting case. In addition, this program is of direct use to samples in which no salts are suspected in the fluid system. In salt-free fluid systems, clathrate melting to form a homogeneous carbonic phase and an aqueous phase is a univariant reaction in a temperature-pressure space. Consequently, this system can be completely defined by measuring only the final clathrate melting temperature.

The use of this program is best illustrated with an example (Table 2, Fig. 6D, Appendix B). The phase behaviour of a fluid inclusion with relative high density carbonic phase is illustrated in Figure 6D. At low temperatures, the inclusion contains a clathrate phase and a carbonic phase, which is either vapour-like or liquid-like. During heating, both phases remain present until the clathrate starts to melt (T_{mCLA} in Fig. 6D). Clathrate melting causes an increase of the density of the carbonic phase, and, consequently, the fluid system will shift towards higher density isochores during further heating. The final clathrate melting temperature (T_{mCLA} in Fig. 6D) defines both pressure and density of the fluid system in the inclusion at the intersection of the clathrate stability curve and a higher density isochore.

The program *NOSALT* also includes final clathrate melting at Q_2 conditions. The homogenisation temperature of the carbonic phases and the final clathrate melting temperature are dependent in this type of melting behaviour. In other words, the density of the carbonic phase is defined at the measured clathrate melting temperature. The program calcu-

lates a final clathrate melting temperature which corresponds to the measured homogenisation temperature, and indicates that this temperature is used in further calculations.

CONCLUSION

Clathrate melting temperatures obtained from $H_2O-CO_2-CH_4-N_2-NaCl-KCl-CaCl_2$ -rich fluid inclusions may give valuable information on salinity and the $V-X$ properties of phases present in fluid inclusions in combination with liquid-vapour equilibria of the gas-rich phases and Raman spectroscopic analysis. Bulk compositions and densities may be obtained with an additional volume fraction estimation. A set of computer programs (*DENSITY*, *ICE*, *Q2*, and *NOSALT*) written in Turbo C++ version 3.0 has been developed to run on a PC for various initiation procedures to calculate clathrate stability conditions, bulk salinities, and bulk compositions and densities of fluid inclusions. The calculations are restricted to fluid compositions less than eutectic salinities. The programs are available publicly and may be downloaded by FTP from the server at IAMG.ORG.

Acknowledgments—Jean Dubessy and Régis Thiery are sincerely acknowledged for their help during this study. I would like to thank Robert McDonnell for discussion and improvements on the English. Larry Diamond and Robert Darling kindly made constructive reviews of the manuscript. This work has been financially supported by the program "Human Capital and Mobility", network HCM, CEE-DG XII-G, contract CT 930198-PL 922279. Most of this work has been accomplished in a position entitled to social security benefit.

REFERENCES

- Adisasmito, S., Frank, R. J. III, and Sloan, E. D. Jr., 1991, Hydrates of carbon dioxide and methane mixtures: Jour. Chemical Engineering Data, v. 36, no. 1, p. 68-71.
- Anderson, F. E., and Prausnitz, J. M., 1986, Inhibition of gas hydrates by methanol: Am. Inst. Chemical Engineering Jour., v. 32, no. 8, p. 1321-1333.
- Angus, S., Armstrong, B., and Reuck, K. M., 1976, International thermodynamic tables of the fluid state: 3. Carbon Dioxide: Pergamon Press, Oxford, 385 p.
- Angus, S., Armstrong, B., and Reuck, K. M., 1978, International thermodynamic tables of the fluid state: 5. Methane: Pergamon Press, Oxford, 251 p.
- Angus, S., Reuck, K. M., and Armstrong, B., 1979, International thermodynamic tables of the fluid state: 6. Nitrogen: Pergamon Press, Oxford, 241 p.
- Bakker, R. J., 1995a, The application of a computerised and optimised clathrate stability model to fluid inclusion studies: ECROFI XIII Barcelona: Boletín de la Sociedad Española de Mineralogía, v. 18, no. 1, p. 15-17.
- Bakker, R. J., 1995b, Improved model for clathrate stability in the $H_2O-CO_2-CH_4-NaCl-KCl-CaCl_2$ system: European Union of Geosciences 8, Terra Abstracts, v. 7, no. 1, p. 70.
- Bakker, R. J., and Thiery, R., 1994, Application of clathrates to fluid inclusion studies, in De Vivo, B., and

- Frezza, M. L., eds., *Fluid Inclusions in Minerals: Methods and Applications: Short Course International Mineralogical Association*, p. 191–208.
- Bakker, R. J., Boiron M. C., Thiéry, R., Dubessy, J., and Cathelineau, M., 1996, Computerised clathrate stability model: specification of metamorphic fluids in inclusions, V.M. Goldschmidt Conference (Abstracts), v. 1, p. 37.
- Bakker, R. J., Dubessy, J., and Cathelineau, M., 1996, Improvements in clathrate modelling I: The $\text{H}_2\text{O}-\text{CO}_2$ system with various salts: *Geochim. Cosmochim. Acta*, v. 60, no. 10, p. 1657–1681.
- Benedict, M., Webb, G. B., and Rubin, L. C., 1949, An empirical equation for thermodynamic properties of light hydrocarbons and their mixtures I. Methane, ethane, propane and n-butane: *Jour. Chem. Phys.*, v. 8, no. 2, p. 334–345.
- Beyer, W. H., 1991, *CRC standard mathematical tables and formulae*: CRC Press, Boca Raton, Florida, p. 9–11.
- Borland, 1992, Turbo C++ (version 3.0) user's guide: Borland International, Scotts Valley, California, 772 p.
- Carroll, J. J., Slupsky, J. D., and Mather, A. E., 1991, The solubility of carbon dioxide in water at low pressure: *Jour. Phys. Chem. Ref. Data*, v. 20, no. 6, p. 1201–1209.
- Carroll, J. J., and Mather, A. E., 1992, The system carbon dioxide–water and the Krichevsky–Kasarnovsky equation: *Jour. Solution Chemistry*, v. 21, p. 607–621.
- Chen, H. S., 1972, The properties of carbon dioxide hydrate: Office of Saline Water, Research and Development Progress Report No. 830, November 1972, p. 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: *Industrial and Engineering Chemistry Fundamentals*, v. 6, no. 4, p. 492–498.
- Collins, P. L. F., 1979, Gas hydrates in CO_2 -bearing fluid inclusions and the use of freezing data for estimation of salinity: *Econ. Geol.*, v. 74, no. 6, p. 1435–1444.
- Darling, R. S., 1991, An extended equation to calculate NaCl contents from final clathrate melting temperatures in $\text{H}_2\text{O}-\text{CO}_2$ -NaCl fluid inclusions: implications for P–T isochore location: *Geochim. Cosmochim. Acta*, v. 55, p. 3869–3871.
- Davidson, D. W., Gough, S. R., Handa, Y. P., Ratcliffe, C. I., Ripmeester, J. A., and Tse, J. S., 1987, Some structural studies of clathrate hydrates: *Jour. Phys. C1*, v. 48, no. 3, p. 537–542.
- Dholabhai, P. D., Kalogerakis, N., and Bishnoi, P. R., 1993, Equilibrium conditions for carbon dioxide hydrate formation in aqueous electrolyte solutions: *Jour. Chem. Eng. Data*, v. 38, no. 4, p. 650–654.
- Diamond, L. W., 1990, Fluid inclusion evidence for P–V–T–X evolution of hydrothermal solutions in late-alpine gold-quartz veins at Brusson, Val d'Ayas, northwest Italian Alps: *Am. Jour. Sci.*, v. 290, p. 912–958.
- Diamond, L. W., 1992, Stability of CO_2 clathrate hydrate + CO_2 liquid + CO_2 vapour + aqueous KCl–NaCl solutions: Experimental determination and application to salinity estimates of fluid inclusions: *Geochim. Cosmochim. Acta*, v. 56, p. 273–280.
- Diamond, L. W., 1994a, Salinity of multivolatile fluid inclusions determined from clathrate hydrate stability: *Geochim. Cosmochim. Acta*, v. 58, no. 1, p. 19–41.
- Diamond, L. W., 1994b, Introduction to phase relations of CO_2 - H_2O fluid inclusions, in De Vivo, B., and Frezzotti, M. L., eds., *Fluid Inclusions in Minerals: Methods and Applications: Short Course International Mineralogical Association*, p. 131–158.
- Duan, Z., Møller, N., and Weare, J. H., 1992a, An equation of state for the CH_4 - CO_2 - H_2O system: I. Pure systems from 0 to 1000°C and 0 to 8000 bar: *Geochim. Cosmochim. Acta*, v. 56, no. 7, p. 2605–2617.
- Duan, Z., Møller, N., and Weare, J. H., 1992b, An equation of state for the CH_4 - CO_2 - H_2O system: II. Mixtures from 50 to 1000°C and 0 to 1000 bar: *Geochim. Cosmochim. Acta*, v. 56, no. 7, p. 2619–2631.
- Dubessy, J., Thiéry, 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: *Eur. Jour. Mineral.*, v. 4, no. 5, p. 873–884.
- Hollister, L. S., and Burruss, R. C., 1976, Phase equilibria in fluid inclusions from the Khtada Lake metamorphic complex: *Geochim. Cosmochim. Acta*, v. 40, no. 2, p. 163–175.
- Jhaveri, J., and Robinson, D. B., 1965, Hydrates in He methane–nitrogen system: *Can. Jour. Chemical Engineering*, April, p. 75–78.
- John, V. T., Papadopoulos, K. D., and Holder, G. D., 1985, A generalized model for predicting equilibrium conditions for gas hydrates: *Am. Inst. Chemical Engineering Jour.*, v. 31, no. 2, p. 252–259.
- Lee, B. I., and Kesler, M. G., 1975, A generalized thermodynamic correlation based on three-parameter corresponding states: *Am. Inst. Chemical Engineering Jour.*, v. 21, no. 4, p. 510–527.
- Ng, H. J., and Robinson, D. B., 1976, The measurement and prediction of hydrate formation in liquid hydrocarbon–water systems: *Industrial and Engineering Chemistry Fundamentals*, v. 15, no. 4, p. 293–298.
- Ng, H. J., and Robinson, D. B., 1977, The prediction of hydrate formation in condensed systems: *Am. Inst. Chemical Engineering Jour.*, v. 23, no. 4, p. 477–482.
- Parrish, W. R., and Prausnitz, J. M., 1972, Dissociation pressure of gas hydrates formed by gas mixtures: *Industrial and Engineering Chemistry, Processes, Design, and Development*, v. 11, no. 11, p. 26–35.
- Peng, D. Y., and Robinson, D. B., 1976, A new two-constant equation of state: *Industrial and Engineering Chemistry Fundamentals*, v. 15, no. 1, p. 59–64.
- Pitzer, K. S., 1992, Ion interaction approach: theory and data correlation, in Pitzer, K. S., ed., *Activity Coefficient in Electrolyte Solutions*: CRC Press, Boca Raton, Florida, p. 76–153.
- Prausnitz, J. M., Lichtenthaler, R. N., and Azevedo, E. G. de, 1986, *Molecular thermodynamics of fluid-phase equilibria*: Prentice Hall Inc., Englewood Cliffs, New Jersey, 600 p.
- Redlich, O., and Kwong, J. N. S., 1949, On the thermodynamics of solutions V: an equation of state. Fugacities of gaseous solutions: *Chem. Rev.*, v. 44, no. 1, p. 233–244.
- Roedder, E., 1963, Studies of fluid inclusions II: Freezing data and their interpretation: *Econ. Geol.*, v. 58, no. 2, p. 167–211.
- Roedder, E., 1984, *Fluid inclusions: Reviews in Mineralogy*, Mineral. Soc. America, v. 12, Blacksburg, 646 p.
- Smith, F. G., 1953, *Historical development of inclusion thermometry*: Univ. Toronto Press, Toronto, Canada, 149 p.
- Soave, G., 1972, Equilibrium constants from a modified Redlich–Kwong equation of state: *Chemical Engineering Science*, v. 27, no. 6, p. 1197–1203.
- Thiery, R., Kerkhof, A. M. van den, and Dubessy, J., 1994, VX properties of CH_4 - CO_2 and CO_2 - N_2 fluid inclusions: modelling for $T < 31^\circ\text{C}$ and $P < 400$ bars: *Eur. Jour. Mineral.*, v. 6, no. 6, p. 753–771.
- Thompson, J. B., Jr., 1967, Thermodynamic properties of simple solutions, in Abelson, P. H., ed., *Researches in Geochemistry*, v. 2: John Wiley & Sons, New York, p. 340–361.

- Waals, J. H. van der, and Platteeuw, J. C., 1959, Clathrate solutions, in Prigogine, I., ed., *Advances in Chemical Physics*, v. 2: Interscience Publishers Inc., New York, p. 1–57.
- 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. Internat.*, v. 30, no. 12, p. 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. Geology*, v. 74, p. 289–308.

APPENDIX A

Program Routines

In order to simplify the program structures, each parameter involved is assigned an individual routine, as illustrated in Figure 1. The routine descriptions give a concise outline of the theoretical models as developed by Dubessy, Thiéry, and Canals (1992), Thiéry, Kerkhof, and Dubessy (1994), Bakker (1995b), Bakker and others (1996), and Bakker, Dubessy, and Cathelineau (1996). For a complete description of the theoretical model, the reader is referred to the study of Bakker, Dubessy, and Cathelineau (1996).

The routine NUMBERS.CPP contains global variables, which are used in both programs and other routines. Additionally, some physical constants, such as Avogadro's number, gas constant, and Boltzmann constant are defined in this routine.

Routine EQUATIONS.CPP is able to solve analytically any quadratic or cubic equation. The results include both real and imaginary numbers. The trigonometric method is used to obtain the solutions of cubic equations (e.g. Beyer, 1991). This method gives exact values in theory; however, computer rounding errors may introduce erratic results.

Routines KELL.CPP, HAAR.CPP, CO2IUPAC.CPP, CH4IUPAC.CPP, and N2IUPAC.CPP include the calculation of the PTV properties of pure H₂O, pure CO₂, pure CH₄, and pure N₂ fluids, respectively, at conditions relevant to clathrate stability conditions. The saturated-liquid and saturated-vapour densities and the vapour pressure along the coexistence curve for pure H₂O and pure CO₂ are calculated with the routines CO2SAT.CPP and H2OSAT.CPP, respectively.

Routines CHUPRA.CPP and SOAVE.CPP are able to calculate *P–T–V–X* properties of H₂O–CO₂–CH₄–N₂ gas mixtures according to the equations of state from Chueh and Prausnitz (1967) and Soave (1972), respectively. These routines use EQUATIONS.CPP to calculate the volumetric properties of fluids from cubic equations at defined temperature, pressure, and composition. Furthermore, the fugacity coefficients of each component in the gas mixture can be calculated, according to the theoretical considerations described by Prausnitz, Lichtenthaler, and Azevedo (1986). These equations of state were originally designed for vapour-like gases and should, therefore, not be used for liquid-like fluids at higher pressures. Routine DUAN.CPP calculates *P–T–V–X* properties and fugacity coefficients of H₂O–CO₂–CH₄ gas mixtures (Duan, Møller, and Weare, 1992a and 1992b), and can be applied to higher pressures.

Routines THIERY.CPP and LEEKESLE.CPP represent a modified Soave equation of state according to Thiéry, Kerkhof, and Dubessy (1994), and a combination of a modified BWR equation of state and Pitzer correlations from Lee and Kesler (1975), respectively. These equations are used in routine LVEQUIL.CPP to calculate liquid–vapour equilibria of gas mixtures. Homogenisation temperatures are converted into densities at bubble and dew-points. At clathrate melting temperatures below homogenisation temperatures, it may calculate the density and composition of coexisting liquid and vapour phases.

The routine THERMO.CPP calculates the Gibbs free energy of pure H₂O (either vapour, liquid, or solid), of hypothetical empty clathrates (either structure I or structure II), and of the gases CO₂, CH₄, and N₂.

Routine LANGMUIR.CPP uses the theory of three-dimensional generalisation of ideal localised adsorption as original proposed by Waals and Platteeuw (1959) and modified by Bakker (1995b), Bakker and others (1996) and Bakker, Dubessy, and Cathelineau (1996) to calculate cell potentials, langmuir constants, and the occupancy of CO₂, CH₄, and N₂ molecules in a clathrate structure, which are used to obtain the chemical potential of H₂O in the clathrate phase.

Routine OSMOTIC.CPP calculates the osmotic coefficient for NaCl-, KCl-, and CaCl₂-bearing solutions according to the model for liquid solutions of Pitzer (1992).

Routine HENRY.CPP calculates the solubility of the gases CO₂ (Carroll, Slupsky, and Mather, 1991) and CH₄, N₂ (Anderson and Prausnitz, 1986) from Henry's constants at selected temperatures, taking into account pressure corrections and salting-out effect.

Routine AQUEOUS.CPP calculates the activity of H₂O in the aqueous solution. The reduction of the activity of H₂O as a consequence of the presence of CO₂, CH₄, N₂, NaCl, KCl, and CaCl₂ in liquid solutions is obtained from gases and salt solubility calculations. The composition of coexisting aqueous and nonaqueous phase are numerically estimated according to the method described by Carroll, Slupsky, and Mather (1991) and Carroll and Mather (1992), based on the equality of chemical potentials for the components in each phase. This routine uses the routines KELL.CPP, HAAR.CPP, CHUPRA.CPP, SOAVE.CPP, DUAN.CPP, OSMOTIC.CPP, and HENRY.CPP.

Routine Q2DEPRI.CPP uses purely empirical equations from Darling (1991), Diamond (1992) and Bakker, Dubessy, and Cathelineau (1996) to calculate the salinity of H₂O–CO₂–salt-rich inclusions from clathrate melting temperatures at Q₂ conditions.

APPENDIX B

DENSITY

Program Density version 10/07/96 R.J.Bakker, CRÉGU, BP 23, 54501 Vandœuvre (France) present address: University Heidelberg (Germany) Filename : density.txt			
CLATHRATE PHASE (at final melting conditions)			
Clathrate Structure 1			
Tm (K)	281.150000	281.250000	281.050000
Pm (MPa)	14.950188	14.905235	14.995195
mole fractions			
H2O	0.856922	0.856948	0.856896
CO2	0.110940	0.111071	0.110810
CH4	0.032137	0.031981	0.032294
N2	0.000000	0.000000	0.000000
NON-AQUEOUS PHASE			
EOS : Duan et al. (1992)			
Vm (cc/mol)	50.769335	50.809052	50.729789
D (g/cc)	0.839285	0.838628	0.839939
Mole fractions			
H2O	0.000068	0.000069	0.000067
CO2	0.949935	0.949934	0.949936
CH4	0.049997	0.049997	0.049997
N2	0.000000	0.000000	0.000000
Fugacity coefficients			
H2O	0.945828	0.943299	0.948385
CO2	0.274416	0.275456	0.273381
CH4	2.900573	2.892135	2.909083
N2	1.000000	1.000000	1.000000
Homogenisation Conditions (In metastable absence of clathrate)			
Vh (cc/mol)	50.769335	50.809052	50.729789
Th (K)	278.150000	278.250000	278.050000
Ph (MPa)	5.199808	5.209580	5.189653
Volume fraction	0.400000	0.360000	0.440000
AQUEOUS SOLUTION (after final clathrate melting)			
EOS : Kell & Whalley (1965)			
Vm (cc/mol)	17.891391	17.891942	17.890841
act(H2O)	0.902596	0.903948	0.901244
Mole fractions			
H2O	0.898410	0.899724	0.897102
CO2	0.023956	0.024048	0.023865
CH4	0.000365	0.000365	0.000364
N2	0.000000	0.000000	0.000000
Salt (K + Cl)	0.077268	0.075862	0.078668
Associated KCl			
Molality	2.387017	2.340152	2.433814
Weight Per.	15.106906	14.854367	15.357590
Henry's constants (MPa)			
CO2	162.678269	162.181972	163.175469
CH4	5942.214677	5900.933424	5983.799801
N2	14188.333841	14085.682551	14291.772904
Volume fraction	0.600000	0.640000	0.560000
TOTAL FLUID INCLUSION			
Vm (cc/mol)	24.148159	23.334150	25.016049
D (g/cc)	0.914047	0.919767	0.908504
mole fractions			
H2O	0.727508	0.750984	0.702469
CO2	0.200118	0.177126	0.224799
CH4	0.009807	0.008571	0.011133
N2	0.000000	0.000000	0.000000
K(+)	0.031284	0.031660	0.030800
Cl(-)	0.031284	0.031660	0.030800
Weight Percentage salt = 100*gram(salt)/gram(total)			
KCl	9.557228	9.907744	9.175928
Molality = mole salt per 1 kg H2O			
KCl	2.386975	2.340117	2.433764

ICE

PROGRAM : ICE version 12/07/96
R.J.Bakker, CREGU, BP 23, 54501 Vandœuvre (France)
present address: University Heidelberg (germany)
Filename : ice.txt

CLATHRATE PHASE (at final melting conditions)

Clathrate Structure 1

Tm (K)	281.850000	0.000000	0.000000
Pm (MPa)	4.593167	0.000000	0.000000
mole fractions			
H2O	0.862330	0.000000	0.000000
CO2	0.120411	0.000000	0.000000
CH4	0.016108	0.000000	0.000000
N2	0.001150	0.000000	0.000000

NON-AQUEOUS PHASE

EOS : Soave (1972) / Thiery et al. (1994)			
Vm (cc/mol)	370.887792	0.000000	0.000000
D (g/cc)	0.106348	0.000000	0.000000
mole fractions			
H2O	0.000539	0.000000	0.000000
CO2	0.819558	0.000000	0.000000
CH4	0.139925	0.000000	0.000000
N2	0.039978	0.000000	0.000000

Volume fraction	0.600000	0.000000	0.000000
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AQUEOUS SOLUTION (after final clathrate melting)

EOS: Kell & Whalley (1965)			
Vm (cc/mol)	17.980081	0.000000	0.000000
act[H2O]	0.963101	0.000000	0.000000
mole fractions			
H2O	0.962122	0.000000	0.000000
CO2	0.024732	0.000000	0.000000
CH4	0.000169	0.000000	0.000000
N2	0.000023	0.000000	0.000000
Salt (Na + Cl)	0.012954	0.000000	0.000000
Associated NaCl			
Molality	0.373677	0.000000	0.000000
Weight Per.	2.137097	0.000000	0.000000
Volume fraction	0.400000	0.000000	0.000000

TOTAL FLUID INCLUSION

Vm (cc/mol)	41.903104	0.000000	0.000000
D (g/cc)	0.473701	0.000000	0.000000
mole fractions			
H2O	0.896938	0.000000	0.000000
CO2	0.078612	0.000000	0.000000
CH4	0.009643	0.000000	0.000000
N2	0.002732	0.000000	0.000000
Na(+)	0.006038	0.000000	0.000000
Cl(-)	0.006038	0.000000	0.000000
Weight Percentage of salt = 100*gram(Salt)/gram(total)			
NaCl	1.746585	0.000000	0.000000
Molality = mole salt per 1 kg H2O			
NaCl	0.373661	0.000000	0.000000

FLUID SYSTEM AT FINAL ICE MELTING

TQ1 (K)	269.050000	0.000000	0.000000
PQ1 (MPa)	1.075468	0.000000	0.000000

CLATHRATE PHASE :

mole fractions			
H2O	0.869056	0.000000	0.000000
CO2	0.119342	0.000000	0.000000
CH4	0.011005	0.000000	0.000000
N2	0.000598	0.000000	0.000000
Volume fraction	0.309736	0.000000	0.000000

NON-AQUEOUS PHASE :

Vm (cc/mol)	1947.694919	0.000000	0.000000
D (g/cc)	0.020252	0.000000	0.000000
mole fractions			
H2O	0.000483	0.000000	0.000000
CO2	0.819604	0.000000	0.000000
CH4	0.139932	0.000000	0.000000
N2	0.039981	0.000000	0.000000
Volume fraction	0.512003	0.000000	0.000000

AQUEOUS PHASE :

Molality NaCl	0.842521	0.000000	0.000000
Weight Per.	4.692642	0.000000	0.000000
Volume fraction	0.176260	0.000000	0.000000

Q2

Program Q2 version 13/07/96
 R.J.Bakker, CREGU BP 23, Vandoeuvre (France)
 present address: University Heidelberg (Germany)
 Filename : q2.txt

CLATHRATE PHASE (at final melting conditions)

Clathrate Structure 1

Tm (K)	280.250000
Pm (MPa)	5.703601

mole fractions	
H2O	0.859541
CO2	0.114892
CH4	0.025567
N2	0.000000

NON-AQUEOUS PHASES

AT HOMOGENISATION CONDITIONS :

Th (K)	292.950000
Ph (MPa)	7.811373
Vh (cc/mol)	68.858795
D (g/cc)	0.598536

xCO2	0.900000
xCH4	0.100000
xN2	0.000000

Volume fraction	0.500000 (± 0.050000)
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AT CLATHRATE MELTING CONDITIONS :

	VAPOUR	LIQUID
Frac (rel)	0.307789	0.692211
Vm (cc/mol)	240.619879	52.267029
x(CO2)	0.817075	0.936872
x(CH4)	0.182925	0.063128
x(N2)	0.000000	0.000000

VAPOUR PHASE IN EQUILIBRIUM WITH CLATHRATE :

EOS : Duan et al. (1992)	
Vm (cc/mol)	261.845809
D (g/cc)	0.148522

Mole fractions	
H2O	0.000206
CO2	0.816906
CH4	0.182887
N2	0.000000

AQUEOUS SOLUTION (after final clathrate melting)

EOS : Kell & Whalley (1965)	
Vm (cc/mol)	17.968462
act[H2O]	0.917678

Mole fractions	
H2O	0.921587
CO2	0.026344
CH4	0.000297
N2	0.000000
Salt (Ca + Cl)	0.051773

Associated CaCl2	
Molality	1.039446
Weight Per.	10.343504

Volume fraction	0.500000 (± 0.050000)
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TOTAL FLUID INCLUSION

Vm (cc/mol)	28.499788	26.921894	30.274158
D (g/cc)	0.776816	0.798012	0.755620

Mole fractions			
H2O	0.730865	0.759440	0.698731
CO2	0.189985	0.165467	0.217556
CH4	0.038092	0.032429	0.044460
N2	0.000000	0.000000	0.000000
Ca(2+)	0.013886	0.014221	0.013084
Cl(-)	0.027372	0.028442	0.026169

Weight Percentage salt = 100*gram(salt)/gram(total)			
CaCl2	6.420727	6.844098	5.969404
Molality = mole salt per 1 kg H2O			
CaCl2	1.039446	1.039446	1.039446

NOSALT

Program NOSALT version 06/07/96
R.J.Bakker, CREGU, BP 23, 54501 Vandœuvre (France)
present address: University Heidelberg (Germany)
Filename : nosalt.txt

CLATHRATE PHASE (at final melting conditions)

Clathrate Structure 1

Tm (K)	285.150000	285.350000	284.950000
Pm (MPa)	7.092901	7.394161	6.813161
mole fractions			
H2O	0.859004	0.858798	0.859208
CO2	0.104534	0.103878	0.105064
CH4	0.036142	0.036892	0.035416
N2	0.000321	0.000333	0.000312

NON-AQUEOUS PHASE

EOS : Soave (1972) / Thierry et al. (1994)
Vm (cc/mol) 206.224402 191.139260 221.195660
D (g/cc) 0.173239 0.186906 0.161517

mole fractions			
H2O	0.000762	0.000813	0.000723
CO2	0.699466	0.699431	0.699494
CH4	0.289779	0.289764	0.289790
N2	0.009992	0.009992	0.009993

fugacity coefficients

H2O	0.252728	0.230373	0.273971
CO2	0.622192	0.606533	0.636566
CH4	0.989264	0.997191	0.983231
N2	1.255087	1.286423	1.229471

Volume fraction	0.800000	0.750000	0.850000
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AQUEOUS SOLUTION (after final clathrate melting)

EOS : Kell & Whalley (1965)
Vm (cc/mol) 17.965179 17.963128 17.967066

mole fractions

H2O	0.974600	0.974443	0.974793
CO2	0.024662	0.024995	0.024689
CH4	0.000529	0.000552	0.000508
N2	0.000010	0.000010	0.000009

Henry's constants (MPa)

CO2	124.161404	125.498181	122.875898
CH4	3645.897692	3872.122112	3821.011672
N2	9050.704309	9109.108640	8995.509814

Volume fraction 0.200000 0.250000 0.150000

TOTAL FLUID INCLUSION

Vm (cc/mol) 66.613748 56.049921 62.025301
D (g/cc) 0.346333 0.399935 0.293042

mole fractions

H2O	0.722948	0.760311	0.667763
CO2	0.199188	0.173324	0.237390
CH4	0.075275	0.064159	0.091691
N2	0.002589	0.002206	0.003156