

CHAPTER 7. COMPUTER MODELING IN FLUID INCLUSION RESEARCH

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INTRODUCTION

The identification of fluid and solid components within individual fluid inclusions is based on both direct (*e.g.*, Raman spectroscopy, infrared spectroscopy, laser ablation techniques) and indirect (*e.g.*, microthermometry) methods. The main objective of these analytical methods is to obtain a bulk composition and density of individual fluid inclusions. The main tools of microthermometry are the use of melting temperatures, dissolution temperatures and homogenization temperatures of specific phases that occur in fluid inclusions during heating and freezing experiments. Equations of state of fluid phases are used to transform microthermometric values into densities and compositions. For example, if a fluid inclusion containing pure water has a homogenization temperature of 247°C into the liquid phase then a bulk density of 0.80 g.cm⁻³ (22.42 cm³.mol⁻¹) can be calculated using the equation of Haar *et al.* (1984). The salinity of aqueous liquid solutions in fluid inclusions can be obtained from the melting temperature of ice (in salt-undersaturated fluids) using purely empirical equations for freezing-point-depression (see also Bodnar 2003). For example, an ice melting temperature of -12.5°C corresponds to a 16.39 mass % NaCl solutionⁱ according to the equation

ⁱ When the word "weight" is used, the intended meaning is clear: weight is a force, for which the SI unit is the newton. In everyday use, weight is usually a synonym for mass, for which the SI unit is the kilogram. The term "mass%" should be used instead of "weight%" for indicating the

from Dubois & Marignac (1997). Most equations of state for fluid systems are extremely complex and not easily applied by most fluid inclusionists. Computer modeling is inevitable for the application of those equations.

Ideally, an equation of state gives a complete description of the physical and chemical properties of fluids, either pure or mixtures. This equation gives the relation between four thermodynamic parameters, *i.e.* temperature (T), pressure (p), volume (V), as density (D) or molar volume (V_m), and composition (x), as amount-of-substance fractionsⁱⁱ, formerly known as mole fraction. The multi-dimensional space (Fig. 7-1) built up from these parameters consists of fields, which are mainly classified as homogeneous (single phase) and heterogeneous fluids (multiple phases). In the homogeneous field, the equation of state is able to reproduce an isochore (line of constant density in a p - T diagram) for a specific fluid inclusion with a constant total volume (Fig. 7-1c). The boundary between the homogeneous

salinity of aqueous solutions (see also Taylor, 1995).

ⁱⁱ Amount of substance is one of the seven base quantities upon which the SI is founded. The symbol for this quantity is n and the SI unit is *mole*. A fraction of n is commonly called "mole fraction" but we prefer the name "amount-of-substance fraction" (symbol x) because it does not contain the name of the unit mole (compare kilogram fraction to mass fraction) (Taylor, 1995). In this paper it is abbreviated with a.s. fraction.

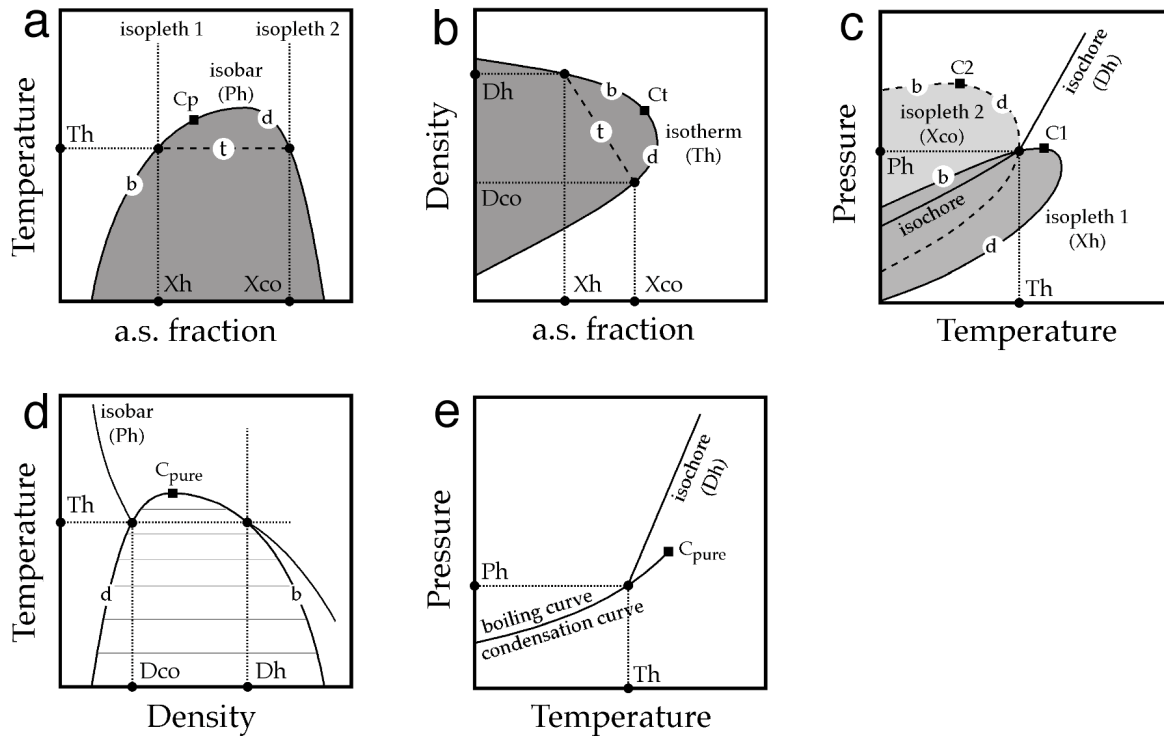


FIG.7-1. Schematic T - x diagram (a), D - x diagram (b) and p - T diagram (c) for fluid mixtures illustrating the relation between the four thermodynamic parameters of fluids. *a.s. fraction* = amount of substance fraction. The shaded areas represent fluid immiscibility. a to c give the complete description of homogenization conditions, *i.e.* temperature (Th), pressure (Ph), density (Dh) and composition (Xh) as predicted by perfect equations of state, which also reproduce the coexisting phases (*isopleths 1* versus *2*, and Xh versus Xco), which are connected by tie lines (t) in a and b. Curves b and d are the bubble point curve (homogenization into the liquid phase) and the dew point curve (homogenization into the vapor phase), respectively. The critical points of *isopleths 1* and *2*, *i.e.* $C1$ and $C2$ respectively, do not correspond to the critical points at the *isotherm* (Ct) and at the *isobar* (Cp), as they occur at different compositions. The fluid properties of pure gases are schematically indicated in a D - T diagram (d) and a p - T diagram (e). See text for further details.

and heterogeneous fields defines the homogenization conditions. At homogenization, melting and dissolution conditions change such that the system crosses a phase boundary and loses a phase. These conditions can be calculated with the same equation of state and can be plotted for specific pressures on a T - x diagram, *i.e.* isobars (Fig.7-1a), for specific temperatures on a D - x diagram, *i.e.* isotherms (Fig. 7-1b) and for specific compositions on a p - T diagram, *i.e.* isopleths (Fig. 7-1c). The schematic example in Figures 7-1a, b and c illustrates homogenization at Th , Ph , Dh and Xh (isopleth 1) into the liquid phase. At this point, the last amount of vapor phase immediately before the homogenization has a composition Xco (*i.e.* isopleth 2) and a

corresponding density Dco . A perfect equation of state would be able to reproduce accurately all the indicated fluid properties, including both isopleths, critical points, tie-lines, dew-point and bubble-point curves. Equations which can predict the homogenization conditions and the fluid properties within the heterogeneous field (both liquid and vapor phases) can also be used to extend the previously mentioned isochore to lower pressures and temperatures (Fig. 7-1c). Pure fluids, which are extremely rare in nature, are described with only three of the four thermodynamic parameters, *i.e.* p , T and V (Fig. 7-1d and e). The isobar for pure fluids lies within the homogeneous field in a T - D diagram (Fig. 7-1d), whereas in mixtures the isobar defines the

boundary between the homogeneous and heterogeneous fields (Fig. 7-1a). The bubble-point and dew-point curves collapse into one single line in a p - T diagram (Fig. 7-1e), which is now indicated as the boiling and condensation curve. The critical point (C_{pure}) is located at the maximum pressure and temperature conditions of this line, unlike critical points in fluid mixtures (c.f. Fig. 7-1a-c). A supreme equation of state for pure gases is able to calculate all the properties illustrated in Fig. 7-1d and e.

Equations of state that give a complete description of fluid systems are rare. They have been developed only for pure gases as highly complex unified Helmholtz-energy functions (e.g., Span & Wagner 1996). Other equations of state only describe parts of fluid systems. As exemplified in Fig. 7-2, the dark-shaded areas schematically illustrate a limited p - T - V - x space to which these equations can be applied (cf. Fig. 7-1a, b and c). The coexistence of a second fluid phase (vapor or liquid) is mostly neglected in these equations, which describe in general either aqueous liquid solutions (melting temperature of ice, and total homogenization into the liquid phase) or homogeneous gas-rich fluids. Modified Redlich-Kwong equations of state (MRK) were originally designed for homogeneous vapor-like phases and are unable to describe a liquid phase or electrolyte solutions accurately. They are based on theoretical equations, as developed by Waals

(1873) and are modified according to empirical considerations (e.g., Holloway 1977). Consequently, phase equilibria in the vicinity of the homogenization conditions cannot be calculated accurately using this type of equation. Theoretically, they can be applied to any fluid mixture by using appropriate mixing rules. However, their accuracy is often not satisfactory, as they are commonly unable to reproduce carefully obtained experimental data. Several purely empirical equations have been developed, mainly for H_2O -salt fluid systems. These types of equations are even more restricted than the previously described semi-empirical MRK equations. The equations are polynomial functions of temperature, and adequately fit only a small part of the p , T , V and x relationships. For example, melting temperatures of ice, hydrohalite and halite can be directly used in simple polynomial functions to calculate salinities of the aqueous liquid solution (e.g., Bodnar 1993), without knowledge of the composition and density of the corresponding vapor phase (e.g., Fig. 7-2a). The density of salt-bearing aqueous solutions, e.g., for the $NaCl$ - $CaCl_2$ - H_2O fluid system (Oakes *et al.* 1990), can be described purely empirical in a very small temperature and salinity range (Fig. 7-2b), without knowing the properties of a coexisting phase. Zhang & Frantz (1987) and Bodnar & Vityk (1994) present relatively simple equations for the construction of

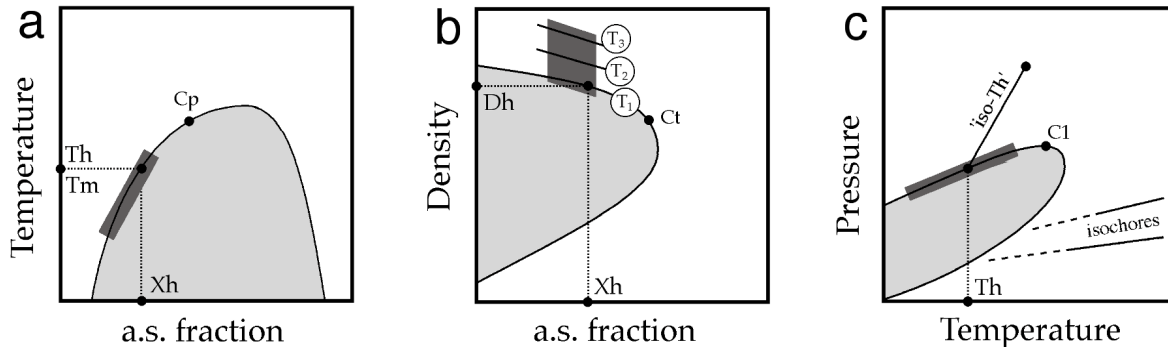


FIG. 7-2. Schematic T - x diagram (a), D - x diagram (b) and p - T diagram (c) for fluid mixtures, similar to Fig. 1a, b and c, indicating the limited space (dark shaded areas) taken into account by most of the available equations of state. Freezing point depression of ice may be represented by a small part of (a). Density of aqueous solution for a limited range of salinities and temperatures (T_1 , T_2 and T_3) can be represented by a small part of b. Total homogenization of an aqueous solution into the liquid phase is represented in a small part of a and c. Calculations of isochores from total homogenization into the liquid phase ($iso-Th$) and of isochores of homogeneous gas-rich mixtures is indicated in c. See text for further details.

isochores in the H_2O -NaCl system. The homogenization temperatures are not explicitly transformed into density values, but 'near-isochores' are directly constructed as 'iso-Th' linesⁱⁱⁱ in a p - T diagram (Fig. 7-2c). These lines can only be applied to fluid systems in natural inclusions that exactly match the experimentally used fluid. Although purely empirical equations have a favorable mathematical simplicity, their application is limited as often extrapolations and even interpolations between the four thermodynamic parameters p , T , V and x are impossible. Knowledge of the limitations of equations of state is a prerequisite for the most effective use of computer programs.

The interpretation of microthermometric data is also restricted by identity of the phases present in the micro-fluid system in inclusions. For example, the melting temperature of ice in the presence of an aqueous liquid solution and a vapor bubble reflects a specific salinity. However, the ice melts metastably at higher temperatures in the absence of the vapor bubble, which may regularly occur in high-density fluid inclusions. Moreover, if a H_2O - CO_2 clathrate phase is present at final ice melting, this temperature does not reflect the total salinity of the aqueous phase, as it is diluted during later melting of the clathrate phase. Melting of an H_2O - CO_2 clathrate in the presence of a CO_2 -rich liquid and vapor phase also reflects a certain salinity. However, the salinity of the system is not defined from clathrate melting in the presence of only a CO_2 -rich vapor or only a CO_2 -rich liquid. Therefore, knowledge of the phases present at specific melting and homogenization temperatures is indispensable for appropriate use of computer programs.

In the following sections we review some of the features of computer programs available to help interpret largely microthermometric data.

PACKAGE CLATHRATES

Fluid inclusions containing H_2O and a gas form gas-hydrates (clathrates) during freezing

ⁱⁱⁱ An 'iso-Th' line connects the experimental conditions of the synthesis of inclusions with a certain fluid composition to their homogenization conditions in a p - T diagram. Iso-Th lines are indicated as "near-isochores" because they are not necessarily parallel terms.

experiments. The conditions under which a clathrate is stable depend on the types of gas present in the vapor phase and the amount of salt present in the aqueous solution, as the salt affects the chemical potential or activity of H_2O . Clathrates are ice-like solid phases that exhibit a freezing-point-depression in the presence of salt, similar to the behavior of water-ice. In a binary H_2O -salt system, the salinity is directly obtained from the melting temperature of ice in the presence of a vapor phase. In a ternary H_2O -gas-salt system, the melting temperature of a clathrate does not, by itself, define the salinity and additional information is needed to fully characterize the system. Bakker (1997) describes several computer programs in the package *CLATHRATES* that handle specific combinations of data, in addition to clathrate melting temperatures, to obtain bulk fluid inclusion densities and compositions in the fluid system H_2O - CO_2 - CH_4 - N_2 - C_2H_6 -NaCl-KCl-CaCl₂-MgCl₂. This package consists of 5 programs: *DENSITY*, *ICE*, *Q2*, *NOSALT* and *CURVES*. The first three programs correspond to three specific types of melting behavior in fluid inclusions (Fig. 7-3), whereas the last two can be used to obtain limiting conditions, *i.e.* in binary H_2O -gas systems or within p - T - x diagrams, respectively.

DENSITY

For fluid inclusions containing a high-density (liquid-like) gas-rich phase and an aqueous liquid solution at room temperature (path **a** in Fig. 7-3), observations can be made in the metastable absence of clathrates in freezing experiments (*i.e.* where a clathrate fails to nucleate on freezing). Clathrate consumes part of the available gas during its nucleation. Consequently, the remaining gas-rich phase becomes less dense with a corresponding higher homogenization temperature. If these homogenization conditions lie within the stability field of the clathrate phase, true density of the gas-rich phase can only be obtained from homogenization temperatures (*e.g.*, $\text{L}_{\text{CO}_2}\text{-V}_{\text{CO}_2} \rightarrow \text{L}_{\text{CO}_2}$) in the metastable absence of a clathrate, which may regularly occur (see also Diamond 1992). Therefore, the melting temperature of the clathrate phase, which subsequently might be nucleated on further cooling the system, must exceed the homogenization temperature of the gas. This method can only be used if the homo-

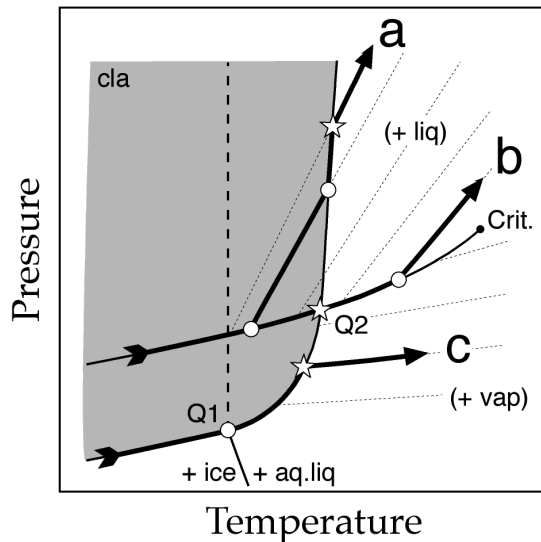


FIG.7-3. Schematic p - T diagram illustrating the stability conditions of a clathrate phase (shaded area, *cla*) in an H_2O - CO_2 fluid system. The stability fields of ice and an aqueous liquid solution (*aq.liq*) in the absence of another fluid species are separated by the dashed line. a, b, c illustrate different p - T paths that may occur in fluid inclusions with different CO_2 densities during heating. The stars indicate the final melting conditions of the clathrate phase. The thin dashed lines are isochores of the carbonic phase. *Crit.* is the critical point of CO_2 . *vap* and *liq* indicate the presence of a vapor-like and liquid-like CO_2 phase. *Q1* and *Q2* refer to the two quadruple points of this system (see also Bakker 1997).

genization temperature of the gas phases exceeds the nucleation temperature of clathrate or ice during cooling (generally lower than -30°C).

ICE

For inclusions containing a low-density gas phase in an aqueous liquid solution, additional observations are required, and include the melting temperature of ice and an estimation of the volume fraction of the vapor bubble after the clathrate has melted (see also Dubessy *et al.* 1992, Bakker *et al.* 1996). When the clathrate melting temperature exceeds the ice melting temperature (path *c* in Fig. 7-3), the initial estimate of the salinity of the aqueous solution is obtained directly from the ice melting temperature. Continued heating and melting of

the clathrate will dilute the aqueous solution. Therefore, a mass balance using both measured final ice and final clathrate melting temperatures in addition to volume fraction estimates (vapor), enables the calculation of the bulk density and composition (including the salinity) of fluid inclusions.

Q2

The presence of coexisting liquid and vapor gas phases (in general CO_2 -rich), as well as an aqueous liquid solution at clathrate melting defines the 'Q2' melting, *i.e.* melting at an invariant point (path *b* in Fig. 7-3). In this configuration the clathrate melting temperature directly reflects the salinity of the aqueous liquid solution. In contrast to the *DENSITY* program, the homogenization temperature of the gas phases must exceed the clathrate melting temperature. The carbonic phase has a density intermediate between the two previously described melting behaviors.

NOSALT

Salt dissolved in an H_2O -gas system depresses the stability field of clathrates to lower temperatures. Consequently, a binary H_2O -gas fluid system exhibits maximum clathrate melting temperatures. The *NOSALT* program can be used to estimate those limiting conditions for any kind of the previously described clathrate melting behavior.

CURVES

The *CURVES* program is used for the construction of p - T - V - x diagrams with clathrate stability curves for any type of gas-hydrate in the system H_2O - CO_2 - CH_4 - N_2 - C_2H_6 , up to eutectic salinities of NaCl - KCl - CaCl_2 - MgCl_2 mixtures dissolved in the aqueous liquid solution.

EXAMPLES OF PACKAGE CLATHRATES

The freezing/heating behavior of a synthetic H_2O - CO_2 fluid inclusion in quartz is illustrated in Fig. 7-4. This inclusion illustrates the characteristics of typical Q2 melting. The melting of the CO_2 -rich phase occurs at -56.6°C in the presence of a vapor phase ($\text{S}_{\text{CO}_2}\text{-V}_{\text{CO}_2} \rightarrow \text{L}_{\text{CO}_2}\text{-V}_{\text{CO}_2}$), indicative of pure CO_2 . Subsequently, the inclusion contains a CO_2 liquid and vapor phase and a clathrate solid phase (Fig. 7-4b). During further heating, the relative volumetric

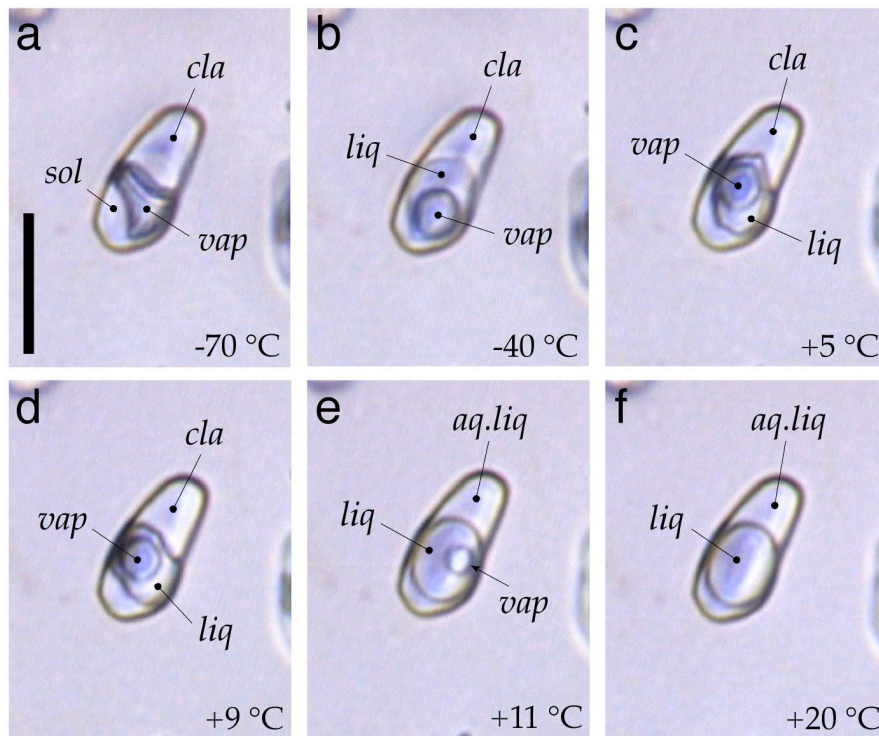


FIG.7-4. A heating sequence of a synthetic H_2O - CO_2 -rich fluid inclusion in quartz, at -70°C (a), -40°C (b), $+5^\circ\text{C}$ (c), $+9^\circ\text{C}$ (d), $+11^\circ\text{C}$ (e) and $+20^\circ\text{C}$ (f). *sol*, *vap*, *liq* and *cla* are the CO_2 solid phase, CO_2 vapor phase, CO_2 liquid phase and clathrate phase, respectively. *aq.liq* is the aqueous liquid solution after clathrate melting. The scale-bar has a length of 10 μm .

proportions of the phases do not change. The clathrate phase recrystallizes continuously, but does not melt. Even at 9°C (Fig. 7-4d) the presence of a solid phase is still noticeable from the deformed meniscus between the clathrate and CO_2 liquid phase. The spherical CO_2 vapor bubble is floating freely in the CO_2 liquid phase. After clathrate melting at 9.9°C , *i.e.* Q2 conditions, CO_2 (liq), CO_2 (vap) and an H_2O -rich liquid solution remain in the inclusion (Fig. 7-4e). The release of CO_2 from the clathrate phase causes a sudden increase of the CO_2 density, *i.e.* a sudden decrease in the CO_2 vapor bubble size. At 17.9°C the CO_2 (liq) and CO_2 (vap) phases homogenize into the liquid phase. At room temperature (Fig. 7-4f) the homogeneous gas bubble (liquid-like) occupies 48 volume % of the inclusion. The properties of this fluid inclusion can be calculated with the *NOSALT* program, or with the *Q2* program if the presence of salts is suspected. Under these circumstances, an additional phase must be present in the inclusions at lower temperatures, *i.e.* a salt-hydrate in Fig. 7-

4a and 4b, and an aqueous liquid solution in Fig. 7-4c and 4d. Consequently, knowledge of the phases present during the reported melting and homogenization temperature are of importance for selecting the calculation procedure. The input proceedings in the *NOSALT* program are illustrated in Fig 7-5. The calculated properties (output) of this fluid inclusion are given in Appendix 7-1. The program has calculated the exact composition and density of the individual phases present after clathrate melting. In addition, the estimated volume fraction of the homogeneous gas bubble allows the calculation of bulk properties. The *NOSALT* program initially requires information on the phase conditions of clathrate melting (Fig. 7-5a). Then, an equation of state has to be selected to calculate gas fugacities at clathrate melting conditions. Bakker (1997, 1998) gives the criteria for this selection procedure. The choice between several equations of state allows the user to perform experimental calculations. Subsequently, the composition of the homogeneous gas phase is introduced (Fig. 7-5b),

a THE CLATHRATE PHASE

Which other phases are present at final clathrate melting?

(0) default
 (1) HLL : gasmixture (liq) + H2O (liq)
 (2) Q2 : gasmixture (liq+vap) + H2O (liq)
 (3) HLV : gasmixture (vap) + H2O (liq)
 (4) Q1 : gasmixture (vap) + H2O (liq+sol)
 (5) HIV : gasmixture (vap) + H2O (sol)

choose number: 2

Equation of state to calculate fugacities in clathrate equilibrium:

(1) Chueh & Prausnitz (1967) : (H2O)-CO2-CH4-N2-C2H6
 (2) Soave (1972) : (H2O)-CO2-CH4-N2-C2H6
 (3) Lee & Kesler (1975) : (H2O)-CO2-CH4-N2-C2H6
 (4) Peng & Robinson (1976) : (H2O)-CO2-CH4-N2-C2H6
 (5) Duan et al. (1992a,b) : H2O-CO2-CH4
 (6) Duan et al. (1996) : H2O-CO2-CH4-N2

choose number: 5

b NON-AQUEOUS PHASE: mixture of CO2-CH4-N2-C2H6

What is the composition of the homogeneous phase?
 (amount-of-substance fractions, number between 0 and 1):

x(CO2) : 1
 x(CH4) : 0
 x(N2) : 0
 x(C2H6) : 0

c THE AQUEOUS PHASE

Is the volume percentage of the aqueous liquid solution known,
 directly after final clathrate melting?

(y/n) : y

Volume percentage (number between 0 and 100%) = 52

d CALCULATION INSTRUCTIONS

The density of the non-aqueous phase is required for Q2 melting

WARNING: Density should correspond to P-T conditions at Q2
 (or Th should exceed clathrate melting temperature)

Density obtained from:

(1) Molar Volume (in cc/mol)
 (2) Density (in g/cc)
 (3) Homogenisation temperature
 (4) Homogenisation pressure

choose number: 3

Equation of state to calculate liquid-vapour equilibria:

Duschek et al. (1990) : pure CO2

Homogenisation temperature (° Celsius) = 17.9

Mode of homogenisation:

(1) vapour
 (2) liquid
 (3) critical

choose number: 2

FIG. 7-5. See caption on following page.

e

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Q2 APPROXIMATION, intersection HLV and liquid-vapour equilibria
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Temperature = 10 °Celsius

Liquid-Vapour equilibrium at clathrate melting

    Fraction vapour = 0.091395
    Vm (liquid) = 51.107819
    Vm (vapour) = 325.629921

Pressure (liquid-vapour) = 4.50196 MPa
    Iteration: 1 2 3 4 5 6 7 8 9
Pressure (clathrate) = 4.641001 MPa

Temperature should be lower for equal pressures
Change temperature approximation? (y/n): y
New temperature (°Celsius) = 9.8091
-----
Temperature = 9.8091 °Celsius

Liquid-Vapour equilibrium at clathrate melting

    Fraction vapour = 0.093048
    Vm (liquid) = 51.024164 cc/mol
    Vm (vapour) = 327.725781 cc/mol

Pressure (liquid-vapour) = 4.48069 MPa
    Iteration: 1 2 3 4 5 6 7 8
Pressure (clathrate) = 4.480652 MPa

Good fit! stop iterations

Results are now available in file: test1

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FIG.7-5 (continued). Calculation instructions for the program *NOSALT*, according to the heating experiment illustrated in Fig. 7-4. The references indicated in this figure are further specified in the appendices and in Bakker (2003).

which can be obtained either by Raman spectrometry, knowledge about triple-point melting or a fictitious composition of the four gas components CO₂, CH₄, N₂ and C₂H₆. The volume fraction of the aqueous liquid solution is optionally required (Fig. 7-5c). Without this information the program will still calculate the properties of the individual phases but not the bulk fluid. Then, the program requires the definition of the gas density, which can be introduced as a known value or as obtained from homogenization conditions (Fig. 7-5d). An equation of state has to be selected manually to analyze the homogenization conditions for gas mixtures, whereas pure gases are calculated with automatically selected equations. Mixtures of CO₂-CH₄-N₂ are best analyzed with the combination of Soave (1972) and Lee & Kesler (1975) as presented in Thiéry *et al.* (1994). The final calculation of clathrate melting at Q2 conditions is illustrated in Fig. 7-5e. It is an iterative procedure, which calculates, at a selected

temperature, the pressure of the clathrate equilibrium and the pressure of CO₂ liquid-vapor equilibrium (including coexisting fluid compositions). The temperature can be adjusted until a satisfactory result is obtained, where the pressure difference becomes minimal. The actually measured temperature of Q2 melting may differ from this calculated temperature. However, it must be kept in mind that this example handles a fluid inclusion with a known gas composition with a fixed invariable point (Q2). In that case, either an inaccurate measurement or imprecision in modeling causes any differences between both temperatures.

A natural fluid inclusion in quartz containing a mixed H₂O-CH₄-NaCl fluid behaves differently at low temperatures (Fig. 7-6) when compared to the previously described H₂O-CO₂ example. At -140°C, the inclusion in this example contains two CH₄-rich phases, *i.e.* liquid and vapor, in addition to a mixed mass of what should be ice, clathrate and hydrohalite (Fig. 7-6a).

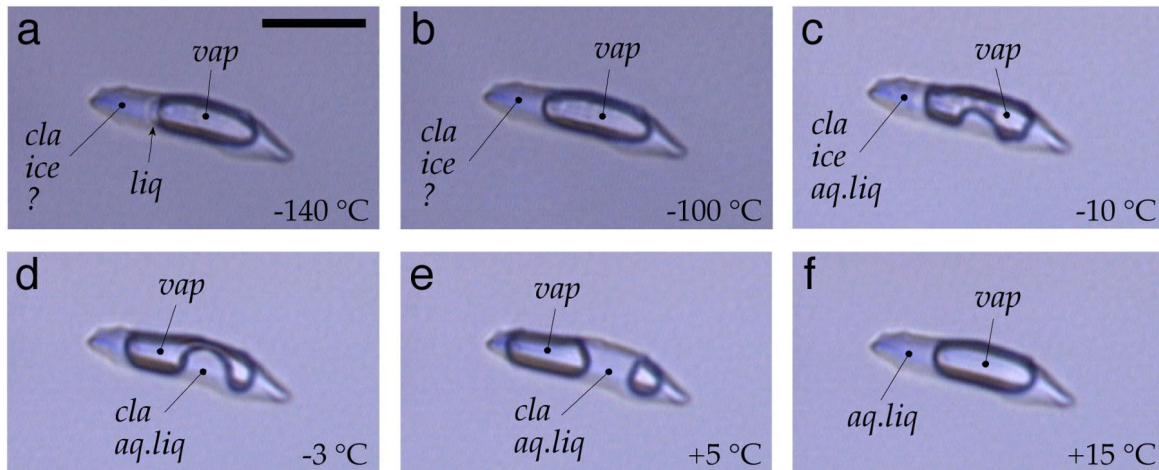


FIG.7-6. A heating sequence of a natural $\text{H}_2\text{O}-\text{CH}_4\text{-NaCl}$ -rich fluid inclusion in quartz, at -140°C (a), -100°C (b), -10°C (c), -3°C (d), $+5^\circ\text{C}$ (e) and $+15^\circ\text{C}$ (f). *ice*, *aq.liq*, *cla*, *liq* and *vap* are the ice phase, aqueous liquid phase, clathrate phase, CH_4 -liquid phase and CH_4 -vapour phase, respectively. The scale-bar has a length of $10\text{ }\mu\text{m}$.

Optically, none of these solid phases can be separately identified. The total amount of hydrohalite is probably very small due to a relatively low bulk salinity value. The CH_4 -rich phases homogenize into the vapor phase at about -110°C (Fig. 7-6b). At the (unknown) eutectic temperature of this system, the hydrohalite is replaced by an aqueous liquid solution. Subsequently, at -10°C (Fig. 7-6c), the inclusion contains ice, clathrate, a saline aqueous liquid and a CH_4 -rich vapor bubble. Ice crystals can be clearly distinguished from clathrate crystals, as ice forms rounded grains whereas clathrate has an irregular and needle-like morphology. Therefore, the melting of ice at -3.5°C is easily observed. At higher temperatures, the presence of clathrate crystals can be inferred from the somewhat irregular shape of the meniscus around the vapor bubble and the separation of the gas phase in multiple bubbles (Fig. 7-6e). Several small clathrate crystals may float in the aqueous liquid solution in contact with the CH_4 vapor bubble. The clathrate finally melts at 12.3°C (Fig. 7-6f). The fluid properties of this inclusion can be calculated by using the *ICE* program, with the addition of an estimated volume fraction of the gas bubble at room temperature, here 55 volume %. The calculation procedures (input) of this program are illustrated in Fig. 7-7. The calculated composition and density of each phase present after clathrate melting, and the bulk properties are given in Appendix 7-2. The *ICE* program requires

the specification of a clathrate melting temperature, the composition of the vapor bubble, and an equation of state to calculate fugacities of the gas mixture at the final clathrate melting temperature (Fig. 7-7a and b). The choice of the equation of state depends on the conditions at clathrate melting, *i.e.* the type of gas mixture present and the p - T conditions (see also Bakker 1998). The dissolved salt has to be chosen for the aqueous solution (Fig. 7-7c), one or more of NaCl , KCl , CaCl_2 and MgCl_2 . The use of equivalent mass % NaCl (formerly known as equivalent weight %) is obtained by assuming that 100% of the salt is NaCl . Any additional information or experimental salt solutions can be used to specify the composition in the computer program. Furthermore, the program requires a final ice melting temperature and an estimation of the volume % of the aqueous liquid solution after clathrate melting (Fig. 7-7c). A specific fluid system has a finite number of possible pairs of final ice and final clathrate melting temperatures. Therefore, the *ICE* program allows a limit check in order to estimate those boundary conditions (Fig. 7-8). First, a maximum ice melting temperature is estimated in a salt-free system. As with dissolved salts, gases also depress the freezing point of water. For example, CH_4 is able to depress this temperature to -0.3°C . A restriction of the clathrate model includes a maximum pressure of clathrate stability at 200 MPa (see also Bakker 1997), above which the

a THE CLATHRATE PHASE

What is the final Clathrate Melting Temperature?

T (°Celsius) = 12.3

Equation of state to calculate fugacities in clathrate equilibrium:

- (1) Chueh & Prausnitz (1967) : (H₂O)-CO₂-CH₄-N₂-C₂H₆
- (2) Soave (1972) : (H₂O)-CO₂-CH₄-N₂-C₂H₆
- (3) Lee & Kesler (1975) : (H₂O)-CO₂-CH₄-N₂-C₂H₆
- (4) Peng & Robinson (1976) : (H₂O)-CO₂-CH₄-N₂-C₂H₆
- (5) Duan et al. (1992a,b) : H₂O-CO₂-CH₄
- (6) Duan et al. (1996) : H₂O-CO₂-CH₄-N₂

choose number: 5

b NON-AQUEOUS PHASE mixture of CO₂-CH₄-N₂-C₂H₆

What is the composition?
(amount-of-substance fraction, number between 0 and 1):

x(CO₂) : 0
x(CH₄) : 1
x(N₂) : 0
x(C₂H₆) : 0

c THE AQUEOUS PHASE mixture of H₂O-NaCl-KCl-CaCl₂-MgCl₂

Relative mass ratio of salts in aqueous solution (0-100%):

NaCl = 100
KCl = 0
CaCl₂ = 0
MgCl₂ = 0

What is the final Ice Melting Temperature?

T (°Celsius) = -3.5

What is the volume percentage of the aqueous liquid solution phase?
(directly after final clathrate melting)

Volume percentage (number between 0 and 100%) = 45

FIG.7-7. Calculation instructions for the program *ICE*, according to the heating experiment illustrated in Fig. 7-6. The references indicated in this figure are further specified in the appendices and in Bakker (2003).

calculations are highly imprecise. At this pressure of 200 MPa, the program calculates a corresponding maximum clathrate temperature in a salt-free system of 39.9°C for the binary H₂O-CH₄ fluid system. Subsequently, the program calculates the minimum ice melting temperature at a eutectic NaCl salinity, *i.e.* 5.463 molal, corresponding to -23.45°C. After these boundary estimations, the first calculation procedure consists of the estimation of the salinity at the final ice melting temperature, in the presence of clathrate, aqueous liquid solution, and a vapor bubble, *i.e.* Q1 melting. Subsequently, the mass balance between final ice melting and final clathrate melting is used to calculate the bulk fluid properties of the fluid inclusion (Appendix 7-2).

A combination of clathrate melting in the presence of ice/vapor (as in the *ICE* program) and at Q2 conditions in a single fluid inclusion is illustrated in Fig. 7-9. A synthetic H₂O-CO₂ fluid inclusion in quartz at -70°C contains CO₂ solid, CO₂ vapor and an ice-glassy substance (Fig. 7-9a). At -56.6°C CO₂ solid has melted and only a CO₂ vapor phase remains present ($S_{\text{CO}_2}\text{-}V_{\text{CO}_2} \rightarrow V_{\text{CO}_2}$) in addition to the glass (Fig. 7-9b), which starts to recrystallize to ice and clathrate around -30°C (Fig. 7-9c). At -1.4°C ice crystals have melted and the presence of a clathrate phase and aqueous liquid solution is suspected from a partly deformed meniscus of the vapor bubble (Fig. 7-9d and 9e). During further heating, the clathrate is continuously decreasing in size, *i.e.* melting and releasing H₂O to the aqueous liquid solution and

```

Do you want a limit check (calculation of maximum temperature)?

(y/n) : y

SALT-FREE FLUID SYSTEM:

Q1 APPROXIMATION, intersection HIV-HLV
-----
Total Molality equivalent = 0 mol salt/kgH2O
Temperature = -2 °Celsius

Iteration: 1 2 3 4 5 6 7
Pressure (HIV) = 2.455606 MPa
Iteration: 1 2 3 4 5 6
Pressure (HLV) = 2.19562 MPa

Temperature should be higher for equal pressures
Change temperature approximation? (y/n): y
New temperature (°Celsius) = -0.3
-----
Total Molality equivalent = 0 mol Salt/kgH2O
Temperature = -0.3 °Celsius

Iteration: 1 2 3 4 5
Pressure (HIV) = 2.583161 MPa
Iteration: 1 2 3 4 5 6 7
Pressure (HLV) = 2.583165 MPa

Good fit! stop iterations

*****
Maximum ice melting temperature = -0.3 °C (at zero salinity)
*****

Iteration: 1 2 3 4

*****
Maximum clathrate melting temperature = 39.876229 °C (at 200 MPa)
*****

EUTECTIC NaCl SYSTEM (molality = 5.463 mol/kgH2O):

Q1 APPROXIMATION, intersection HIV-HLV
-----
Total Molality equivalent = 5.463 mol salt/kgH2O
Temperature = -13 °Celsius

Iteration: 1 2 3 4 5 6
Pressure (HIV) = 1.743052 MPa
Iteration: 1 2 3 4 5 6 7
Pressure (HLV) = 3.590291 MPa

Temperature should be lower for equal pressures
Change temperature approximation? (y/n): y
New temperature (°Celsius) = -23.453
-----
Total Molality equivalent = 5.463 mol Salt/kgH2O
Temperature = -23.453 °Celsius

Iteration: 1 2 3 4 5
Pressure (HIV) = 1.225639 MPa
Iteration: 1 2 3 4 5
Pressure (HLV) = 1.225659 MPa

Good fit! stop iterations

*****
Minimum ice melting temperature = -23.453 °C (at 5.463 mole NaCl/kgH2O)
*****

```

FIG.7-8. Calculation instruction in the program *ICE* for the estimation of boundary condition of the selected fluid system.

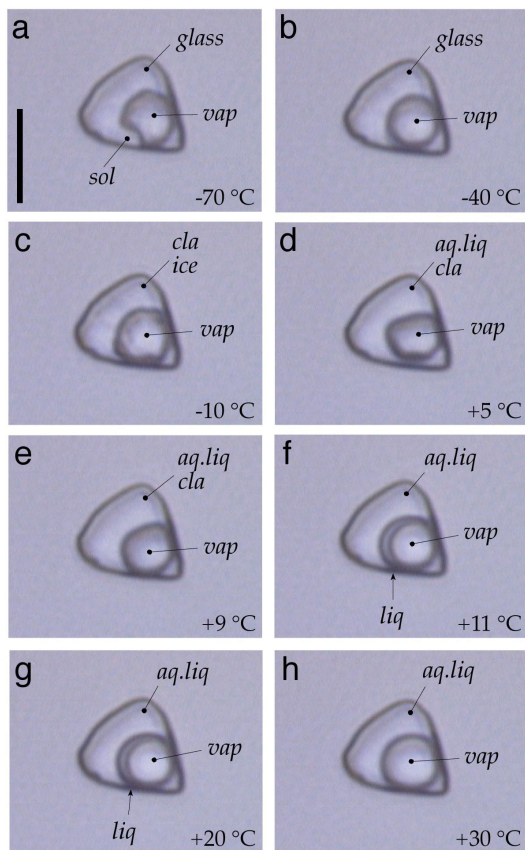


FIG.7-9. A heating sequence of a synthetic H₂O-CO₂-rich fluid inclusion in quartz, at -70°C (a), -40°C (b), -10°C (c), +5°C (d), +9°C (e), +11°C (f), +20°C (g) and +30°C (h). *ice*, *aq.liq*, *cla*, *sol*, *liq* and *vap* are the ice phase, aqueous liquid phase, clathrate phase, CO₂-solid phase, CO₂-liquid phase and CO₂-vapor phase, respectively. The scale-bar has a length of 10 μ m.

CO₂ to the vapor bubble. The final clathrate melting occurs at 9.8°C, and the CO₂ released to the bubble causes a phase separation of CO₂ (liq) and CO₂ (vap) (Fig. 7-9f and g). These phases homogenize at 23.3°C into the vapor phase (Fig. 7-9h). In this specific example the *Q2* program must be used to calculate bulk fluid properties, because both CO₂ (liq) and CO₂ (vap) are present at the final clathrate melting temperature.

PACKAGE FLUIDS

Fluid inclusions that do not have observed clathrate melting temperatures can be interpreted by using the computer package *FLUIDS* (Bakker 2003). Moreover, this package

provides a digital library and workshop for all available equations of state and thermodynamic modeling of fluid systems. This package consists of five sets of computer programs: *BULK*, *ISOC*, *TEST*, *Loners*, and *AqSo*. The package includes the fluid components H₂O, CO₂, CH₄, N₂, C₂H₆, H₂S, NH₃, H₂, O₂ and CO in addition to the salt components NaCl, KCl, CaCl₂ and MgCl₂.

BULK

This program calculates bulk densities (and molar volumes) and bulk compositions of fluid inclusions, using information obtained from microthermometry, micro-Raman spectroscopy, cation ratios and volume fraction estimates. In complex fluid systems including H₂O, gases and salts, the formation of stoichiometric hydrates (*i.e.* salt hydrates) and non-stoichiometric hydrates (*i.e.* clathrates) is expected in freezing experiments. Consequently, the package *CLATHRATES* is more likely to be applicable to these types of fluids. However, the hydrate phases may be metastably absent or not observable, which makes the use of the *BULK* program necessary.

ISOC

Isochores of fluid systems, *i.e.* lines of constant density (or molar volume) in a *p-T* diagram, can be constructed in the *ISOC* program for a selected fluid composition. Compositional information for the fluid system is obtained either from the *BULK* program or from the package *CLATHRATES*. Additionally, a hypothetical bulk composition and density may be used as inputs. Isochores can be corrected for the compressibility and expansivity of the mineral hosting the fluid inclusion.

Loners

This is a group of programs consisting of individual equations of state. Each program is able to calculate *p-T-V-x* properties for a specific equation of state. In addition, other thermodynamic properties like Helmholtz energy, entropy, enthalpy, Gibbs energy, heat capacity, speed of sound and Joule-Thomson coefficient can also be calculated from unified Helmholtz-energy functions. A list of all equations of state included in this group is given in Bakker (2003).

AqSo

The properties of aqueous liquid solutions can be calculated with the group *AqSo*, which consist of three parts: 1. programs that use Henry's law and salting-out coefficients to calculate the solubility of gases in H₂O; 2. programs that use osmotic coefficients to calculate the properties (e.g., solubilities, activity coefficients, excess Gibbs energies, molar volumes) of an aqueous liquid solution containing dissolved salts; and 3. programs using purely empirical equations for salinity calculation directly obtained from freezing point depression. Further specifications are found in Bakker (2003).

EXAMPLES OF THE PACKAGE *FLUIDS*

A natural fluid inclusion in quartz (Fig. 7-10) contains a mixture of CH₄ and CO₂. These components did not freeze when cooled to -190°C, a metastability commonly observed in most gas-rich fluid inclusions. Consequently a melting temperature could not be measured. At -190°C, a CH₄-rich vapor bubble coexists with a liquid phase with a higher CO₂/CH₄ ratio; these homogenize at -77°C into the vapor. A Raman peak-area analysis of the homogeneous fluid at room temperature reveals a composition of approximately 93 amount-of-substance % CH₄ and 7 amount-of-substance % CO₂. Either the *BULK* program or one of the *Loner* programs, using only that equation of state that reproduces accurately the CO₂-CH₄ homogenization conditions, can calculate the properties of this inclusion. Fig. 7-11 illustrates the steps used to run the *BULK* program with the above fluid information. The program has nine predefined fluid systems, with up to four components (Fig. 7-

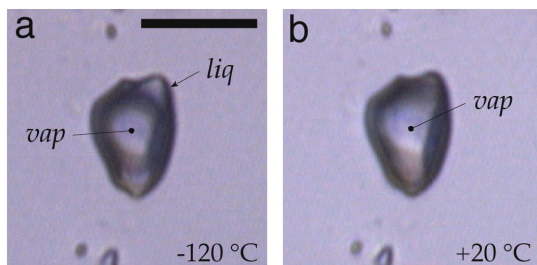


FIG.7-10. A heating sequence of a natural CH₄-CO₂-rich fluid inclusion in quartz, at -120°C (a), +20°C (b). *liq* and *vap* are the liquid phase and vapor phase, respectively. The scale-bar has a length of 10 μ m.

11a). They include the most common fluid systems found in natural fluid inclusions. Other fluid systems including any combinations of the components H₂O-CO₂-CH₄-N₂-C₂H₆-H₂S-NH₃-H₂-O₂-CO-NaCl-KCl-CaCl₂-MgCl₂ can be introduced manually. After choosing a system, the composition of the homogeneous non-aqueous phase is entered into the program (Fig. 7-11b) as is its density, here constrained by the homogenization temperature of the CH₄-rich phases. The program then provides a list of equations of state that can be used to analyze the observed homogenization behavior. Similar to the previously described example in the package *CLATHRATES*, a combination of equations of state as presented by Thiéry *et al.* (1994) (i.e. choice 9 in Fig. 7-11b), is the best available equation to transform homogenization temperatures into densities for this specific fluid system. Fig. 7-11c illustrates the iterative approach involved in this procedure. The first iteration series results in a trivial solution, where both CH₄-CO₂ vapor and liquid phases have similar compositions and densities. The selection of new initial parameters depends on knowledge of the topology of fluid properties in the *p-T-V-x* space. A coexisting liquid phase slightly below homogenization conditions always contains a higher fraction of the component with a higher critical temperature, in this case CO₂. Therefore, the CO₂ enriched liquid phase is initially estimated at a composition of $x(\text{CO}_2) = 0.2$. The new pressure approach can only be deduced from knowledge of morphology of the immiscibility region of CH₄-CO₂ fluids (e.g., Fig. 3 in Bakker 1997). The program gives the possibility to repeat the initiation until an acceptable result is obtained. The real solution is obtained in a second series at 4.325 MPa with a coexisting CO₂-richer liquid phase (17.58 amount-of-substance % CO₂) at the point of homogenization (for further explanation see Fig. 2 in Bakker, 2003). The molar volumes of the coexisting phases are distinctively different, corresponding to typically vapor- and liquid-like phases. According to the calculation method of Thiéry *et al.* (1994) the real molar volume is obtained from using the calculated *p-T-x* values in the equation of state according to Lee & Kesler (1975), yielding a bulk molar volume of 192.47 cm³.mole⁻¹. The results (output) of this example are illustrated in Appendix 7-3. In addition to bulk fluid properties,

a

```

FLUIDS, package of computer programs for fluid inclusion studies

Program 1: BULK, version 08/02
Product Development Ronald J. Bakker

Included components:

    1. Fluids : H2O-CO2-CH4-N2-C2H6-H2S-NH3-H2-O2-CO
    2. Salts  : NaCl-KCl-CaCl2-MgCl2-FeCl2

Bulk fluid V-X properties of inclusions are calculated from:

    - Homogenisation temperatures/pressures
    - Ice melting temperatures
    - Volume fraction estimates

Properties of individual phases are calculated at room temperature

-----
Component definition:

    (1) predefined systems
    (2) manually defined system

        choose number: 1

    (1) H2O
    (2) H2O-NaCl
    (3) H2O-CO2
    (4) H2O-CO2-NaCl
    (5) H2O-CH4
    (6) H2O-CH4-NaCl
    (7) CO2-CH4
    (8) H2O-CO2-CH4
    (9) H2O-NaCl-CO2-CH4
    (10) changed my mind

        choose number: 7

```

b

```

Non-aqueous phase: mixture CO2 CH4

Composition of the homogeneous non-aqueous phase
(amount-of-substance fraction, number between 0 and 1):

    x(CO2) = 0.07
    x(CH4) = 0.93

Density of non-aqueous phase is obtained from:

    (1) Density (g/cc)
    (2) Molar Volume (cc/mol)
    (3) Homogenisation Temperature
    (4) Homogenisation Pressure

        choose number: 3

Homogenisation Temperature (°Celsius) = -77

Mode of homogenisation:

    (1) Vapour
    (2) Liquid
    (3) Critical

        choose number: 1

Equation of state for homogenisation conditions of the non-aqueous phases:

    (1) Redlich & Kwong (1949) any gas mixture
    (2) Chueh & Prausnitz (1967) CO2-CH4-N2-C2H6-H2S-H2
    (3) Soave (1972) any gas mixture
    (4) Lee & Kesler (1975) CH4-C2H6-H2S-H2
    (5) Peng & Robinson (1976) any gas mixture
    (6) Holloway (1977, 1981) Flowers (1979) any gas mixture
    (7) Bowers & Helgeson (1983), Bakker (1999) any gas mixture
    (8) Duan et al. (1992) H2O-CO2-CH4
    (9) Thiery et al. (1994), Soave (1972) CO2-CH4-N2
    (10) Duan et al. (1996) H2O-CO2-CH4-N2-C2H6-H2S-H2-O2-CO

        Choose number : 9

```

FIG. 7-11. See caption on following page.

C

```

*****
Homogenisation conditions are numerically analysed. Conversion depends on
the chosen initial parameters. The trivial solution may regularly occur,
especially if the temperature exceeds the immiscibility field.
You may adjust the initiation until you reach a satisfying result.

Iteration number: 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19
*****
Result of Liquid-Vapour Equilibria Calculations

Temperature = 196.15 K, -77 °C
Pressure = 7.89673 MPa, 78.9673 bar
Zero function = -1.17795e-13
Number of iterations : 19

Phase 1      63.2349 cc/mol
x(CO2)       0.0700001 (f = 0.0724819 MPa)
x(CH4)       0.93 (f = 3.67113 MPa)

Phase 2      63.2349 cc/mol
x(CO2)       0.07 (f = 0.0724817 MPa)
x(CH4)       0.93 (f = 3.67113 MPa)

Warning: phases have nearly equal compositions, possible trivial solution
Warning: phases have nearly equal densities, possible trivial solution

Do you want to change the numerical approximation? (y/n) y

    Initial liquid composition (amount-of-substance fractions):

x(CO2) = 0.2
x(CH4) = 0.8

    New Pressure Approach (in MPa) = 2.5

    New Precision (default is 1e-12) = 1e-12

Iteration number: 44 45 46 47 48 49 50 51 52 53 54 55 56 57 58 59 60 61 62
63 64 65 66 67 68 69 70 71 72 73 74 75 76 77 78 79 80 81 82 83 84 85 86
*****
Result of Liquid-Vapour Equilibria Calculations

Temperature = 196.15 K, -77 °C
Pressure = 4.32529 MPa, 43.2529 bar
Zero function = -2.04059e-13
Number of iterations : 86

Phase 1      64.3344 cc/mol
x(CO2)       0.175803 (f = 0.135217 MPa)
x(CH4)       0.824197 (f = 2.89235 MPa)

Phase 2      201.733 cc/mol
x(CO2)       0.07 (f = 0.135217 MPa)
x(CH4)       0.93 (f = 2.89235 MPa)

Do you want to change the numerical approximation? (y/n) n

Gas mixture calculations:

    Homogenisation temperature = 196.15 K (-77 °C)
    Homogenisation pressure = 4.32529 MPa (43.2529 bar)
    Molar volume = 192.467 cc/mole
    Density = 0.0935249 g/cc

Calculation fluid inclusion properties at 20 °C

Total Homogenisation and Volume Fractions

Gas mixture:

    Total homogenisation at 196.15 K (-77 °C)
    Molar Volume = 192.467 cc/mol

Write results in file : test3

```

FIG.7-11. Calculation instructions in the program *BULK*, according to the heating experiment illustrated in Fig. 7-10. The references indicated in this figure are further specified in the appendices and in Bakker (2003).


```

Aqueous Solution:
Thermodynamic model for aqueous solution:

  H2O (+ Gases according to Henry's law)

Henry's Law:

  CO2 : Carroll et al. (1991), Carroll & Mather (1992)
  CH4 : Rettich et al. (1981)

-----
Calculation fluid inclusion properties at 20 °C

  Only the solubility of CO2 and CH4 are taken into account for
  density calculations: Duan et al. (1992), H2O-CO2-CH4 system

Pressure calculation of gas mixture at 20 °C

  P (MPa) = 10.3652 (103.652 bar)

-----
Total Homogenisation and Volume Fractions

*****
WARNING!
Accurate equations of state are not available for H2O-Gas-Salt systems.
Volume % of the aqueous liquid phase wetting the inclusion wall has to be
introduced for bulk fluid calculation!
*****

  Percentage of aqueous liquid phase at 20°C (0-100 vol%) = 10

-----
Write results in file : test3a

```

FIG.7-12. Calculation instructions for the aqueous liquid solution in the program *BULK*, for the inclusion illustrated in Fig. 7-10, assuming a 10 volume% H₂O rim. The references indicated in this figure are further specified in the appendices and in Bakker (2003).

the result file gives the properties of the fluid inclusion at 20°C including the number of phases with their volumetric proportions and the internal pressure.

Analysis of the same fluid inclusion at room temperature using micro-Raman spectroscopy revealed the presence of an optically unobserved H₂O rim. The formation of clathrate was, however, not observed. The bulk properties of this inclusion can also be calculated with the *BULK* program, assuming a certain volume percentage of H₂O. In a relatively dark fluid inclusion (Fig. 7-10) with optically 'thick' phase boundaries, at least 10 volume % H₂O may be hidden wetting the inclusion walls. This value is used here as an approximation of the unknown actual amount of water. The calculation procedure is similar to the previously described example, with the addition of the estimated volume fraction of the H₂O phase. The predefined system H₂O-CO₂-CH₄ has to be selected in the first step of the input (see Fig. 7-11a). The program automatically selects a thermodynamic model for the aqueous liquid solution according to Henry's law, as only gases are involved (Fig. 7-12). The density of the CH₄- and CO₂-bearing aqueous liquid solution is

calculated with the equation of state from Duan *et al.* (1992a, b). The internal pressure at 20°C is calculated from the CH₄-CO₂ gas mixtures with a known density (see also Fig. 7-11c). The volume fraction of the aqueous liquid solution at room temperature is introduced in the following step (Fig. 7-12). A total homogenization temperature was not measurable in this fluid inclusion because the aqueous phase was invisible. Even if it had been measured, it would not have been very useful for the homogenization calculations, as an accurate equation of state is not available for this ternary fluid system. The results (output) of the calculations are given in Appendix 7-4. The inclusion contains 54 amount-of-substance % H₂O, a remarkable amount given that it is optically invisible.

The calculation steps of the *BULK* program for a natural aqueous inclusion in calcite (Fig. 7-13) are illustrated in Figure 7-14. At room temperature, the inclusion contains a vapor bubble of approximately 8 volume % (Fig. 7-13f). During cooling, the vapor bubble disappears at -52°C, which marks the nucleation of ice in the metastable absence of salt-hydrate and a vapor bubble (Fig. 7-13a). During heating a mixture of

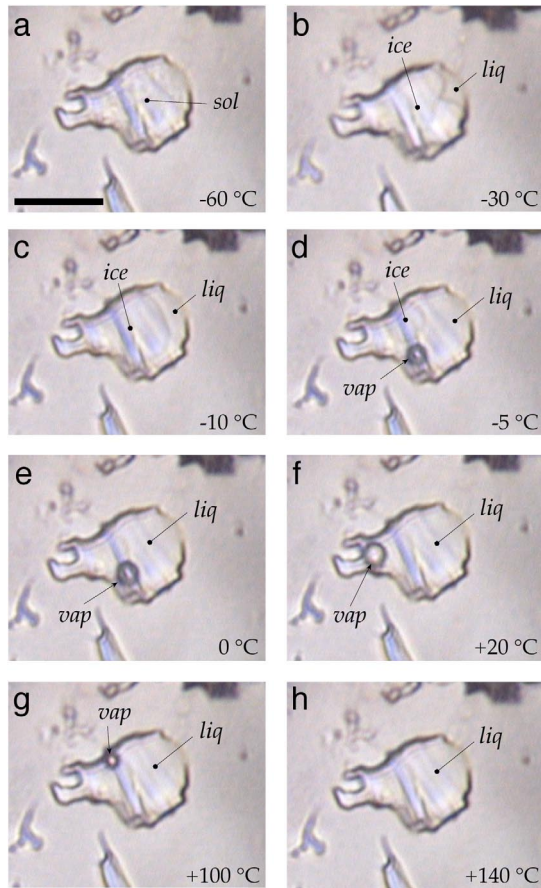


FIG.7-13. A heating sequence of a natural H₂O-NaCl-rich fluid inclusion in calcite, at -60°C (a), -30°C (b), -10°C (c), -5°C (d), 0°C (e), +20°C (f), +100°C (g) and +140°C (h). *ice*, *liq* and *vap* are the ice phase, aqueous liquid phase, and vapor phase, respectively. The scale-bar has a length of 10 μ m.

an aqueous liquid solution and ice remains in the inclusion up to -5°C (Fig. 7-13b and c). At this temperature, the volumetric effect of the melting (or shrinkage) of the ice crystal is sufficient to nucleate a vapor bubble (Fig. 7-13d), and the inclusion returns to a stable phase configuration. The ice finally melts at -3.9°C (Fig. 7-13e). Total homogenization occurs at 130.2°C into the liquid phase (Fig. 7-13h). During cooling to room temperature, the vapor bubble nucleates at approximately 47°C. The calculation procedure in *BULK* differs from the previously described example because the fluid system can be represented by a water-salt binary. As no salt-hydrates were formed (no detection by micro-

Raman spectroscopy, even at -190°C), the type of dissolved ions could not be directly determined, and it is assumed that NaCl is the dominant dissolved species, forcing the use of equivalent mass%. The aqueous solution can be modeled using purely empirical or ion interaction models (Fig. 7-14a). As no gases are suspected in the vapor bubble (no double freeze was observed) and a simple NaCl solution is assumed, a purely empirical equation is here adopted (*e.g.*, Bodnar 1993, *i.e.* number 4 in Fig. 7-14a). The program provides seven empirical equations that differ minimally in the binary H₂O-NaCl system. Subsequently, the program requires a salinity constraint, here microthermometry provides an ice melting temperature. Salinities exceeding eutectic values are not included in modeling the aqueous solution, consequently only final ice melting temperatures are taken into account. A salinity of 6.30 mass % NaCl is obtained from the selected equation (Fig. 7-14b). Then, the program requires information for the calculation of the density of the aqueous solution at room temperature, *i.e.* 20°C (Fig. 7-14c). Again, the user is able to select from four equations, which are mainly based on the ion interaction model presented by Pitzer (1991). The model from Krumgalz *et al.* (1996) is selected, which represents the most accurate equation for undersaturated NaCl solutions. Unlike the H₂O-CO₂-CH₄ mixture in the previously described example, the total homogenization in a H₂O-NaCl fluid system can be used to calculate bulk densities (Fig. 7-14d), according to the equation from Zhang & Frantz (1987), which is the only equation available in this binary fluid system. The result of the calculation is illustrated in Appendix 7-5.

The results from *BULK* program given in Appendix 7-4 are used to illustrate the steps in the *ISOC* program (Fig. 7-15). The fluid system can be defined by amount-of-substance fractions of all the components involved (Fig. 7-15a) or by using molality values or mass % of dissolved salts. These numbers are always recalculated in terms of ion amount-of-substance. fractions of the dissociated salt. Subsequently, the program requires a bulk fluid density value or molar volume (Fig. 7-15b). The program directly calculates the non-specified value, *i.e.* the density in this case. Then, an equation of state has to be selected to construct the isochore (Fig. 7-15c).

a

Aqueous Solution:

Thermodynamic model for aqueous solution:

- (1) H2O-Salts
Purely empirical, dissolved gases and P neglected
- (2) H2O-Salts
Ion interaction model, osmotic coefficients (Pitzer, 1992)

choose number: 1

Purely empirical equation:

- (1) Potter et al. (1978) NaCl
- (2) Hall et al. (1987) NaCl-KCl
- (3) Oakes et al. (1990) NaCl-CaCl2
- (4) Bodnar (1993) NaCl
- (5) Naden (1996) NaCl-CaCl2
- (6) Bakker et al. (1996) KCl or CaCl2
- (7) Dubois & Marignac (1997) NaCl-MgCl2

choose number: 4

Salinity of dissolved salts:

- (1) ice melting temperature
- (2) molality
- (3) mass%
- (4) amount-of-substance fraction associated salt (relative to H2O)

choose number: 1

 WARNING!: do not exceed eutectic temperatures:
 pure NaCl solution: -21.2 °C

Final melting temperature of ice (in °Celsius) = -3.9

b

Relative mass ratio of salts in solution (0-100%) as obtained from
 e.g. hydrohalite melting:

NaCl = 100

Purely empirical equations

Successfull calculation of salinity of aqueous solution

Mass% NaCl = 6.30276

c

Calculation fluid inclusion properties at 20 °C

Equation of state aqueous system:

- (1) Oakes et al. (1990): H2O-NaCl-CaCl2
- (2) Archer (1992): H2O-NaCl
- (3) Krumgalz et al. (1996): H2O-NaCl-KCl-CaCl2-MgCl2
- (4) Holmes et al. (1997): H2O-CaCl2-MgCl2

choose number: 3

d

Total Homogenisation and Volume Fractions

- (1) Homogenisation Temperature
- (2) Volume Fraction

choose number: 1

Homogenisation temperature (°C) = 130.2

Mode of homogenisation:

- (1) Vapour
- (2) Liquid
- (3) Critical

choose number: 2

Equation of state to analyse total homogenisation:

Zhang & Frantz (1987) : H2O-NaCl-KCl-CaCl2

FIG.7-14. Calculation instructions in the program *BULK*, according to the heating experiment illustrated in Fig. 7-13. The references indicated in this figure are further specified in the appendices and in Bakker (2003).

The program automatically presents a selection of those equations that include the components specified in Figure 7-15a. The program defines the limitations of the selected equation of state,

and offers the opportunity to change the selection. Optionally, the program will correct the fluid isochore for the compressibility and expansivity of the host mineral (Fig. 7-15d). For the selected

a

Selection of fluid system

(1) amount-of-substance fractions of all components
 (2) molalities-mass% of salts and a.s. fractions of gases
 (3) molalities-mass% (always relative to H2O)

choose number : 1

Composition of fluid, in amount-of-substance fractions (0 to 1),
 salts are introduced as dissociated ions (like Na+ and Cl-)

H2O = 0.540547
 CO2 = 0.033430
 CH4 = 0.426023
 N2 = 0
 C2H6 = 0
 H2S = 0
 NH3 = 0
 H2 = 0
 O2 = 0
 CO = 0

Na+ = 0
 K+ = 0
 Ca++ = 0
 Mg++ = 0
 Cl- = 0 (calculated)

b

Bulk fluid density

(1) Value in cc/mole
 (2) Value in g/cc

choose number : 1

Molar Volume (cc/mole) = 97.72527

Density = 0.184639 g/cc

c

Equation of state for isochore calculation

(1) Redlich & Kwong (1949) : any gas-mixture
 (2) Holloway (1977), Flowers (1979) : any gas-mixture
 (3) Jacobs & Kerrick (1981), Kerrick & Jacobs (1981) : H2O-CO2-CH4
 (4) Bakker (1999) : any gas-mixture + NaCl
 (5) Duan et al. (1992a, 1992b) : H2O-CO2-CH4
 (6) Duan et al. (1992, 1996) : H2O-CO2-CH4-N2-CO-H2-O2-H2S

choose number : 3

Details Reference:

Kerrick & Jacobs (1981), Am.J.Sci., 281:735-767
 Jacobs & Kerrick (1981), Geochim.Cosmochim.Acta, 45:607-614
 Composition : H2O-CO2-CH4
 Limits: pure H2O 293-1173 K and 100-890 MPa
 pure CO2 673-1073 K and 50-1500 MPa
 pure CH4 320-670 K and 5-860 MPa

Would you like to continue with this equation of state? (y/n) y

FIG. 7-15. See caption on following page.

d

```

VOLUMETRIC DATA of HOST MINERAL (Compressibility, Expansion)

    Quartz : Hosieni et al. (1985)
    other minerals : Berman (1988)

In which mineral group is the fluid trapped:

    (0) not specified
    (1) Quartz
    (2) Carbonate
    (3) Olivine
    (4) Al2SiO5
    (5) Garnet
    (6) Feldspar
    (7) Pyroxene
    (8) Amphibole
    (9) Oxides
    (10) Cyclo-silicate
    (11) Sphene

                                choose number : 1

Further specification of mineral:

    alpha-beta transition is included in calculations

Isochore corrections starting point:

    (1) Default (25 °C and 1 bar)
    (2) Other temperature/pressure

                                choose number : 1

-----
TEMPERATURE RANGE

Automatical correction

    1. if lower limit is below homogenisation conditions
    2. if calculation results in negative pressures

    Lower T (°C) = 300
    Upper T (°C) = 600

    Number of steps (integer) = 30

-----
Write results in file (drive + filename) : test5

```

FIG.7-15. Calculation instructions in the program *ISOC*, applied to the example given in Appendix 7-4. The references indicated in this figure are further specified in the appendices and in Bakker (2003).

host mineral quartz, the program indicates that the alpha-beta transition is taken into account. The correction of the isochore needs a starting point, *i.e.* p - T conditions where the molar volume of fluid in the inclusion is defined. Default p - T conditions are selected in this example (Fig. 7-15d), however, usually homogenization conditions define this starting point. A reversed correction can be obtained from selecting the trapping conditions of the fluid inclusion. Finally, a temperature range has to be defined within which the isochore is calculated. The range can be

chosen independently from the indicated limits of the selected equation of state. The calculations are partially displayed on the screen. The result of this example is given in Appendix 7-6.

The molar volume of the CH₄ vapor bubble calculated with the *ICE* program for the fluid inclusion illustrated in Figure 7-6 and Appendix 7-2 is 184.72 cm³.mol⁻¹. At the ice melting temperature, this CH₄ phase has a molar volume of 901.29 cm³.mol⁻¹. The molar volume of the CH₄ phase can also be directly obtained from its homogenization temperature, *i.e.* -110°C

into the vapor phase, using the *Loner19* program (see also Bakker 2003). This program handles the thermodynamic properties of CH₄ according to the unified Helmholtz energy function from Setzmann & Wagner (1991). The program offers 15 calculation procedures as illustrated in Figure 7-16a, of which number 5 is chosen here, *i.e.* calculation of homogenization conditions. A non-solution is found after the first iteration series as the sum of the amount-of-substance fractions is not equal to 1 (Fig. 7-16b). The program offers the possibility to start a new approach, by selecting a new initial pressure of 1 MPa, according to the criteria indicated in the previous paragraph. After 41 iterations the solution is found at 1.803 MPa and a molar volume of 552.13 cm³.mol⁻¹ (Fig. 7-16c). The program gives a warning that both phases have equal compositions, which can be ignored in the case of pure gases. Comparison of the molar volumes of the CH₄ phase at different temperatures indicates the presence or metastable absence of a clathrate phase, which contains approximately 14.7 amount-of-substance % CH₄. The clathrate phase was probably partly nucleated during the freezing experiment, resulting in a lower molar volume at CH₄-homogenization than at the ice melting temperature. The total volume differences between ice and water in the inclusion has only minor effect on the density of the volatile phase in the remaining space. This example has illustrated the use of one of the *Loners* program to calculate the properties of portions of fluid inclusions and fluid properties in general.

The use of the program group *AqSo* is illustrated with *AqSo1e* program (Fig. 7-17). This program handles purely empirical equations for H₂O-salt systems, *i.e.* the H₂O-NaCl-KCl system and for a small part of the H₂O-NaCl-CaCl₂ system (*e.g.*, Bodnar *et al.* 1989). The proportions of both monovalent and divalent salts in natural fluid inclusions is difficult to estimate, however the ternary system can be used to perform experimental ‘what if’ calculations for those inclusions that deviate in fluid properties from the binary H₂O-NaCl system. For example, ice-like material is nucleated in an aqueous fluid inclusion during a freezing experiment at -80°C, and a vapor bubble remains present. During heating, the presence of a liquid phase becomes noticeable around -22°C. At -21.5°C rounded crystals dissolve completely, and irregular crystals finally

melt at -5.4°C. This information is sufficient to assume a ternary fluid system of H₂O-NaCl-KCl where hydrohalite is the last phase to melt. The eutectic point of this system is -22.9°C, which is generally impossible to observe exactly. The observation of a first melt slightly above this point is consistent with this fluid system. For comparison, the binary H₂O-NaCl system has a eutectic point at -21.2°C, which is not consistent with the observation of liquid at -22°C. As nucleation occurs at a very low temperature, the aqueous solution is suspected to contain a large amount of dissolved salt. The morphology of the last melting crystals is different from pure ice, and cubic crystals were not observed. Therefore, it is hypothesized that hydrohalite is the last melting phase. The identification of the last melting phase is critical for the interpretation of salinity. The combination of micro-Raman spectroscopy and microthermometry (*e.g.*, Bakker 2001, 2002) provides such information, as hydrohalite has a spectrum substantially different from ice. To interpret the above observations, first the fluid system has to be defined in the program (Fig. 7-17a), then the calculation steps are identified, *i.e.* either the salinity is derived from melting temperatures or vice versa. The cotectic lines can be obtained from exact field intersection calculations or from second phase purely empirical equations according to Bodnar *et al.* (1989). The program requires identification of which phases actually melted, *i.e.* the ice and hydrohalite crystals (Fig. 7-17b). The program indicates the limits of the melting temperatures for each phase. Then, the program calculates the properties of the aqueous solution at both cotectic melting conditions and final melting conditions (Fig. 7-17c). This inclusion contains a 25.1 mass % NaCl and 0.9 mass % KCl aqueous solution.

MacFlinCor

MacFlinCor was developed to process and interpret laboratory data gathered on fluid inclusions and to calculate P-T isochores for geologically important fluids composed of H₂O, CO₂, CH₄, NaCl, KCl and N₂. Within the program, interactive diagrams are available to describe those chemical systems which cannot be adequately constrained numerically. The user can choose from among multiple published equations of state describing fluid behavior and can easily compare the results obtained by using different

a

```

Program LONER19, version 06/02

FLUIDS: package of computer programs for fluid inclusion studies
Product Development Ronald J. Bakker

Program for individual equation of state:

    Setzmann U, Wagner W (1991) J.Phys.Chem.Ref.Data, 20:1061-1155.

    Temperature: -182.5 to 351.9 °C
    Maximum pressure: 1000 MPa

Calculation of properties of pure CH4

Calculation procedure:

    (1) Molar volume (density) at selected P-T conditions
    (2) Pressure at selected V-T conditions
    (3) Temperature at selected P-V conditions
    (4) Fugacity and coefficients
    (5) Homogenisation conditions
    (6) Liquid-Vapour equilibrium
    (7) Helmholtz energy
    (8) Entropy
    (9) Internal Energy
    (10) Enthalpy
    (11) Gibbs Energy
    (12) Heat Capacity (at constant volume)
    (13) Heat Capacity (at constant pressure)
    (14) Speed of Sound
    (15) Joule-Thomson coefficient
    (16) Exit

                                choose number: 5

```

b

```

The chosen bulk fluid composition puts restrictions on the maximum
homogenisation temperature and pressure of the system. Be sure that
temperatures and pressures lie within the limits of the immiscibility field.

Select homogenisation:

    (0) Temperature
    (1) Pressure

                                choose number: 0

    Homogenisation temperature (°Celsius) = -110

What is the mode of homogenisation:

    (0) vapour
    (1) liquid
    (2) critical

                                choose number: 0

*****
Homogenisation conditions are numerically analysed. Conversion depends on
the chosen initial parameters. The trivial solution may regularly occur,
especially if the temperature exceeds the immiscibility field.
You may adjust the initiation until you reach a satisfying result.

Iteration number: 1
*****
Result of Liquid-Vapour Equilibria Calculations

Temperature = 163.15 K, -110 °C
Pressure = 1.79982 MPa, 17.9982 bar
Zero function = -0.00102297
Number of iterations : 1

Phase 1      48.8002 cc/mol
x(CH4)       0.998977 (f = 1.43253 MPa)

Phase 2      553.424 cc/mol
x(CH4)       1 (f = 1.43106 MPa)

No solution: summation of a.s.fractions is not equal to 1

Do you want to change the numerical approximation? (y/n) y

```

FIG. 7-16. See caption on following page.

C

```

Initial liquid composition (amount-of-substance fractions):
x(CH4) = 1

New Pressure Approach (in MPa) = 1

New Precision (default is 1e-12) = 1e-12

Iteration number:  2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23
24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41
*****
Result of Liquid-Vapour Equilibria Calculations

Temperature = 163.15 K, -110 °C
Pressure = 1.80258 MPa, 18.0258 bar
Zero function = -3.97238e-13
Number of iterations : 41

Phase 1      48.7984 cc/mol
x(CH4)      1 (f = 1.43267 MPa)

Phase 2      552.132 cc/mol
x(CH4)      1 (f = 1.43267 MPa)

Warning: phases have nearly equal compositions, possible trivial solution

Do you want to change the numerical approximation? (y/n) n

Homogenisation conditions:

Th = 163.15 K (-110 °C)
Ph = 1.80258 MPa (18.0258 bar)
Vh = 552.132 cc/mol
Dh = 0.029056 g/cc

```

FIG.7-16. Calculation instructions in the program *Loner19*, for a pure CH₄ fluid according to the equation of state from Setzmann & Wagner (1991).

equations. It should be noted that this program is substantially older than those described in the first part of this paper and it is not as compositionally comprehensive. However it does have a user friendly interface that is conducive to use while making the microthermometric measurements. Used in this mode, the program essentially prompts the user for the needed observations and allows the analyst to make sensitivity calculations while gathering the data. This latter point should not be overlooked – microthermometry can be very time consuming. Having measured a homogenization temperature (at a rapid heating rate) of say 145°C, should you spend the time to determine whether it was really 144.6°C (or even if it is 142°C) by a much slowed heating experiment? Answering this question depends on the nature of your study but being able to see the effects of making the more careful measurement by doing a quick "what if" calculation in MacFlinCor can help decide the question. In the following paragraphs some of the features of the program are elucidated using, where possible, the same inclusions described earlier in this chapter.

MacFlinCor was developed in HyperCard which operates on the model of index cards with each card providing an entry in a

simple but powerful database. (Historical digression – when this program was first conceived in 1991, HyperCard was distributed with every Macintosh computer – this is no longer the case but Hypercard still functions under operating Systems through 9.2 and it runs in Classic mode under System X.) This index-card, database approach is ideal for working with fluid inclusions because each "card" in a data "stack" can be used to record all the information about a single inclusion while the microthermometry is being done. The program *MacFlinCor* is composed of two files: *MacFlinCor* itself which contains the template data cards and *FlinCalc* which stores compiled Pascal code for some of the more involved calculations and is called as needed by data cards in the *MacFlinCor* stack. The heart of the program, and the only cards that the user should see, are the cards making up the *MacFlinCor* stack. Eleven of these cards are tailored to specific chemical systems that may be represented by individual fluid inclusions and for which sufficient experimental data is available to attempt to interpret laboratory observations. These cards serve as templates that are copied automatically as needed from the *MacFlinCor*

a

Program AqSole, version 07/01
 FLUIDS: package of computer programs for fluid inclusion studies
 Product development Ronald J. Bakker

Program 1e for aqueous solutions at low temperatures:

List of publications from Virginia Polytechnic Institute:
 (1) Hall et al. (1987) Econ. Geol., 83, 197-202
 (2) Sterner et al. (1988) Geochim. Cosmochim. Acta, 52, 989-1005
 (3) Bodnar et al. (1989) Comp. Geosc., 15, 19-41
 (4) Oakes et al. (1990) Geochim. Cosmochim. Acta, 54, 603-610
 (5) Bodnar (1993) Geochim. Cosmochim. Acta, 57, 683-684

Calculations are based on purely empirical best-fits
 No fundamental thermodynamic modelling involved

Fluid system:

(1) H2O-NaCl
 (2) H2O-KCl
 (3) H2O-CaCl2 (partly)
 (4) H2O-NaCl-KCl
 (5) H2O-NaCl-CaCl2 (partly)

choose number: 4

Calculation procedure:

(1) salinities from melting temperatures
 (2) melting temperatures from salinities

choose number: 1

Cotectic lines in ternary systems:

(1) Exact, intersections of fields
 (2) Best-fit from Bodnar et al. (1989)

choose number: 1

b

Final melting temperature available for (2 phases):

ice (y/n) : y
 hydrohalite (y/n) : y
 halite (y/n) : n
 sylvite (y/n) : n

Limits cotectic line: -21.2 to -22.9 °C
 Limits Ice: 0 to -22.9 °C
 Limits Hydrohalite: -22.9 to +0.1 °C

Tm(ice) in °C = -21.5
 Tm(hydrohalite) in °C = -5.4

c

Result of calculations

Cotectic melting at -21.5 °C:

NaCl: 22.75 mass%
 KCl: 0.875007 mass%
 Mass ratio (fraction NaCl) = 0.962963

Final melting at -5.4 °C:

Sterner et al. (1988)
 NaCl: 25.074 mass% (5.72419 molality)
 KCl: 0.90295 mass% (0.122188 molality)
 Mass ratio (fraction NaCl) = 0.96524

FIG.7-17. Calculation instructions in the program *AqSole*, according to purely empirical equations for aqueous liquid solutions.

stack into a user's data stack. Each of these cards may be accompanied, at the user's discretion, by a second card that can be used to: (1) determine pressures via the use of independent geothermometers, and (2) make pressure

corrections to measured homogenization temperatures for aqueous inclusions. Most of the rest of the cards are figures redrawn from the literature which have been made interactive by the addition of moving crosshairs. Examples

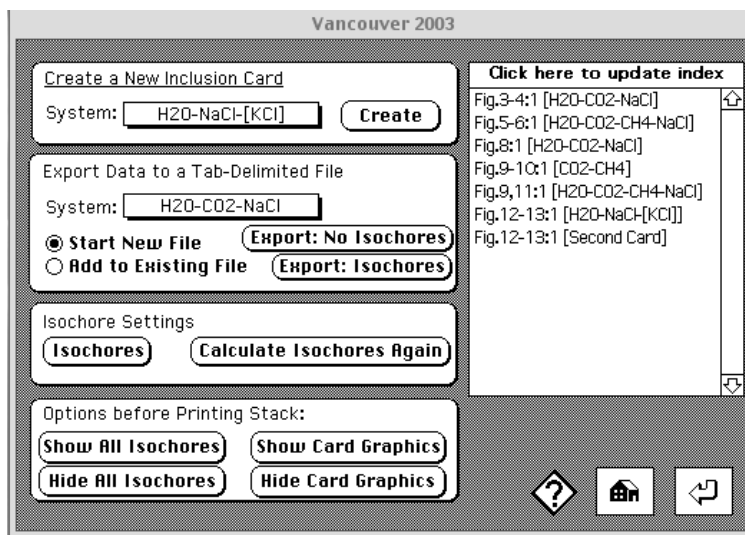


FIG.7-18. Index card of a data deck after adding several cards for measured inclusions.

of these card types are provided below.

After starting *MacFlinCor*, the user may choose between opening a previously created data file or beginning a new one. In this example, we create a new data file and input representative data from several inclusions to illustrate some of the features of *MacFlinCor*. Upon clicking the "Start a New Database" button, the user is prompted for a file name and a data stack is created (Fig. 7-18).

This stack initially contained only the index card shown in Figure 7-18. From this Index, data cards are created for appropriate chemical systems (7 are shown here), decisions are made about the order in which data will be exported, and the parameters for calculating isochores may be set. Clicking on the "Isochores" button allows the user to change the default values. In addition the user may return to this card at any time and change the isochore parameters; the changed values will be in effect for any further calculations done in the stack. The "Calculate Isochores Again" button lets one recalculate isochores for every card in the data stack if, after gathering a mass of data, the user decides to change the isochore limits or intervals. The buttons on the bottom left of the card are designed to simplify printing of the stack. HyperCard can print multiple (up to 32) cards per page and these pages of miniature images of the data cards provide a convenient hard copy of the data gathered on a single sample or population of inclusions.

Clicking and holding the mouse button while pointing at the shadowed box in the upper left portion of the screen produces a pop-up menu that allows one of nine chemical systems to be chosen (Fig. 7-19). Separate data cards for the various systems have been designed because of the different input parameters and output calculations that are appropriate for different groups of chemical compounds. After highlighting the desired menu item and releasing the mouse button, the sought-after data card can be created by clicking on the "Create" button (Fig. 7-18). We begin here by creating a card for the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ (Fig. 7-20).

Each of the data cards (e.g., Fig. 7-20, 7-21) has essentially the same screen layout. In the upper left corner, a pop-up menu permits the choice of an equation of state for the chemical system at hand. Below this is a large area

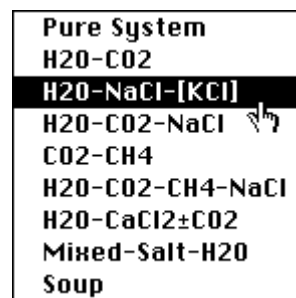


FIG.7-19. Systems menu.

Vancouver 2003

H₂O-CO₂-NaCl

Bowers & Helgeson

Notes: ☒ Text ☐ Graphic

If you have measured a total homogenization temperature for this inclusion, the determination of the bulk composition is over defined. Therefore you may wish to substitute the Th(total) measurement for the Estimated Volume Fraction 'measurement'. At this point in time this will require you to use some diagrams (which don't yet work) to solve for the bulk composition. I would suggest that you try both methods if you have gathered all the required information.

Sample ID: **Fig.3-4**

Inclusion Number:

Inputs:

Clath. Melt Temp.

Th CO₂(L-V):

Th to: ☒ liquid ☐ vapor

Est. VolFrac CO₂: at C

☐ Use Th(Tot)? Th Total:

Σ ☐ Isochores

<u>Aqueous phase</u>		Density	0.993
		Molality NaCl	0.038
		Weight % NaCl	0.223
		Mole Fraction NaCl	0.001
<hr/>			
<u>Carbonic phase</u>		<u>Bulk Inclusion</u>	
Density	0.796	XH ₂ O	0.767
Mol Vol	55.316	XCO ₂	0.233
		XNaCl	0.001
		Density	0.898
		Mol Vol	26.811

FIG.7-20. Data card created for inclusion fluids in the system H₂O-CO₂-NaCl. Compare the output calculations to those shown in Figures 4 and 5 and Appendix 7-1.

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H₂O-NaCl-[KCl]

Zhang & Frantz

Notes: ☐ Text ☒ Graphic

Sample ID: **Fig.12-13**

Inclusion Number: **1**

Inputs:

☒ Freezing pt. depression

☐ NaCl dissolution temp.

V.Frac Th (L-V): L

NaCl / (NaCl + KCl) ratio:

T Eutectic: Melt 2:

☐ Hydrohalite melt temp.

KCl dissolution temp.:

Σ ☐ Isochores ☒ from Th?

➡ Molality Salt	1.14
➡ Weight % Salt	6.23
➡ Mole fraction Salt	0.02
Crit. Temp. <input type="text" value="432"/>	Crit. Press. 371
Molar Volume	19.33
Density	0.974
P at Th along L-V-NaCl Sol. Curve	2

FIG.7-21. Data card for the system H₂O-NaCl-[KCl]. Compare the results here to those shown in Figures 13 and 14 and Appendix 7-5.

designed for two purposes. The default use is as a notebook for recording observations in the laboratory during heating and freezing runs. (The template cards come with some notes about the use and/or development of the card – this can/should be replaced by the user.) Secondly, clicking on the "Graphic" button above the text box causes the text to be temporarily hidden and be replaced by a white board upon which simple sketches of the inclusion in question, its relationship to fractures and other inclusions, and other data can be recorded (e.g., Fig. 7-21).

HyperCard provides a set of drawing tools that are adequate for simple illustrative purposes. This becomes a permanent part of the data entry for this inclusion.

The right hand half of the card provides fields for data entry and calculated output. For the undersaturated H₂O-CO₂-NaCl system (Fig. 7-20), three observations serve to characterize the inclusion fluids: a clathrate melting temperature (for salinity), a CO₂ liquid-vapor homogenization temperature (for carbonic phase density) and either a liquid-vapor volume percent estimate or a

total H₂O-CO₂ temperature (for bulk density). Clicking on the "Σ" button will result in one of three responses: (1) a message requesting some additional data that is required for the calculation, (2) an error message requesting a change in one of the inputs because some value is out of range, or (3) the calculation will take place. Error messages are context sensitive and will generally inform the user of the appropriate range of values and, after dismissing the message box, the input cursor will be returned to the offending entry.

Output also varies with the chemical system; here data for the separate aqueous and carbonic phases are presented as well as for the bulk inclusion. In addition, the isochore for the fluid is calculated (using the parameters set on the Index card) and, for lack of screen space, its field is hidden behind the rest of the output. Clicking on the "Isochores" check box will show the field and its contents.

One of the goals of *MacFlinCor* is to provide the user with an opportunity to calculate derived quantities and isochores from hypothetical fluids. For the chemical system H₂O-NaCl-[KCl] (Fig. 7-21) the user may enter as inputs, values for quantities that are normally outputs when working with fluid inclusions: molality, weight %, or mole fraction salt. Clicking on one of the arrows next to these outputs produces a dialog box in which a value may be entered. Closing this dialog box results in calculations of the rest of the output parameters.

Across the bottom of the card are buttons for returning to the "Index", making a "Copy" of the current card (retaining the Sample ID and any graphics drawn under the Text window), making a "New" blank card from the current one, and "Delete" the current card.

An inclusion formed in a non-boiling system will undergo total homogenization at a pressure and temperature below that at which it was trapped in nature. The locus of possible trapping conditions is given by the isochore that locates the path in P-T space consistent with the molar volume and compositional data derived in the laboratory (Diamond, 2003, this volume). Independent temperature or pressure data is required to fix the other unknown and fully characterize the trapping conditions. Such independent temperature data could be derived from calcite-dolomite, arsenopyrite, or various silicate geothermometers. Independent pressure

data could be derived from sphalerite-pyrite-pyrrhotite geobarometry, stratigraphic reconstruction, or data from other groups of fluid inclusions. To facilitate making these types of "corrections" second data cards have been created for each of the important chemical systems. These second cards are created and accessed initially from an individual data card; note the "More P/T Info" button on Fig. 7-21.

Figure 7-22 shows the result of creating a second card for the card shown in Figure 7-21. Isochore information is automatically transferred to this card and independent temperature data can be entered in the top half of the card. The source of this data can be recorded by choosing from a list on a pop-up menu; here for example arsenopyrite geothermometry gives 275°C. The lower half of Figure 7-22 provides interactive use of the figures from Potter (1977) to make pressure corrections for H₂O-NaCl fluids. Figure 7-23 is the card for 5 % NaCl and, after setting the crosshairs for the measured Th and independent pressure, returns the ΔT and the corrected trapping temperature.

MacFlinCor provides a comprehensive data gathering and reduction environment that provides both the novice and experienced user guidance during the measurement and interpretation of fluid inclusions in geological materials. See Brown and Hagemann (1994, 1995) for a more detailed introduction to the workings of this program, including its application to a suite of Archean lode gold deposit fluid inclusions.

FLINCOR

FLINCOR was the first broad-based attempt to provide a computer program to calculate fluid inclusion properties from microthermometry measurements (Brown, 1989). The program was written for early versions of the Windows operating environment and has not kept up with changes in Windows. Although a knowledgeable computer tinkerer can get it to function in most versions of the operating system, the program's lack of upkeep makes it not very useful any longer.

Concluding remarks

The computer programs described in this manuscript offer the possibility of calculating the properties of fluid inclusions. The complexity of

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H₂O-NaCl-[KCl] 2

Zhang & Frantz

T	P (Zhang & Frantz)
130.2	4
200	1450
300	3521
400	5592
500	7662
600	9733
700	11804
800	13875
900	15946
1000	18017

If you have independent pressure information (e.g. stratigraphic reconstruction) you can generate a 'pressure correction' which, when added to the Th, may give the trapping temperature.

Sample ID: **Fig.12-13**
 Inclusion Number: **1**

Independent T Info: T P
 Stable Isotopes: 250 2485
 Arsenopyrite: 275 3003
 Other:
 Other:
 Other:

Independent P Info: P ΔT
 Other FI's: 1750 140
 Trapping Temp: 270.

Calc Wt.%: 6.23 ☐ 1% ☒ 5% ☐ 10% ☐ 15% ☐ 20% ☐ 25%

Index
Asp Thermo
Potter (1977) NaCl-H₂O

FIG.7-22. The "second" card for the system H₂O-NaCl-[KCl]. Here independent temperature or pressure data can be entered and applied to the calculated isochore to generate a pressure- or temperature-"correction" for inclusions trapped under non-phase separating conditions. In addition, the diagrams from Potter (1977) can be employed to correct measured homogenization temperatures.

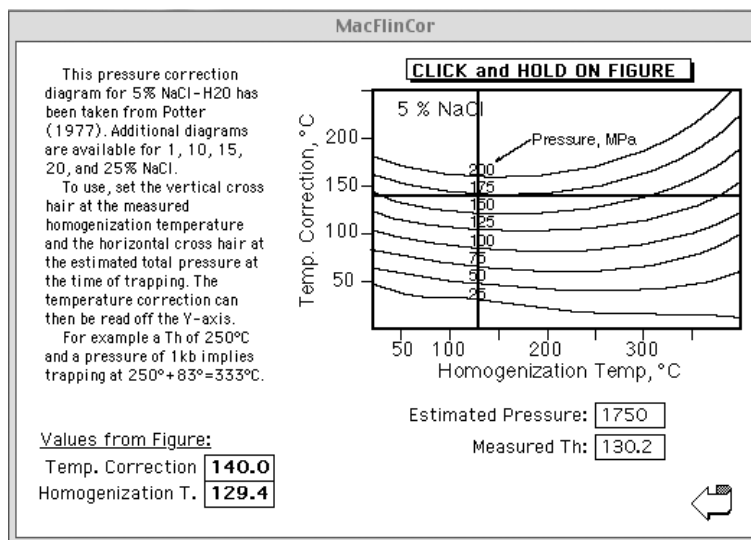


FIG.7-23. Diagram from Potter (1977) providing a pressure correction for a 5 mass% NaCl-H₂O solution. The correction of 140°C must be added to the measured Th to get to the actual trapping temperature, here 270°C.

equations of state that describe fluid systems makes the development and use of computer programs highly desirable. The limitations of the programs are defined by the knowledge of specific fluid systems, which often may be insufficient for the studied fluid inclusions. The presented programs run on Macintosh, Windows-based and DOS-based platforms. A complete list of the programs included in the package *FLUIDS*

is given in Bakker (2003), where also the thermodynamic background of the programs is further explained. The packages *CLATHRATES* and *FLUIDS* are also available on the University of Leoben website <http://www.unileoben.ac.at/~buero62/minpet/ronald>, which is regularly updated.

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CHAPTER 7: APPENDIX 7-1

CLATHRATES, package of computer programs for fluid inclusions studies

Program 1: NOSALT version 11/02

Product development Ronald J. Bakker

Filename : test1

CLATHRATE PHASE (at final melting conditions)

Q2 melting system

Clathrate Structure 1

Tm (K)	282.959100
Pm (MPa)	4.480652
Vm (cc/mol)	22.409591
D (g/cc)	0.976885

amount-of-substance fractions

x(H2O)	0.850880
x(CO2)	0.149120

Equation of state for fugacity calculations in clathrate equilibrium:

Duan et al. (1992a,b) Geochim.Cosmochim.Acta, 56, 2605-2617 and 2619-2631.

NON-AQUEOUS PHASE (after final clathrate melting)

Volume fraction vapour	0.044663
Volume fraction liquid	0.435337

Bulk properties (partial homogenisation):

Th (K)	291.050000
Ph (MPa)	5.451783
Vh (cc/mol)	55.374469

amount-of-substance fractions:

x(CO2)	1.000000
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Equation of state for liquid-vapour equilibria:

Duschek et al. (1990) J.Chem.Thermodyn., 22, 841-864.

Coexisting liquid-vapour fluids at clathrate melting temperature

	Vapour	Liquid
rel.Frac.	0.093048	0.906952
Vm (cc/mol)	327.725781	51.024164
x(H2O)	0.000581	0.000000
x(CO2)	0.999419	1.000000

AQUEOUS SOLUTION (after final clathrate melting)

Volume fraction 0.520000

EoS Approximation: Duan et al. (1992a,b) H2O-CO2-CH4

Vm (cc/mol)	18.721938
D (g/cc)	1.004141

amount-of-substance fractions

x(H2O)	0.969832
x(CO2)	0.030168

TOTAL FLUID INCLUSION

Vm (cc/mol)	27.439994
D (g/cc)	0.903640

amount-of-substance fractions

x(H2O)	0.739153
x(CO2)	0.260847

CHAPTER 7: APPENDIX 7-2

CLATHRATES, package of computer programs for fluid inclusion studies
Program 3: ICE version 12/02
Product development Ronald J. Bakker
Filename : test2

CLATHRATE PHASE (at final melting conditions)

Clathrate Structure 1

Tm (K) 285.650000
Pm (MPa) 10.480653
Vm (cc/mol) 22.415620
D (g/cc) 0.790728

amount-of-substance fractions

x(H2O) 0.852665
x(CH4) 0.147335

NON-AQUEOUS PHASE (after final clathrate melting)

Volume fraction 0.550000

EoS : Duan et al. (1992a,b) Geochim. Cosmochim. Acta, 56, 2605-2617 and 2619-2631.

Vm (cc/mol) 184.720081
D (g/cc) 0.086854

amount-of-substance fractions

x(H2O) 0.000470
x(CH4) 0.999530

AQUEOUS SOLUTION (after final clathrate melting)

Volume fraction 0.450000

EoS Approximation: Duan et al. (1992a,b) H2O-CO2-CH4

Vm (cc/mol) 17.858902
D (g/cc) 1.017046

Activity(H2O) 0.985155

amount-of-substance fractions

x(H2O) 0.984154
x(CH4) 0.002251
x(Na+) 0.006797
x(Cl-) 0.006797

Salinity Aqueous Phase (associated salt molecules)

	Mass%	Molality
NaCl	2.192231	0.383386

TOTAL FLUID INCLUSION

Vm (cc/mol) 35.492464
D (g/cc) 0.505440

amount-of-substance fractions

x(H2O) 0.880201
x(CH4) 0.107641
x(Na+) 0.006079
x(Cl-) 0.006079

FLUID SYSTEM AT FINAL ICE MELTING

TQ1 (K) 269.650000
PQ1 (MPa) 2.347148

CLATHRATE PHASE :

Volume fraction 0.388183
Vm (cc/mol) 22.320838
amount-of-substance fractions
x(H2O) 0.853444
x(CH4) 0.146556

NON-AQUEOUS PHASE :

Volume fraction 0.427562
Vm (cc/mol) 901.289870
amount-of-substance fractions
x(H2O) 0.000008
x(CH4) 0.999992

AQUEOUS PHASE :

Volume fraction 0.184250
Vm (cc/mol) 17.871820
amount-of-substance fractions
x(H2O) 0.965838
x(CH4) 0.000935
x(Na+) 0.016613
x(Cl-) 0.016613

CHAPTER 7: APPENDIX 7-3

FLUIDS, package of computer programs for fluid inclusion studies
Program 1: BULK, version 08/02
Product development Ronald J. Bakker
Filename : test3

BULK FLUID INCLUSION

Vm (cc/mol) 192.467013
D (g/cc) 0.093525

amount-of-substance fractions
x(CO2) 0.070000
x(CH4) 0.930000

Fluid inclusion at room temperature (20 °C)

Internal pressure : 10.365190 MPa

Fluid phases present :
1. vapour-like gas mixture 100.000000 vol.%

VAPOUR-LIKE GAS MIXTURE (at 20 °C)

Equation of state: Lee & Kesler (1975)

Vm (cc/mol) 192.467013
D (g/cc) 0.093525

amount-of-substance fractions
x(CO2) 0.070000
x(CH4) 0.930000

HOMOGENISATION CONDITIONS OF NON-AQUEOUS PHASES

Equation of state: Thiéry et al. (1994), Soave (1972), Lee & Kesler (1975)

Th (K) 196.150000 (-77.000000 °C)
Ph (MPa) 4.325289 (43.252894 bar)
Vh (cc/mol) 192.467013
Dh (g/cc) 0.093525

amount-of-substance fractions
x(CO2) 0.070000
x(CH4) 0.930000

CHAPTER 7: APPENDIX 7-4

FLUIDS, package of computer programs for fluid inclusion studies
Program 1: BULK, version 08/02
Product development Ronald J. Bakker
Filename : test3a

BULK FLUID INCLUSION

Volume fraction estimates are used for bulk fluid calculations

Vm (cc/mol) 97.725270
D (g/cc) 0.184640

amount-of-substance fractions

x(H2O) 0.540547
x(CO2) 0.033430
x(CH4) 0.426023

Fluid inclusion at room temperature (20 °C)

Internal pressure : 10.365190 MPa

Fluid phases present :

1. liquid rim aqueous solution 10.000000 vol.%
2. vapour-like gas mixture 90.000000 vol.%

VAPOUR-LIKE GAS MIXTURE (at 20 °C)

Equation of state: Lee & Kesler (1975)

Vm (cc/mol) 192.467013
D (g/cc) 0.093525

amount-of-substance fractions

x(CO2) 0.070000
x(CH4) 0.930000

HOMOGENISATION CONDITIONS OF NON-AQUEOUS PHASES

Equation of state: Thiéry et al. (1994), Soave (1972), Lee & Kesler (1975)

Th (K) 196.150000 (-77.000000 °C)
Ph (MPa) 4.325289 (43.252894 bar)
Vh (cc/mol) 192.467013
Dh (g/cc) 0.093525

amount-of-substance fractions

x(H2O) 0.000729
x(CO2) 0.069949
x(CH4) 0.929322

AQUEOUS SOLUTION (at 20 °C)

Equation of state for volumetric properties: Duan et al. (1992)

Henry constant CO2: Carroll et al. (1991), Carroll & Mather (1992)

Henry constant CH4: Rettich et al. (1981)

Vm (cc/mol) 17.996481
D (g/cc) 1.004671

amount-of-substance fractions

x(H2O) 0.995437
x(CO2) 0.002656
x(CH4) 0.001907

CHAPTER 7: APPENDIX 7-5

FLUIDS, package of computer programs for fluid inclusion studies
Program 1: BULK, version 08/02
Product development Ronald J. Bakker
Filename : test4

BULK FLUID INCLUSION

Total homogenisation conditions:

Th (K) 403.350000 (130.200000 °C)
Ph (MPa) 0.448508 (4.485080 bar)

Equation of state: Zhang & Frantz (1987)

Vm (cc/mol) 19.341692
D (g/cc) 0.973889

amount-of-substance fractions

x(H2O) 0.960193
x(Na+) 0.019903
x(Cl-) 0.019903

Fluid inclusion at room temperature (20 °C)

Internal pressure : 0.002339 MPa

Fluid phases present :

1. liquid rim aqueous solution 91.434307 vol.%
2. vapour-like gas mixture 8.565693 vol.%

VAPOUR-LIKE GAS MIXTURE (at 20 °C)

Equation of state: Wagner & Pruss (1993)

Vm (cc/mol) 1040596.392950
D (g/cc) 0.000017

amount-of-substance fractions

x(H2O) 1.000000

AQUEOUS SOLUTION (at 20 °C)

Equation of state for volumetric properties: Krumgalz et al. (1996)

Vm (cc/mol) 17.684970
D (g/cc) 1.043923

amount-of-substance fractions

x(H2O) 0.960193
x(Na+) 0.019903
x(Cl-) 0.019903

ICE MELTING CONDITIONS

Purely empirical equation for salinity calculation: Bodnar (1993)

Tm (K) 269.250000 (-3.900000 °C)
Pm (MPa) 0.000014 (0.000141 bar)

Salinity Aqueous Phase (associated salt molecules)

	Molality	Mass%
NaCl	1.150606	6.302759

CHAPTER 7: APPENDIX 7-6

FLUIDS, package of computer programs for fluid inclusion studies
Program 2: ISOC, version 08/02
Product Development Ronald J. Bakker

Filename : test5

Equation of state : Jacobs & Kerrick (1981), Kerrick & Jacobs (1981)
Host Mineral : Quartz

Bulk fluid composition:

x(H₂O) = 0.540547

x(CO₂) = 0.033430

x(CH₄) = 0.426023

Molar Volume = 97.725270 cc/mol

Density = 0.184639 g/cc

T(K)	T(°C)	P(MPa)	P(bar)	V(cc/mol)
573.150000	300.000000	36.186627	361.866267	98.821994
583.150000	310.000000	37.379627	373.796273	98.870559
593.150000	320.000000	38.653572	386.535716	98.919526
603.150000	330.000000	39.964802	399.648025	98.969141
613.150000	340.000000	41.296888	412.968881	99.019568
623.150000	350.000000	42.641406	426.414056	99.070956
633.150000	360.000000	43.993301	439.933013	99.123454
643.150000	370.000000	45.349227	453.492274	99.177217
653.150000	380.000000	46.706805	467.068050	99.232407
663.150000	390.000000	48.064250	480.642504	99.289195
673.150000	400.000000	49.420166	494.201664	99.347760
683.150000	410.000000	50.773417	507.734170	99.408291
693.150000	420.000000	52.123048	521.230481	99.470987
703.150000	430.000000	53.468234	534.682342	99.536057
713.150000	440.000000	54.808243	548.082426	99.603718
723.150000	450.000000	56.142407	561.424070	99.674200
733.150000	460.000000	57.470109	574.701088	99.747738
743.150000	470.000000	58.790763	587.907629	99.824582
753.150000	480.000000	60.103807	601.038074	99.904988
763.150000	490.000000	61.408695	614.086946	99.989223
773.150000	500.000000	62.704885	627.048852	100.077564
783.150000	510.000000	63.991843	639.918427	100.170296
793.150000	520.000000	65.269030	652.690300	100.267716
803.150000	530.000000	66.535905	665.359052	100.370130
813.150000	540.000000	67.776795	677.767947	100.497455
823.150000	550.000000	69.004101	690.041014	100.632381
833.150000	560.000000	70.203167	702.031666	100.792721
843.150000	570.000000	71.361854	713.618543	100.991966
853.150000	580.000000	72.453051	724.530509	101.260930
863.150000	590.000000	73.359277	733.592770	101.736957
873.150000	600.000000	74.336334	743.363340	102.110874