Schriftliche Habilitationsleistung zum Thema

Optimal Interpretation of Microthermometrical Data from Fluid Inclusions:

Thermodynamic Modelling and Computer Programming

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"... en in plaats van vragen te beantwoorden, die de natuur ons stelt, houdt men zich bezig met het antwoord te geven op vragen, die men zich zelven gesteld heeft...

...Maar als deze overweging er toe leiden moest een dieper onderzoek naar het wezen deze lichamen achterwege te laten, uit vrees van buiten den kring der onomstootelijke waarheden te geraken, dan zou men moedwillig een der wegen om nieuwe waarheden te vinden gesloten houden..."

Johannes Diderik van der Waals (1873)

CONTENTS

Abstract

In this habilitation script new chemical and physical concepts and thermodynamical modelling are applied to microthermometry, to enable improved interpretations obtained from fluid inclusion studies in general. Traditionally, empirical analysis has been preferred in fluid inclusion studies. Therefore, the significance of melting temperatures, homogenisation temperatures and other measurable phase changes is not well understood. The infinite number of compositional combinations in fluids makes the empirical approach inappropriate, and therefore does not contribute to a better understanding of natural fluid systems. Recent developments within chemistry and physics allow a fundamental analysis and interpretation of fluid properties observed in fluid inclusions. This study presents several improved equations of state which can be used to interpret fluid mixtures of H_2O-CO_2-CH_4-N_2 and salt (NaCl), that may be applied for the construction of isochores. more gas components can be easily included to this system. This equation of state forms the sole equation that can be applied to complex natural fluid systems, including a salt solution, in addition to a gas mixture. Thermodynamic modelling of homogenisation temperatures is not yet effective for fluid mixtures, like H_2O-CO_2. The lack of experimental data and inconsistencies between several data sets are the main cause for this deficiency. Therefore, a V-X diagram with several smoothed isotherm is presented in this study to obtain graphically bulk fluid properties for the H_2O-CO_2 system, based on recently published experimental data. The clathrate phase, i.e. a solid solution of gas and water, remains one of the most ignored phase that appears within fluid inclusions. Although it may provide important information on bulk fluid properties, its melting behaviour has been one of the most incorrectly interpreted. Inaccurate thermodynamic modelling and observational difficulties are the main causes for this deficiency. A new thermodynamic model is presented in this study for the fluid system H_2O-CO_2-CH_4-N_2-C_2H_6-NaCl-KCl-$CaCl_2$-$MgCl_2$ which accurately reproduces all experimental data on clathrate melting up to 200 MPa. The model has been specially adapted for fluid inclusion studies. Computer programs in C++ are presented that can handle the extensive numerical and analytical procedures which form part of the above mentioned thermodynamic models. Four programs associated with clathrate melting (**Density**, **Ice**, **Q2** and **Nosalt**) are presented for the specific melting behaviour in fluid inclusions. The properties of each phase are calculated, which include also the salinity of the aqueous solution present during clathrate melting. The program **Homogen** can be used for the calculation of bulk fluid properties in fluid inclusions obtained from homogenisation temperatures (for pure fluid systems), melting temperatures of ice and optically estimated volume fractions of the phases present in inclusions at room temperature. Known bulk fluid compositions and densities can be introduced in the program **Isochor** to calculate isochores. This program also includes the possibility to correct fluid density due to expansion and compressibility of the host mineral. Furthermore, this program incorporates the most recently published equations of state which more accurately represents the properties of fluids. These new thermodynamic models and computer programs present a significant advance for enabling the improved geological interpretations of fluid inclusion data

1. Introduction

The changes in temperature, pressure and chemical conditions within specific parts of rock is directly related to geological processes of any scale. Rocks that suffer from a complex geological history may contain the remains of several successive geological events. Mineral assemblages, as well as entrapped fluids, may represent equilibrated traces of these conditions. Although, the reliability of fluid inclusion studies may appear doubtful because of the relatively high reactivity and the volatile character of fluids, it has been shown that fluid inclusions may preserve fluids over millions of years, which remain representative of original near surface, crustal or mantle conditions. Fluid inclusions in natural rock are samples of such fluids that once circulated within the pore spaces between minerals. In addition, the movement of fluids may be localised through preferred orientated cracks, faults, or shear zones within rock, where they may be preserved in vein-forming minerals. Crystal growth and the formation of closely related fluid inclusions, can be a relative fast process. Fluid entrapment is, therefore, an instantaneous process in terms of geological time. Although the amount of different types of fluids that may be entrapped can be numerous, especially in older rock that have experienced multiple geological events, grains usually contain a restricted number of different types of inclusions, which are related to only a few geological processes, as defined by deformation and metamorphism. Apart from fluid flow through fault zones, this may illustrate that the fluid present in rock is not likely to change its properties very fast, and that fluid-mineral interactions are probably buffering, and therefore control both fluid and mineral compositions.

Since the awareness of the importance of fluid inclusions, the small size of these structures and the inferior nature of analytical methods have hindered rapid advancement of this well practised approach in geology. Most of all, a thorough analysis and generative study of particular inclusions was of the least interest, and a few fluid properties have served only as a tool to study the origin of rocks and minerals. However, during the last decades many analytical techniques have been improved in order to meet the need of fluid inclusionists to measure extremely small amounts of material within single fluid inclusions. A technique which has been very powerful since the first fluid inclusion studies is microthermometry. The use of this technique is strongly dependent on scientific developments within chemistry and physics because it involves the direct observation of phase changes of components that form part of the entrapped fluid. Many of these observations could only be interpreted after the chemistry of the fluid system became known, and the thermodynamics was thoroughly described.

The direct application of studied phase behaviour in chemistry appears to be problematic for most fluid inclusionists. The use of microthermometry has been generally accepted as a powerful tool to describe fluid inclusions, however, the obtained temperatures for phase changes remain poorly interpreted, which has had major consequences for the geological interpretations of the rocks studied. The principle objective of this study is to narrow the gap between chemistry and geology for an improved interpretation of microthermometrical data. The question at hand is historically illustrated, and treated with several newly developed thermodynamic models and computer programming. These thermodynamical models and computer programs present an advance for enabling improved geological interpretations of the individual fluids found in inclusions.

The objectives of this study are evolved and handled in four sections:

1. Concise *historical review* on the development of the use of microthermometry in fluid inclusion studies. This section illustrates the poor application of physicochemical concepts in microthermometry and the state of the art (see Chapter 2).

2. *Equations of state* for complex fluid systems. Established thermodynamic models for fluid systems are scrutinized and analysed on mathematical limitations and inaccuracies. In this study, new modifications to the Redlich-Kwong type of equation of state are introduced for complex H_2O-CO_2-CH_4-N_2 fluid mixtures (Chapter 3) which are applicable over a wider temperature-pressure range than previously published equations. Equations for relatively simple fluid systems, including only H_2O, CO_2 and NaCl are expanded with CH_4 and N_2 by Bakker (1999; see Chapter 8.1). This adaptation allows isochore calculation for more realistic geological fluid systems, which include often certain amounts of both gas components in addition to salt-bearing solutions. The transformation of homogenization temperatures in to densities, i.e. P-T-V-X relations of the solvus, is only effective for pure component fluid systems. Inconsistent experimental data and thermodynamic models of the solvus of H_2O-CO_2 fluid mixtures has been critically examined by Bakker (in press; see Chapter 8.2). A new empirical V-X diagram is presented which can be directly used to obtain graphically bulk density and composition from microthermometrical data from binary H_2O-CO_2 fluid inclusions.

3. *Clathrate modelling*. In this study, established thermodynamic models on clathrate stability, i.e. gas hydrates, have been improved and extended to complex fluid system, including mixtures of H_2O, CO_2, CH_4, N_2, C_2H_6, NaCl, KCl, $CaCl_2$, and $MgCl_2$ (see Chapter 4). Melting of a clathrate phase may give valuable information on the density and composition of fluid inclusions. Bakker et al. (1996; see Chapter 8.4) present the effect of clathrate freezing point depression of the CO_2 gas hydrate from several salts, and Bakker (1998; see Chapter 8.5) introduce a new excess energy term for mixed gas hydrates, both of which are able to reproduce all available experimental data accurately. These models have been specially adopted for fluid inclusion, which in general contain a clathrate phase during cooling runs (Bakker, 1997; see Chapter 8.6).

4. *Computer programming*. The complexity of the newly developed thermodynamical models produces the necessity of computer programming. In this study, programs in C++ have been designed to perform extensive calculations and to present general applicable procedures (see Chapter 5). As previously mentioned, Chapter 8.6 presents four programs associated with specific types of clathrate melting in fluid inclusions (Bakker, 1997) : DENSITY, ICE, Q2 and NOSALT. The calculation of bulk density and composition of fluid inclusions from microthermometrical data and occasionally optical volume fraction estimates is obtained in program HOMOGEN (see Chapter 5). Finally, program ISOCHOR (see Chapter 5) produces isochores for known bulk compositions and densities, including the thermal expansion and compressibility of the host mineral. These programs include recently published equations of state, which allow calculations of high accuracy.

2. Historical Review

2.1. Development of microthermometry before 1900

One of the first known fluid systems to mankind was air, petroleum, blood, and atmospheric H_2O containing several easily dissolved salts. Their properties and phase changes at 1 atmosphere were used to design efficient thermometers (Fahrenheit, 1724; Celsius, 1742), which evidently formed the basis of the apparatus in microthermometry. These fluids were also initially assumed to be present in gems (Boyle, 1672), which contained large fluid inclusions, clearly visible with the naked eye. Due to Boyle's interest in experimental work, he was also one of the first to characterize systematics for the physical properties of gases and he also laid the foundations for the ideal equation of state for fluids (Boyle, 1661). The systematic and mathematical description of fluid properties form the fundamentals for microthermometry.

At the beginning of the 19th century, the chemical and physical properties of fluids in cavities was addressed by Davy (1822), who mentioned that water, and all fluids at usual temperatures, are more expansive upon heating than earthy matters. This specific fluid property was already experimentally proven for gases by Boyle (1661) and Gay-Lussac (1808) as expressed in the ideal gas law. Subsequently, Davy (1822) postulated the generation of a bubble at room conditions in aqueous inclusions which have been formed at higher temperatures and atmospheric pressures. During cooling to room temperatures the contraction of the fluid in cavities generated a vacuum. In accordance to his hypothesis, the low internal pressure inside fluid inclusions was indeed noticeable during opening procedures. Brewster (1823) reversed this prediction and measured the temperature of filling, i.e. homogenisation temperature. He was the first to recognize the potential of microthermometry:

> *"And though I have employed only the microscope, and the agency of heat and light, I have been led to results of considerable generality and interest. This physical method of determining the properties of minute quantities of matter, though often very difficult, and sometimes perplexing in its manipulations, carries with it a degree of evidence not inferior to that of chemical analysis; while it possesses the advantage of examining the substance in its original and unchanged condition, and may be applied, in many cases, where the chemist cannot avail himself of any of the resources of his art"*

Brewster (1823) described the disappearance of bubbles in fluid inclusions, i.e. the expansion of the fluid, by hand warming until they disappear completely (Fig.1). He build the first elementary heating stage, which included no more than a container of heated water, and measured the reappearance temperature of "*vacuities*" during cooling, which was apparently almost the same as the temperature of filling. Metastabilities during cooling runs were not yet recognized. The first fluid inclusions observed by Brewster (1823) contained a fluid for which no readily available explanation was present from chemistry and physics. He measured homogenisation temperatures between 23.3° and 29°C, and an expansibility of this "*New Fluid*" in two phase (Fig.1) and three phase inclusions (Fig.2), which was about 30 times higher than values known for water solutions. Later, the pressure inside these assumed vacuities appeared to exceed atmospheric pressures. At this time, the existence of liquid CO_2 was not yet known in chemistry.
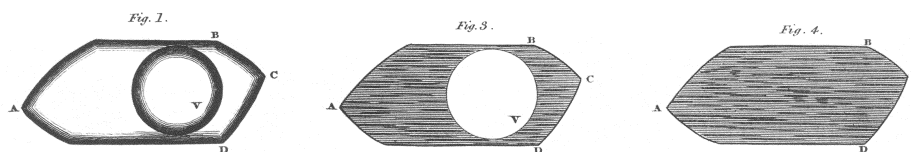
Fig.1. *"Cavity in New Holland topaz, filled with a colourless and transparent fluid (ABCD) with a vacuity (V), of a circular form, which moves by an inclination of the plate. The vacuity V vanishes in a brilliant speck at a temperature of 80°F, leaving the whole of the cavity ABCD of the same uniform tint " (from Brewster, 1823).*
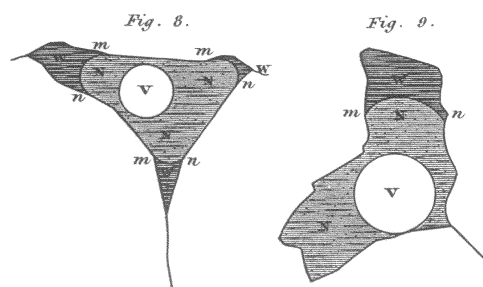
Fig.2. *"Topaz, V is the vacuity, N the new fluid, and W another fluid, which we shall distinguish by the name of the Second Fluid." (from Brewster, 1823).*

The application of microthermometry in geology became evident from experiments of Sorby (1858) who described the use of melting temperatures and homogenisation temperatures of water-rich fluids in natural inclusions. Heating of the sample was done in a bath of paraffin. From experiments with several types of salts he concluded that, provided the temperature of inclusion formation was not known, it may be approximated by determining what increase of heat is required to expand the fluid to fill the cavities. The pressure of the rock during formation was obtained from the elastic forces of the vapour of water at homogenisation temperatures, i.e. the pressure along the boiling curve. Sorby (1858) referred to some specific fluid properties which are indicative of the composition of the enclosed fluid. In addition to pure H_2O inclusion, which melted exactly at 0.0°C, he also noted the presence of dissolved salts in the cavities from crushing experiments on natural rock, and consequently, explained the failure to freeze the fluid in some very excellent fluid-cavities at a temperature of about –20°C. He also noticed the increase of homogenisation temperatures as a result of the presence of salts in the water. In Sorby's studies, the optical estimation of filling degrees, i.e. volume-fractions of the fluid in cavities, is an important tool for analytical procedures of fluid inclusions. Sorby (1858) designed some purely empirical equations to convert these filling-degrees into homogenisation temperatures (Fig. 3). These equations are equivalent to the boiling curve of H_2O at constant total volume, as described in chemistry.

About fifty years after the description of the *"New Fluid"* by Brewster (1823), Simmler (1858) was the first to offer an interpretation, comparing the expansibility of liquid CO_2 to that of the liquids in crystals, as described by Brewster (1823). Vogelsang (1869) was able to determine that the peculiar fluid in three phase inclusions (i.e. *"Brewsterlinite"*), was indeed liquid CO_2.: the presence of CO_2 was positively identified after the crystals were broken and the spectrum of the fluid was measured, by passing electric sparks through it.

$$V = Bt + Ct^2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{equation (1)}$$

$$= \frac{v + \cdot00000271p}{1 - \cdot00000271p} \ldots\ldots\ldots\ldots\ldots\ldots \text{(2)}$$

$$t = \frac{\sqrt{4CV + B^2} - B}{2C} \ldots\ldots\ldots\ldots\ldots\ldots \text{(3)}$$

$$= \frac{\sqrt{4C\frac{v + \cdot00000271p}{1 - \cdot00000271p} + B^2} - B}{2C} \ldots\ldots\ldots \text{(4)}$$

$$v = (Bt + Ct^2)(1 - \cdot00000271p) - \cdot00000271p \ldots \text{(5)}$$

$$p = 369,000\frac{V - v}{1 + V} \ldots\ldots\ldots\ldots\ldots\ldots \text{(6)}$$

$$e = 13\cdot2\{1 + \cdot007153(t - 100)\}^5 \ldots\ldots\ldots\ldots \text{(7)}$$

If $p = 0$, $v = V$.

1. Water .... $V = \cdot0001344t + \cdot000003245t^2$
2. „ with 10 p. c. of chloride of potassium .. $V = \cdot0001868t + \cdot000002524t^2$
3. „ „ 25 p. c. of chloride of potassium.... $V = \cdot0003006t + \cdot000001410t^2$
4. „ „ 12½ p. c. of chloride of potassium + } $V = \cdot0003280t + \cdot000001422t^2$
   12½ p. c. of chloride of sodium..
5. „ „ 25 p. c. of chloride of sodium...... $V = \cdot0003520t + \cdot000001370t^2$
6. „ „ 25 p. c. of sulphate of soda........ $V = \cdot0003077t + \cdot000001644t^2$
7. „ „ 25 p. c. of mixed salts, being the } $V = \cdot0003221t + \cdot000001461t^2$
   mean of 3, 4, 5, & 6..........

*Fig.3. Empirical equations of Sorby (1858). **V** is the relative size of the vacuity at 0°C, **v** is the actually observed relative size, **t** is temperature in °C, **p** is pressure in feet of rock (1 atm = 13.2 feet), **e** is the elastic force of the vapour of water at t. Values of **B** and **C** for the expansion of several pure H_2O and salt-bearing fluids.*

By the mid 1800's, chemistry and physics provided new evidence (Thilorier, 1835; Gore 1861; Andrews 1869, Waals 1873) to interpret these observations and the occurrence of three phase fluid inclusions. The physiochemical properties of liquid CO_2 were described by Thilorier (1835) and Gore (1861). Andrews (1869) described the surface of demarcation between the liquid and gas CO_2, which disappeared at the *"Critical Point"* of 30.92 °C. Liquefaction does not occur at temperatures a little above this point, and the fluid appears to be perfectly homogeneous (Fig.4). The continuity of gaseous and liquid states was then kinetically and mathematically described by Waals (1873) who introduced a highly effective modification of the ideal gas law from purely theoretical considerations (Fig.5). He postulated that all substances have a critical temperature, above which it is a permanent gas.
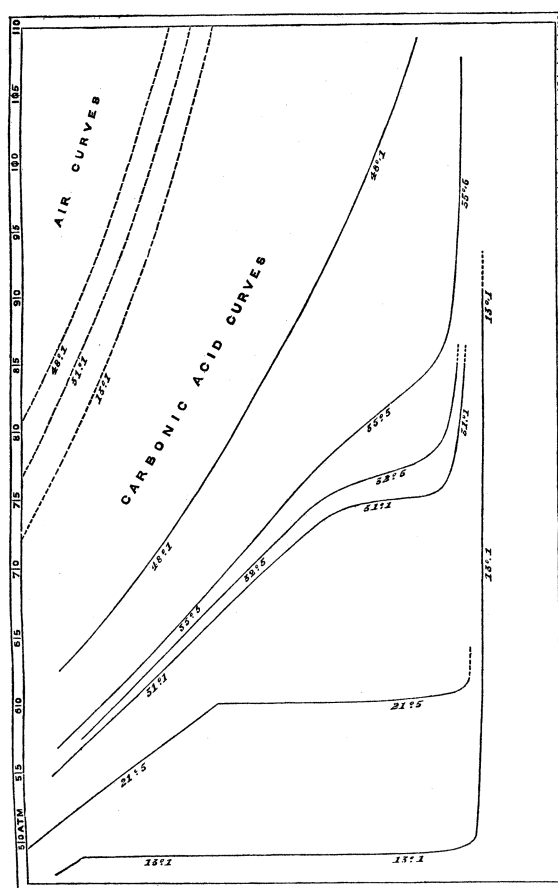
Fig.4. PV diagram with isotherms for CO_2 and air, from Andrews (1869).
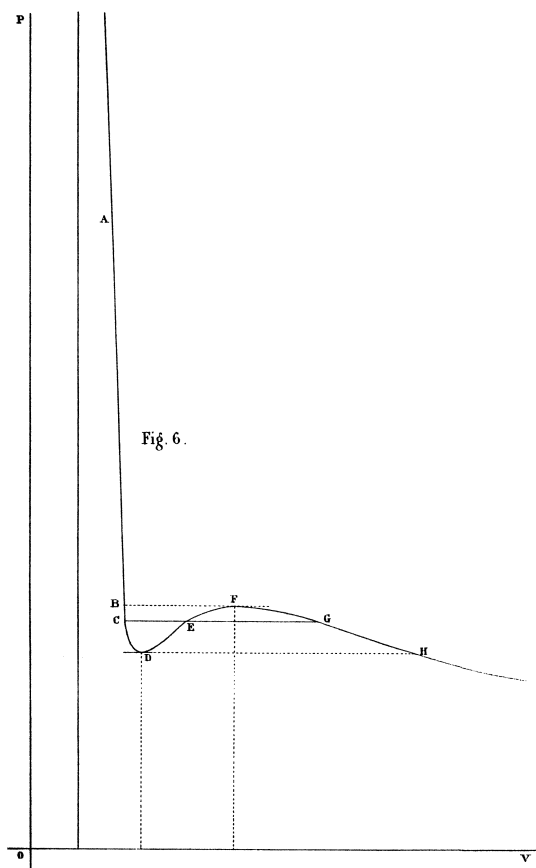
Fig.5. *General PV diagram from Waals (1873) with an isotherm for sub-critical conditions. Liquid (density C) is in equilibrium with gas (density G) at a defined pressure.*

Zirkel (1873) extensively described the occurrence of fluid inclusions in rock and minerals and he developed the state of the art in microthermometry. A heating stage designed by Vogelsang was presented with controlled electric heating up to 200°C (Fig.6). Zirkel (1873) summarized the two major types of fluids observed during heating of samples: those that considerably expand (CO_2-rich fluids) and those that show hardly any expansion (H_2O-salt-rich fluids).

According to Sorby's experimental work, only the homogenization temperatures were considered to be of most geological interest, although chemistry and physics provided the tools to calculate densities and isochores from these temperatures. Microthermometry remained restricted to oversimplified explanations, where homogenization temperatures were measured or calculated from highly inaccurate filling degree estimates, and they were interpreted as directly relating to the formation conditions. Complications were already recognized as inclusion populations occurred with widely varying degrees of filling. CO_2 homogenisation up to 32 °C was mainly used as a qualitative identification of the presence of CO_2 in fluid inclusions. Zirkel (1893) showed that the application of microthermometry was still at a primitive level, despite many new discoveries within physics and chemistry. The presence of other gases, like CH_4, N_2, H_2 and CO was erroneously suspected because homogenization occurred
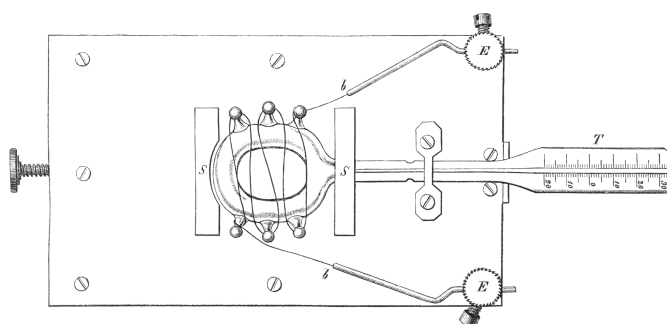

Fig.6. *"heizbare Objecttisch" from Vogelsang, as shown in Zirkel (1873). S are connecting pieces (Stege); T is a mercury thermometer; E are electrodes; b is copper wire.*

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occasionally in the vapour phase (e.g. Tilden, 1897). The actual arguments for this assumption were the results from bulk analysis, viz. extracting gases by heating of the rock in a vacuum. Only few geologists (e.g. Hartley, 1876a,b, 1877a,b) seriously combined the knowledge of chemical and physical phenomena with their microthermometrical observation in fluid inclusions. Hartley studied the constant vibration of minute bubbles, and the variation of the critical point of CO_2 as a consequence of the presence of small amounts of other gases.

During this time, developments in chemistry and physics were almost completely ignored. For example, phase changes at critical conditions in closed tubes, which may be regarded as substitute fluid inclusions, were described by Ramsay (1880) and Hannay (1880). The disappearance of capillarity near the critical point illustrates the disappearance of the liquid meniscus in fluid inclusions at critical homogenization. Their experiments provided important data on possible phase changes and other physio-chemical properties of fluid inclusions in minerals. The pure CO_2 system was further described in some detail by Amagat (1892, 1893) who presented PVT data from which isochores can be constructed in PT-diagrams up to 258 °C and 1000 atmosphere.

2.2. Development of microthermometry after 1900

Following the experiments of Sorby (1858), homogenisation temperatures of aqueous inclusions were still interpreted as reflecting the formation conditions of fluid cavities and parts of minerals at the beginning of the 20th century (e.g. Königsberger, 1901; Königsberger & Müller, 1906). The origin of two phase H_2O-CO_2 fluid inclusions was misinterpreted and considered to directly relate to pure H_2O fluid properties. Two phase inclusions with a H_2O-rich liquid and a CO_2-rich vapour bubble, as deduced from destructive spectral analysis, were believed to be formed from a homogeneous water-rich fluid in which all the CO_2 is dissolved at homogenization temperatures and saturated steam pressures (Konigsberger & Müller, 1906). The design of a heating stage had been improved by Königsberger & Müller (1906), who gave a careful description of the experimental set-up for accurate and precise measurements.

Hunt (1903) had a pleasant manner of expressing the scientific discrepancy between geology and chemistry, and he stimulated the application of chemical phenomena to fluid inclusion studies. He recognized that geologists ignored, disproved and rejected physical evidence:

> *"Being, however, an undoubted crock, I am extremely disinclined to come between the geological pots and the chemical kettles; and I need only say that my sympathies are with the chemical kettles, because they seem to me to account for all the phenomena which I have observed with my antiquated microscopes."*

The state of water above critical temperatures was still disregarded, and it was assumed to be completely dissolved in the rock. The critical point of H_2O (374.1 °C) was often interpreted as the formation conditions of granites, which contain aqueous fluid inclusions.

Johnsen (1919) was one of the first to explain in detail the relation between homogenisation temperature and total density of pure CO_2 inclusions in amethyst crystal, using the data of Amagat (1892) and the equation of state from Waals (1873). He combined optical volume fraction estimations with tabled values of CO_2 vapour and

liquid densities at 20°C to calculate the total density during the assumed formation of the crystal (Fig.7). This density turned out to be exactly the density of liquid CO_2 at the homogenisation temperature, i.e. the temperature of complete filling. The depth and pressure of the formation conditions of the minerals were then calculated with known *"geotherme Tiefenstufe"* of 1°C per 30 meter and known *"geobare Tiefenstufe"* of 1 atmosphere per 4 meter, which apparently differed greatly from the pressure of the fluid.

Tabelle A[1]).

Temperatur in Celsiusgraden	Dichte ϱ_d des gesättigten CO_2-Dampfes	Dichte ϱ_f der flüssigen CO_2.
0	0,096	0,914
+ 5	0,114	0,888
+10	0,133	0,856
+15	0,158	0,814
+20	0,190	0,766
+25	0,240	0,703
+30	0,334	0,598
+31,3	0,464	0,464

Fig.7. CO_2 density table from Johnsen (1919).

The interpretation of microthermometrical data was clearly improved by Nacken (1921), who critisized the then widely accepted assumption that homogenisation temperatures are equal to the formation conditions of minerals. He explained the processes and phase changes that occur during heating and cooling in fluid inclusion, assuming then to be constant volume containers and, therefore, act as isochoric systems (Fig. 8). He applied available chemical data on phase diagrams for CO_2 from Amagat (1893) and the much less known system of H_2O from Holborn & Baumann (1910). Nacken (1921) clearly stated that fluid inclusions are formed somewhere along the isochore of its fluid system, and that homogenisation temperatures represent the minimum trapping conditions:
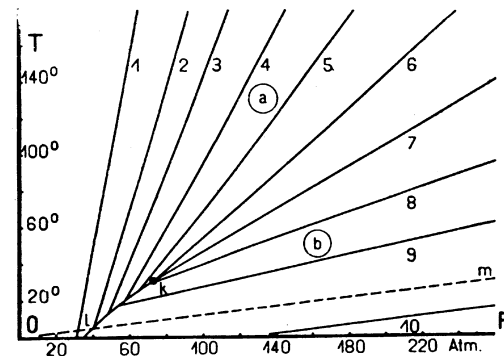
Fig. 1.

Fig.8. CO_2 isochores from Nacken (1921).

"Eine eindeutige Bestimmung der Bildungs-Bedingungen ist auf diesem Wege nicht möglich. Das gilt besonders für die Entstehungstemperatur und für den hierbei herrschenden Druck und damit auch für die Tiefe, in der die Einschlüsse entstanden. Nur eine untere Temperaturegrenze läßt sich durch das Verschwinden der Libelle festlegen."

Nacken (1921) was also the first to elucidate the possible phase transition for mixed CO_2-H_2O fluid inclusions from theoretical phase diagrams (Roozeboom, 1904) (Fig. 9); experimental data were not available for this system. Furthermore, heterogeneous trapping was considered as a possible mechanism of the entrapment of nearly pure CO_2 fluids. Droplets of the discontinuous fluid phase might cling to a growing crystal face until it was enclosed by the mineral. Alternatively, the growing face might enclose

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some of the continuous phase. This mechanism might account for the observed variable ratio of the two phases when examined under the microscope at room temperature.

Fig. 5.

Fig.9. *Theoretical mixed CO$_2$-H$_2$O fluid properties from Nacken (1921).*

The implications of homogenization of H$_2$O-rich inclusions at higher temperatures were not well understood, and erroneous compromises were developed. For example, in samples with a mixed population of H$_2$O-rich and CO$_2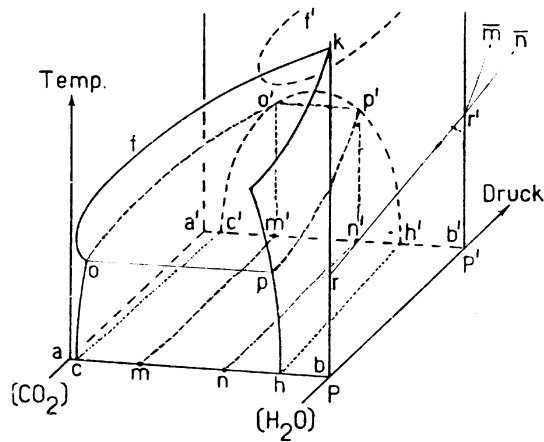$-rich fluid inclusions Holden (1925) constructed isochores for pure CO$_2$ inclusions according to the method of Johnsen (1919). He then used the homogenisation temperatures of H$_2$O-rich inclusions to estimate the pressure on the CO$_2$ isochores, which were believed to reflect formation conditions. Unfortunately, homogenisation temperatures of liquid inclusions remained mistakenly interpreted as trapping conditions, especially within the field of ore-geology (e.g. Newhouse, 1933), where compositional specification of the enclosed fluid was fully neglected.

Outside the field of fluid inclusion research, the characteristics of H$_2$O-rich fluids in rocks above critical conditions were firstly clarified by Ingerson (1934) and Morey & Ingerson (1937). They were the first to apply the concept of critical and supercritical fluids within geology. In studying hydrothermal processes in association with the solubility of silicates, Morey & Ingerson (1937) illustrated qualitatively aqueous systems at high temperatures, approaching and above the critical temperature of H$_2$O (Fig.10). These theoretical phase diagrams can also have been applied to H$_2$O-CO$_2$ mixtures.
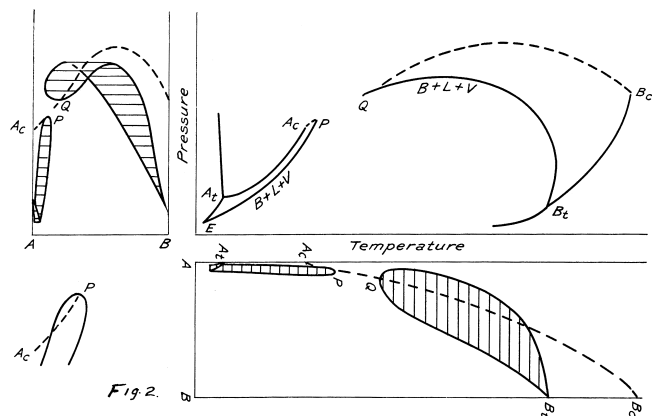
FIGS. 1 AND 2.   Projections on the temperature-concentration, temperature-pressure, and pressure-concentration planes of a solid model which gives a diagrammatic representation of the phase equilibrium relationships in a binary system with components of widely different volatility, in which the critical or plait point curve in Fig. 1 (upper) *is not* intersected by the solubility curve. A_t and A_c, and B_t and B_c, represent the triple and critical points for the two components, respectively. E is the binary eutectic.

Fig.10. *Theoretical phase diagrams from Morey & Ingerson (1937).*

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Ingerson (1947) introduced pressure corrections for the homogenization temperatures of H_2O-rich inclusions using available P-V-T data, which are no more than a construction of isochores for pure H_2O fluids, similar to those calculation for CO_2 undertaken by Johnsen (1919).

The general application of these concepts, however, remained somewhat restricted. Complete ignorance and mystification was even increased by the development of decrepigraphs (e.g. Scott, 1948; Smith, 1948). During heating, decrepitation noises were recorded with a microphone, and the corresponding temperatures were believed to represent formation conditions, which believed to represent homogenization temperatures or temperatures of complete filling. This erroneous approach was revised by Kennedy (1950a) who questioned fundamental assumptions in the use of vacuoles, i.e. fluid inclusions, in geologic thermometry:

> "The question that the writer wishes to raise are primarily intended as a caution against the too ready acceptance of far-reaching conclusions based on what appears to the writer to be insufficiently compelling evidence."

Kennedy (1950a) recognized the need for exact chemical and physical data on fluids for the effective interpretation of microthermometrical data. Subsequently, he presented accurate P-V-T diagrams for pure H_2O (Kennedy, 1950b) containing isochores labeled with homogenization temperatures, which differed substantially from previously published data (Fig.11). Furthermore, Kennedy questioned the isolated character of fluid inclusions in natural rock, as experimentally observed in a fluorite sample. Homogenisation temperatures appeared to be lowered by 10°C from the original value of about 200 °C in the same inclusions after the fluorite had been subjected to a pressure of approximately 1500 bar and 150°C.
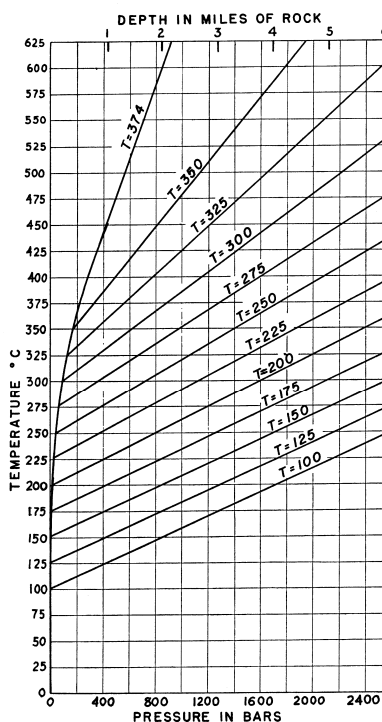
Fig. 3. Curve showing relation of temperature of disappearance and pressure at time of formation.

Fig.11. P-T diagram for pure H_2O with several isochores, from Kennedy (1950a)

Since the beginning of systematic fluid inclusion research, the analysis of salts within fluid inclusions has been mainly based on extraction methods, and not related to microthermometry. Again, developments within chemistry and physics were not recognized in geology, and data on for example the freezing point depression were

ignored. For higher temperatures, data on the H_2O-salt solution series were firstly compiled by Brönsted (1928) and Schroeder et al. (1935) who gave the temperature dependence for the solubility of several salts, like NaCl, KCl, $CaCl_2$, Na_2SO_4, K_2SO_4, $CaSO_4$, Na_2CO_3, and $NaHCO_3$ at 1 atmosphere. Although these results were only rough approximations for microthermometry because of the chemical complexity of most fluids and the higher pressure for isochoric vapour saturated conditions, it was generally believed that these amounts of salts probably occur in aqueous solutions in fluid inclusions in minerals. The effect of increased critical temperature of H_2O solutions with salts (e.g. Chitarow & Iwanow, 1936) were not applied in any fluid inclusion study. Knowledge of the salt-H_2O system was greatly improved by Keevil (1942) who presented experimental work conducted at higher pressures. Although the importance of H_2O in many geological processes was generally accepted, Keevil noticed the lack of details concerning composition, temperature and pressure of hydrothermal reactions. His experiments simulated processes and phase changes that may occur in fluid inclusions. However, entrapped fluids in minerals were not part of this study.

A thorough review on published data available for microthermometry was given by Smith (1953). This work clearly indicates the basic level of interpretations for microthermometrical data at that time. Exact chemical and physical approaches were discouraged by the erroneous opinion that there is no need for exact and practical graphs of P-V-T data of water and carbon dioxide. The potential of microthermometry was further hampered by the absence of an exact method for determining directly either the temperature or the pressure of crystallization of minerals by measurements of inclusions.

2.3. Enhanced chemical awareness in fluid inclusion studies

About a century after the first experiments from Sorby (1858), the application of microthermometry had not developed significantly further. Only homogenization temperatures of liquid-like aqueous inclusions, decrepitation temperatures and homogenisation temperatures of CO_2 around 31 °C were measured. Homogenizations near room temperatures were used as a qualitative identification for the presence of CO_2. Furthermore, the interpretation of these temperatures remained highly speculative, and the chemical composition and density were still of minor interest to many fluid inclusionists. Although many fluid systems, including phase diagrams were already known in chemistry and physics, fluid inclusion studies failed to apply this highly useful information. The complexity of fluid systems in natural inclusions was believed to be beyond the relatively simple experimentally studied fluids in chemistry. This resulted in an almost complete blocking of constructive evaluation of possible phase changes in fluid inclusions. By the mid 1950's the application of microthermometry to analyse fluid inclusions in density and composition was realised and several fluid systems were described in more detail and readily available for the measured temperatures of phase changes in fluid inclusions.

H_2O-Gas

Traditionally, the CO_2 gas system was firstly investigated in more detail. Roedder (1963) described some new methods on the identification of CO_2 in fluid inclusions, and

expanded the application of microthermometry to H_2O-gas-rich inclusions. The triple point of pure CO_2 (-56.6°C) was already characterised by Quinn & Jones (1936), but frozen CO_2 crystals were not yet observed in fluid inclusions which has been freezed down to -78.5°C. This metastability was overcome by cooling with liquid N_2 down to -196°C. Consequently this triple point can be used to identify the presence of CO_2. In addition, Roedder (1963) mentioned the melting of CO_2 hydrate in several natural samples between +7.5 and +11.1°C. He described extensively the melting behaviour of this phase in fluid inclusions, and gave detailed observations on visible and invisible CO_2 hydrate crystals (Fig.12).
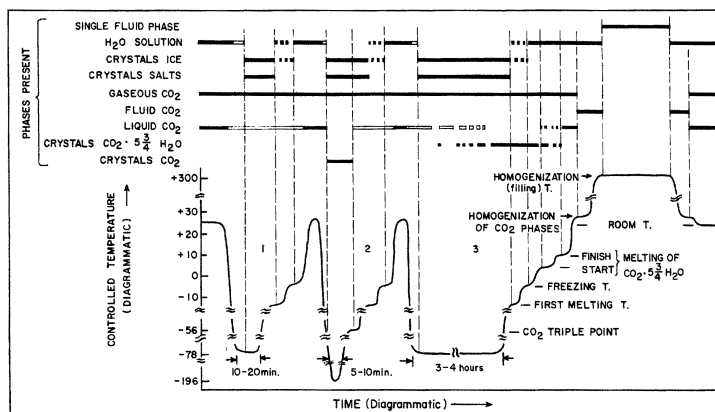
Fig.12. Heating and freezing behaviour of fluid inclusions, from Roedder (1963).

FIG. 2. Diagram showing the phase assemblages during three cooling (and one heating) runs on sample containing $CO_2 + H_2O$ solution. The solid bars indicate stable phases, and the open bars metastable ones. In run 1, neither CO_2 crystals nor $CO_2 \cdot 5\frac{3}{4}H_2O$ crystals form. In run 2, CO_2 crystals form at liquid nitrogen temperatures, but the time is inadequate to form $CO_2 \cdot 5\frac{3}{4}H_2O$ crystals. In run 3, $CO_2 \cdot 5\frac{3}{4}H_2O$ crystals form slowly. The crystals of salts were not seen, but were assumed to be present on the basis of the freezing data. The diagram was drawn for sample ER61-9B, but is generally applicable.

Apparently gas hydrate, or clathrate, melting data had never been used in studying the composition of fluid inclusions in minerals, although the existence of clathrates was already known since Davy (1811) discovered the chlorine hydrate. Wroblewski (1882) found that CO_2 and H_2O form a solid compound, i.e. the CO_2 gas hydrate, which melted at 8°C (Hempel & Seidel, 1898). Unfortunately, clathrates still remain as one of the most ignored phases that appear within fluid inclusions, and its melting behaviour remains as one of the most wrongly interpreted.

The immiscibility of H_2O-CO_2 fluids, as theoretically illustrated by Morey & Ingerson (1939) was experimentally studied by Tödheide & Franck (1963), Takenouchi & Kennedy (1962) and Sterner & Bodnar (1991). The topology of this fluid system within TPX diagrams (Fig.13) represents total homogenization conditions for binary H_2O-CO_2 mixtures Although volume and density were in general not included in these studies, these diagrams provide a foundation for the interpretation of phase behaviour in fluid inclusions. Unfortunately, these data set are inconsistent and the presented data did not allow the interpretation of homogenisation temperatures of binary H_2O-CO_2 mixtures.

The presence of additional gases, like CH_4 and N_2 in natural fluid inclusions remained problematic for the analysis of microthermometrical data. Therefore, Swanenberg (1980) introduced the concept of *"CO_2-equivalent density"* to derive approximate isochores. Hollister & Burruss (1976) noticed the gap between available

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PTX data in the fluid system CO_2-CH_4-H_2O-NaCl, and its application to fluid inclusion studies. They introduced the CO_2-CH_4 *subsystem* at lower temperatures, where the H_2O component is essentially confined to either solid ice or solid clathrate and "*inert*" with respect to the equilibria involved. Lowering of the melting temperature of solid CO_2 in the presence of CO_2-CH_4 gas defines the total amount of CH_4 present in the subsystem, using the partition coefficients of Donnelly & Katz (1954), and measurements of volume percentages of liquid and gas phases. This concept has been

Abb. 3. Das Zweiphasengebiet und die kritische Kurve im System Kohlen-dioxid—Wasser (qualitativ). - - - - kritische Kurve, ——— Dampfdruckkurven. Übrige Bezeichnungen siehe Text

Fig.13. Qualitative PTX diagram for the H_2O-CO_2 system, from Tödheide & Franck (1963).

further developed by Kerkhof (1988), Thièry et al. (1994) and Kerkhof & Thièry (1994) in VX diagrams, which can be used to estimate graphically the composition and density from melting and homogenisation temperature for binary mixtures of CO_2-CH_4 and CO_2-N_2. It should be noted that the presence of any H_2O may seriously change these graphs.

Hollister & Burruss (1976) also give an extensive discussion on changes of the CO_2 clathrate stability as a consequence of the presence of additional CH_4 or NaCl. Only approximate numbers were given on the amount of influence. The effect of salts on the depression of pure CO_2 clathrate melting temperatures were defined by Darling (1991) and Diamond (1992) in purely empirical equations, which can be directly applied to fluid inclusion data. The complication of additional gases was then elucidated by Diamond (1994) by extrapolating isochores in the metastable absence of a clathrate phase, in combination with Raman spectrographical analysis of the gas mixture and clathrate melting temperature. Dubessy et al. (1994) applied a similar combination of techniques in addition to ice melting temperatures and volume fraction estimations. Inclusion density and composition were obtained from complex calculations, which could only be performed with efficient computer programs. The combination of microthermometry and Raman spectroscopy is currently a common practise for the non-destructive analysis of fluid inclusions containing complex gas mixtures and salt-bearing aqueous solutions.

H_2O-Salt

The freezing point depression of ice in salt-bearing solutions of fluid inclusions in beryl found within pegmatites was first considered by Cameron et al. (1953) to estimate salinities. The sample was frozen with a gas flow cooled by liquid air, and melting temperatures were measured between –5°C and –12°C. Because the type of salt had to be guessed, the concentrations of the solutions could only be roughly estimated.

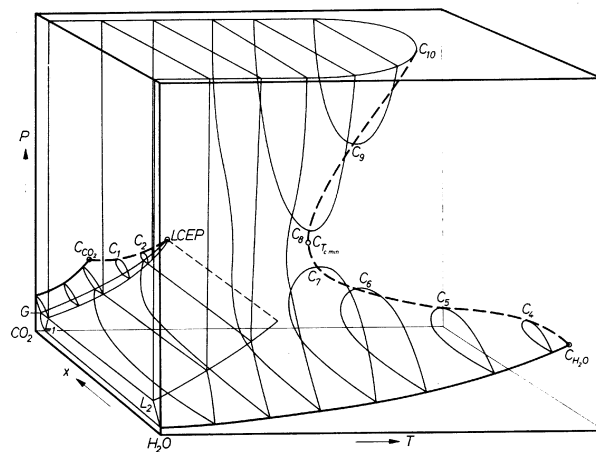Recorded data on the melting points of solutions with various salts in water pointed to concentrations in the range between 2.7 and 6.5 molar. The type of salts were not specified further. The first systematic approach to using microthermometry for compositional analysis without extracting material from inclusions was described by Roedder (1962). A newly designed heating-freezing stage allowed accurate and precise measurements of samples in the range –35°C to +250°C, and hence low temperature phase changes could be measured. Temperature gradients were minimized by total immersion of the sample in circulating thermostated fluid. Roedder described in detail the method of measuring ice melting temperatures and highlighted some special techniques to improve the precision and accuracy. Roedder (1962) gives a complete impression on the problems and merits of metastable supercooling of fluid inclusions. He described inclusion textures which are indicative for first melting of the fluid, and which may express the type of salt present. Furthermore, fluid inclusion phase appearances during final melting were described, which is a measure of the salinity. Fluid inclusions are generally multicomponent systems, as previously obtained from various bulk chemical procedures for extracted fluids. Therefore, Roedder (1962) mentioned that the depression of the freezing point for pure solutions of NaCl can be used as a crude guide, introducing the *eq. wt% NaCl*. He further stressed the need for a combination of several methods for a complete analysis:

> *"The combination of chemical analytical data on leachates, giving the ratios of the various salts present in inclusions, with freezing data, giving the concentration of salts, makes possible much more complete characterization of the included fluids than would be possible from either type of data alone."*

Roedder (1962) presents a TX-diagram for the H_2O-NaCl system from the International Critical Tables IV (1928) which can be readily used to read off graphically the salinities from final ice melting temperatures (Fig.14). Although this diagram had been developed for 1 atmosphere total pressure, higher internal pressures in fluid inclusions as obtained from the presence of liquid CO_2 are assumed to only slightly lower the freezing point.
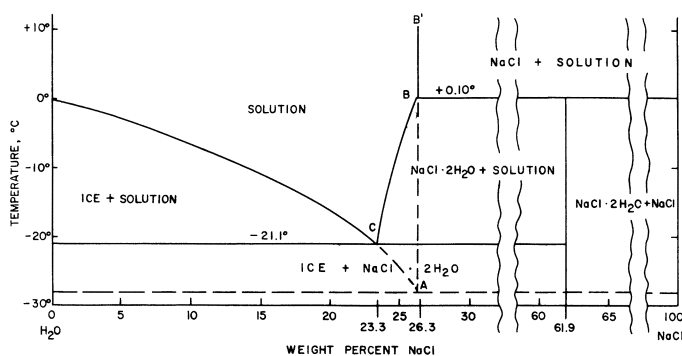
Fig.14. *Freezing point depression, from Roedder (1962).*

FIG. 4. The system H_2O-NaCl. Data from various sources (Int. Crit. Tables IV, p. 235, 1928).

Several purely empirical equations have been developed for the freezing point depression in the H_2O-NaCl system as shown in Fig.14 (Potter et al., 1978; Hall et al., 1988; Oakes et al. 1990; Bodnar, 1993; Dubois & Marignac, 1997). Difference between these equations resulted from the amount of experimental data included, and different values for the eutectic point (Table 1). The empirical approach has been applied to some

binary salt mixture as well, like NaCl-CaCl$_2$-H$_2$O (Oakes et al., 1990), NaCl-KCl-H$_2$O (Hall et al. 1988), and NaCl-MgCl$_2$-H$_2$O (Dubois & Marignac, 1997).

Table 1. Eutectic salinity and temperatures for the H$_2$O-NaCl system

	wt.% NaCl	Melting Temperature (°C)
Rodebush (1918)	23.31	-21.12
Potter et al. (1978)	23.225	-20.81
Hall et al. (1988)	23.20	-21.21

As mentioned in the previous paragraph, the maximum amount of salt which can dissolve in liquid H$_2$O was measured as a function of temperature (e.g. Keevil, 1942). The measured values of vapour saturated solubility of NaCl, i.e. the three phase stability curve, range from the incongruent melting point of hydrohalite to higher salinities. Sourirajan & Kennedy (1962) made an extensive study on the NaCl-H$_2$O system at higher temperatures and pressures (Fig. 15) and provided a large dataset. Chou (1987), Sterner et al. (1988) and Bodnar (1992) provided some more data for one particular phase boundary, and defined empirically best-fit curves along the three-phase curve. This allows salinity calculations from the measured temperature of halite daughter crystal dissolution in the presence of both liquid and vapour, which neglects the amount of salt dissolved in the vapour phase. Most of these empirical polynomes include too many terms for relatively straight lines. These considerations do not take into account any equilibrium conditions between phases. Consequently, substantial errors in salinity calculations may be present at higher temperatures because the amount of dissolved salt the H$_2$O vapour phase is neglected.
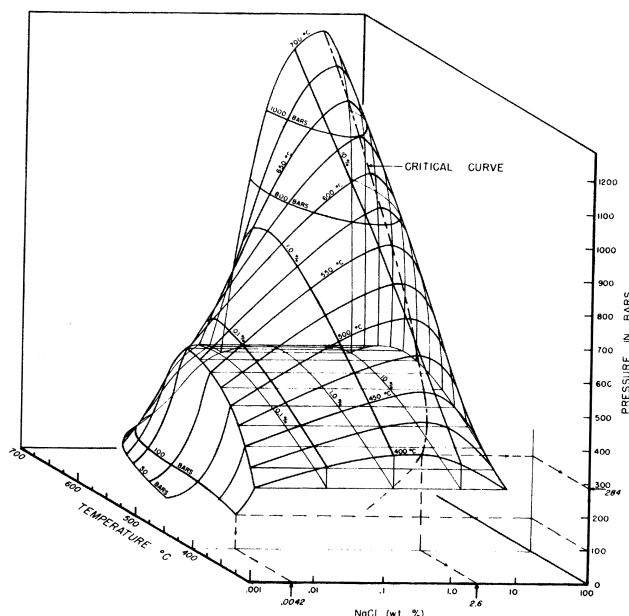
Fig. 17. Temperature-pressure-composition model of the system H$_2$O–NaCl.

Fig.15. P-V-T diagram for the H$_2$O-NaCl fluid system, from Sourirajan & Kennedy (1962)

2.4. In conclusion

The previous section has illustrated the poor use of chemical concepts within microthermometry. Only a few relatively simple fluid systems have been sufficiently adopted in fluid inclusion studies. However, for most natural fluid inclusions it is still

impossible to calculate densities of the fluids from the homogenization temperatures or to estimate compositions and salinities from the melting temperatures, although chemistry provide sufficient experimental data and theoretical models for similar phase changes.

In the line of the pioneering studies from Sorby (1858), purely empirical best-fits to experimental data are the easiest way for modelling fluid properties, and this method has been favoured during the last four decades. The infinite compositional combinations, however, require a more thorough approach for the interpretation of natural fluid inclusions. The purely empirical approach does not result in a better understanding of the fundamental properties of fluids, and, therefore, does not result in a better prediction of those properties at defined conditions and compositions. Moreover, the estimation of empirical polynomes includes generally only one intensive variable, usually temperature, and too many terms for relatively straight lines. These polynomes are merely a description of symptoms, and absolutely useless for any extrapolation.

Thermodynamics provide several fundamental models to predict fluid behaviour in fluid inclusions, which have been omitted in geology. For example, the identification of possible molecular and ionic interactions provides the foundation of modelling observable phase transitions and fluid properties. Recently developed equations of state for pure fluid systems include these interactions (e.g. Span & Wagner, 1996), and mixed fluids are currently studied on modelling the complex interaction of unlike molecules. Thermodynamics of aqueous electrolyte solutions has given the tools for more substantial modelling in salt-bearing solutions (e.g. Pitzer, 1992). According to the model of Debye & Hückel (1923), dissolved electrolytes affect the activity of H_2O in aqueous solutions, which is determined by the product of the osmotic coefficient and the amount of dissolved ions. Both activity and osmotic coefficient expressions are derivatives of the excess free energy. These expressions are polynomes in temperature and pressure and can be used for any type of salt mixture (Spencer et al., 1990; Dubessy et al., 1992; Bakker et al., 1996).

The complexity of these models do not allow a relatively simple application, but require the use of computer-programming to treat all elementary defined physical parameters. The drawback in geology of the application of thermodynamical modelling is mainly based on this complexity. As previously mentioned, this study adapts and improves several thermodynamic models for fluid inclusion studies, which can be easily applied with newly developed computer programs.

3. Improving equations of state

Originally, equations of state were designed to describe mathematically the relation between temperature, pressure and density of homogeneous gas systems. They are, therefore, suitable to isochore calculations. The application to liquid-like fluids became evident after the discovery of the continuity between vapour and liquid (Andrews, 1869; Waals, 1873). According to thermodynamics, this mathematical relation is closely related to other measurable fluid properties, like heat capacity and viscosity, and newly developed equations are, therefore, also designed for liquid-vapour equilibria.

3.1 Modified Redlich-Kwong equation of state

In the previous section it was mentioned that experimental data from Amagat (1892,1893) and the equation of state from Waals (1873) were the first approaches to calculate isochores. Modelling of the saturation curves, i.e. liquid-vapour equilibria remained purely empirical. Many modifications on the equation of state have been developed in order to include more data over a wider temperature and pressure span. For example, Redlich & Kwong (1949) modified empirically the theoretical equation of Waals (1873) and obtained better fits for vapour-like gases:

$$P \quad = \quad \frac{RT}{V} \qquad\qquad\qquad \text{Ideal gas}$$

$$P \quad = \quad \frac{RT}{V-b} - \frac{a}{V^2} \qquad\qquad \text{van der Waals}$$

$$P \quad = \quad \frac{RT}{V-b} - \frac{a}{V(V-b)\sqrt{T}} \qquad \text{Redlich-Kwong}$$

where P, T, and v are pressure, temperature, and molar volume, respectively: R is the gas-constant; and a and b are specific constants defined by the type of gas. Many definitions for a and b causes widespread variations in modified equations of state. Originally, a and b were calculated as constant values from critical conditions (see the exact definition in Bakker, 1999; Chapter 8.1). Soave (1972) and Santis et al. (1974) were the first to introduce a temperature dependence for the a-values. Holloway (1977, 1981) only defined the empirical polynome to the values estimated by Santis et al. (1974). Holloway (1977) concentrated on the thermodynamical calculation of equilibrium compositions of fluids at high temperature and pressure according to the method of French (1966). Holloway (1977) noticed the lack of experimental data on thermodynamic properties of the geologically important fluid phase species, and he promoted the use of relatively simple equations of state. The empirical best-fit methods (Fig.16) by Holloway (1977, 1981, 1987) is inconsistent with the intended polynomes proportionally to $1/T^2$, and many constant values for $a(T)$ and a_0 appear to be erroneously cited and doubly defined. In this study, new empirical equations for a in true reciprocal temperature are developed for H_2O, CO_2, CH_4 and N_2 (Fig.17) for an

accurate description of intermolecular forces which meet physical restrictions and is applicable over a wider temperature span:

$$a(T)_{H_2O} = \left[9.4654 - \frac{2024.6}{T} + \frac{1.4928 \times 10^6}{T^2} + \frac{7.57 \times 10^8}{T^3}\right] \times 10^6$$

$$a(T)_{CO_2} = \left[-1.2887 + \frac{5936.3}{T} - \frac{1.4124 \times 10^6}{T^2} + \frac{1.1767 \times 10^8}{T^3}\right] \times 10^6$$

$$a(T)_{CH_4} = \left[-1.1764 + \frac{3521.6}{T} - \frac{1.155 \times 10^6}{T^2} + \frac{1.4775 \times 10^8}{T^3}\right] \times 10^6$$

$$a(T)_{N_2} = \left[0.060191 - \frac{200.59}{T} + \frac{0.15386 \times 10^6}{T^2}\right] \times 10^6$$

where T is temperature in Kelvin, and the dimension of $a(T)$ is $cm^6 MPaK^{0.5}mol^{-2}$. These equations allow more realistic extrapolation and interpolation due to the proportionality with reciprocal temperature, meaning an asymptotical decrease as temperature rises.
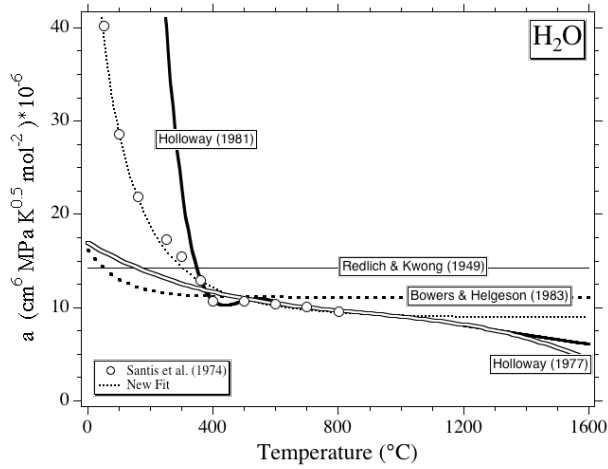
Fig.16. a-T diagram for H₂O with several polynomes from the indicated references. The new fit is according to the above presented equation
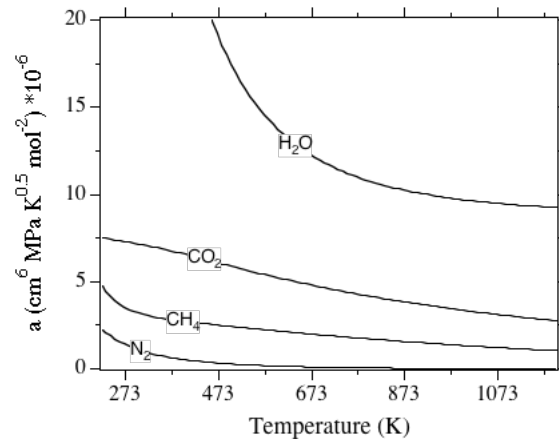
Fig.17. a-T diagram for H₂O, CO₂, CH₄ and N₂ according to this study.

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Natural fluid systems contain usually dissolved salts in addition to gas mixtures as described by equations of state. Modified Redlich-Kwong equations of state are only developed for gas mixtures and the effect of any dissolved salts is not included in fitting procedures. Bowers & Helgeson (1983) were the first to introduce a salt to the modified Redlich-Kwong equation of state, in order to fit experimental data of Gehrig (1980) for H_2O-CO_2-NaCl fluids. Bakker (1999, see Chapter 8.1) adapted their equations for more complex fluid systems, and introduced CH_4 and N_2. The presence of salt effects only the *a-b* parameters for H_2O due to the strong interactions between these molecules. The interactions between NaCl and CO_2-CH_4-N_2 molecules are neglected. Bakker's empirical modifications allow isochore construction for realistic geological fluid systems which are often found in fluid inclusions, and which involve several gas components and salts.

3.2. Modified Lee-Kesler equation of state

Another successful type of equations of state are modifications to the equation developed by Lee & Kesler (1975):

$$P = RT\left[\frac{1}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \frac{D}{V^6} + \frac{F}{T^3V^3}\left(\beta - \frac{\gamma}{V^2}\right)\exp\left(-\frac{\gamma}{V^2}\right)\right]$$

This equation was originally designed for hydrocarbon gases, but Duan et al. (1992a,b) extended its application to other gases, like H_2O, CO_2 and CH_4. In this study, these modifications are critically analysed and checked on its accuracy and mathematical correctness. This modified Lee-Kesler equation of state appears to be applicable to both isochore calculations and liquid-vapour equilibria, i.e. solvus. Experimental data from pure gases are accurately reproduced, however, some mathematical problems may occur at lower temperatures. For example, at 473.15 K and a selected pressure, only one value for the molar volume of H_2O should be obtained. However, the calculated isotherm gives in certain pressure domains four possible solutions (Fig.18).
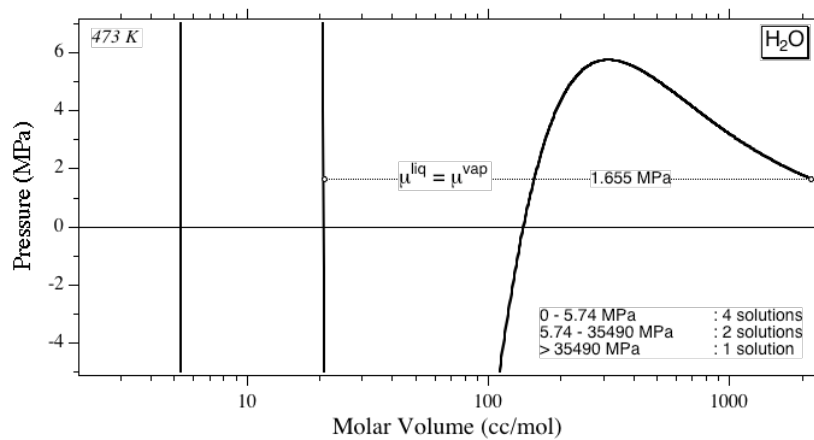
Fig.18. *PV-diagram for pure H_2O with the calculated 473 isotherm. The liquid-vapour equilibrium is calculated at 1.655 MPa, where the chemical potentials of the components in each phase are equal.*

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The calculated PV properties for pure H_2O at liquid-vapour equilibrium are 5-7% off from the steam-tables according to Haar et al. (1985). The mathematical assumptions from Duan et al. (1992b) for H_2O-CO_2-CH_4 gas mixtures appear to be highly erroneous, and the presented solvus diagrams of binary gas mixtures are incorrect. They have defined complex mixing rules, which are mathematically undefined for occasionally occurring negative numbers. The binary interaction parameters are

Fig.19. Binary interaction parameters k_1, k_2, and k_3 for H_2O-CO_2 mixtures

claimed to be continuous switching fitting functions across certain temperature intervals, however the presented functions are highly discontinuous (Fig.19). Moreover, the calculated solvi and isochores of binary gas mixtures were completely erroneous at certain temperature-pressure conditions (Fig.20 and 21). Consequently, Duan et al. (1992a,b) did not succeed in presenting an equation of state that can predict both phase equilibrium and volumetric properties with accuracy close to that of experimental data.

Fig.20. PX diagram for CO_2-CH_4 gas mixtures with the solvus at 0 °C (solid line) calculated from Duan et al. (1992a,b). The dashed line is the published curve by Duan et al. (1992a,b), at erroneously -1.7 °C.
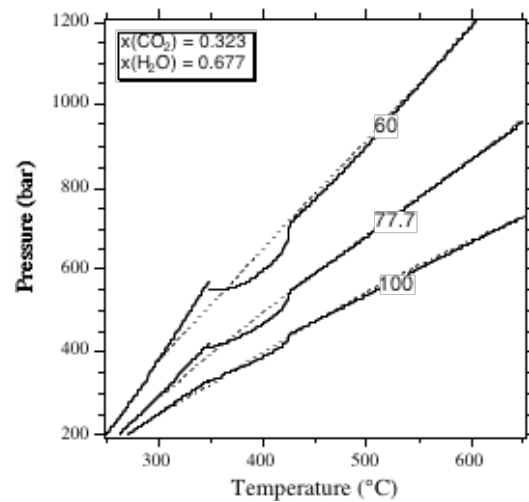
Fig.21. TP diagram for H_2O-CO_2 gas mixture with several isochores (solid lines) calculated from Duan et al. (1992a,b). The dashed lines are the published isochores by Duan et al. (1992a,b).

This example shows that accurate modelling of fluid properties of gas mixtures near solvus conditions still needs improvement and that recently published equations of state must be handled with scepticism.

3.3. Unified Helmholtz energy functions

Equations of state for pure substances have been developed to a high precision. The international thermodynamic tables of the fluid state from the *IUPAC*, as compiled by Angus et al. (1976, 1978, 1979) introduced a complete list of measurable properties of pure gases like CO_2, CH_4, and N_2. An equation of state was developed that was able to reproduce PVT data, information on the *saturation curves*, the *second virial coefficient*, and *isobaric heat capacity* as well as other thermodynamic intensive variables, which include a maximum of 45 disposable constants. For the critical region, several modification were introduced in critical equations and switching functions. The complexity of these equations do not allow isochore and liquid-vapour equilibria calculations without the use of a computer code. From these type of equations a new generation of equations of state was developed for the representation of the thermodynamic properties of pure gases: a fundamental equation explicit in the *Helmholtz energy* (e.g. Haar et al., 1984; Setzman & Wagner, 1991; Span & Wagner, 1996). The fundamental equation is expressed in the *dimensionless Helmholtz energy* with two independent variables, density ρ and temperature T:

$$\Phi(\rho,T) \;=\; \frac{A}{RT} \;=\; \Phi^0(\delta,\tau) + \Phi^r(\delta,\tau)$$

$$P(\delta,\tau) \;=\; \rho RT\left(1 + \delta\left[\frac{\partial \Phi^r}{\partial \delta}\right]_\tau\right)$$

$$G(\delta,\tau) \;=\; RT\left(1 + \delta\left[\frac{\partial \Phi^r}{\partial \delta}\right]_\tau + \Phi^0 + \Phi^r\right)$$

$$c_P(\delta,\tau) \;=\; R\left\{-\tau^2\left(\left[\frac{\partial^2 \Phi^0}{\partial \tau^2}\right]_\delta + \left[\frac{\partial^2 \Phi^r}{\partial \tau^2}\right]_\delta\right) + \frac{\left(1 + \delta\left[\frac{\partial \Phi^r}{\partial \delta}\right]_\tau - \delta\tau\left[\frac{\partial^2 \Phi^r}{\partial \delta \partial \tau}\right]\right)^2}{1 + 2\delta\left[\frac{\partial \Phi^r}{\partial \delta}\right]_\tau + \delta^2\left[\frac{\partial^2 \Phi^r}{\partial \delta^2}\right]_\tau}\right\}$$

where δ is the reduced density and τ is the inverse reduced temperature. Φ^0 is the ideal gas behaviour and Φ^r is the residual fluid behaviour, which are calculated from multi-component equations. P, T, and R are pressure, temperature, and the gas constant, respectively. G is the Gibbs free energy and c_P is the isobaric heat capacity. The accuracy of the unified Helmholtz energy functions is superior to all formerly published equations due to its general thermodynamic application. Unfortunately, these equations have not yet been developed for gas mixtures, and relative simpler equations of state, like modified Redlich-Kwong, remain a valuable tool in isochore construction.

3.4. Solvus estimations

The lack of experimental data for fluid mixtures, including a complete set of P-T-V-X properties of solvus conditions is the main cause of the inaccuracy in thermodynamic modelling. Solvus conditions reflect homogenization temperatures of fluid inclusions, which can be directly used to calculate inclusion bulk densities. Therefore, microthermometry comprises an accurate method of the characterization of the entrapped fluids within fluid inclusion studies. However, for most fluid systems, the use of total homogenization temperatures has a limited application, due to the previously describe deficiency.

In this study, this problem is illustrated on binary fluid systems, in this particular case the H_2O-CO_2 solvus (see Chapter 8.2) is chosen for comparison of available experimental data sets and thermodynamic modelling. Experimental data on the exact P-T-X conditions of the H_2O-CO_2 solvus are inconsistent, moreover, volumetric fluid properties (densities) were completely ignored in most previous studies. Thermodynamical modelling appears only to be effective in a small temperature range at relative low pressures, and is highly inaccurate at pressures exceeding 30 MPa. The inconsistencies in experimental data sets can be illustrated with the estimated P-T-X position of the critical curve and its temperatures minimum, i.e. saddle point of the solvus. Tödheide & Franck (1963) estimiated this minimum for a 41.5 mole% CO_2 mixture at 266 °C and 2450 bar. Takenouchi & Kennedy (1964) obtained a temperature minimum at 265 °C and 2150 bar for a 31 mole% CO_2 mixture. This solvus was reexamined by Sterner & Bodnar (1991) using a new technique to analyse fluid systems: the experimental synthesis of fluid inclusion in quartz (Bodnar & Sterner, 1987). Fluid inclusions with defined compositions were synthesized at selected temperatures and pressures. The bulk density of the fluid mixture was obtained from measured partial homogenization temperature of the CO_2 phases and calculated density and compositions of the aqueous phase in the presence of this homogenization. The solvus pressure was calculated by using a non-published modified Redlich-Kwong equation of state (Connelly & Bodnar, 1983), which was assumed to represent accurately experimental data near the solvus. However, these pressure calculations must be regarded as the main source of uncertainties in their calculation procedures, because experimental data are hardly available and inconsistent. Although Sterner & Bodnar (1991) provide the possibility to interpret the solvus of H_2O-CO_2 directly in V-X properties, they prefered a calculated P-T-X representation of this fluid system. After careful reexamination of the spread in measured homogenization temperatures and inaccuracies in calculated pressures, their highly interpretative smoothed P-X diagram (see Fig.13 in Sterner & Bodnar, 1991) does not correspond accurately to their experimental data. The claimed position of the saddle point at 269 °C, 2000 bar and 37 mole% CO_2 does not appear in a newly developed P-X diagram in this study (Fig.22), based on their experimental data.

The differences between all data sets and several thermodynamic models are futher investigated in detail in Chapter 8.2 (Bakker, in press). Bulk density estimations from Sterner & Bodnar (1991) are taken into account, and a new V-X diagram is presented in Fig.6 from Chapter 8.2, which can be directly used to obtain graphically bulk density and composition from measured partial CO_2 homogenization and total homogenization of H_2O-CO_2 phases.

A successful attempt to model solvus conditions thermodynamically was performed by Thiéry et al. (1994) for binary mixtures of CO_2-CH_4 and CO_2-N_2. They modified the equation of state according to Soave (1972) with an empirical correction term for overcomplicated mixing rules. The individual parameters, like molar volume, become meaningless in their equations, and could only be calculated by using the equation of state according to Lee & Kesler (1975). This method is dissuaded from being applied to thermodynamic modelling, because the coherence of all independent parameters is lost.

Compared to the circumstances described in Chapter 2, chemistry does not supply an accurate thermodynamic model for liquid-vapour equilibria of fluid mixtures at relatively high temperatures and pressures that may regularly occur in fluid inclusions. Surprisingly, the need for such models is mainly satisfied within geology itself.
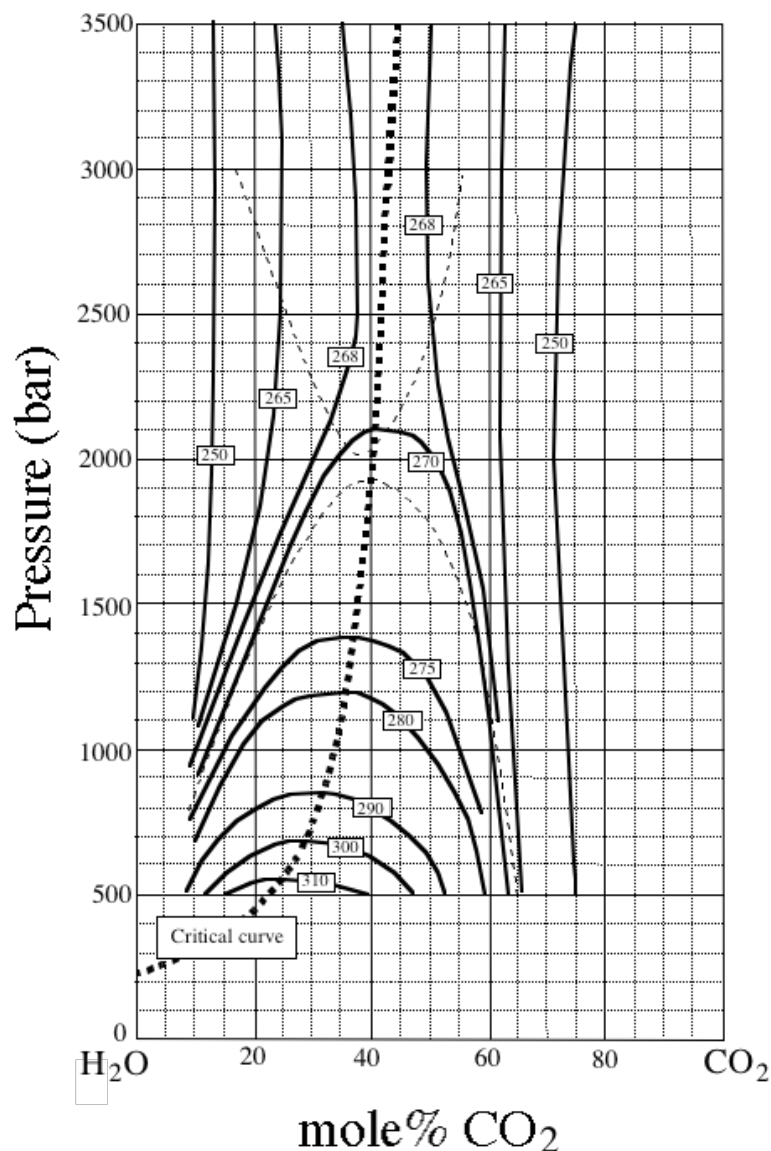
Fig. 22. *Reinterpreted isotherms (in °C) of the H_2O-CO_2 solvus in a P-X diagram. The thin dashed curve represents the 270 °C isotherm according to Sterner & Bodnar (1991).*

27

4. Improved clathrate modelling

The occurrence of clathrates in fluid inclusions during microthermometrical measurements is a common phenomena. Each inclusion that contains a mixture of H_2O and other gases will form clathrates at lower temperatures (Fig.23). Roedder (1962) was the first to notice this in mixed H_2O-CO_2-rich fluid inclusions. The first systematic approach to using clathrate melting temperatures were given by Dubessy et al. (1992) and Diamond (1992), in combining a set of observations, including the clathrate melting temperature, to calculate bulk fluid densities and compositions.
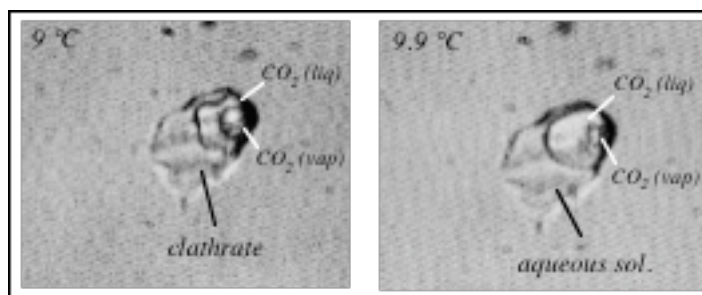
Fig.23. *Melting behaviour of CO_2-H_2O-rich synthetic fluid inclusion at Q2 conditions, i.e. in the presence of CO_2 liquid and vapour, clathrate, and an aqueous solution. The density increase of the gas phases after clathrate melting is evident from the decreased size of the CO_2(vap) bubble.*

Like many chemical substances, the discovery of gas hydrates, or clathrates, was a laboratory curiosity (Davy, 1810), and it was more than a century before clathrates were systematically investigated in detail in relation to industrial interests (Hammerschmidt, 1934). The discovery of clathrates in gas transmission lines stimulated the natural gas industry to estimate the conditions of clathrate stability in order to prevent blocking. Recently, clathrates now recognized as a world-wide energy resource, due to massif occurrences in permafrost regions and on the ocean seabed (Kvenvolden, 1988). Clathrates, are delicate networks of H_2O molecules with a cubic or hexagonal crystal structure and several types of molecular cavities. The presence of gas molecules in only part of these cavities stabilize the structures. Clathrates are non-stoichiometric compounds and the amount of enclosed gas is temperature and pressure dependent.

4.1. Thermodynamic Modelling

The behaviour of fluid systems at variable temperature and pressure can be perfectly visualized in phase diagrams. Consequently, phase diagrams can be used to predict equilibrium conditions and phase changes. The topology of complex systems can be schematically drawn to predict how normal equilibrium assemblages may change as a function of the imposed conditions (Bakker & Thiéry, 1994; see Chapter 8.3). These qualitative diagrams form a fundamental part of any systematic clathrate modelling, which subsequently can be used to quantify exact phase transitions.

A first approach to modelling consisted of representing clathrate stability conditions using smoothed values, non-specified best-fit curves, and purely empirical polynomal functions (e.g. Deaton and Frost, 1946). Relatively simple empirical relations are still used for mathematical comfort, e.g. Bozzo et al. (1975) and Dholabhai et al. (1993), although this approach gives erroneous results for conditions and fluid systems other than those used to prepare them. Moreover, the nonstoichiometry and the infinite compositional combinations of clathrates require a more thorough approach for interpolations and extrapolations of clathrate stability conditions in natural systems.

Modifications of classical adsorption statistical mechanics were the first substantial approach to fundamental modelling of clathrates in equilibrium with vapour-like and supercritical fluids (Platteeuw & Waals, 1958; Waals & Platteeuw, 1959). This was only possible after intense studies of the crystallographic structure of the solid clathrate phase (Stackelberg & Müller, 1954). The basic concept of this model is further discussed in Chapter 8.3 (Bakker & Thiéry, 1994). Characteristic aspects of this model were improved or adjusted by McKoy & Sinanoglu (1963), Saito et al. (1964), Parrish & Prausnitz (1972), Ng & Robinson (1976), Holder et. al. (1980), Dharmawardhama et al. (1980), John et al. (1985), Munck et al. (1988), and Dubessy et al. (1992). Many of these modifications did not improve the simplicity and predictability of the model. In Chapter 8.4 and 8.5 (Bakker et al., 1996; Bakker, 1998) these published modifications have been scrutinized, and apparent differences are identified as a reflection of the amount of experimental data used to fit parameters.

Problematic parameters in clathrate modelling are:

- Thermodynamic properties of H_2O in liquid phase
Molar volume and heat capacity of liquid H_2O are mainly defined at temperatures above 0 °C. Clathrate modelling also requires such parameters at temperatures below 0 °C, in the metastable liquid region. Only a few studies report these properties.

- Thermodynamic properties of the clathrate phase
Molar volumes, heat capacities, entropies, and standard thermodynamic constants of clathrate phases are usually only indirectly obtained.

- Fugacity coefficients of gases
Although many equations of state are available, only those that accurately reproduce fugacity coefficients in mixtures of H_2O and gases like CO_2 and CH_4 at clathrate melting conditions are used in the model. This accuracy is difficult to estimate and not many equations are designed for gas mixtures including H_2O.

- Solubility of gases in aqueous solutions
Solubility have to be calculated with Henry's law because equations of state are not able to deal accurately with both coexisting liquid and vapour phases. Published data on Henry's constant are inconsistent and nonsystematically obtained.

- Intermolecular potentials
Mathematical description of intermolecular forces are based on dilute gases. Statistical mechanics is used to describe and average these highly idealized forces in clathrate cavities. Several molecular models are available for the description of the potential

energy between molecules. In general, these models represent oversimplified molecule models mainly defined for the interaction of similar molecules. Arbitrarily mixing rules are used for unlike molecule interactions.

- *Dimension cavities*

Idealized spherical cavities are used in clathrate modelling, although real cavities have more irregular forms with various diameters in different directions. Moreover, cavities can be deformed and may show varying diameter.

- *Mixed gas hydrates*

Clathrate models can be applied to fluid systems including more than one type of enclosed gas molecule, e.g. a mixture of H_2O-CO_2-CH_4. However, the mixing rules are purely arbitrary, and stability calculations are extremely inaccurate.

- *Osmotic coefficient*

The activity of H_2O in the aqueous solution is effected by dissolved electrolytes, which can be characterized by the model of Debye & Hückel (1923). This model was improved by Pitzer (1992), who introduced high order polynomial equations to calculate osmotic coefficients, usually only as a function of temperature.

- *Salting-out coefficients*

Not much is known on the decreased solubility of gases in aqueous solution as a result of the presence of dissolved electrolytes. Only a few purely empirical equations are available.

- *Experimental data sets*

Especially salt-bearing solutions give inconsistent experiment data sets on the stability of clathrates, which makes accurate thermodynamical modelling not yet possible.

None of the previously published clathrate stability models take fully into account optimal estimations of these parameters. Moreover, insufficient amounts of experimental data have been included to test the accuracy of these models. An extensive revision of various models was performed by Bakker et al. (1996), and Bakker (1997, 1998), as presented in this study (see Chapter 8.4, 8.5 and 8.6). The most accurate estimations of the previously mentioned parameters were assessed, and a large amount of experimental data from independent sources for fitting procedures were used. The predictability and accuracy up to 200 MPa of the newly developed modifications are more accurate than other models for a complex fluid system including H_2O-CO_2-CH_4-N_2-C_2H_6 and several salts, NaCl-KCl-$CaCl_2$-$MgCl_2$. Figs. 24, 25, 26, and 27 demonstrate the quality of the proposed modifications and its ability to calculate accurately stability conditions for pure gas clathrates of CO_2, CH_4, N_2, and C_2H_6, respectively. In salt-bearing systems, including NaCl, KCl, $CaCl_2$ and $MgCl_2$, the improved clathrate stability model appears to reproduce average values. However, it should be noted that the available experimental data are inconsistent (Fig.28).
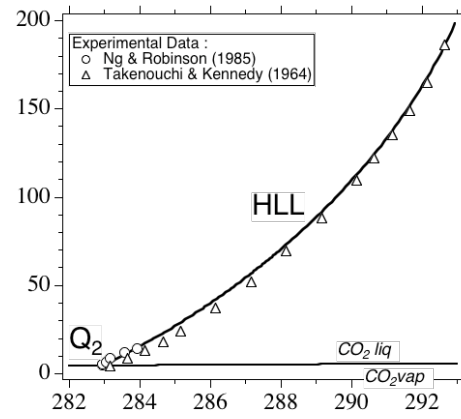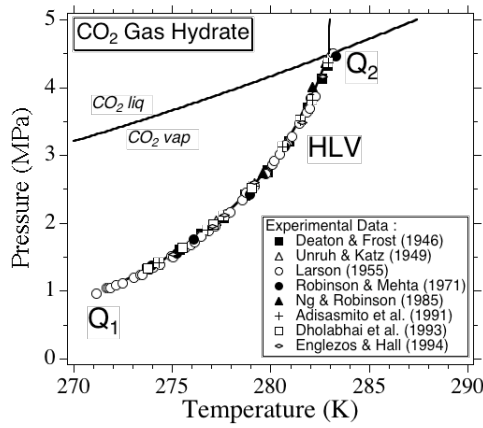
Fig.24. Comparison of experimental data and thermodynamical modelling of clathrate stability conditions in the H_2O-CO_2 fluid system. HLV represent clathrate melting in the presence of an aqueous liquid solution and CO_2 (vap), HLL in the presence of an aqueous liquid solution and CO_2 (liq).
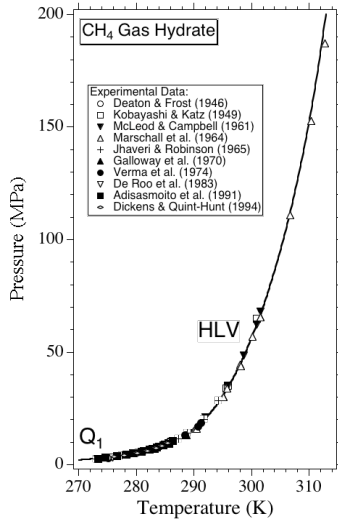
Fig.25. Similar to Fig.23, for CH_4 clathrate
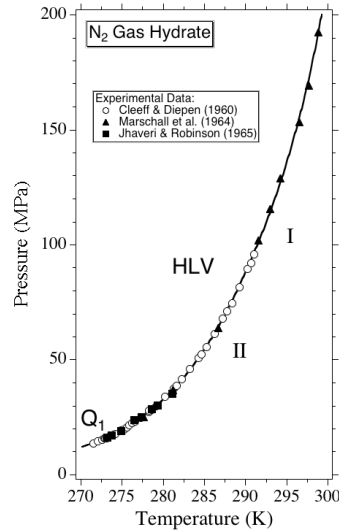
Fig.26. Similar to Fig.23, for N_2 clathrate. I and II represent different clathrate crystal structures.
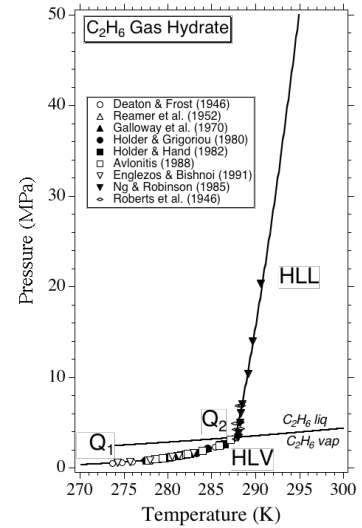
Fig.27. Similar to Fig.23, for C_2H_6 clathrate.
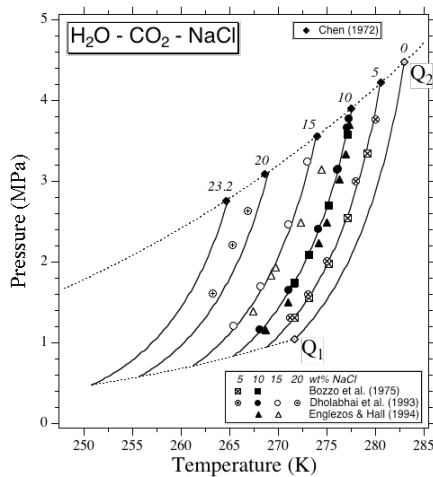
Fig.28. Freezing-point depression of clathrate stability conditions in the H_2O-CO_2-NaCl fluid system, for 0, 5, 10, 15, 20, and eutectic salinity of 23.2 wt% NaCl.

For mixed gas hydrates of CO_2-CH_4, CH_4-N_2 and CH_4-C_2H_6, excess Gibbs free energy functions are introduced in this study (Bakker, 1998; see Chapter 8.5) to obtain a good fit to experimental data. The excess free energy must be a result of mixing the binary end-members to form the solid clathrate solution. The excess thermodynamical functions are asymmetric modifications of the Margules model (Thompson, 1967), describing the composition and temperature dependence of this energy function. Fig.29. illustrates the accuracy of this clathrate model for CO_2-CH_4 clathrates (Adisasmito et al., 1991) and CH_4-N_2 clathrates (Jhaveri & Robinson, 1965).
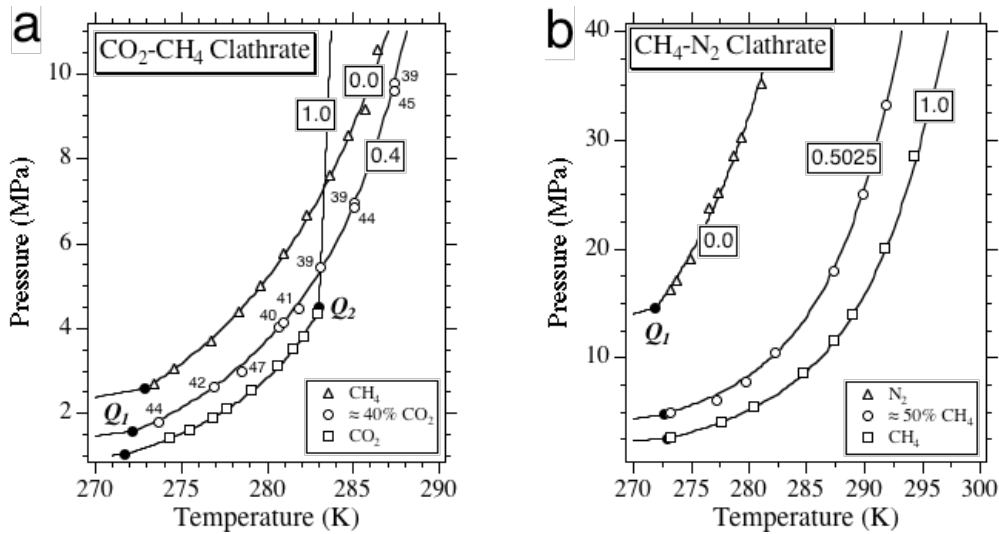
Fig.29. *T-P diagrams with stability curves for pure gas and mixed gas clathrates.*

4.2. Conclusions

A clathrate stability model is presented in this study which is based on the large amount of available experimental data over a wide temperature and pressure range. Clathrate melting temperatures can be readily interpreted in complex fluid systems, including H_2O-CO_2-CH_4-N_2-C_2H_6-$NaCl$-KCl-$CaCl_2$-$MgCl_2$, which regularly occur in fluid inclusions. The accuracy attained is higher than previously published models, as illustrated in Chapter 8.4, 8.5 and 8.6, which were mainly not developed for fluid inclusions studies. Due to complex mathematical procedures, computer programs have been developed to perform the many numerical and analytical procedures in clathrate modelling, as will be explained in the next section.

5. Computer modelling in C++

A principle objective of fluid inclusion research is to determine the bulk density and composition, i.e. the VX properties of the enclosed fluid. Temperature measurements of phase changes provide an important tool for this purpose. However, the mathematical complexity of physical and chemical modelling does not permit easy calculations of fluid systems in natural rock. Furthermore, the large amount of independent thermodynamical intensive variables, and, consequently, the large amount of different theoretical models used to describe these parameters, make computer programming unavoidable. Many models depend on methods of numerical computing due to the complexity of the included equations. Structured programming is an essential part for the transparency of the organization of extensive computer programs, and is only possible in computer languages like Pascal, C, and C++.

In this study, computer programming is performed in C++ language, using TURBO C++, version 3.0 (Borland, 1992), on IBM PC systems. A library of individual published thermodynamic models has been developed, which can be included in any desired main program, adjusted to the specific question presented (Fig.30). The libraries include also the numerical procedures involved, physical constants, equations of state and solubility models.
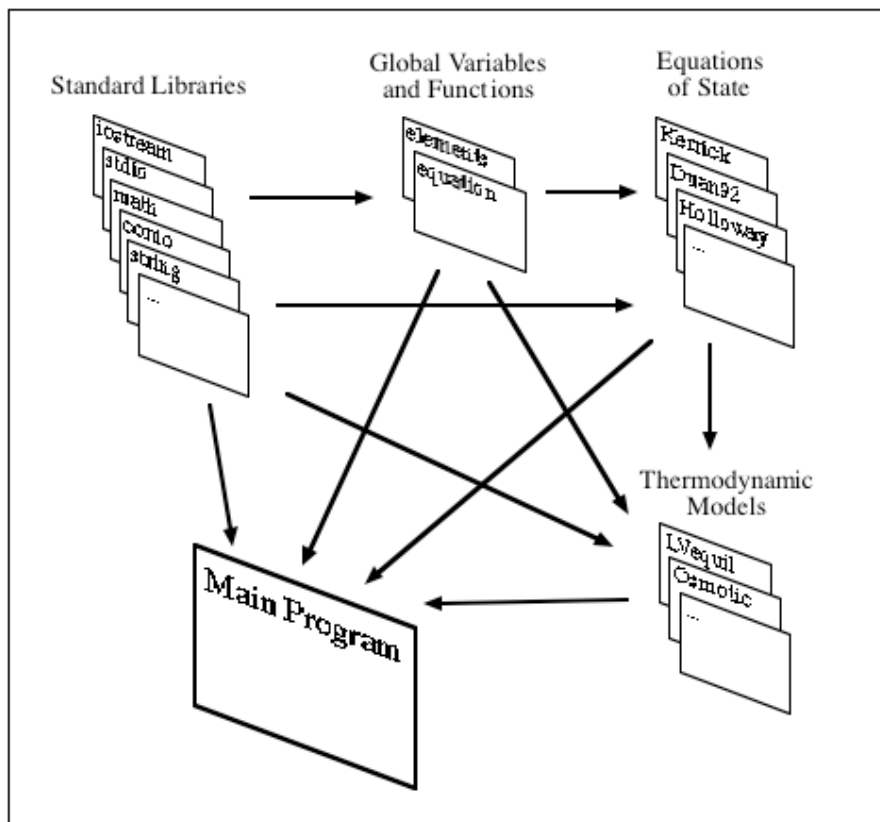
Fig.30. Structured programming in C++ with several groups of libraries, which are partly interconnected, and which are included in a 'Main Program'. File names correspond to some files described in the next paragraph.

5.1. Libraries

Files are grouped in libraries of similar topics, as illustrated in Fig.30. Standard libraries are provided by Borland (1992) and contain various support routines, e.g. *iostream* in Fig.30. In this study, the library of equations of state has been developed. This library is of major importance and is constantly increasing in size due to the large supply of publications. Newly published equations of state are currently being include in this library. Each file listed in Table 2 includes procedures to calculate for any type of fluid mixture:

a) pressure as a function of temperature and molar volume,
b) molar volume as a function of temperature and pressure,
c) fugacity coefficients as a function of temperature, pressure and molar volume.

Table 2. *Equations of state for different fluid systems ordered in files according to specific publications, which can be included in any main program.*

Filename	Fluid system	Reference
ANDERKO.CPP	H_2O-NaCl	Anderko & Pitzer (1993a,b)
ANGUS76.CPP	CO_2	Angus et al. (1976)
ANGUS78.CPP	CH_4	Angus et al. (1978)
ANGUS79.CPP	N_2	Angus et al. (1979)
BELON.CPP	H_2O-CO_2-CH_4-CO-H_2-O_2	Belonoshko & Saxena (1991a,b)
BODNAR.CPP	H_2O-NaCl	Bodnar & Vityk (1994)
		Knight & Bodnar (1989)
BOWERS.CPP	H_2O-CO_2-NaCl	Bowers & Helgeson (1983)
	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3-H_2-O_2-NaCl	Bakker (1999)
CHUEH.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S	Chueh & Prausnitz (1967)
CHRISTO.CPP	H_2O-CO_2-CH_4-N_2	Christoforakos & Franck (1986)
DUAN92.CPP	H_2O-CO_2-CH_4	Duan et al. (1992a,b)
DUAN96.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3-H_2-O_2	Duan et al. (1992c, 1996)
DUAN95.CPP	H_2O-CO_2-NaCl	Duan et al. (1995)
FRIEND.CPP	C_2H_6	Friend et al. (1991)
GALLAGHER.CPP	H_2O-CO_2	Gallagher et al. (1993)
HAAR.CPP	H_2O	Haar et al. (1984)
HOLLOWAY.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3-H_2-O_2	Santis et al. (1974)
		Holloway (1977, 1981, 1987)
		Flowers (1979)
KELL.CPP	H_2O	Kell (1967)
		Hare & Sorensen (1987)
		Kell & Whalley (1965)
KERRICK.CPP	H_2O-CO_2-CH_4	Kerrick & Jacobs (1981)
		Jacobs & Kerrick (1981)
KESTIN.CPP	H_2O	Kestin & Sengers (1986)
LEE.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3	Lee & Kesler (1975)
LVOV.CPP	H_2O-NaCl	Lvov et al. (1990)
		Lvov & Wood (1990)
PENG.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3-H_2-O_2	Peng & Robinson (1976)
REDLICH.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3-H_2-O_2	Redlich & Kwong (1949)
SAXEN87a.CPP	H_2O-CO_2-CH_4-N_2-CO-H_2-O_2	Saxena & Fei (1987a)
SAXEN87b.CPP	H_2O-CO_2	Saxena & Fei (1987b)
SETZMANN.CPP	CH_4	Setzmann & Wagner (1991)
SHMONOV.CPP	CO_2	Shmonov & Shmulovich (1974)
SOAVE.CPP	H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S-NH_3	Soave (1972)
SPAN.CPP	CO_2	Span & Wagner (1996)
SPYCHER.CPP	H_2O-CO_2-CH_4-H_2	Spycher & Reed (1988)
STERNER.CPP	H_2O-CO_2	Sterner & Bodnar (1991)
THIERY.CPP	CO_2-CH_4-N_2	Thiery et al. (1994a,b)
ZHANG.CPP	H_2O-NaCl-KCl-$CaCl_2$	Zhang & Frantz (1987)

In addition to this set of equations of state, other thermodynamical models, numerical procedures and physical constants are defined in this study in:

1. ELEMENTS.CPP
Fundamental physical constants are defined in this file: light constant, permeability in vacuum, permittivity in vacuum, Planck's constant, elementary charge, Rydberg's constant, electron mass, proton mass, Avogadro's number, Faraday's constant, gas constant in different dimensions, Boltzman constant, electronvolt, atmosphere and newton. The moleweights of H_2O, CO_2, CH_4, N_2, C_2H_6, H_2S, NH_3, H_2, O_2, NaCl, KCl, $CaCl_2$, and $MgCl_2$ are given in this file. Global variables, which are used in many procedures and functions in several libraries, are also defined.

2. EQUATION.CPP
General numerical procedures are defined in this file. The analytical solution of quadratic, cubic and quartic equations is given, several integration functions, i.e. Gaussian Quadratures and Multidimensional Intergrals, special functions like the Gamma Function, Beta Function, Incomplete Gamma Function, Error Function, Cumulative Poisson Function, root finding equations (Newton-Raphson Method and Sectant Method), least squares modelling of data and fittings to a straight line.

3. GASSOL.CPP
Henry constants and the solubility of CO_2, CH_4, N_2 and C_2H_6 in water are calculated in this file, as a function of temperature, pressure and salinity. The thermodynamic models are derived from Carroll et al. (1991), Carroll & Mather (1992), Cramer (1982), Yasunishi & Yoshida (1979), Rettich et al. (1981), Stoessell & Byrne (1982), Byrne & Stoessell (1982), Benson & Kraus (1976) and Moore et al. (1982). The properties of both liquid and vapour phases are simultaneously obtained from equilibrium calculations.

4. LANGMUIR.CPP
A theoretical model for clathrate structure and a three dimensional generalization of the ideal localized adsorption are defined in this file. The molecular model and thermodynamic constants are obtained from Waals & Platteeuw (1959), McKoy & Sinanoglu (1963), John & Holder (1985), Avlonitis (1994), Bakker et al. (1996), and Bakker (1997, 1998). The Langmuir constants are numerically estimated according to the Gauss integration method. Fugacities are calculated with several equations of state listed in Table 2. The chemical potential of a hypothetical empty clathrate structure is calculated with these variables.

5. LVEQUIL.CPP
This file includes bubble-dew point estimations according to Raoult's law and liquid-vapour equilibrium calculations using identical equations of state for both phases. Homogenization temperatures and pressures can be transformed into densities and molar volumes for known fluid compositions. Furthermore, the estimation of composition and density of coexisting liquid and vapour within the fluid immiscibility field can be calculated. The numerical approach of equalizing chemical potentials in both phases is extensive and may occasionally result in trivial solutions. Therefore, the

possibility is presented to change several parameters and accuracy to arrive at equilibrium conditions.

6. OSMOTIC.CPP

The effect of electrolytes in aqueous solutions is calculated in this file. Procedures are developed for the ionic strength and the Debye-Hückel parameter, according to the model from Debye & Hückel (1924a, b). The thermodynamic model according to Pitzer (1991) is transformed in several procedures and functions to calculate the osmotic coefficient, excess Gibbs free energy, activity coefficients and mean activity coefficients, using experimentally obtained constants from Bradley & Pitzer (1979), Pitzer et al. (1984), Holmes & Mesmer (1983), Harvie et al. (1984), and Möller (1988).

7. SATURATION.CPP

Liquid-vapour equilibria of pure substances, H_2O (Keenan et al., 1969; Wagner & Pruss, 1993), CO_2 (Duschek et al. 1990), CH_4 (Setzmann & Wagner, 1991), N_2 (IUPAC tables), and C_2H_6 (Friend et al., 1991) are given in semi-empirical equations. Homogenization temperatures can be directly transformed into densities, molar volumes and saturation pressures.

8. THERMO.CPP

Thermodynamic intensive variables for several phases are calculated in several functions for isobaric heat capacity, entropy, enthalpy and Gibbs free energy. Thermodynamic data on liquid H_2O is obtained from Giauque & Stout (1936), Osborne et al. (1939), and Angell et al., (1973). Clathrate and pure ice data are obtained from Ginnings & Gorruccini (1947), and Avlonitis (1994). The thermodynamic standard values for gases are obtained from CODATA values (Cox et al., 1989).

5.2. Application of libraries

Several self-instructive computer programs have been developed for geological applications of these libraries, mainly for the direct interpretation of microthermometrical data from fluid inclusions.

Bakker (1997, see Chapter 8.6) has developed four programs associated with clathrate melting in fluid inclusions: DENSITY, ICE, Q2, and NOSALT. These four programs represent four specific types of clathrate melting behaviour, which may be observed in fluid inclusions. In addition to final clathrate melting temperature, program DENSITY and Q2 use the homogenisation temperatures of the carbonic phase, while program ICE includes a final ice melting temperature. These data are used to calculate the properties of each phase, which includes also the salinity of the aqueous phase present during final clathrate melting. Bulk compositions and densities are only obtained with an additional volume fraction estimation of the carbonic vapour bubble and the rim of aqueous solution after final clathrate melting. If microthermometry illustrates the presence of a gas mixture, as obtained from the freezing point depression of pure CO_2, the gas composition of the carbonic phase should be estimated from additional methods, like Raman spectroscopy. The program NOSALT is directly used for salt-free fluid system and can be used as a limiting case for problematic calculations in the other clathrate programs. These programs provide a highly accurate estimation of fluid inclusion properties, which can be readily used to interpret the thermal histories of

selected regions, geothermometry and geobarometry, as well as the source regions of fluids and sedimentary rock.

The programs have been developed to run in IBM-PC compatible computers having DOS as operating system, and consist of a direct question-answer principle, where any erroneous input is recognized in correction procedures. The first screen display of these programs is a general introduction, giving the version number which is the datum of the last updating of the program, a list of the required input, calculation limits, and a list of publications which form the fundaments of the programs (Fig.31).

```
CLATHRATES, package of computer programs for fluid inclusion studies
Program DENSITY, version 15/03/98
Research Project : Clathrate Stability Conditions.
Ronald J. Bakker (University Heidelberg, Germany)

The fluid system H2O-CO2-CH4-N2-C2H6 with NaCl-KCl-CaCl2-MgCl2
Limits of the model are between 0-200 MPa and 250-320 K.
Input of the program includes :
        1. final clathrate melting temperature
        2. composition of the homogeneous non-aqueous phase
        3. density of the non-aqueous phase
        4. composition of salt
Optionally:
        5. volume-fractions of the non-aqueous phase

This program will calculate the properties of the individual phases
present in fluid inclusions, and properties of the total inclusion,
if the volume-fractions are known.
This program is NOT suitable for clathrate melting at Q2 conditions.
Ref.:   - Bakker RJ, Thiery R (1994) IMA Short Course, p.191-214.
        - Bakker RJ et al. (1996) Geochim.Cosmochim.Acta, v.60, 1657-1681.
        - Bakker RJ (1997) Computers & Geosciences, v.23, 1-18.
        - Bakker RJ (1998) Geol. Soc., London, Spec. Publ, v.137, 75-105.

                                              Press any key to continue
```

*Fig.31. Introduction screen display of the program **DENSITY**.*

Than, the final melting temperature of the clathrate phase and the equation of state to calculate the fugacity of gas molecules enclosed in the clathrate phase are asked for in the next screen display (Fig.32). The choice of equation is dependent on the gas system, as specific equations are only representing certain gas mixtures and some are more accurate then others (see also Bakker, 1998; Chapter 8.5).

```
THE CLATHRATE PHASE

What is the final Clathrate Melting Temperature?
        T (°Celsius) = 8.1

Equation of state to calculate fugacities in clathrate equilibria:
        (0) Chueh & Prausnitz (1967) : (H2O)-CO2-CH4-N2-C2H6
        (1) Soave (1972) : (H2O)-CO2-CH4-N2-C2H6
        (2) Lee & Kesler (1975) : (H2O)-CO2-CH4-N2-C2H6
        (3) Duan et al. (1992a,b) : H2O-CO2-CH4
        (4) Duan et al. (1996) : H2O-CO2-CH4-N2-C2H6
                                                       choose number:
3
```

Fig.32. Input of the properties of the clathrate phase. In this example, the clathrate melts at 8.1 °C, and the equation of state according to Duan et al (1992a,b) is chosen.

Subsequently, the properties of the non-aqueous phase, i.e. carbonic phase in the vapour bubble, are required (Fig.33). Several corrections to erroneous input are illustrated in this example. First, the composition of the carbonic gas mixture did not sum up to a

100%. The program includes an endless loop until the sum of the mole percentages is exactly 100%.

```
NON-AQUEOUS PHASE (CO2-CH4-N2-C2H6)

What is the composition (0-100 mole%), based on a H2O-free system:
        x(CO2) = 95
        x(CH4) = 4
        x(N2) = 0
        x(C2H6) = 0

ERROR : sum of mole percentage is not equal to 100
        x(CO2) = 95
        x(CH4) = 5
        x(N2) = 0
        x(C2H6) = 0

Density of homogeneous CO2-CH4-N2-C2H6 is obtained from :
        (0) Molar Volume (in cc/mol)
        (1) Density (in g/cc)
        (2) Homogenisation Temperature (in metastable absence of clathrate)
        (3) Homogenisation Pressure (in metastable absence of clathrate)
                                                            choose number: 3

        Homogenisation Temperature (°C) = 9

ERROR : Th exceeds the clathrate melting temperature
        Homogenisation Temperature (°C) = 7
        Mode of homogenisation :
                (0) Vapour
                (1) Liquid
                (2) Critical
                                                            choose number: 1

Equation of state to calculate liquid-vapour equilibrium:
        (0) Redlich & Kwong (1949): CO2-CH4-N2-C2H6
        (1) Chueh & Prausnitz (1967) : CO2-CH4-N2-C2H6
        (2) Soave (1972) : CO2-CH4-N2-C2H6
        (3) Lee & Kesler (1975) : CO2-CH4-N2-C2H6
        (4) Holloway (1977, 1981) Flowers (1979) : H2O-CO2-CH4-N2-C2H6
        (5) Bowers & Helgeson (1983) : H2O-CO2-CH4-N2-C2H6
        (6) Duan et al. (1992a,b) : H2O-CO2-CH4
        (7) Thiery et al. (1994) : CO2-CH4-N2
        (8) Duan et al. (1996) : H2O-CO2-CH4-N2-C2H6
                                                            choose number: 7

Is the gas volume fraction known?, after clathrate melting
        (y/n): y
        Percentage (0-100 vol%) = 106

ERROR : percentage should have a value between 0-100%
        Percentage (0-100 vol%) = 40
```

Fig.33. Input screen for the non-aqueous phase, with several error-procedures.

The density of the carbonic mixture, which is a mixture of CO_2, CH_4, N_2 and C_2H_6, can either be directly introduced in values of cc/mol and g/cc, or it can be calculated from partial homogenization temperatures and pressures. The program **DENSITY** is based on the theoretical consideration from Diamond (1992), therefore, homogenization temperatures in the metastable absence of the clathrate phase must be lower than the final clathrate melting temperature. The example in Fig.33 shows the error indication, and the possibility for correction. A second list of equations of state is illustrated, which is used for liquid-vapour equilibrium calculations, completely independent of the previously mentioned equations of state for the clathrate phase. These equations are used to calculate densities from homogenization temperatures of gas mixtures. For the example in Fig.33, the equation of state according to Thiéry et al. (1994) for a mixture of CO_2 and CH_4 is chosen, which gives an accurate estimation of solvus conditions. The

introduction of the volume fraction of the non-aqueous phase after clathrate melting, i.e. the vapour bubble, is optionally, with, again, an error-procedure. In the next screen display, the type of salt-mixture in the aqueous phase is introduced (Fig.34). The relative composition represents ratios of different types of salt in the solution, as obtained from e.g. crush-leach test, or careful microthermometrical observation of the melting behaviour of ice and hydrated salt ions. In the absence of any further specification of the type of ions that are present in the inclusions, wt% eq. NaCl is obtained by choosing a 100% NaCl solution.

```
AQUEOUS PHASE

Relative composition of salt (0-100 mole%) :
        NaCl = 60
        KCl = 0
        CaCl2 = 41
        MgCl2 = 0

ERROR: sum of mole percentage is not equal to 100
        NaCl = 60
        KCl = 0
        CaCl2 = 40
        MgCl2 = 0
```

Fig.34. Input of the aqueous phase.

The filename that contains the results of these calculations is introduced in the next screen display. Than, the program starts a sub-program to analyse the homogenization temperature of the carbonic gas mixture (Fig.35). This subprogram illustrates the possibility of erroneous results if trivial solutions occur, which depends highly on the initially estimation of the pressure during homogenization. The initial estimated pressure of 7 MPa gives an erroneous result after 12 iterations. The error is obvious from the calculated composition of both vapour and liquid, which appear to be identical (Fig.35). The vapour should be richer in the more volatile component of the mixture, i.e. that component with a lower critical point. A new approximation can be introduced by new definitions of the initial pressure and accuracy , in addition to an upper and lower limit of pressure estimations. After careful examination of the immiscibility curves of CO_2-CH_4 mixtures (Bakker, 1997; see Chapter 8.6), the initial pressure is graphically estimated at 5.5 MPa. After 11 iteration a solution is found at 5.3 MPa. The correctness of this result is obvious from the molar volume and composition of both liquid and vapour phase. The program has now successfully transformed homogenization temperature into molar volume and density. Finally the program is ready to combine

```
PROPERTIES OF THE CARBONIC PHASES (CO2-CH4-N2-C2H6)

Homogenisation conditions are numerically analysed. conversion depends on
the chosen initial parameter. The trivial solution may regularly occur,
especially if the temperature exceeds the LV-region.
You must adjust the initiation until you reach a satisfying results.

        Initial Pressure (MPa) = 7

0 1 2 3 4 5 6 7 8 9 10 11 12
******************************************************************
Result Liquid-Vapour Equilibria Calculations

Temperature  = 279.15 K, 6 Celsius
Pressure = 6.31 MPa, 63.101 bar

Zero function = 1.429e-10
Amount of iterations : 12

              Vapour        Liquid        Fugacity (MPa)
Vm            106.768       50.355
xCO2          95            95            3.122
xCH4          5             5             1.048
sum           100           100

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

        Minimum Pressure (MPa) = 4
        Maximum Pressure (MPa) = 8
        First Pressure Approach (in MPa) = 5.5
        Accuracy (1e-9) = 1e-9

0 1 2 3 4 5 6 7 8 9 10 11
******************************************************************
Result Liquid-Vapour Equilibria Calculations

Temperature  = 279.15 K, 6 Celsius
Pressure = 5.3 MPa, 53.001 bar

Zero function = 1.302e-11
Amount of iterations : 11

              Vapour        Liquid        Fugacity (MPa)
Vm            266.895       50.355
xCO2          83.867        95            3.042
xCH4          16.133        5             0.881
sum           100           100

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

Do you want to stop this iteration step? (y/n) y

******************************************************************
```

Fig.35. Screen display of the sub-program to calculate liquid-vapour equilibria.

the clathrate melting temperature and the previously obtained results to calculate bulk fluid properties of this specific fluid inclusion. The results are illustrated in Fig.36.

```
Program Density version 15/03/98
R.J.Bakker, University Heidelberg (Germany)
email: ronald.bakker@urz.uni-heidelberg.de
Filename : test1
_____
CLATHRATE PHASE (at final melting conditions)

Clathrate Structure 1

Tm (K)              281.250000
Pm (MPa)            14.545083
Vm (cc/mol)         22.374787
D (g/cc)            0.930621

mole fractions
H2O                 0.857227
CO2                 0.110455
CH4                 0.032319
N2                  0.000000
C2H6                0.000000

Equation of state for fugacity calculations in clathrate equilibria:
Duan et al. (1992a,b) Geochim.Cosmochim.Acta, 56, 2605-2617 and 2619-2631.

_____
NON-AQUEOUS PHASE (after final clathrate melting)

Mole fractions
H2O                 0.004754
CO2                 0.945484
CH4                 0.049762
N2                  0.000000
C2H6                0.000000

Fugacity coefficients
H2O                 0.875897
CO2                 0.280100
CH4                 2.947390

Volume fraction     0.400000

Homogenization conditions, in metastable absence of clathrate:

Th (K)              279.150000
Ph (MPa)            5.300077
Vh (cc/mol)         51.141179
D (g/cc)            0.833213

Equation of state for liquid-vapour equilibria:
Thiery et al. (1994) Eur.J.Mineral., 6, 753-771

_____
AQUEOUS SOLUTION (after final clathrate melting)

EOS : Duan et al. (1992a,b)
Vm (cc/mol)         18.584298
D (g/cc)            1.009643
act[H2O]            0.902057

Mole fractions
H2O                 0.907870
CO2                 0.026939
CH4                 0.000207
N2                  0.000000
C2H6                0.000000
Na+                 0.016246
K+                  0.000000
Ca++                0.010831
Mg++                0.000000
Cl-                 0.037908

Molality associated salt molecules:
NaCl                0.993323
KCl                 0.000000
CaCl2               0.662215
MgCl2               0.000000

Volume fraction     0.600000

_____
TOTAL FLUID INCLUSION

Vm (cc/mol)         24.933425
D (g/cc)            0.898790

mole fractions
H2O                 0.731748
CO2                 0.206070
CH4                 0.009871
N2                  0.000000
C2H6                0.000000
Na+                 0.013078
K+                  0.000000
Ca++                0.008719
Mg++                0.000000
Cl-                 0.030515
```

Fig.36. Result-file of the example defined in Fig.31, 32, 33 and 34. See text for further details.

40

The composition and molar volume of each phase that is present at clathrate melting is given in the result file (Fig.36). The program has calculated which clathrate structure is the most stable, i.e. has the lowest chemical potential according to the theoretical consideration presented by Bakker (1998; see Chapter 8.5). The salinity of the aqueous solution is given in ionic-concentration, assuming complete dissociation of the salt molecules. The bulk composition and molar volume is obtained from the optical estimation of volume fraction of the vapour bubble after melting of the clathrate phase. Subsequently, these values can be used to calculate an isochore for the specific fluid inclusion. The programs ICE, Q2, and NOSALT have similar calculation procedures, as described in detail by Bakker (1997; see Chapter 8.6).

Microthermometrical data from fluid inclusions in the absence of any clathrate phases can be modelled using the program HOMOGEN. Homogenization temperatures for certain fluid systems are directly transformed in densities and molar volumes. Salinities are calculated from freezing point depression of water. Optical volume fraction estimations of the phases present in fluid inclusions are used to calculate bulk fluid properties for fluid systems including more than one component. Most equations of state are not yet able to transform homogenisation temperatures of binary mixtures in to densities (for example H_2O-CO_2 mixtures, see Chapter 8.2). Only gas mixtures of CO_2-CH_4, and CO_2-N_2 can be treated according to fluid modelling of Thiery et al. (1994a, b). Similar to the previously described programs, HOMOGEN runs on DOS according to the question-answer principle. The first screen display of this program (Fig.37) illustrates the version number of the program, i.e. the latest update, and the fluid system for which the program can be used, i.e. the system H_2O-CO_2-CH_4-N_2-C_2H_6-NaCl-KCl-$CaCl_2$. Furthermore a list is given of the required input.

The inclusion data are introduced in the next screen displays. First of all, the aqueous phase is specified (Fig.38), than the properties of the vapour bubble are introduced (Fig.39). A non-aqueous fluid inclusion is identified by a negative response to the aqueous rim observation (see Fig.38). The presence of several types of salts in the aqueous solution can be specified and, subsequently, the final ice melting temperature is enquired. The calculations are restricted to fluid compositions less then

```
Program HOMOGEN, version 10/03/99
Ronald J. Bakker (University Heidelberg, Germany)

Fluid system H2O-CO2-CH4-N2-C2H6-NaCl-KCl-CaCl2

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

        (1) Homogenization temperatures/pressures
        (2) Ice melting temperatures
        (3) Volume fraction estimates
```

Fig.37. *First screen display of the program* **HOMOGEN.**

Fig.38. *Specification of the aqueous solution in fluid inclusions.*

```
AQUEOUS SOLUTION

Is at room temperature a rim of aqueous liquid phase present?
                                                      (y/n)  :
y

What type of salt is present in the aqueous solution:
        (0) none
        (1) NaCl
        (2) KCl
        (3) CaCl2
                                choose number: 1

What is the melting temperature of ice (in Celsius) : -25

ERROR: Ice-melting T cannot be lower than -21.2 C

What is the melting temperature of ice (in Celsius) : -9.8

What is the volume precentage of this aqueous rim (0-100%): 40
```

eutectic salinities, therefore, an error indication appears if the eutectic temperature of the specific fluid system is exceeded, as illustrated in Fig. 38. Finally, the optical estimated volume percentage of the aqueous rim is introduced.

```
VAPOUR BUBBLE

What is the composition of the homogeneous gas-rich bubble (0-100
mole%):

        H2O = 0
        CO2 = 95
        CH4 = 5
        N2 = 0
        C2H6 = 0

Partial density of non-aqueous bubble is obtained from:
        (0) density (g/cc)
        (1) molar volume (cc/mol)
        (2) homogenisation temperature
        (3) homogenisation pressure
                                                choose number: 2


        T (Celsius) = 21.2

        Mode of homogenisation:
                (0) Vapour
                (1) Liquid
                (2) Critical
                                                choose number: 0
```

Fig.39. Screen display for the vapour bubble properties

The composition of the vapour bubble is introduced in mole percentage (Fig.39). If evidence for the presence of any type of gas is not obtained from microthermometrical analysis and the inclusion has characteristics of only an aqueous fluid system, the composition of the gas-rich bubble is 100 mole% H_2O. Otherwise, the density of the carbonic gas mixture in the vapour bubble can be introduced in values of g/cc, cc/mol, or from homogenization temperatures and pressures of the gas mixture. The next calculation procedures are based on the information introduced according to Figs. 38 and 39. In pure fluid systems, total homogenization temperatures are directly transformed into densities, and volume fractions of the phases present at room temperature are calculated. H_2O-salt fluid systems are analysed according to the calculation methods presented Bodnar & Vityk (1994) and Zhang & Frantz (1987). The gas mixture presented in the example in Fig.39 is analysed according to the method revealed in Fig.35, where the liquid-vapour equilibrium of the CO_2-CH_4 mixture is numerically estimated. The results are only displayed on the screen, as illustrated in Fig.40, which can be readily used in the program **ISOCHOR**, for the calculation of isochores of the specific fluid system. The V-X properties of both the vapour bubble and the aqueous rim are separately illustrated. The salinity of the solution is indicated in molality and weight percentage. The V-X properties of the total inclusion in this specific example is obtained from the optical volume percentage estimations. Complete dissociation of the salt molecule in the solution is expected, therefore, mole

```
RESULTS (Inclusion properties at 293 K)

1. VAPOUR BUBBLE
        Vol.% = 60
        Vm (cc/mol) = 823.990225
        x(H2O) = 0.001171
        x(CO2) = 0.948887
        x(CH4) = 0.049941

2. AQUEOUS PHASE, liquid rim
        Vol.% = 40
        Vm (cc/mol) = 18.249343
        x(H2O) = 0.900883
        x(CO2) = 0.010754
        x(CH4) = 2.233208e-5
        NaCl : 2.721646 molal (13.723276
wt%)

3. TOTAL INCLUSION
        Vm (cc/mol) = 44.156425
        x(H2O) = 0.871954
        x(CO2) = 0.040918
        x(CH4) = 0.001627
        x(Na+) = 0.04275
        x(Cl-) = 0.04275
```

*Fig.39. Result of the program **HOMOGEN**.*

fraction of the ions are displayed.

Program **ISOCHOR** calculates isochores for known bulk fluid compositions and densities of inclusions. Isochores of the entrapped fluids can be traced to high temperatures and pressures, and changes of the host mineral volume, i.e. thermal expansion and compressibility are taken into account. Calcite, quartz, cordierite muscovite, fayalite, forsterite, andalusite, and kyanite are included as possible host minerals. Depending on the fluid system, a wide collection of equations of state is presented for the calculations. Details and limiting conditions for each equation are illustrated to facilitate the selection. The advantage of the program **ISOCHOR** in comparison to FLINCOR (Brown, 1989) and MacFlinCor (Brown & Hageman, 1994) is the host mineral correction and the use of recently published equations of state. Furthermore, the program **ISOCHOR** is continuously updated, according to the state of art in chemistry, physics and geology (see Table 2).

Similar to the other programs, **ISOCHOR** has been developed to run in IBM-PC compatible computers having DOS as operating system and consist of a question-answer principle, where any erroneous input is recognized in correction procedures. The program is introduced with general information, including version number and fluid systems (Fig.41).

The fluid properties, as obtained from the program **HOMOGEN** can be readily introduced in the next screen display. The results presented in the previous section (Fig.40) are used to illustrate the course of action. First, the type of salt and salinity are introduced, than the

```
Program ISOCHOR, version 10/03/99
Ronald J. Bakker, University Heidelberg (Germany)

Isochore calculation in complex gas system

Fluid system:   H2O-CO2-CH4-N2-C2H6-H2S-NH3-H2-O2
                NaCl-KCl-CaCl2


Salinities are introduced as either weight% or molality
Densities  are  introduced  as  g/cc  or  cc/mol (molar
volume)
Compressibility and expansion of host mineral are
included
```

Fig.41. *Introduction of the program* **ISOCHOR**.

bulk composition and density of the specific fluid system are enquired (Fig.42). The composition of the gas mixture is based on a salt-free system. For example, the

```
Which type of salt is present:
        (0) none
        (1) NaCl
        (2) KCl
        (3) CaCl2
                                        choose number : 1


Salinity is obtained from:
        (0) value in Weight%
        (1) value in Molality (mol salt / kg H2O)
                                        choose number : 0


        Weight% = 13.723

What is  the Bulk Composition (0-100 mole%), based on a salt-free
system:
        H2O = 95.348
        CO2 = 4.474
        CH4 = 0.178
        N2 = 0
        C2H6 = 0
        H2S = 0
        NH3 = 0
        H2 = 0
        O2 = 0


Bulk Fluid Density is obtained from :
        (0) Value in cc/mol
        (1) Value in g/cc
                                        choose number : 0


        Molar Volume (cc/mol) = 44.156
```

Fig.42. *Input of bulk V-X fluid properties.*

inclusion in Fig.40 contains 4.275 mole% Cl⁻ and 4.275 mole% Na⁺ ions. The remaining gas species form only 91.45 mole% of the total inclusion. The percentage H_2O, CO_2 and CH_4 of that part are 95.348, 4.474 and 0.178 mole%, respectively.

      The program **ISOCHOR** makes a selection of those equations of state that include the specific fluid system introduced in the previous section (Fig.43). Only the equation of state modified by Bakker (1999, see Chapter 8.1) is suitable for isochore calculation of fluid mixtures including H_2O, CO_2, CH_4 and NaCl. Details of the desired equation of state are revealed on the screen, and subsequently , the program includes the possibility to change this choice, and to select another equation of state included in the list.

```
Which Equation of State is prefered :

        (0) Bakker (1999) : any gas-mixture + NaCl

                                                    choose  number  :
0

Details Reference:
        Bowers & Helgeson (1983), Geochim.Cosmochim.Acta, 47:1247-1275.
        Bakker (1999) Chem. Geol., 154:225-236.
        Composition : any gas-mixture + NaCl
        Limits : 623-873 K and 50-200 MPa (extended by Bakker, 1999)

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

Fig.43. Screen display for the selection of an equation of state.

Than, the host mineral of the fluid inclusion can be specified (Fig.44). Compressibility and expansion data of several minerals (Hosieni et al., 1985; Berman, 1988) are included to correct the fluid density as a consequence of the change in total volume of the cavities. The host mineral molar volume must be specified at those conditions where the fluid density was calculated. Data obtained from microthermometry can be approximately represented by standard conditions of 25 °C and 1 bar, i.e. choice *0* in Fig.44.

```
Volumetric data (Compressibility, Expansion) on host mineral

In which mineral is the fluid trapped:
        (0) not specified
        (1) Quartz (Hosieni et al., 1985)
        (2) Calcite (Berman, 1988)
        (3) Cordierite (Berman, 1988)
        (4) Muscovite (Berman, 1988)
        (5) Fayalite (Berman, 1988)
        (6) Forsterite (Berman, 1988)
        (7) Andalusite (Berman, 1988)
        (8) Kyanite (Berman, 1988)
                                                    choose  number  :
1

At which conditions are the bulk fluid density estimated:
        (0) Homogenization conditions (approx. 25°C and 1bar)
        (1) Other temperature/pressure
                                                    choose  number  :
0
```

Fig.44. Host mineral volumetric data.

The temperature interval for the isochore, the amount of calculation steps, and the filename that contains the results of these calculations is introduced in the next screen display. The result file (Fig.45) include all the information that has been introduced in the previous paragraph, in addition to the calculated isochore of the specific fluid

system. This result can be readily introduced in any commercially available plotting and matrix program for the graphical presentation of isochoric systems.

```
PROGRAM ISOCHOR, version 10/03/99
Ronald J. Bakker, University Heidelberg (Germany)

Filename : test2

EOS : Bowers & Helgeson (1983), Bakker (1996)
Host Mineral : Quartz

Composition :
H2O = 0.953480
CO2 = 0.044740
CH4 = 0.001780

Type of Salt : NaCl
Molality = 2.721583 mol(salt)/kgH2O
Weight = 13.723000

Molar Volume = 44.156000 cc/mol
Density = 0.473962 g/cc

T(K)            T(C)            P(MPa)          V(cc/mol)
298.150000      25.000000       0.100000        44.156000
298.150000      25.000000       0.100000        44.156000
298.150000      25.000000       0.100000        44.156000
298.150000      25.000000       0.100000        44.156000
298.150000      25.000000       0.100000        44.156000
298.150000      25.000000       0.100000        44.156000
623.150000      350.000000      10.405819       44.818517
648.150000      375.000000      20.405071       44.869285
673.150000      400.000000      30.314187       44.923841
698.150000      425.000000      40.069160       44.983459
723.150000      450.000000      49.619741       45.049538
748.150000      475.000000      58.934771       45.123577
773.150000      500.000000      68.003160       45.207167
798.150000      525.000000      76.829890       45.301983
823.150000      550.000000      85.397639       45.425737
848.150000      575.000000      93.656519       45.603595
873.150000      600.000000      100.915716      46.115226
```

Fig.45. Result File from program **ISOCHOR**.

The previously described programs are included in the 3.5 inch disk in this manuscript. Six executable files are included: *NOSALT.EXE*, *DENSITY.EXE*, *ICE.EXE*, *Q2.EXE*, *HOMOGEN.EXE* and *ISOCHOR.EXE*. The programs are directly executable from this disk without any additional hardware or software requirements.

6. Conclusions

Microthermometry provides an excellent tool to analyse bulk fluid densities and composition of fluid inclusions in minerals. The measured temperatures of phase changes, including the melting behaviour of enclosed solids and the homogenization temperature of liquid and vapour phases are important monitors for the formation conditions of both fluid inclusions and host mineral. However, the interpretation of these temperatures remains highly speculative and estimated bulk fluid properties are highly inaccurate for most fluid systems after about 150 years of fluid inclusion research.

Historically, developments within chemistry are poorly adapted in geology for microthermometrical studies. Fluid inclusion studies are mainly restricted to direct geological interpretation of only homogenization temperatures. Purely empirical relations are used for many different specific fluid systems, however infinite compositional combinations require a more thorough approach to interpret natural fluid inclusions. Chemistry provides many thermodynamical models to predict fundamental fluid properties.

A modified Redlich-Kwong equation of state is developed with temperature dependent values for the *a* parameter of H_2O, CO_2, CH_4, and N_2, which are applicable over a wide temperature and pressure range to calculate isochores in complex fluid system. These equations allow accurate descriptions of intermolecular forces, which meet physical restrictions. In addition, the Bowers & Helgeson (1983) equation of state is modified to include NaCl for complex natural fluids. These modifications present the sole possibility to construct isochores for realistic geological fluid system which involve several gas components and salt.

A modified Lee-Kesler equation of state, as newly developed by Duan et al. (1992a, b) has a great potential of predicting both isochores and liquid-vapour equilibria. However, many erroneously defined variables in Duan et al. (1992a, b) do not allow accurate fluid properties calculation at the specific solvus conditions and closely related isochores. Accurate modelling of gas mixtures near solvus conditions still needs improvement, and recently published equations of state must be critically examined.

Unified Helmholtz energy functions have been developed to a high precision to predict all measureable fluid properties. The accuracy of these functions is superior to all formerly published equations due to its general thermodynamical application. Unfortunately, these equation have not yet been developed for gas mixtures.

Solvus conditions are poorly known for most gas mixtures, therefore, total homogenization temperatures can not be directly used to calculate inclusion bulk densities. Thermodynamical modelling of solvus conditions does not give the required accuracy due to inconsistent experimental data sets. A new V-X diagram with smoothed isotherms of the H_2O-CO_2 system is presented based on data from Sterner & Bodnar (1991), which can be directly used to obtain graphically bulk density and composition from measured partial CO_2 homogenization temperature and total homogenization of H_2O-CO_2 phases.

A clathrate phase occurs in any fluid inclusion having a mixture of H_2O and gases, and its melting behaviour provides important information on bulk fluid densities and compositions. Thermodynamic modelling has been modified to improve the accuracy for complex fluid systems including H_2O, CO_2, CH_4, N_2, C_2H_6, NaCl, KCl,

$CaCl_2$, and $MgCl_2$. The calculation of individual thermodynamical parameters included in clathrate stability model has been improved, according to recent developments within chemistry. None of the previously published models take fully into account optimal estimations of these parameters, and insufficient amounts of experimental data have been included to test the accuracy of these models. Excess Gibbs free energy functions are developed for mixed gas hydrates, including gas mixtures of CO_2-CH_4, CH_4-N_2 and CH_4-C_2H_6. The effect of salts on this fluid system is expressed in lowering the water activity according to osmotic coefficient calculations.

Computer programs in C++ have been developed to perform the many numerical and analytical procedures in fluid modelling. The mathematical complexity of physical and chemical modelling does not permit easy calculations of fluid system in natural rock. Self instructive computer programs have been developed to run in IBM-PC compatible computers having DOS as operating system. Four programs represent four specific types of clathrate melting behaviour in fluid inclusions, i.e. **DENSITY**, **ICE**, **Q2** and **NOSALT**. Microthermometrical data, optical volume percentage estimations and Raman spectrographical data from fluid inclusions in the absence of any clathrate phase can be modelled in the program **HOMOGEN**. Isochores of a complex fluid system, including H_2O, CO_2, CH_4, N_2, C_2H_6, H_2S, NH_3, H_2, O_2, NaCl, KCl, and $CaCl_2$, are calculated in program **ISOCHOR**. This program includes a correction for volume changes of the host mineral, and the use of recently published equations of state.

7. References

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