Package *FLUIDS* 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties

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Abstract

The computer package *FLUIDS* contains five sets of computer programs written in C++ for the calculation of fluid properties. Both model fluids and data from fluid inclusions can be analysed in the programs. Bulk density, molar volume and composition of fluid inclusions are calculated with the program *BULK*, which uses microthermometric data, micro-Raman spectroscopic data, cation ratios and volume-fraction estimations as input. The program offers a broad variety of equations of state, which are selected according to the fluid system or the temperature and pressure conditions of interest. The isochores that correspond to the output or test $V - x$ properties of fluid inclusions are calculated by the program *ISOC*. In calculating the isochores, this program takes account of the compressibility and expansion of selected host minerals. The program *TEST* allows different equations of state to be compared directly with experimental data, thereby facilitating selection of the most adequate model in the programs *BULK* and *ISOC*. *Loner* is a group of programs that handle individual equations of state (EoS) for all fluid systems presented in the programs *BULK* and *ISOC*. *Aqso* is a group of programs that allows purely empirical modelling of electrolyte-bearing aqueous solutions, Henry's law for dilute gas-bearing aqueous solutions, and osmotic coefficients for dilute electrolyte-bearing aqueous solutions. The programs are available on the University of Leoben web site at http:/www.unileoben.ac.at/~buero62/minpet/ronald.
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1. Introduction

Direct, nondestructive analysis of fluids trapped in microcavities in minerals depends on visible phase transitions using microthermometry, in addition to component identification with Raman spectroscopy. The latter also allows a semiquantitative approach, in which gas ratios can be estimated. In addition, other analytical methods like laser ablation coupled to ICP-MS and crush-leach may provide information about the components within fluid inclusion. These analytical techniques provide numbers, which must be integrated to determine the bulk composition and density of the fluid trapped in the inclusions. This is one of the primary goals of fluid inclusion studies.

Equations of state (EoS) for fluids are of major importance for the analysis of phase transition temperatures and the construction of isochores. Ideally, an

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EoS relates pressure (p), temperature (T), molar volume (V_m) and composition (x). In practice, however, most EoSs only yield part of this relation, and they are usually restricted to very narrow temperature and pressure ranges. The number of published EoSs has increased sharply during the past few decades, and it has become a time-consuming task to find and to apply the most suitable EoS for a specific research problem.

The aim of this paper is to present the computer package *FLUIDS*, which has been written in C++ (Borland, Turbo C++ version 3.0; CodeWarrior, version 7.0) for the interpretation of fluid inclusion data. The package can also be used for the calculation of fluid properties in general. Experimental data on specific fluid properties can be directly compared to EoSs, which may improve the interpretation of fluid inclusion studies. The program structure is flexible, and is readily modified to allow use of alternative or additional EoSs. This paper is the first in a series, which describes the thermodynamic modelling and EoSs used in the package. Most of the published EoSs had to be modified and improved to make them suitable for fluid inclusion research.

2. Published computer programs on fluid systems

In addition to computer programs that mainly treat thermodynamic data of minerals like *Ge0-Calc* (Berman et al., 1987; Brown et al., 1989) and *THERMO-CALC* (Powell et al., 1998), several programs are restricted to calculate fluid properties only. Many of those programs are applicable only to fluid systems with a small number of components, mainly H_2O, CO_2 and NaCl (e.g. Jacobs and Kerrick, 1981a; Bowers and Helgeson, 1985; Nicholls and Crawford, 1985; Hurai, 1989; Cavarretta and Tecce, 1995).

Calculations of complex fluid mixtures including a large number of gas components are restricted to isochore estimation at supercritical conditions. For example, the program *ISOCHORE* (Holloway, 1981) is confined to one modified Redlich–Kwong EoS originally developed by Holloway (1977), and calculates an isochore for supercritical fluid mixtures of known composition. Other programs offer a wider range of calculational options and include more EoSs. For example, the program *SUPERFLUID* (Belonoshko et al., 1992) can calculate Gibbs free energies

and molar volumes at selected p–T conditions of supercritical fluid mixtures in the C–H–O–N–S–Ar system. Two specific EoSs, i.e. Belonoshko and Saxena (1992) and Shi and Saxena (1992), are used for pure gases, in addition to low pressure substitute EoSs for pure H_2O, CO_2 and CH_4 (i.e. Saul and Wagner, 1989; Kerrick and Jacobs, 1981; Jacobs and Kerrick, 1981b, respectively). Gas mixture properties are defined according to Saxena and Fei (1988) and Shi and Saxena (1992). The programs *GEO-FLUIDS* (http://geotherm.ucsd.edu/geofluids/) are developed to calculate fluid properties, i.e. isochores and liquid–vapour equilibria, solely with the EoS from Duan et al. (1992a,b, 1996a).

FLINCOR (Brown, 1989) and *MacFLINCOR* (Brown and Hagemann, 1994) are specially designed for fluid inclusion studies. Data obtained directly from microthermometry and volume fraction estimations are used for isochore and bulk density and composition calculations. H_2O, CO_2, CH_4, N_2, H_2S, H_2, SO_2, CO, NaCl, KCl, and $CaCl_2$ are the fluid components included in the programs, which are described by about 12 EoSs. However, not every compositional combination of those components is included, and calculations are mainly restricted to the H_2O–CO_2–CH_4–N_2–NaCl system. The use of clathrate melting temperatures in *FLINCOR* can only be applied to pure CO_2 clathrates. The programs contain several interactive phase-diagrams to avoid complex calculation procedures. Most of the equations of state in these programs have become obsolete and describe only a small part of the previously mentioned fluid mixtures. The programs offer extrapolation possibilities outside the range of defined compositions or conditions for specific EoSs.

Thermodynamic properties of H_2O and aqueous species can be calculated with *SUPCRT92* (Johnson et al., 1992). Some purely empirical equations on melting behaviour of fluid inclusions in the system H_2O–NaCl–KCl and H_2O–NaCl–$CaCl_2$ are presented in the programs *SALTY* (Bodnar et al., 1989) and *CalcicBrine* (Naden, 1996), respectively.

Bulk fluid composition and density in equilibrium with specific mineral assemblages at higher temperatures and pressures are calculated with the programs *FLEVOL* (Bakker, 1992) and *GEOFLUID* (Larsen, 1993). Both are based on fluid modelling according to French (1966) in which individual gas fugacities are controlled by solid-phase buffers. *FLEVOL* calculates

fluid properties in the system C−O−H−N using several types of EoSs, whereas *GEOFLUID* includes the C−O−H fluid system using the EoS of Saxena and Fei (1987a,b).

Recent EoSs have superseded many of the formulations developed by earlier investigators, with higher accuracy over larger temperature and pressure ranges. The computer package, *FLUIDS* presented in this study is designed as a digital library and workshop for all available EoSs and thermodynamic modelling of fluid systems, and will be regularly updated.

3. Program structure

The computer programs in the package *FLUIDS* are organised according to the programming structure in Fig. 1 (see also Bakker, 1999a). The programs use various files (so-called libraries), which operate independently. In addition to a standard library (included in C++ software packages), four supplementary libraries have been developed: (1) Global variables and mathematical functions, which can be used in any kind of (sub) program. Also, physical constants are defined in this section. (2) Equations of state, a group of files handling individual EoSs. (3) Thermodynamic modelling, a group of files including osmotic coefficients, Henry's constants, excess Gibbs energy models and liquid−vapour equilibrium (LVE) calculations

(see Appendices A−F). (4) Experimental data on fluid systems.

Global variables are defined uniquely in the file *NumDef.CPP* and they are applied to all libraries. They include the definition of macros for the identification of phases, components, and EoSs. The properties of elements, i.e. atomic number, relative atomic mass, and oxidation states, are encapsulated in a class-type object. The properties of gases and salts are summarised in a struct-type object. They included the definitions of relative molecular mass, critical-point conditions, and triple-point conditions. In addition, the amount-of-substance fraction (commonly termed "mole fraction"), fugacity, fugacity coefficient, and activity in specific phases are stored in this object. The file *Equation.CPP* gives the analytical solutions of quadratic, cubic and quartic equations, including complex number solutions (Beyer, 1991). Nonlinear equations are numerically solved with the secant method (Press et al., 1997).

Components of the libraries can be introduced in any kind of main program, which is developed according to the physicochemical properties to be calculated. The advantage of this program structure is that recently published thermodynamic models can be easily included, without changing the overall program structure. Moreover, development of new main programs with a different objective can be accomplished quickly and efficiently.

4. The programs

At present, the package *FLUIDS* treats the fluid components H_2O, CO_2, CH_4, N_2, C_2H_6, H_2S, NH_3, H_2, O_2, CO, and the salt components NaCl, KCl, $CaCl_2$, $MgCl_2$. Salts dissolved in water can be defined as corresponding anions and cations, i.e. Na^+, K^+, Ca^{2+}, Mg^{2+} and Cl^-. The package consists of five main groups of programs, developed for the Macintosh, Windows-based and DOS-based platforms: *BULK*, *ISOC*, *TEST*, *Loner* and *Aqso*.

4.1. BULK

The program *BULK* uses information obtained directly from fluid inclusions to calculate bulk fluid density and composition.
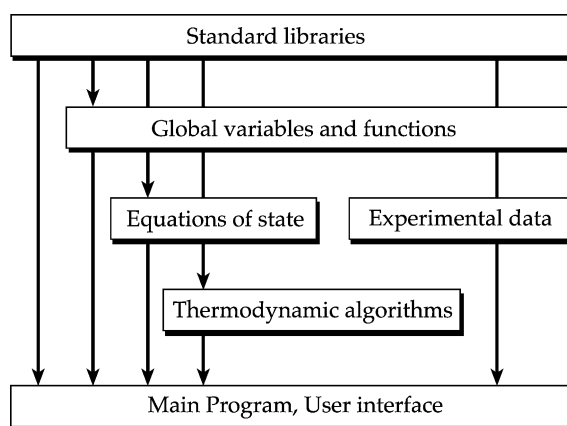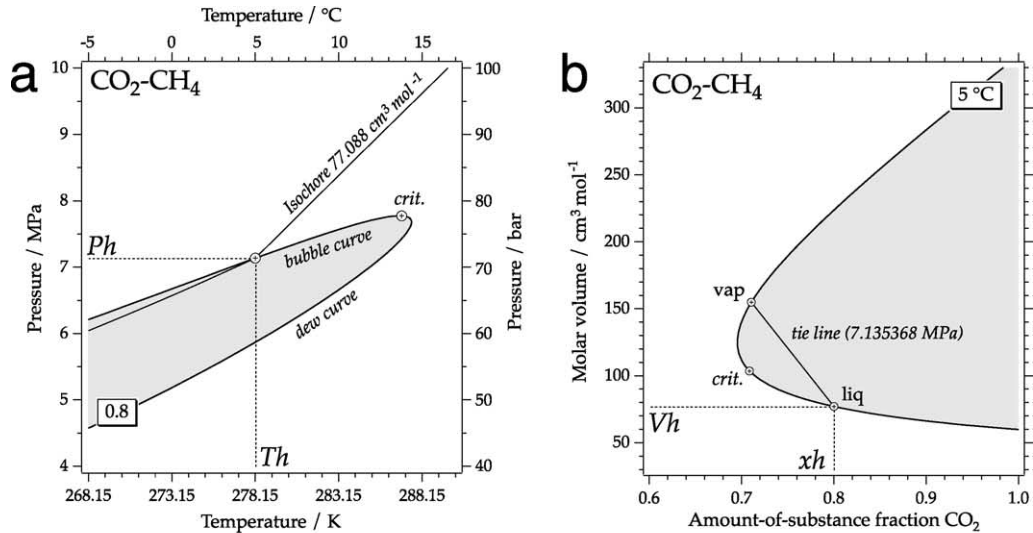

Fig. 1. General structure of the *FLUIDS* computer programs, which are divided into several libraries, i.e. standard libraries, global variables and functions, equations of state, thermodynamic algorithms, experimental data, and the user interface.

a CO_2-CH_4

Temperature / °C

Isochore 77.088 cm³ mol⁻¹

crit.

bubble curve

Ph

dew curve

0.8

Th

Pressure / MPa — Pressure / bar — Temperature / K

b CO_2-CH_4

5 °C

vap

tie line (7.135368 MPa)

crit.

liq

Vh

xh

Molar volume / cm³ mol⁻¹ — Amount-of-substance fraction CO_2

c
```
Result of Liquid-Vapour Equilibria Calculations

Temperature = 278.15 K, 5°C
Pressure = 8.343195 MPa, 83.431955 bar
Zero function = 1.972933e-11
Number of iterations : 12

        phase 1      phase 2      Fugacity (MPa)
CO2     0.8          0.8          2.97249
CH4     0.2          0.2          2.26589
Vm      69.577       69.578

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

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

d
```
        Initial vapour composition (mole fractions)

        CO2 = 0.7
        CH4 = 0.3

        New Pressure Approach (in MPa) = 7

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

e
```
Result of Liquid-Vapour Equilibria Calculations

Temperature = 278.15 K, 5°C
Pressure = 7.135368 MPa, 71.353683 bar
Zero function = -1.305622e-13
Number of iterations : 55

        phase 1      phase 2      Fugacity (MPa)
CO2     0.8          0.71065      2.91544
CH4     0.2          0.28935      2.0257
Vm      77.088       154.857

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

The nonaqueous vapour or liquid bubble is specified by its composition and density, as obtained from micro-Raman spectroscopy and homogenisation temperatures. In addition, hypothetical compositions and densities of the vapour bubble can be introduced in the program if these data are missing. The calculation of densities at the input homogenisation temperatures is done according to the LVE calculations in the file *LVequil.CPP* (see Appendix A). Alternatively, this file also offers the possibility to calculate densities from input homogenisation pressures.

The program *BULK* offers several EoSs for the analysis of homogenisation conditions. The difficulties associated with solving the equilibrium equations depend primarily on the selected initial values for the parameters used in LVE calculations. Multiple solutions may appear at a selected homogenisation temperature. Furthermore, LVE calculations in the vicinity of the critical point in multi-component systems are extremely sensitive to the initial conditions because both liquid and vapour have nearly equal compositions and densities. After a successful calculation, the program displays the solution on the screen. Possible trivial solutions, i.e. when both liquid and vapour phase have equal composition and density, are signalled with a warning sign. The LVE calculation can be restarted by choosing new initial values for the parameters in order to avoid this trivial solution. The fugacity of a component is calculated with the same EoS for both phases, which therefore must accurately describe both liquid- and vapour-like fluids at similar temperature–pressure conditions. The accuracy of the selected EoS at homogenisation conditions should be tested against experimental data (see main program *TEST*). In one-component fluid systems, such as pure H_2O, CO_2, CH_4, N_2, C_2H_6, NH_3, O_2 and CO, purely empirical equations (file *Saturation.CPP*) can be used to calculate saturation fluid properties at homogenisation conditions (see Appendix F).

An example of LVE calculations in the binary CO_2–CH_4 fluid system is illustrated here, with the EoS of Redlich and Kwong (1949), because novices are often confused by this kind of calculation. It should be noted that this equation does not accurately describe this fluid system at liquid-like conditions but the calculations are easily reproduced and they illustrate the general procedures well. We consider a mixture with an amount-of-substance fraction of 0.8 CO_2 and 0.2 CH_4 that homogenises at 5 °C in the liquid phase (Fig. 2a and b). After 11 iterations in the LVE calculation, a trivial solution appears on the screen (Fig. 2c), where both phases have a similar composition and density. New values of the initial guess are introduced for the composition of the coexisting vapour phase and for pressure (Fig. 2d). A true solution is found after several iterations (Fig. 2e), when phase 1 (liquid) and phase 2 (vapour) have clearly distinct compositions and molar volumes. The EoS of Redlich and Kwong (1949) gives a solution of 77.088113 cm^3/mol at a pressure of 7.135368 MPa, where the fugacity of CO_2 in both phases equals 2.91544 MPa.

Clathrate-melting temperatures are not included in the program *BULK* because they require an extra analytical procedure that would unnecessarily complicate the program structure. Based on similar program structuring, Bakker (1997, 1999a) has already presented several computer programs, which were designed to handle different types of clathrate melting in fluid inclusions for a H_2O–CO_2–CH_4–N_2–C_2H_6–$NaCl$–KCl–$CaCl_2$ fluid system.

The aqueous solution can be specified by introducing an ice-melting temperature or a known molality or mass percentage of specific salts. At present, only aqueous solutions up to eutectic compositions are included in the program *BULK*. In the presence of a multiple salt solution, the ratio of salts can be obtained from the peritectic and cotectic melting temperatures. For example, in a fluid inclusion containing a mixture of dissolved $NaCl$ and $MgCl_2$, hydrohalite melts completely at −24 °C, whereas ice melts at −4.3 °C. The peritectic melting of hydrohalite defines the mass ratio of $NaCl$/$MgCl_2$ at 61:39 (Dubois and Marignac, 1997). This ratio or selected test values is entered in the program. The test value allows the use of equivalent mass % for the presence of an unknown salt.

Fig. 2. Example of liquid–vapour equilibrium calculations in the computer package *FLUIDS*. The *pT*-diagram (a) and *Vx*-diagram (b) illustrate the physical parameters which are to be determined at homogenisation conditions (Th, Ph, Vh and xh). Screen read-out (c) illustrates the trivial solution after the first calculation procedures. Screen read-out (d) gives the correction possibility, changing the first guess of composition, pressure and accuracy. Screen read-out (e) illustrates the final solution of liquid–vapour equilibrium calculations (see text for further details).

Table 1
References and corresponding fluid systems and program numbers in the group *Loner*

Reference	Program	Fluid System	Limits	Fit
Anderko and Pitzer (1993a,b), Duan et al. (1995)	Loner15	$H_2O-CO_2-NaCl-KCl$	573 to 1200 K, <500 MPa	LVE+SVP
Angus et al. (1976)	Loner17	CO_2	216 to 1100 K, <100 MPa	LVE+SVP
Angus et al. (1978)	Loner21	CH_4	90 to 620 K, <100 MPa	LVE+SVP
Angus et al. (1979)	Loner25	N_2	63 to 1100 K, <100 MPa	LVE+SVP
Belonoshko and Saxena (1991a,b)	Loner23	$H_2O-CO_2-CH_4-CO-H_2-O_2$	400 to 4000 K, 500 to 1000 MPa	SVP
Belonoshko and Saxena (1992), Shi and Saxena (1992)	Loner40	$H_2O-CO_2-CH_4-N_2-$ $H_2S-NH_3-H_2-O_2-CO$ $(S_2-SO_2-COS-Ar)$	400 to 4000 K, 0.5 to 100 GPa	SVP
Bodnar and Vityk (1994), Bodnar (1992, 1994), Knight and Bodnar (1989)	Loner32	$H_2O-NaCl$[a]	323 to 973 K, <600 MPa	SVP
Bowers and Helgeson (1983), Bakker (1999a,b)	Loner8	$H_2O-CO_2-NaCl,$ $H_2O-CO_2-CH_4-N_2-C_2H_6-$ $H_2S-NH_3-H_2-O_2-CO-NaCl$	623 to 773 K[b], 50 to 150 MPa[b]	SVP
Christoforakos and Franck (1986)	Loner26	$H_2O-CO_2-CH_4-N_2$ (Xe)[c]	500 to 650 K, <250 MPa	LVE
Chueh and Prausnitz (1967)	Loner2	$H_2O-CO_2-CH_4-N_2-C_2H_6-H_2S$[d]	n.s.	LVE
Duan et al. (1992a,b, 1996b)	Loner9	$H_2O-CO_2-CH_4-H_2S-(NaCl)$	273 to 1273 K, <800 MPa	LVE+SVP
Duan et al. (1992c, 1996a)	Loner10	$H_2O-CO_2-CH_4-N_2-$ $H_2S-H_2-O_2-CO$ (Ar)	273 to 2000 K, <2000 MPa	SVP
Friend et al. (1991)	Loner20	C_2H_6	90 to 625 K, <70 MPa	LVE+SVP
Gallagher et al. (1993)	Loner27	H_2O-CO_2	400 to 1000 K, <100 MPa	LVE+SVP
Goodwin (1985)	Loner28	CO	68 to 1000 K, <100 MPa	LVE+SVP
Haar and Gallagher (1978)	Loner29	NH_3	195 to 750 K, <500 MPa	LVE+SVP
Haar et al. (1984)	Loner14	H_2O	273 to 1273 K, <1000 MPa	LVE+SVP
Holloway (1977, 1981, 1987), de Santis et al. (1974), Flowers (1979)	Loner5	$H_2O-CO_2-CH_4-N_2-C_2H_6-$ $H_2S-NH_3-H_2-O_2-CO$[d]	673 to 1573 K, <200 MPa	SVP
Jacobsen et al. (1986)	Loner22	N_2	126 to 2000 K, <1000 MPa	LVE+SVP
Kell (1967), Kell and Whalley (1965)	Loner16	H_2O	273 to 423 K, <100 MPa	SVP
Kerrick and Jacobs (1981), Jacobs and Kerrick (1981b)	Loner6	$H_2O-CO_2-CH_4$	673 to 1073 K, <1500 MPa	SVP
Kestin and Sengers (1986)	Loner30	H_2O (D_2O)	277 to 800 K, <100 MPa	LVE+SVP
Lee and Kesler (1975)	Loner7	$H_2O-CO_2-CH_4-$ $N_2-C_2H_6-H_2S-NH_3$[d]	T_r=0.3 to 4, P_r=0 to 10	LVE+SVP
Lvov et al. (1990), Lvov and Wood (1990)	Loner31	$H_2O-NaCl$[e]	273 to 973 K, 0.1 to 1000 MPa	SVP
Peng and Robinson (1976)	Loner4	$H_2O-CO_2-CH_4-N_2-C_2H_6-$ $H_2S-NH_3-H_2-O_2-CO$[d]	n.s.	LVE+SVP
Redlich and Kwong (1949)	Loner1	$H_2O-CO_2-CH_4-N_2-C_2H_6-$ $H_2S-NH_3-H_2-O_2-CO$[d]	$>T_c$, $>P_c$	SVP
Saxena and Fei (1987a, 1988)	Loner24	$H_2O-CO_2-CH_4-$ $N_2-CO-H_2-O_2$	>400 K	SVP
Saxena and Fei (1987b, 1988)	Loner33	$H_2O-CO_2-CH_4-N_2-$ $CO-H_2-O_2$ $(Ar-Xe)$	<3000 K, <100 GPa	SVP
Setzmann and Wagner (1991)	Loner19	CH_4	90 to 625 K, <1000 MPa	LVE+SVP
Shi and Saxena (1992)	Loner39	$H_2O-CO_2-CH_4-H_2S-$ H_2-O_2 (S_2-SO_2-COS)	n.s.	SVP
Shmonov and Shmulovich (1974)	Loner13	CO_2	373 to 1273 K, 200 to 1000 MPa	SVP
Soave (1972)	Loner3	$H_2O-CO_2-CH_4-N_2-C_2H_6-$ $H_2S-NH_3-H_2-O_2-CO$[d]	n.s.	LVE
Span and Wagner (1996)	Loner18	CO_2	216 to 1100 K, <800 MPa	LVE+SVP

Table 1 (continued)

Reference	Program	Fluid System	Limits	Fit
Spycher and Reed (1988)	Loner34	$H_2O-CO_2-CH_4-H_2$	289 to 1273 K, <100 MPa	SVP
Sterner and Bodnar (1991)	Loner12	H_2O-CO_2[a]	673 to 973 K, 200 to 600 MPa	SVP
Stewart et al. (1991)	Loner35	O_2	54 to 300 K, <80 MPa	LVE+SVP
Thiéry et al. (1994a,b)	Loner11	$CO_2-CH_4-N_2$[d]	<304 K, <40 MPa	LVE
Tillner–Roth et al. (1993)	Loner36	NH_3	223 to 573 K, <1000 MPa	LVE+SVP
Tillner–Roth and Friend (1998)	Loner37	H_2O-NH_3	200 to 600 K, <40 MPa	LVE+SVP
Zhang and Frantz (1987)	Loner38	$H_2O-NaCl-KCl-CaCl_2$[a,f]	453 to 973 K, <300 MPa	SVP

Gas components in brackets are originally included in the references, but not used in the programs. Temperature–pressure limits for each EoS are indicated (n.s.—not specified). T_r and P_r are the reduced temperature and pressure, T_c and P_c are the critical temperature and pressure. The type of experimental data to which the equations were fitted is denoted as liquid–vapour equilibria (LVE) or single-phase volumetric properties (SVP).

[a] Data obtained from synthetic fluid inclusion studies.
[b] Extended by Bakker (1999a,b).
[c] Only for binary systems H_2O–gas.
[d] More gases can be incorporated.
[e] More salts can be incorporated.
[f] Only for binary systems H_2O–salt.

Final ice-melting temperatures are analysed with thermodynamic models, either by using the ion-inter-action model (e.g. Pitzer, 1991), with osmotic coefficients calculated in file *Osmotic.CPP* (see Appendix C), or by using purely empirical models (e.g. Bodnar, 1993). The disadvantage of purely empirical models for electrolyte solutions is that they can only be applied to restricted predefined compositions and conditions. They can provide salinity in terms of equivalent mass percentage, and they do not take into account the total pressure and the presence of dissolved gases. True salinities are, therefore, overestimated using such models. Henry's constants are used to calculate the solubility of gases (e.g. Carroll et al., 1991), including salting-out coefficients (e.g. Cramer, 1982) in the file *GasSol.CPP* (see Appendix B). The activity of H_2O in complex solutions is obtained by combining the models for dissolved electrolytes and gases, according to the theoretical considerations in Bakker et al. (1996).

The program *BULK* calculates the composition and density of the vapour bubble and the aqueous solution at room temperature (20 °C) according to the previously described procedures. If an additional liquid CO_2-rich phase is present at this temperature, the program calculated the relative proportions according to the LVE calculations. The density of the H_2O-rich liquid solution at room temperature is calculate from several thermodynamic models that account for either dissolved gases (e.g. Duan et al., 1992a,b) or dissolved electrolytes (e.g. Krumgalz et al. 1996).

Finally, bulk compositions and densities of individual fluid inclusions can be obtained from estimations of volume fractions of phases present at room temperature, as described in the previous paragraph. Volume fraction estimates are a source of errors with magnitudes that are presently unknown, but sensitivity calculations can be easily performed with the program *BULK*. Bulk densities can also be obtained from total homogenisation temperatures, however, it can mainly be applied to one-component fluids, for which accurate thermodynamic models are available, e.g. Wagner and Pruß (1993) for H_2O (see Appendix F, Table F1). Most EoSs were not designed to predict solvus conditions, i.e. homogenisation conditions, of multi-component fluid systems. Therefore, highly incorrect values for bulk density are obtained by using such equations to predict Th values, whereas bulk densities based on volume fraction estimation of phases at room temperature provide more reliable, albeit approximate values. Except for single component fluids and $NaCl-H_2O$ mixtures, the program *BULK* inquires input of volume fraction estimates.

4.2. ISOC

The information obtained from the program *BULK*, or a hypothetical bulk composition and density, are entered into the program *ISOC* to calculate corresponding isochores. This program includes many different types of EoSs (Table 1), and the relevant equations are automatically selected according to the

fluid composition. The user is able to select one of the EoSs for the isochore calculation. Each selection is accompanied by an indication of limits of applicability of the EoS, as specified in the original publication. The selection can be changed arbitrarily if those limits do not correspond to the required $p-T$ conditions.

Included in the program is an option to correct fluid isochores for reversible changes in the absolute volume of the host minerals. Compressibility and expansion of 18 possible host minerals (e.g. quartz, carbonates, Al_2SiO_5 polymorphs, olivines, garnets, feldspars, and pyroxenes) are included (Hosieni et al., 1985; Berman, 1988). Isochore calculations are defined by the user over a certain temperature interval with selected step sizes.

The differences in prediction of the selected EoSs and the effect of isochore corrections are illustrated in Fig. 3. For comparison, two EoSs have been selected, i.e. Duan et al. (1992a,b), EoS^{DMW}, and Holloway (1977, 1981), EoS^H, for a binary H_2O-CO_2 fluid mixture. The precision of both EoSs at higher temperature and pressure is tested against an experimental datum from Sterner and Bodnar (1991), for which $x(H_2O)$ is 0.38 and $x(CO_2)$ is 0.62, and molar volume is 46.8 cm^3 mol^{-1} at 700 °C and 300 MPa. With these fixed $V_m - x$ values, the EoS^{DMW} overestimates the experimental pressure by 14 MPa, whereas the EoS^H underestimates the pressure by 21 MPa (Fig. 3). The isochore according to EoS^H is nearly a straight line in a $p-T$ diagram (Fig.3), whereas EoS^{DMW} has irregularities at low temperature (below 450 °C) and a negative slope at high temperatures (above 890 °C). The EoS^{DMW} appears to be more accurate for the example experimental datum. However, extrapolation of this equation to lower and higher temperatures evidently yields unrealistic isochore slopes.

If we assume that this example fluid is trapped in quartz at the specified experimental conditions, then the $p-T$ path of cooling can be predicted by taking into account the compressibility and thermal expan-
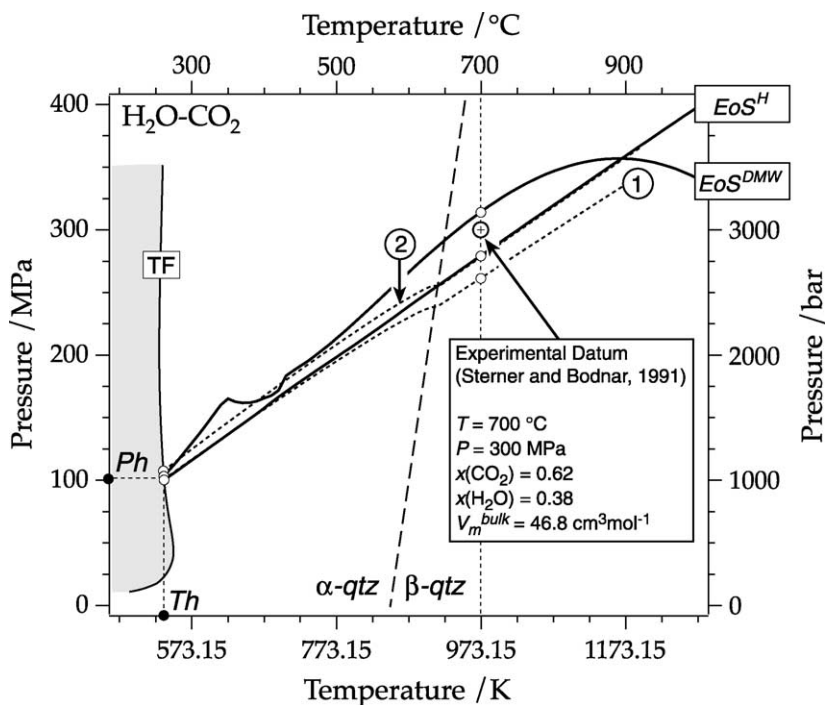

Fig. 3. Pressure–temperature diagram with isochores (solid curves) for a fixed bulk composition and molar volume. Short-dashed curves illustrate the change in $p-T$ paths of a hypothetical fluid inclusion as a consequence of the expansion of the host mineral at higher temperatures and pressures. The cross represents an experimental datum for 700 °C and 300 MPa from Sterner and Bodnar (1991). The shaded area indicates the immiscibility field of the specified fluid mixture according to the experiments of Tödheide and Franck (1963) (TF). The long-dashed line is the phase boundary between α- and β-quartz (see text for further details).

Table 2
Purely empirical equations for freezing-point-depression of aqueous solutions with one or two dissolved salts, and the corresponding program numbers in the group *Aqso*

Reference	Program	Fluid System
Bakker et al. (1996)	Aqso4e	H_2O-KCl, $H_2O-CaCl_2$
Dubois and Marignac (1997)	Aqso3e	$H_2O-NaCl-MgCl_2$
Naden (1996)	Aqso2e	$H_2O-NaCl-CaCl_2$
Potter et al. (1978)	Aqso5e	$H_2O-NaCl$
VPI: Hall et al. (1988), Sterner et al. (1988), Bodnar et al. (1989), Oakes et al. (1990), Bodnar (1993)	Aqso1e	$H_2O-NaCl$, $H_2O-NaCl-KCl$, $H_2O-NaCl-CaCl_2$

sion of quartz. By graphically intersecting the path with the experimentally determined solvus of Töd-heide and Franck (1963) (curve TF in Fig. 3), the homogenisation conditions are predicted to be about 261 °C and 101 MPa (Th and Ph in Fig. 3). The calculation predicts a bulk molar volume of 45.3 cm³ mol⁻¹ at these conditions. These $V_m - x$ numbers could also have been obtained, using the program *BULK*, from the homogenisation temperature of the CO_2 phases at 25.1 °C (in the liquid) and from the vapour bubble volume fraction of 0.843 (see also Bakker and Diamond, 2000).

Host mineral corrections of isochores are illustrated only for the EoS[H] in Fig. 3. It should be noted that corrected isochores have a variable molar volume. Therefore, they are not strictly isochores, but specific fluid inclusion $p-T$ paths. As a second example of such calculations, we now assume that the molar volume of the fluid inclusion is 46.8 cm³ mol⁻¹, as determined from the measured homogenisation conditions (e.g. Bakker and Diamond, 2000). The host mineral correction now tends towards lower pressures at higher temperatures (dashed curve 1 in Fig. 3). At 700 °C, the molar volume of the fluid has changed to 48.3 cm³ mol⁻¹ at 262 MPa. Alternatively, if we assume that at 700 °C the inclusion has a molar volume of 46.8 cm³ mol⁻¹, as obtained from experimental data, than the isochore is corrected towards higher pressures at lower temperatures (dashed curve 2 in Fig. 3). The homogenisation conditions for this specific fluid mixture are at a similar temperature but at higher pressures, 109 MPa, whereas the molar volume has decreased to 45.3 cm³ mol⁻¹.

4.3. TEST

Both programs *ISOC* and *BULK* permit the user to choose among different EoSs and thermodynamic models. As mentioned above, the program *ISOC* includes limit indications for the selected EoSs as stated in the source publications. The program *TEST* provides extra information on the limitations of specific EoSs, as obtained from mathematical restrictions and comparison with experimental data. These data can be selected from a program library, which has been specially designed in C++ for storing published experimental data on fluid systems, or they can be entered by the user. The accuracy, precision, extrapolation possibilities and improvements of the EoSs will be discussed elsewhere (Bakker, in preparation) are further discussed in the papers following the general introduction to the computer package *FLU-IDS*.

4.4. Loner

Loner is a group of programs (Table 1) that handles individual EoSs. These programs can be used to

Table 3
Dilute aqueous solutions according to Henry's law for several dissolved gases and the salting-out effect, with corresponding references and program numbers in the group *Aqso*

Reference	Program	Fluid System
Anderson and Prausnitz (1986)	Aqso1h	$H_2O-CH_4-N_2$
Benson and Krause (1976)	Aqso2h	$H_2O-N_2-O_2$
Carroll et al. (1991), Carroll and Mather (1992)	Aqso3h	H_2O-CO_2
Cramer (1982)	Aqso4h	$H_2O-CO_2-CH_4-O_2-NaCl$
Crovetto (1991)	Aqso5h	H_2O-CO_2
Drummond (1981)	Aqso6h	$H_2O-CO_2-CH_4-H_2S-H_2-NaCl$
Prini and Crovetto (1989)	Aqso7h	$H_2O-CH_4-N_2-C_2H_6-H_2-O_2$
Rettich et al. (1981)	Aqso8h	$H_2O-CH_4-C_2H_6$
Stoessell and Byrne (1982), Byrne and Stoessell (1982)	Aqso9h	$H_2O-CH_4-NaCl-KCl-CaCl_2-MgCl_2$
Teng et al. (1997)	Aqso10h	H_2O-CO_2

evaluate temperature, pressure, molar volume (and excess molar volume), fugacity, activity and liquid–vapour equilibrium from known variables using a single EoS. Excess molar volumes and activity coefficients of fluid mixtures can be calculated from the mixing rules used in the source publications or from standard excess Gibbs energy functions in the file *Gexcess.CPP* (see Appendix D). Additionally, unified Helmholtz energy functions (e.g. Span and Wagner, 1996) allow the calculation of Helmholtz energy, entropy, internal energy, enthalpy, Gibbs energy, isochoric heat capacity, isobaric heat capacity, speed of sound and Joule–Thomson coefficient.

4.5. Aqso

Aqso contains three groups that calculate the properties of dilute aqueous solutions at relatively low temperatures. Each group is the application of a specific thermodynamical model: (1) purely empirical equation for H_2O–salt fluid systems (Table 2); (2) Henry's law and salting-out coefficients for H_2O–gas and H_2O–gas–salt fluid systems (Table 3, see Appendix B); (3) electrolyte solution models with osmotic coefficients (Table 4, see Appendix C). Similar to EoSs, the accuracy of these thermodynamic models, their extrapolation possibilities and improvements will be discussed elsewhere (Bakker, in preparation).

5. Concluding remarks

The computer package *FLUIDS* has been developed for the analysis of fluid inclusion data (programs *BULK* and *ISOC*) and for the calculation of bulk fluid properties in general (programs *TEST*, *Loner*, *Aqso*). The programs run on Macintosh, Windows-based and DOS-based platforms. The package contains a broad variety of EoSs and thermodynamic modelling. Those that have not yet been included in this paper may be easily inserted into these programs, without changing the overall program structure. The package is designed as a digital library and workshop for fluid properties. The programs are available on the University of Leoben web site http://www.unileoben.ac.at/~buero62/minpet/ronald, which also includes several worked examples of each type of program. To ensure reproducibility of calculations and to provide correct documentation, users of the *FLUIDS* program package should cite not only this publication and program version number, but also the original publications of the selected EoSs or empirical equations.

Appendix A. Liquid–vapour equilibrium

The phase equilibrium between vapour and liquid phases at constant temperature and pressure is calculated in file *LVEquil.CPP* according to the method of Prausnitz et al. (1980), and is described by the equality of chemical potentials (or fugacities) of a

Table 4
Electrolyte solution models based on osmotic coefficients with corresponding references and program numbers in the group *Aqso*

Reference	Program	Fluid System
Archer (1992, 1999)	Aqso3c	H_2O–NaCl, H_2O–KCl
Bakker et al. (1996)	Aqso10c	H_2O–NaCl–KCl–$CaCl_2$–$MgCl_2$
Conceicao et al. (1983)	Aqso11c	H_2O–NaCl–$MgCl_2$[a]
Harvie et al. (1984)	Aqso4c	H_2O–CO_2–NaCl–KCl–$CaCl_2$–$MgCl_2$[a]
Holmes and Mesmer (1983)	Aqso8c	H_2O–KCl[a]
Holmes et al. (1994, 1997)	Aqso9c	H_2O–$CaCl_2$
Krumgalz et al. (1996)	Aqso5c	H_2O–NaCl–KCl–$CaCl_2$–$MgCl_2$[a]
Møller (1988)	Aqso6c	H_2O–NaCl–$CaCl_2$[a]
Phutela and Pitzer (1983)	Aqso7c	H_2O–$CaCl_2$
Pitzer et al. (1984), Pitzer (1991)	Aqso1c	H_2O–NaCl–KCl–$CaCl_2$–$MgCl_2$[a]
Spencer et al. (1990)	Aqso2c	H_2O–NaCl–KCl–$CaCl_2$–$MgCl_2$[a]

[a] More salts can be incorporated.

component in each phase (Eqs. (A1), (A2a) and (A2b)).

$$f_i^{\text{vapour}} = f_i^{\text{liquid}} \tag{A1}$$

$$f_i^{\text{vapour}} = \vartheta_i y_i P \tag{A2a}$$

$$f_i^{\text{liquid}} = \psi_i x_i P \tag{A2b}$$

where P is pressure, ϑ_i and ψ_i are the fugacity coefficients in the vapour and liquid phase, respectively; y_i and x_i are the amount-of-substance fractions (commonly termed mole fractions) in the vapour and liquid phase, respectively. The ratio of this fraction can be expressed in a K value (Eq. (A3)).

$$K_i = \frac{y_i}{x_i} = \frac{\psi_i}{\vartheta_i} \tag{A3}$$

During phase separation, the amount-of-substance fractions in each phase are not independent (Eq. (A4)).

$$X_i^{\text{bulk}} = \frac{n^{\text{vap}} y_i + n^{\text{liq}} x_i}{n^{\text{vap}} + n^{\text{liq}}} \tag{A4}$$

where X_i^{bulk} is the bulk amount-of-substance fraction of component i; n^{vap} and n^{liq} are the total number of moles in the vapour and liquid phase, respectively. Substitution of Eq. (A3) in Eq. (A4) and defining the sum of n^{vap} and n^{liq} as n^{bulk} results in Eqs. (A5a–5d).

$$X_i^{\text{bulk}} = \frac{n^{\text{vap}}}{n^{\text{bulk}}} K_i x_i + \frac{n^{\text{bulk}} - n^{\text{vap}}}{n^{\text{bulk}}} x_i \tag{A5a}$$

$$x_i = \frac{X_i^{\text{bulk}}}{x^{\text{vap}}(K_i - 1) + 1} \tag{A5b}$$

$$y_i = \frac{K_i X_i^{\text{bulk}}}{x^{\text{vap}}(K_i - 1) + 1} \tag{A5c}$$

$$x^{\text{vap}} = \frac{n^{\text{vap}}}{n^{\text{bulk}}} \tag{A5d}$$

where x^{vap} is the amount-of-substance fraction of the vapour phase in the bulk system. The bubble and dew point, i.e. homogenisation into the liquid and vapour phase, respectively, are calculated at a fixed temperature, i.e. the homogenisation temperature, and by setting x^{vap} at 0 or 1, respectively. The homogenisation pressure and density are numerically obtained (secant method) using the restriction of the mass balance. The fugacity coefficients for both the liquid and vapour phase (ψ_i and ϑ_i) are calculated from the same EoS. A first guess of K values is obtained from both Raoult's law and the Wilson approximation (Michelsen, 1993). Liquid–vapour equilibrium within the immiscibility region of a certain fluid mixture is obtained at selected temperatures by numerical calculation (secant method) of pressure and x^{vap} simultaneously, which may vary between 0 and 1. The relation between x^{vap} and volume fractions φ of the phases is given in Eqs. (A6a–6c).

$$\varphi^{\text{vapour}} = \frac{n^{\text{vap}} V_{\text{m}}^{\text{vap}}}{n^{\text{vap}} V_{\text{m}}^{\text{vap}} + n^{\text{liq}} V_{\text{m}}^{\text{liq}}} \tag{A6a}$$

$$\varphi^{\text{vapour}} = \frac{x^{\text{vap}} V_{\text{m}}^{\text{vap}}}{x^{\text{vap}} V_{\text{m}}^{\text{vap}} + (1 - x^{\text{vap}}) V_{\text{m}}^{\text{liq}}} \tag{A6b}$$

$$\varphi^{\text{liquid}} = 1 - \varphi^{\text{vapour}} \tag{A6c}$$

where V_{m} is the molar volume of the superscripted phase.

Appendix B. Gas solubility in aqueous solutions

The solubility of gases in dilute aqueous solutions is calculated with Henry's law (e.g. Prausnitz et al., 1986) in the file *GasSol.CPP*. Similar to the previous section, equilibrium calculations are based on the equality of fugacities of components in each phase they are present (cf. Eq. (A1)). The solvent, i.e. H_2O, and solutes, i.e. dissolved gases are treated separately (Eqs. (B1a) and (B1b)).

$$f_{\text{gas}}^{\text{vapour}} = f_{\text{gas}}^{\text{liquid}} \tag{B1a}$$

$$f_{H_2O}^{\text{vapour}} = f_{H_2O}^{\text{liquid}} \tag{B1b}$$

The solution of both equations gives the compositions of the coexisting aqueous solution and gas-rich vapour phase, which is numerically calculated (secant method). The fugacities of a component in the liquid and vapour phase are defined by Eqs. (B2a) and (B2b) (cf. Eqs. (A2a) and (A2b)).

$$f_i^{liquid} = \psi_i x_i P = x_i \gamma_i f_i^0 \equiv H_{i,w} x_i \tag{B2a}$$

$$f_i^{vapour} = \vartheta_i y_i P \tag{B2b}$$

where γ_i is the activity coefficient of the component i, and f_i^0 is the fugacity of i at the standard state, $H_{i,w}$ is the Henry's constant of component i in water. The pressure effect on the gas solubility in aqueous solutions is obtained from the definition of fugacity coefficient (Eq. (B3)).

$$RT\ln\left(\frac{f_i}{x_i P}\right) = \int_0^{P^{sat}}\left(v_i - \frac{RT}{P}\right)dP$$
$$+ \int_{P^{sat}}^P\left(v_i - \frac{RT}{P}\right)dP \tag{B3}$$

where v_i is the partial molar volume of component i in the liquid phase, R is the gas constant and T is temperature in K. The integral has been split up at the saturation pressure of the water, P^{sat}. Eq. (B3) can be rewritten to include the Henry's constant as defined in Eq. (B2a).

$$\ln\left(\frac{f_i}{x_i P}\right) = \ln\left(\frac{f_i^{sat}}{x_i^{sat} P^{sat}}\right) + \frac{1}{RT}\int_{P^{sat}}^P v_i dP - \ln\left(\frac{P}{P^{sat}}\right)$$
$$\tag{B4a}$$

$$\ln\left(\frac{f_i}{x_i P}\right) = \ln\left(\frac{f_i^{sat}}{x_i^{sat} P}\right) + \frac{1}{RT}\int_{P^{sat}}^P v_i dP \tag{B4b}$$

$$\ln\left(\frac{f_i}{x_i}\right) = \ln(H_{i,w}^{sat}) + \frac{1}{RT}\int_{P^{sat}}^P v_i dP \tag{B4c}$$

The remaining integral in Eq. (B4c) can be replaced by Eq. (B5), assuming that v_i in the aqueous solution is independent of pressure.

$$\frac{1}{RT}\int_{P^{sat}}^P v_i dP = \frac{v_i^{\infty}(P - P^{sat})}{RT} \tag{B5}$$

where v_i^{∞} is the partial molar volume of component i at infinite dilution. The v_i^{∞} values for CO_2, CH_4, N_2 and C_2H_6 are partly dependent on temperature and are obtained from Bakker (1998). Summarised, the fugacity of H_2O and a gas component in the liquid phase are defined by Eqs. (B6a) and (B6b).

$$f_{H_2O}^{liquid} = x_{H_2O} P^{sat} \psi_{H_2O}^{sat} \exp\left(\frac{v_{H_2O}(P - P^{sat})}{RT}\right) \tag{B6a}$$

$$f_{gas}^{liquid} = x_{gas} H_{gas,w}^{sat} \exp\left(\frac{v_{gas}^{\infty}(P - P^{sat})}{RT}\right) \tag{B6b}$$

where $\psi_{H_2O}^{sat}$ is the fugacity coefficient of pure H_2O at its saturation pressure, which is 1 at low temperatures. The fugacities of H_2O and gas in the vapour phase are obtained from the EoS of Redlich and Kwong (1949). At temperatures below 0 °C, the saturation pressure of water is set equal to the saturation pressure of ice, i.e. sublimation curve (Wagner et al., 1994).

The temperature dependence of the Henry's constant is expressed in a general formula for CO_2, CH_4, N_2 and C_2H_6 (Eq. (B7)).

$$\ln(H_{i,w}^{sat}/MPa) = a_0 + \frac{a_1}{T} + \frac{a_2}{T^2} + \frac{a_3}{T^3} + \frac{a_4}{T^4} \tag{B7}$$

where the constants a_0, a_1, a_2, a_3 and a_4 are defined according to Bakker (1998).

The solubility of gases decreases if salts are also dissolved in the aqueous solution. Therefore, the Henry's constant for gases is corrected with the salting-out coefficient, k_s (Eqs. (B8a–8c)).

$$\ln\left(\frac{H_{i,w}^{salt}}{H_{i,w}}\right) = k_s b_{salt} \tag{B8a}$$

$$k_s(CO_2)/(mol^{-1}\ kg) = 0.11572 - 0.00060293t$$
$$+ 3.5817 \times 10^{-6}t^2$$
$$- 3.7772 \times 10^{-9}t^3 \tag{B8b}$$

$$k_{\mathrm{s}}(\mathrm{CH}_4)/(\mathrm{mol}^{-1}\ \mathrm{kg}) = 3.38828 - 0.0318765T$$
$$+ 0.000122003T^2$$
$$- 2.31891 \times 10^{-7}T^3$$
$$+ 2.22938 \times 10^{-10}T^4$$
$$- 8.83764 \times 10^{-14}T^5 \quad \text{(B8c)}$$

where b_{salt} is the molality of a dissolved salt, t and T are the temperature in °C and K, respectively. Eqs. (B8b) and (B8c) are empirical fits to the data from Cramer (1982), and represent the salting-out coefficient of CO_2 and CH_4 in NaCl solutions, valid between 0 and 300 °C. For KCl solutions, a constant value of 0.04 and 0.026 (Stoessell and Byrne, 1982) is subtracted from k_{s} in Eqs. (B8b) and (B8c), respectively. A constant value of 0.075 and 0.066 is subtracted for $CaCl_2$ solutions, and a constant value of 0.075 and 0.074 is subtracted for $MgCl_2$ solutions in Eqs. (B8b) and (B8c), respectively. It is assumed that all salts are distributed in the liquid phase, and that the vapour phase is free of salts.

Appendix C. Osmotic coefficients

The file *Osmotic.CPP* calculates the osmotic coefficients, activity coefficients and mean activity coefficients of H_2O and dissolved salts in electrolyte solutions according to the thermodynamic model of Pitzer (1991). The chemical potential of a component in a certain phase is expressed as in Eq. (C1).

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j} = \mu_i^0 + RT\ln\left(\frac{f_i}{f_i^0}\right) \quad \text{(C1)}$$

where the superscript 0 refers to standard conditions, G is the Gibbs energy, f_i and n_i are the fugacity and the amount-of-substance of component i, respectively, R is the gas constant and T is temperature in K. The ratio of the fugacity of a component in the mixture and the pure component at p–T is defined as the activity. Furthermore, the activity a_i can be expressed as the product of amount-of-substance fraction x_i and activity coefficient γ_i (Eqs. (C2a) and (C2b)).

$$\frac{f_i}{f_i^0} = a_i \quad \text{(C2a)}$$

$$a_i = \gamma_i x_i \quad \text{(C2b)}$$

In dilute solutions the logarithm of Eq. (C2b) is simplified as follows:

$$\ln(a_i) = \ln(\gamma_i x_i) = \Phi_i \ln(x_i) \quad \text{(C3)}$$

where Φ_i is the osmotic coefficient of component i. Eqs. (C4a) and (C4b) give the definition of the osmotic coefficient for water, as obtained from Eq. (C3), again by separating solvent and solute components.

$$\Phi_{\mathrm{H_2O}} = \frac{-x_{\mathrm{H_2O}}}{\sum_j x_j}\ln(a_{\mathrm{H_2O}}) \quad \text{(C4a)}$$

$$\lim_{x_j \to 0}\left[\frac{-x_{\mathrm{H_2O}}}{\sum_j x_j}\ln(x_{\mathrm{H_2O}})\right] = 1 \quad \text{(C4b)}$$

where x_j is the amount-of-substance fraction of dissolved electrolytes in water. Eq. (C4b) is a combination of Eqs. (C3) and (C4a), which indicates that it can only be applied to dilute solutions. The derivation of Eqs. (C4a) and (C4b) can also be illustrated by expressing the amount-of-substance fraction of H_2O in molalities (b_i) of the corresponding components in the aqueous solution (Eq. (C5)).

$$x_{\mathrm{H_2O}} = \frac{n_{\mathrm{H_2O}}}{n_{\mathrm{total}}} = \frac{n_{\mathrm{H_2O}}}{n_{\mathrm{H_2O}} + \sum_j n_j}$$
$$= \frac{1}{1 + \frac{M_{\mathrm{r}}(\mathrm{H_2O})}{1000}\sum_j b_j} \quad \text{(C5)}$$

where $M_{\mathrm{r}}(\mathrm{H_2O})$ is the relative molar mass of water. The logarithm of this equation can be simplified for dilute solutions (Eqs. (C6a) and (C6b)).

$$\ln(x_{\mathrm{H_2O}}) = -\ln\left(1 + \frac{M_{\mathrm{r}}(\mathrm{H_2O})}{1000}\sum_j b_j\right) \quad \text{(C6a)}$$

$$-\ln\left(1 + \frac{M_r(H_2O)}{1000}\sum_j b_j\right) \approx -\frac{M_r(H_2O)}{1000}\sum_j b_j \tag{C6b}$$

Subsequently, the osmotic coefficient can be expressed as a function of molalities by substitution of Eqs. (C6a) and (C6b) into Eq. (C3):

$$\Phi_{H_2O} = \frac{-1}{\frac{M_r(H_2O)}{1000}\sum_j b_j}\ln(a_{H_2O}) \tag{C7}$$

The total molar Gibbs energy of the aqueous solution is expressed in Eqs. (C8a) and (C8b).

$$G_m = \sum_i x_i\mu_i = x_{H_2O}\mu_{H_2O} + \sum_j x_j\mu_j \tag{C8a}$$

$$G_m = x_{H_2O}[\mu_{H_2O}^0 + RT\ln(a_{H_2O})] + \sum_j x_j[\mu_j^0 + RT\ln(a_j)] \tag{C8b}$$

The excess molar Gibbs energy is obtained by subtracting the ideal mixing Gibbs energy from Eqs. (C8a) and (C8b).

$$G_m^{excess} = RT\left[x_{H_2O}\ln(\gamma_{H_2O}) + \sum_j x_j\ln(\gamma_j)\right] \tag{C9}$$

The activity coefficient of water is obtained by combining Eqs. (C2b), (C6a), (C6b) and (C7):

$$\ln(\gamma_{H_2O}) = (1 - \Phi_{H_2O})\frac{M_r(H_2O)}{1000}\sum_j b_j$$

$$= -\sum_j x_j\frac{\Phi_{H_2O}}{x_{H_2O}} - \ln(x_{H_2O}) \tag{C10a}$$

$$G_m^{excess} = RT\left[\sum_j x_j(1 - \Phi_{H_2O}) + \sum_j x_j\ln(\gamma_j)\right] \tag{C10b}$$

$$\frac{G_m^{excess}}{RT} = x_{H_2O}\frac{M_r(H_2O)}{1000}$$

$$\times \left[(1 - \Phi_{H_2O})\sum_j b_j + \sum_j b_j\ln(\gamma_j)\right] \tag{C10c}$$

The excess Gibbs energy can be obtained from experimental data, which are reproduced by relatively simple mathematical functions dependent on composition and temperature, such as the Margules equation and the Redlich–Kister equation (e.g. Prausnitz et al., 1986). From statistical mechanics, some rough physical significance can be assigned to the parameters that appear in these equations. The excess Gibbs energy function for dilute electrolyte solutions is modelled according to two major assumptions. (1) The interaction between dissolved salt molecules is a function of its potential, and (2) the interaction of individual H_2O molecules is ignored. The function is described by two- and three-body interactions (Eqs. (C11a) and (C11b)).

$$G_m^{excess} = A + \sum_i\sum_j x_ix_jB_{ij} + \sum_i\sum_j\sum_k x_ix_jx_kC_{ijk} \tag{C11a}$$

$$\frac{G_m^{excess}}{RT} = x_{H_2O}\frac{M_r(H_2O)}{1000}$$

$$\times \left[f(I) + \sum_i\sum_j b_ib_j\lambda_{ij}(I)\right.$$

$$\left. + \sum_i\sum_j\sum_k b_ib_jb_k\mu_{ijk}\right] \tag{C11b}$$

where f and λ_{ij} are the transformed Debye–Hückel term and binary interaction parameters (i.e. short-range interaction between two solute molecules), respectively. Both are functions of the ionic strength (I). μ_{ijk} is the triple interaction parameter, which is independent of I. This equation can be rearranged in order to obtain experimentally determinable quantities (see Pitzer, 1991). Values for the osmotic coefficient and the activity coefficient of dissolved salts are obtained from partial differentiation of Eq. (C11b).

The file *Osmotic.CCP* includes the possibility to calculate the ionic strength, the electrostatic term (Debye–Hückel parameter) and several empirical fits of the parameters that occur in Eqs. (C11a) and (C11b) of many dissolved components.

Appendix D. Excess Gibbs energy and Lattice theory

The file *Gexcess.CPP* calculates excess properties of fluid mixtures, i.e. excess functions for molar volume, enthalpy, entropy, Helmholtz energy and Gibbs energy, according to a combination of the van Laar equation (e.g. Wohl, 1946) and lattice theory (e.g. Guggenheim, 1966). The excess Gibbs energy is directly related to the activity coefficients of the components in the solution (Eqs. (D1a) and (D1b), cf. Eqs. (C8a), (C8b) and (C9)).

$$G_{\mathrm{m}} = \sum_i x_i \left[\mu_i^0 + RT\ln(a_i) \right] \tag{D1a}$$

$$G_{\mathrm{m}}^{\mathrm{excess}} = RT \sum_i x_i \ln(\gamma_i) \tag{D1b}$$

where a_i and γ_i are the activity and the activity coefficient of component i, respectively, and the subscript m denotes a molar basis. According to the theory of van Laar (1910), the excess Gibbs energy can be expressed as in Eqs. (D2a–2e).

$$\frac{G_{\mathrm{m}}^{\mathrm{excess}}}{RT \sum_i x_i q_i} = \sum_i \sum_{j \neq i} a_{ij} z_i z_j \tag{D2a}$$

$$z_i \equiv \frac{x_i q_i}{\sum_i x_i q_i} \tag{D2b}$$

$$a_{ij} \equiv a_{ji} \tag{D2c}$$

$$\frac{q_i}{q_j} \equiv \frac{V_i}{V_j} \tag{D2d}$$

$$\sum_i q_i \equiv 1 \tag{D2e}$$

where a_{ij} represents the energy of interaction between a molecule of type i and j, $2z_i z_j$ is the probability that any nearest neighbours are a pair of molecules i and j, q_i is a measure of the size of molecule i. The lattice theory treats a liquid as a quasicrystalline state, where molecules tends to stay in a small region (Guggenheim, 1966; Prausnitz et al., 1986). The total potential energy of this liquid is the summation of all molecular pairs. The interaction between two unlike molecules is described by the interchange energy w (Eq. (D3)).

$$w_{ij}/\mathrm{J} \equiv Z \left[\Gamma_{ij} - \frac{1}{2} (\Gamma_{ii} + \Gamma_{jj}) \right] \tag{D3}$$

where Z is the coordination number ($=10$), and Γ_{ij} is the intermolecular potential between molecule i and j. The total potential energy can be transformed by the canonical partition function into thermodynamic properties, such as excess Helmholtz energy (Eqs. (D4a) and (D4b)).

$$\frac{A_{\mathrm{m}}^{\mathrm{excess}}}{RT} = \frac{1}{kT} \sum_i \sum_{j \neq i} \frac{1}{2} w_{ij} x_i x_j \tag{D4a}$$

$$A_{\mathrm{m}}^{\mathrm{excess}} = N_{\mathrm{A}} \sum_i \sum_{j \neq i} \frac{1}{2} w_{ij} x_i x_j \tag{D4b}$$

where k is the Boltzmann constant, and N_{A} is Avogadro's number. Eqs. (D4a) and (D4b) is equivalent to the two-suffix Margules excess function. Application of this principle to the van Laar excess function (Eqs. (D2a–2e)) results in a direct relation between w_{ij} and a_{ij} (Eq. (D5)).

$$2a_{ij} = \frac{N_{\mathrm{A}} w_{ij}}{RT} \tag{D5}$$

A general formulation of the intermolecular potential energy is described by a combination of the Lennard–Jones-, Kihara-, and Stockmayer-potential (Eq. (D6)).

$$\Gamma_{ij}/\mathrm{J} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij} - 2a_{ij}}{r_{ij} - 2a_{ij}} \right)^{12} - \left(\frac{\sigma_{ij} - 2a_{ij}}{r_{ij} - 2a_{ij}} \right)^6 \right] - \frac{\mu_{ij}^2}{r_{ij}^3} \tag{D6}$$

Table F1
Purely empirical equations of vapour-saturated fluid properties of
pure gases in the file *Saturation.CPP*

Fluid system	Reference
H_2O	Wagner and Pruß (1993)
CO_2	Duschek et al. (1990)
CH_4	Setzmann and Wagner (1991)
N_2	Jacobsen et al. (1986)
C_2H_6	Friend et al. (1991)
H_2S	This paper (Eqs. (F1) and (F2))
NH_3	Haar and Gallagher (1978)
O_2	Stewart et al. (1991)
CO	Goodwin (1985)

where ε is the minimum energy corresponding to the equilibrium separation, r the intermolecular distance, σ is the intermolecular distance where $\Gamma = 0$, a is the radius of the spherical molecular core and μ is the dipole moment. This equation reduces to a Lennard–Jones potential if $a_{ij} = 0$ and $\mu_{ij} = 0$, to a Stockmayer potential if only $a_{ij} = 0$, and to a Kihara potential if only $\mu_{ij} = 0$. The distance between molecules is obtained from the molar volume of pure gases V_m^{pure} (Kohler, 1957), assuming that each molecule occupies the same cube of space (Eq. (D7)).

$$r/m = \sqrt[3]{\frac{V_m^{pure}}{N_A}} \tag{D7}$$

The mixing rules, i.e. geometric mean assumption (with Bertholot's mixed parameter) and arithmetic average, are applied to these molecular parameters (Eqs. (D8a–8f)).

$$r_{ij} = \frac{1}{2}(r_i + r_j) \tag{D8a}$$

$$a_{ij} = \frac{1}{2}(a_i + a_j) \tag{D8b}$$

$$\sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \tag{D8c}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j} \tag{D8d}$$

$$\mu_i^* = \frac{\mu_i}{\sqrt{\varepsilon_i \sigma_i^3}} \tag{D8e}$$

$$\mu_{ij}^* = \sqrt{\mu_i^* \mu_j^*} \tag{D8f}$$

where μ^* is the reduced dipole moment.

The excess functions for molar volume, entropy, enthalpy and Helmholtz energy are obtained from classical thermodynamic derivations of the excess Gibbs energy (Eqs. (D9a–9d)).

$$V_m^{excess} = \left(\frac{\partial G_m^{excess}}{\partial P}\right)_T \tag{D9a}$$

$$S_m^{excess} = \left(\frac{\partial G_m^{excess}}{\partial T}\right)_P \tag{D9b}$$

$$H_m^{excess} = G_m^{excess} + T S_m^{excess} \tag{D9c}$$

$$A_m^{excess} = G_m^{excess} - P V_m^{excess} \tag{D9d}$$

These excess functions can be applied to mixtures of all fluid components included in the *FLUIDS* computer package. Pure fluid properties can be obtained from any of the EoSs mentioned in the text.

Table F2
Empirical constants for pure H_2S in Eqs. (F1) and (F2)

i	a	b (vap)	b (liq)
1	− 5.7856	1.1411	1.4933
2	− 9.4242	− 22.088	− 22.741
3	16.381	35.292	42.079
4	− 48.551	71.91	62.138
5	–	− 332.78	− 267.42
6	–	323.15	228.43
7	–	–	–
8	–	–	–
9	–	− 131.37	− 51.943

Appendix E. Thermodynamic properties of minerals and fluids

Heat capacity, entropy, enthalpy and Gibbs energy at 0.1 MPa (1 bar) and various temperatures of both pure minerals and pure fluids are calculated in the file *Thermo.CPP*. Heat-capacity functions, standard state Gibbs energy and enthalpy of formation from the elements, and entropy at standard-state conditions are taken from Robie et al. (1978) and Berman (1988). A general formula for heat capacity has been adopted in this study, which combines all formulations presented in literature:

$$C_P/\text{J K}^{-1}\ \text{mol}^{-1} = C_0 + \frac{C_1}{\sqrt{T}} + \frac{C_2}{T} + \frac{C_3}{T^2} + \frac{C_4}{T^3} + C_5\sqrt{T} + C_6 T + C_7 T^2 + C_8 T^3 \quad \text{(E1)}$$

Subsequently, entropy, enthalpy and Gibbs energy are obtained from the integration of this function according to classical thermodynamics.

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \quad \text{(E2a)}$$

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \quad \text{(E2b)}$$

$$G = H - TS \quad \text{(E2c)}$$

The effect of pressure on the volumetric properties of minerals is calculated with the equations of Berman (1988).

Appendix F. Vapour-saturated single-component liquids

The file *Saturation.CPP* calculates the liquid–vapour equilibrium of pure gases implemented in this computer package (Table F1). Calculations are based on purely empirical equations of fluid properties. Saturation pressure and densities (liquid or vapour) are calculated at selected temperatures, whereas a saturation temperature can be obtained from either a selected pressure or density. The saturation properties of pure H_2S are fitted to experimental data (West, 1948; Reamer et al., 1950), according to the equations:

$$\ln\left(\frac{P}{P_C}\right) = \sum_{i=1}^{4} a_i \left(1 - \frac{T}{T_C}\right)^i \quad \text{(F1)}$$

$$\ln\left(\frac{V}{V_C}\right) = \sum_{i=1}^{9} b_i \left(1 - \frac{T}{T_C}\right)^{i/3} \quad \text{(F2)}$$

where T_C, P_C and V_C are the critical temperature (373.539 K), critical pressure (9.00455 MPa) and critical molar volume (97.6998 $\text{cm}^3\ \text{mol}^{-1}$), respectively. Eq. (F2) is used for both the liquid and the vapour phases. The empirical constants a and b in Eqs. (F1) and (F2) are defined in Table F2.

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