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Package FLUIDS. Part 3: correlations between equations of state, thermodynamics and fluid inclusions

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ABSTRACT

The computer package FLUIDS (Bakker 2003) has been revised to calculate fluid properties in pores and inclusions. The programs are provided with a Graphical User Interface (GUI) and are adapted to new operating systems, including MacOS, Windows and Linux. The van der Waals equation of state has been added to the group *Loners* and is used to illustrate a large variety of calculation procedures for many thermodynamic parameters and properties. The mathematical transformations can be applied to any equation of state with the form $p(V,T,n)$, i.e. the pressure of a multi-component fluid is expressed as a function of volume, temperature and amount of substance. The fluid properties that are usually observed in microthermometric analyses of fluid inclusions, such as phase separation, phase coexistence and stability, can be predicted with these equations of state by using its spinodal and critical point calculations, in addition to fugacity calculations of liquid and vapour phases. The computer program *LonerW* can be freely downloaded from the website: http://fluids.unileoben.ac.at/Computer.html.

Key words: computer modelling, fluid inclusions, fluid properties, thermodynamics, van der Waals equation of state

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INTRODUCTION

The knowledge of the physical and chemical properties of fluids is of major interest in understanding a variety of geological processes, such as diagenesis, metamorphism, deformation, magmatism and ore formation. Most geological fluids mainly consist of water and two groups of components, i.e. gases (e.g. CO_2, N_2, CH_4) and salts (e.g. NaCl, KCl, $CaCl_2$). The properties of those fluids can be mathematically expressed in an equation of state that includes the relationship between intensive[1] thermodynamic parameters, such as temperature, pressure, composition and molar volume (e.g. Holloway 1977). Another type of equation of state uses purely empirical 'best-fit' polynomials with variables and constants that are indirectly related to these intensive variables (e.g. Driesner & Heinrich 2006).

Bakker (2003) presented the computer package FLUIDS to analyse fluid properties in pores and inclusions. This package includes a large variety of equations of state that can be individually analysed in the program group *Loners*. Several detailed examples of the application of these programs were presented by Bakker & Brown (2003). The full calculation potential of most equations of state to estimate fluid properties has received limited attention in the literature, and the validity of most equations of state is unknown. The group *Loners* allows researchers to perform mathematical experiments with equations of state that have been published since van der Waals (1873) presented one of the first equations that describes all phase states of fluids. The present study gives recent improvements in computer modelling of the group *Loners* (Bakker 2003). This group was originally designed with a rather inflexible SIOUX interface (Simple Input/Output User Exchange, Metrowerks Corporation), and is now provided with a Graphical User Interface (GUI, REALBasic 2007). The equation of state according to van der Waals (1873,

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[1] Intensive parameters are independent of the mass, size or shape of a phase.

abbreviated as *WeoS*) is selected to illustrate its calculation potential.

The number of published equations of state is immense (e.g. Bakker 2003 and references therein). The application of most equations of state is, however, limited because of three restrictions: (i) the limited experimental data that are used to design the mathematical equations; (ii) the type of mathematical formula (polynomials, hyperbolas, parabolas, exponentials, etc.); and (iii) the lack of a complete exploration of their calculation potential. The latter restriction (iii) has been disposed of with the development of unified equations of state based on Helmholtz energy functions. These equations of state have been developed for pure gases, such as H_2O (e.g. Haar *et al.* 1984) and CO_2 (Span & Wagner 1996), based on many measurable fundamental physical properties of molecules. These equations can be used to calculate a variety of fluid properties, including internal energy, entropy, heat capacity, enthalpy, Helmholtz energy, Gibbs energy, chemical potentials, fugacity, activity and pressure (see also Bakker 2003). The most common type of equation of state is expressed as a function for pressure that is defined by molar volume and temperature (Eqn 1).

$$p(T, V, n) \tag{1}$$

where p is pressure, T is temperature, V is total volume and n is the amount of substance (also known as moles). This function can be transformed to calculate all thermodynamic properties of fluid mixtures, as indicated above.

FROM EQUATION OF STATE TO THERMODYNAMIC PROPERTIES

The computer package FLUIDS (Bakker 2003) includes the group *Loners* that handles a large variety of individual equations of state. In the latest version, the equation of state of van der Waals (1873), *WeoS* (Eqn 2) has been added to this list and is selected to illustrate mathematical transformations to calculate thermodynamic properties of fluid mixtures.

$$p = \frac{RT}{v - b} - \frac{a}{v^2} \tag{2}$$

where p is pressure (in MPa), T is temperature (in Kelvin), v is the molar volume (in $\mathrm{cm^3\ mol^{-1}}$), R is the gas constant ($8.31451\ \mathrm{J\ mol^{-1}\ K^{-1}}$), a is a measure of the attractive forces between molecules and b is a measure of the volume of a molecule. Equation 2 can be reorganized in terms of total volume (V) and total amount of substance (n_T):

$$p = \frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{V^2} \tag{3}$$

The new set of programs in the group *Loners* uses the initials of authors of the published equation of state in the name of the program, instead of a number, which was used in the first version (Bakker 2003). The program that uses *WeoS* is named *LonerW* (Fig. 1). The mathematical transformations illustrated in this paper will be applied to all equations of state included in the group *Loners* from Bakker (2003). In theory, the *WeoS* can be applied to any gas phase; however, the program *LonerW* includes only the components H_2O, CO_2, CH_4, N_2, C_2H_6, H_2S, NH_3, H_2, O_2 and CO.

In fluid mixtures with multiple components, the parameters a and b are defined according to quadratic interpolation as derived from the virial theorem (Lorentz 1881) (Eqn 4) and the arithmetic average (van der Waals 1890) (Eqn 5), respectively.

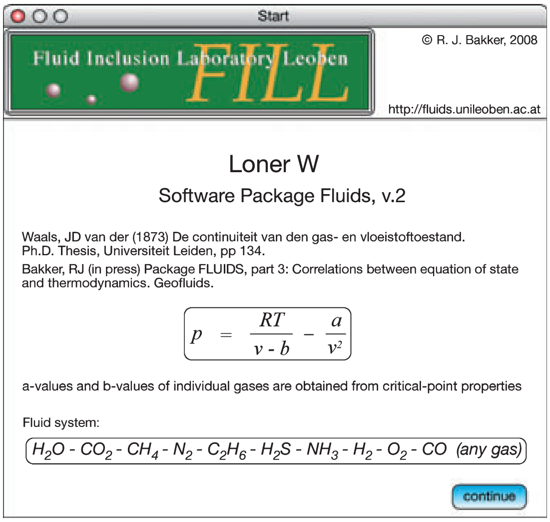
$$a = \sum_i \sum_j x_i x_j a_{ij} \tag{4a}$$

$$n_T^2 a = \sum_i \sum_j n_i n_j a_{ij} \tag{4b}$$

$$b = \sum_i x_i b_i \tag{5a}$$

$$n_T b = \sum_i n_i b_i \tag{5b}$$

where x is the amount-of-substance fraction (also known as *mole* fraction), and i and j are the number of components. These mixing rules have a major impact on the



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http://fluids.unileoben.ac.at

Loner W

Software Package Fluids, v.2

Waals, JD van der (1873) De continuiteit van den gas- en vloeistoftoestand. Ph.D. Thesis, Universiteit Leiden, pp 134.

Bakker, RJ (in press) Package FLUIDS, part 3: Correlations between equation of state and thermodynamics. Geofluids.

$$p = \frac{RT}{v - b} - \frac{a}{v^2}$$

a-values and b-values of individual gases are obtained from critical-point properties

Fluid system:

H_2O - CO_2 - CH_4 - N_2 - C_2H_6 - H_2S - NH_3 - H_2 - O_2 - CO (any gas)

Fig. 1. The 'Start' window of the program *LonerW*, indicating the equation of state that is used in this program (van der Waals 1873) and the components included in the fluid system.

expansion of phase equilibria and critical points of fluid mixtures in the pressure–temperature parameter space.

The program *LonerW* allows the calculation of a large variety of thermodynamic properties of fluid mixtures. The principal thermodynamic considerations are based on Maxwell's equations for thermodynamic variables (Eqn 6), which can be used to obtain the total internal energy (U) and entropy (S) from the *WeoS* (see also Prausnitz *et al.* 1986).

$$dS = \left(\frac{\partial p}{\partial T}\right)_{V,n_T} dV \tag{6a}$$

$$dU = \left[T\left(\frac{\partial p}{\partial T}\right)_{V,n_T} - p\right] dV \tag{6b}$$

The integration in Eqn (6a) at constant temperature results in a mathematical formulation for the entropy of gas mixtures if the boundary conditions for the integration are fixed (Eqn 7)

$$S_1 = S_0 + n_T R \ln\left(\frac{V_1 - n_T b}{V_0 - n_T b}\right) \tag{7}$$

where the subscripts '0' and '1' represent the lower and upper limit, respectively. A lower limit of $p_0 = 0$ leads to $V_0 = \infty$, and results in an undefined number for the entropy, so p_0 is generally defined at some positive low pressure, e.g. 1 bar (0.1 MPa) for a mixture of perfect gases. The *WeoS* (Eqn 3) has to be divided into a perfect gas part and a differential part, i.e. the pressure difference between a real gas mixture and a perfect gas mixture, to be able to apply this lower limit definition (Eqn 8)

$$p = p^{\text{perfect}} + \Delta p \tag{8a}$$

$$p = \frac{n_T RT}{V} + \left[\frac{n_T RT}{V - n_T b} - \frac{n_T^2 a}{V^2} - \frac{n_T RT}{V}\right] \tag{8b}$$

The use of Eqn (8) in the differentiation and subsequent integration in Eqn (6a) results in:

$$S_1 = S_0 + n_T R \ln\left(\frac{V_1}{V_0}\right) + n_T R \ln\left[\frac{(V_1 - n_T b)V_0}{(V_0 - n_T b)V_1}\right] \tag{9}$$

A mathematical simplification can be applied to Eqn (9) by assuming that the total volume of a perfect gas at the lower limit of integration is relatively large (Eqn 10).

$$\lim_{V_0 \to \infty}\left(\frac{V_0}{V_0 - n_T b}\right) = 1 \tag{10a}$$

$$S_1 = S_0 + n_T R \ln\left(\frac{V_1}{V_0}\right) + n_T R \ln\left(\frac{(V_1 - n_T b)}{V_1}\right) \tag{10b}$$

The mathematical accuracy of the approximation in Eqn (10a) is about 0.2% for gases at 0.1 MPa and 25°C. The part on the left-hand side in Eqn (10b) gives the change in entropy of a perfect gas. Expansion, or shrinkage from V_0 to V_1 corresponds to an entropy change according to Eqn (11):

$$\Delta S = n_T R \ln\left(\frac{V_1}{V_0}\right) \tag{11}$$

In a mixture of perfect gases, each gas expands from its partial volume ($n_i \cdot \bar{v}_i$, where $\bar{v}_i$ is the partial molar volume of component i in the mixture) to the total volume (V) at a total pressure of 1 bar (p_0) (Eqn 12)

$$\Delta_{\text{mix}} S = \sum_i \left[n_i R \ln\left(\frac{V}{n_i \bar{v}_i}\right)\right] = \sum_i \left[n_i R \ln\left(\frac{p_0 V}{n_i RT}\right)\right] \tag{12}$$

The total volume after expansion still represents a perfect gas mixture, which simplifies Eqn (12) to Eqn (13):

$$\Delta_{\text{mix}} S = \sum_i \left[n_i R \ln \frac{n_T}{n_i}\right] = -\sum_i [n_i R \ln x_i] \tag{13}$$

Finally, Eqn (10) can be replaced by Eqn (14) to express the entropy at any selected temperature and total volume according to the equation of state from van der Waals (1873).

$$S_1 = S_0 + n_T R \ln\left(\frac{V - n_T b}{V}\right) + \sum_i \left[n_i R \ln\left(\frac{p_0 V}{n_i RT}\right)\right] \tag{14}$$

where V_1 is replaced by V, which is the molar volume at the selected temperature. The corresponding pressure is obtained from Eqn (3). It should be noted that the pressure p_0 and the gas constant R must be expressed in compatible units, e.g. $p_0 = 0.1$ MPa and $R = 8.31451$ J mol^{-1} K^{-1}. The entropy of a mixture of perfect gases at the lower limit conditions (S_0) is defined according to the arithmetic average principle (Eqn 15).

$$S_0 = \sum_i n_i s_i^0 \tag{15}$$

where s_i^0 is the molar entropy of a pure component i as a perfect gas.

In conclusion, the entropy of fluid mixtures, and all other thermodynamic properties, at any selected temperature and pressure are calculated according to two procedures: (i) the integration at constant pressure (0.1 MPa) between 298.15 K and the selected temperature for perfect gases (*path 1* in Fig. 2); and (ii) the integration at this constant temperature from standard pressure to the pressure of interest (*path 2* in Fig. 2). *Path 1* is calculated using the heat capacity (C_p) of pure gases and standard-state properties (Eqn 16) (e.g. Robie *et al.* 1979) and *path 2* is obtained from the previously described procedure (see Eqns 7 to 14).

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T} \tag{16a}$$

$$\left(\frac{\partial H}{\partial T}\right)_p = C_p \tag{16b}$$

The heat capacity at constant pressure is usually expressed as a polynomial function of temperature (e.g. Bakker 2003).

The internal energy of a gas mixture is obtained from the integration of Eqn (6b) at a constant temperature:

$$\int_{U_0}^{U_1} \mathrm{d}U = \int_{V_0}^{V_1} \frac{n_T^2 a}{V^2} \mathrm{d}V \tag{17a}$$

$$U_1 = U_0 - \frac{n_T^2 a}{V_1} + \frac{n_T^2 a}{V_0} \tag{17b}$$

where the subscripts '0' and '1' refer to the lower and upper limit, respectively, of the integration. As in the entropy calculation (Eqn 9), a lower limit of 0.1 MPa is selected; the last term on the right-hand side in Eqn (17) can be neglected because it will approach 0 at high values of V_0 (Eqn 18).

$$U_1 = U_0 - \frac{n_T^2 a}{V} \tag{18}$$

The internal energy of a mixture of perfect gases at the lower limit of integration (U_0) is defined according to an equation similar to Eqn (15). The enthalpy (H) can be directly obtained from the sum of the internal energy and the product of pressure and total volume according to Eqn (19):

$$H = U + PV \tag{19a}$$

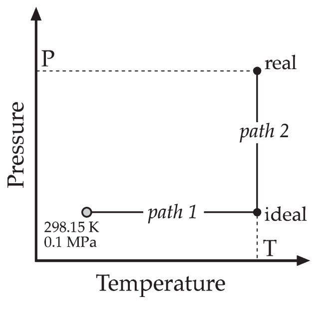


Fig. 2. Schematical temperature–pressure diagram illustrating the perfect gas mixture calculation procedure along *path 1*, i.e. from standard conditions 298.15 K and 0.1 MPa to ideal. *path 2* reflects the calculation procedure from an ideal gas mixture to a real gas mixture (*real*) at the selected temperature and pressure conditions.

$$H_1 = U_0 + \frac{n_T RTV}{V - n_T b} - \frac{2n_T^2 a}{V} \tag{19b}$$

HELMHOLTZ ENERGY, GIBBS ENERGY, CHEMICAL POTENTIAL AND FUGACITY

The Helmholtz energy can be calculated from Eqn (20) in combining the internal energy and entropy, or by direct integration of the pressure in Eqn (3) in terms of total volume according to Eqn (20b).

$$A = U - TS \tag{20a}$$

$$-p = \left(\frac{\partial A}{\partial V}\right)_{T,n_T} \tag{20b}$$

Both approaches result in Eqn (21), which will play a major role in phase-equilibria calculations in this study.

$$\begin{aligned} A_1 = {} & U_0 - TS_0 - \frac{n_T^2 a}{V} - n_T RT \ln\left(\frac{V - n_T b}{V}\right) \\ & - RT \sum_i \left[n_i \ln\left(\frac{V}{n_i RT}\right)\right] \end{aligned} \tag{21}$$

The Gibbs energy is calculated in a similar procedure according to its definition (Eqn 22):

$$G = U + PV - TS \tag{22a}$$

$$\begin{aligned} G_1 = {} & U_0 - TS_0 - \frac{2n_T^2 a}{V} - n_T RT \ln\left(\frac{V - n_T b}{V}\right) \\ & + \frac{n_T RTV}{V - n_T b} - RT \sum_i \left[n_i \ln\left(\frac{V}{n_i RT}\right)\right] \end{aligned} \tag{22b}$$

The chemical potential (μ) of a specific component in a gas mixture is obtained from the partial derivative of the Helmholtz energy (Eqn 21) with respect to the amount of substance of this component (n_i) (Eqn 23).

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j} \tag{23a}$$

$$\begin{aligned} \mu_i = {} & \frac{-1}{V} \sum_j 2n_j a_{ij} - RT \ln\left(\frac{V - n_T b}{V}\right) \\ & + n_T RT \left(\frac{b_i}{V - n_T b}\right) - RT \ln\left(\frac{V}{n_i RT}\right) \\ & + RT + u_i^0 - Ts_i^0 \end{aligned} \tag{23b}$$

The fugacity (f) is directly obtained from the chemical potentials (Eqn 23) according to its definition:

$$RT \ln\left(\frac{f_i}{f_i^0}\right) = \mu_i - \mu_i^0 \tag{24a}$$

$$\begin{aligned} RT\ln\left(\frac{f_i}{x_i p}\right) &= \frac{-1}{V}\sum_j 2n_j a_{ij} \\ &\quad - RT\ln\left(\frac{V-n_T b}{V}\right) + n_T RT\left(\frac{b_i}{V-n_T b}\right) \\ &\quad - RT\ln\left(\frac{V x_i p}{n_i RT}\right) \end{aligned} \tag{24b}$$

where μ_i^0 and f_i^0 are the chemical potential and fugacity, respectively, of component i at standard conditions (0.1 MPa). It should be noted that the fugacity definition no longer includes the mathematical approximation for the lower limit of integration that was used in Eqns (9) and (17). Subsequently, the fugacity coefficient (φ) is defined according to Eqn (25).

$$\varphi_i = \frac{f_i}{x_i p} \tag{25a}$$

$$\begin{aligned} RT\ln(\varphi_i) &= \frac{-1}{V}\sum_j 2n_j a_{ij} - RT\ln\left(\frac{V-n_T b}{V}\right) \\ &\quad + n_T RT\left(\frac{b_i}{V-n_T b}\right) - RT\ln\left(\frac{pV}{n_T RT}\right) \end{aligned} \tag{25b}$$

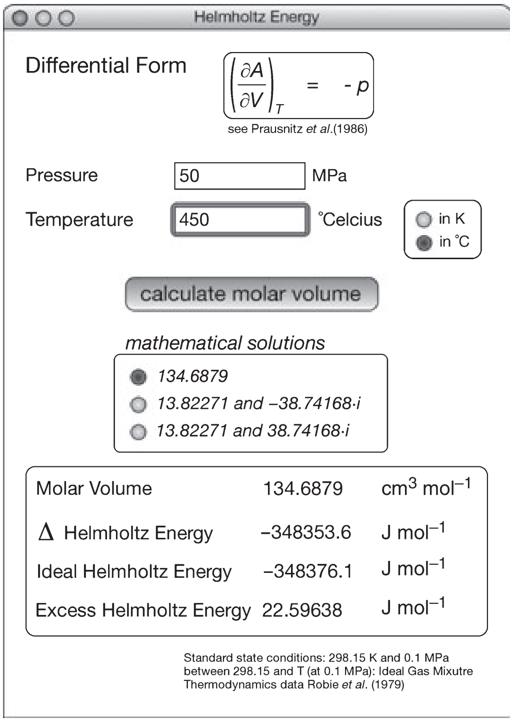
An example of the program *LonerW* to calculate Helmholtz energy of a fluid mixture with $x(CO_2) = 0.5$, $x(CH_4) = 0.3$ and $x(N_2) = 0.2$ at 450°C and 50 MPa is illustrated in Fig. 3. From the given temperature/pressure values the program calculates three possible molar volumes, of which two are a conjugate set of complex numbers. At lower temperatures and pressures (below critical conditions) the mathematical solution may include three real numbers. In the example (Fig. 3), the real number must be selected to calculate the Helmholtz energy. The Helmholtz energy is given as a number relative to standard conditions (indicated with the symbol Δ). Furthermore, the program calculates the Helmholtz energy of an ideal mixture, and the excess energy of a real mixture, according to Eqn (26).

$$A_m(T, V, x_i, x_j, \cdots) = A_{ideal} + A_{excess} \tag{26a}$$

$$A_{ideal} = \sum_i x_i A_i^{pure} + RT\sum_i x_i \ln x_i \tag{26b}$$

where A_m is the molar Helmholtz energy.

Using the same fluid composition to calculate thermodynamic properties at lower temperatures and pressures, e.g. −52°C and 5 MPa, respectively, results in three real mathematical solutions for the molar volume at 89.08, 148.63 and 172.12 $cm^3\ mol^{-1}$, respectively. In other words, at these conditions the fluid exists in the liquid, intermediate and vapour phase, respectively. Either the liquid or the vapour phase can be selected to obtain its corresponding thermodynamic properties.



Differential Form $\left(\frac{\partial A}{\partial V}\right)_T = -p$
see Prausnitz *et al.*(1986)

Pressure 50 MPa
Temperature 450 °Celcius
○ in K
● in °C

mathematical solutions
● *134.6879*
○ *13.82271 and −38.74168·i*
○ *13.82271 and 38.74168·i*

Molar Volume	134.6879	$cm^3\ mol^{-1}$
Δ Helmholtz Energy	−348353.6	$J\ mol^{-1}$
Ideal Helmholtz Energy	−348376.1	$J\ mol^{-1}$
Excess Helmholtz Energy	22.59638	$J\ mol^{-1}$

Standard state conditions: 298.15 K and 0.1 MPa
between 298.15 and T (at 0.1 MPa): Ideal Gas Mixutre
Thermodynamics data Robie *et al.* (1979)

Fig. 3. The calculation procedure *Helmholtz Energy* window of the program *LonerW*. See text for further details.

ACTIVITY

The activity of components in a mixture is defined according to Lewis & Randall (1923), i.e. the ratio of the fugacity of a component and its fugacity in an arbitrary standard state. Consequently, the activity number is dimensionless and depends on which standard state is selected. A commonly selected standard state condition is the fugacity of pure components of the mixture at the same temperature and pressure conditions (e.g. Nordstrom & Munoz 1985; Spear 1995). Figure 4A shows a plot of the activity of H_2O and CO_2 in a variety of mixtures at 500°C and 3000 MPa, according to the *WeoS*, calculated with the program *LonerW*. This diagram illustrates the near-ideal behaviour of solvents and the Henry law behaviour of solutes in dilute solutions. Alternatively, the fugacity of the real gases at the same temperature and a pressure of 0.1 MPa can be selected as standard conditions, which results in completely different numbers for the activities of H_2O and CO_2. (Fig. 4B).

SPINODAL

The Helmholtz energy and the Gibbs energy functions are described by three independent parameters, i.e. n–T–V and n–T–p, respectively. The curvature of these functions in two-, three- or multi-dimensional parameter space (e.g.

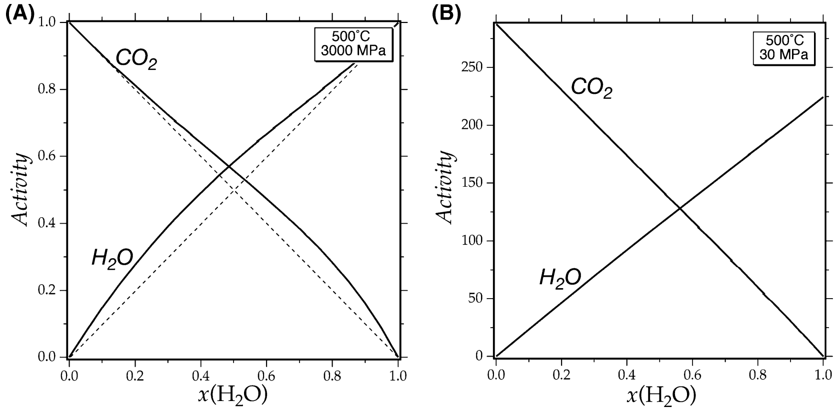


Fig. 4. Activity–composition diagrams for binary H_2O-CO_2 fluid mixtures, at 500°C–3000 MPa (A) and 500°C–30 MPa (B). The dashed diagonal lines in (A) represent ideal mixing behaviour.

van der Waals 1890; van Laar 1905) is used to determine the conditions for phase coexistence, stability and criticality of fluid mixtures. These are the fluid properties that are often observed in fluid inclusion studies during microthermometrical measurements.

Phase separation, e.g. the formation of a bubble in a homogeneous fluid, usually does not occur at the binodal (i.e. the dew and bubble curve; see Diamond 2003), but at conditions inside the stability limits of the fluid mixture. The stability limits are defined by the spinodal line, i.e. the locus of points on the surface of Helmholtz-energy or Gibbs-energy functions that are inflection points (e.g. Levelt-Sengers 2002 and reference therein). In binary fluid mixtures, these conditions are defined by Eqn (27) (see also van Laar 1905).

$$\left(\frac{\partial^2 A_{\mathrm{m}}}{\partial x^2}\right)_v \cdot \left(\frac{\partial^2 A_{\mathrm{m}}}{\partial v^2}\right)_x - \left(\frac{\partial^2 A_{\mathrm{m}}}{\partial x \partial v}\right)^2 = 0 \tag{27a}$$

$$\left(\frac{\partial^2 G_{\mathrm{m}}}{\partial x^2}\right)_{T,p} = 0 \tag{27b}$$

where the subscript ‘m’ refers to molar parameters, x is the mole fraction of one of the two components. In multicomponent fluid systems, non-molar parameters are generally used in addition to the amount of substance (n), instead of fractions. The partial derivatives of the Helmholtz energy with respect to volume and amount of substance of each component can be arranged in a matrix that has a determinant (D_{spin}) equal to zero (Eqn 28) at spinodal conditions.

$$D_{\mathrm{spin}} = \begin{vmatrix} A_{VV} & A_{n_1V} & A_{n_2V} & \cdots \\ A_{Vn_1} & A_{n_1n_1} & A_{n_2n_1} & \cdots \\ A_{Vn_2} & A_{n_1n_2} & A_{n_2n_2} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \tag{28}$$

The individual components of this matrix are defined according to Eqn (29), and are directly obtained from differentiation of Eqn (21). The exact formulations of partial derivatives obtained from the *WeoS* are given in the Appendix.

$$A_{VV} = \left(\frac{\partial^2 A}{\partial V^2}\right)_{n_1 n_2 \cdots} \tag{29a}$$

$$A_{n_1 n_1} = \left(\frac{\partial^2 A}{\partial n_1^2}\right)_{V n_2 \cdots} \tag{29b}$$

$$A_{n_2 n_2} = \left(\frac{\partial^2 A}{\partial n_2^2}\right)_{V n_1 \cdots} \tag{29c}$$

$$A_{n_1 V} = \left(\frac{\partial^2 A}{\partial n_1 \partial V}\right)_{n_2 \cdots} = A_{V n_1} \tag{29d}$$

$$A_{n_2 V} = \left(\frac{\partial^2 A}{\partial n_2 \partial V}\right)_{n_1 \cdots} = A_{V n_2} \tag{29e}$$

$$A_{n_1 n_2} = \left(\frac{\partial^2 A}{\partial n_1 \partial n_2}\right)_{V \cdots} = A_{n_2 n_1} \tag{29f}$$

The size of the matrix depends on the number of components in the fluid system. The matrix is square and contains q columns, where q is the number of differentiation variables, i.e. volume and number of components minus 1. It should be noted that in a pure system only the A_{VV} term remains in the matrix. In binary and ternary fluid mixtures, the spinodal is defined by Eqn (30a) and (30b), respectively.

$$A_{VV} \cdot A_{n_1 n_1} - (A_{n_1 V})^2 = 0 \tag{30a}$$

$$\begin{aligned} A_{VV} \cdot A_{n_1 n_1} \cdot A_{n_2 n_2} - A_{n_1 n_1} \cdot (A_{n_2 V})^2 \\ + A_{n_1 V} \cdot A_{n_1 n_2} \cdot A_{n_2 V} - A_{VV} \cdot (A_{n_1 n_2})^2 \\ + A_{n_2 V} \cdot A_{n_1 V} \cdot A_{n_1 n_2} - A_{n_2 n_2} \cdot (A_{n_1 V})^2 = 0 \end{aligned} \tag{30b}$$

The calculation of the determinant from Eqn (28) using the Laplacian expansion with *minors* and *cofactors* (e.g.

Beyer 1991) consumes increasing amounts of computation time as more components are involved in the fluid mixture. Therefore, the LU decomposition (e.g. Horn & Johnson 1985) has been used in the program *LonerW*.

Figure 5 illustrates the spinodal of a binary H_2O–CO_2 fluid mixture with $x(CO_2) = 0.1$ calculated with *WeoS*. The spinodal has a small loop near the critical point of this fluid mixture and it clearly differs from the binodal, which is also known as the dew curve and the bubble curve. The spinodal extends into that part of the diagram which has negative pressures, whereas the binodal remains within the positive pressure part.

CRITICAL POINT

The critical point, also known as the plait point (see e.g. Korteweg 1903) marks the highest temperature and pressure that boiling can occur in a pure system. Beyond the critical point, i.e. at higher temperatures and pressures, the fluid is in a homogeneous supercritical state. Every fluid mixture with a specific composition has a critical point. In binary mixtures, the critical points of all possible compositions can be represented by a critical curve or locus of critical points. The critical point can be obtained from the Helmholtz energy function (e.g. Baker & Luks 1980; van Konynenburg & Scott 1980), and it marks that part of this surface where the two inflexion points of the spinodal coincide (see previous paragraph). Therefore, the conditions for the spinodal calculation (Eqn 28) are also applied to the critical point. In addition, the critical curve of multi-component fluid mixtures is also defined by the determinant (D_{crit}) of the following matrix:

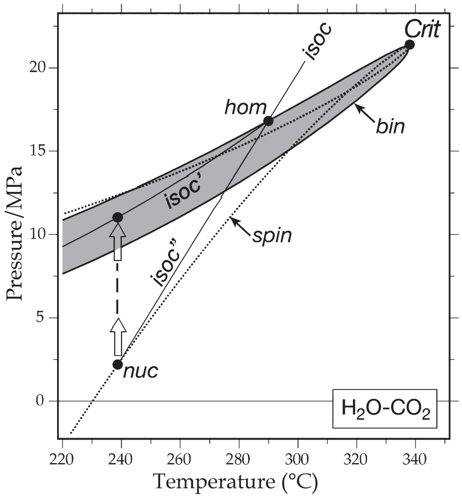


Fig. 5. Temperature–pressure diagram of a binary fluid mixture of H_2O and CO_2 with $x(CO_2) = 0.1$, calculated according to van der Waals (1873). The dashed curve is the spinodal (*spin*), the shaded area are *T–p* conditions of immiscibility, which is limited by the isopleth (*bin*, i.e. dew curve, critical point and bubble curve). The isochore 60.8013 $cm^3 \, mol^{-1}$ is illustrated (*isoc*) that crosses the isopleth at *hom* (homogenization conditions). The metastable extension of this isochore towards the spinodal is illustrated with *isoc''*. *nuc* is the intersection of *isoc''* and the spinodal and reflects the minimum nucleation temperature of a vapour bubble in the fluid inclusion. *isoc''* is the stable continuation of *isoc* in the two-phase field.

$$D_{\mathrm{crit}} = \begin{vmatrix} A_{VV} & A_{n_1 V} & A_{n_2 V} & \cdots \\ A_{V n_1} & A_{n_1 n_1} & A_{n_2 n_1} & \cdots \\ \vdots & \vdots & \vdots & \vdots \\ D_V & D_{n_1} & D_{n_2} & \ddots \end{vmatrix} = 0 \qquad (31)$$

The matrix in Eqn (31) is square and contains q columns, where q is the number of differentiation variables, i.e. volume and number of components minus 1 (c.f. Eqn 28). The number of rows is defined according to the differentiation variables volume and number of components minus 2, and the last row is reserved for the partial derivatives of the determinant D_{spin} from Eqn (28):

$$D_V = \left(\frac{\partial D_{\mathrm{spin}}}{\partial V} \right) \qquad (32a)$$

$$D_{n_1} = \left(\frac{\partial D_{\mathrm{spin}}}{\partial n_1} \right) \qquad (32b)$$

$$D_{n_2} = \left(\frac{\partial D_{\mathrm{spin}}}{\partial n_2} \right) \qquad (32c)$$

The derivatives of the spinodal determinant (see also Baker & Luks 1980) are calculated from the sum of the element-by-element products of the matrix of cofactors (or adjoint matrix) of the spinodal (Eqn 33) and the matrix of third derivatives of the Helmholtz energy function (Eqn 34).

$$\begin{vmatrix} C_{VV} & C_{n_1 V} & C_{n_2 V} & \cdots \\ C_{V n_1} & C_{n_1 n_1} & C_{n_2 n_1} & \cdots \\ C_{V n_2} & C_{n_1 n_2} & C_{n_2 n_2} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \qquad (33)$$

where C_{xy} are the individual elements in the matrix of cofactors, as obtained from the Laplacian expansion.

$$\begin{vmatrix} A_{VVK} & A_{n_1 VK} & A_{n_2 VK} & \cdots \\ A_{V n_1 K} & A_{n_1 n_1 K} & A_{n_2 n_1 K} & \cdots \\ A_{V n_2 K} & A_{n_1 n_2 K} & A_{n_2 n_2 K} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \qquad (34)$$

where the subscript K refers to the variable that is used in the third differentiation, i.e. volume and amount of substance of the components 1 and 2, as indicated in Eqn (32a), (32b) and (32c), respectively. For example, in unary and binary fluid systems, the determinant of Eqn (31) is given by Eqn (35a) and (35b), respectively.

$$A_{VVV} = 0 \tag{35a}$$

$$\begin{aligned} &-(A_{n_1n_1} \cdot A_{n_1V}) \cdot A_{VVV} + \left(A_{n_1n_1} \cdot A_{VV} + 2A^2_{n_1V}\right) \cdot A_{n_1VV} \\ &- 3 \cdot (A_{n_1V} \cdot A_{VV}) \cdot A_{n_1n_1V} + \left(A^2_{VV}\right) \cdot A_{n_1n_1n_1} = 0 \end{aligned} \tag{35b}$$

As with Eqn (28), to reduce computation time in the program *LonerW*, the LU decomposition has been used to calculate the determinant in Eqn (31). In conclusion, the two determinants given in Eqns (28) and (31) are used to calculate the critical point of any fluid mixture. However, the computation time is significantly increased for mixtures containing more than seven components.

The example in Fig. 5 illustrates the critical point of a fluid mixture of $x(CO_2) = 0.1$ and $x(H_2O) = 0.9$ at 338.085°C and 21.39 MPa with a molar volume of 90.2345 cm^3 mol^{-1}, as obtained from the *WeoS*. This point is located on both the spinodal (obtained from Eqn 28) and the binodal, i.e. the boundary T–p conditions of phase separation.

PSEUDO-CRITICAL POINT

The pseudo-critical conditions are defined according to a different concept to the critical point (see previous paragraph) and are directly obtained from the mathematical equation that defines pressure (Eqn 3):

$$\left(\frac{\partial p}{\partial V}\right)_{T,n} = 0 \tag{36a}$$

$$\left(\frac{\partial^2 p}{\partial V^2}\right)_{T,n} = 0 \tag{36b}$$

In pure systems, the pseudo-critical conditions are equal to the critical point calculation described in the previous section (Eqns 28 to 35). In fluid mixtures, the pseudo-critical point always underestimates the true critical point in temperature and pressure. These conditions have been used in literature to relate directly the true critical point conditions to the a and b parameter in Eqn (3), and they are the principles of the corresponding state theory (e.g. van der Waals 1880; Pitzer 1939).

$$v_{pc} = 3b \tag{37a}$$

$$p_{pc} = \frac{a}{27b^2} \tag{37b}$$

$$T_{pc} = \frac{8a}{27bR} \tag{37c}$$

Alternatively, the a and b parameters can be replaced by the critical values of pure systems (Eqn 38).

$$a = \frac{27}{64} \cdot \frac{R^2 T_c^2}{p_c} \tag{38a}$$

$$b = \frac{1}{8} \cdot \frac{RT_c}{p_c} \tag{38b}$$

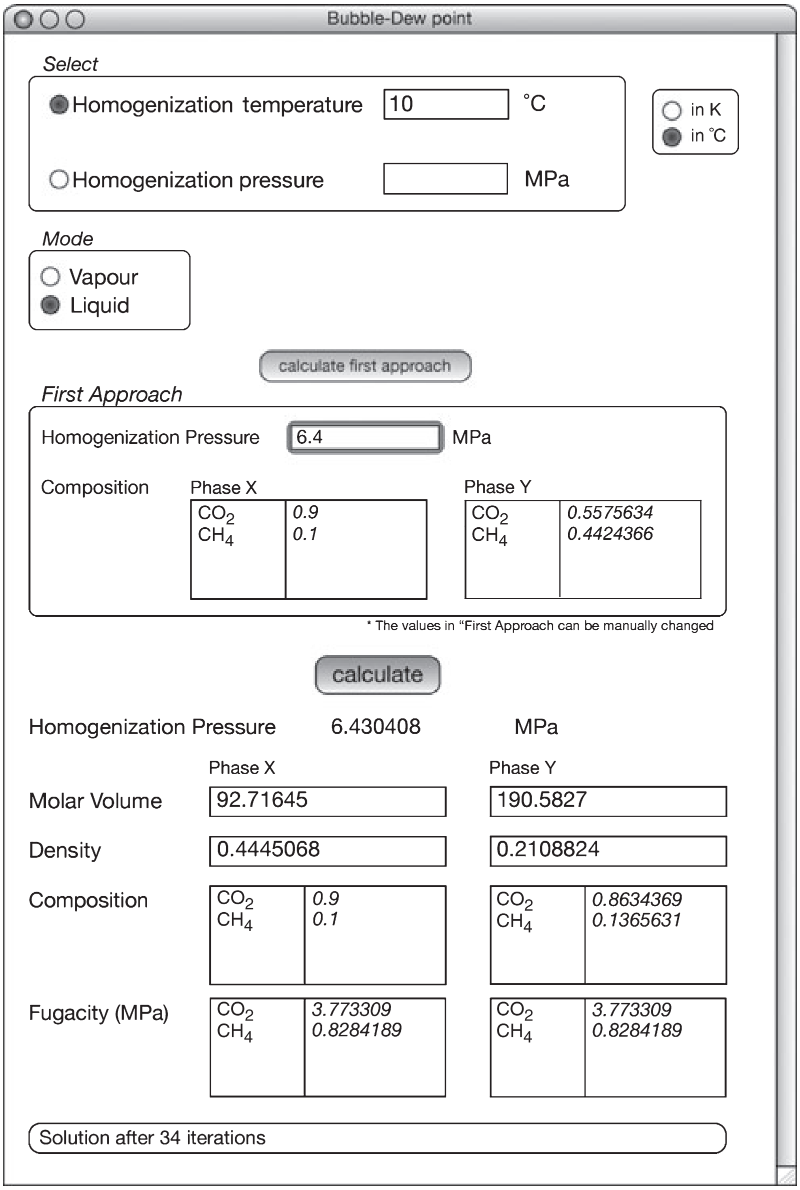
The true critical molar volume of pure systems is not included in the calculations in Eqn (36). In general, the mathematically obtained critical molar volume differs significantly from the measured critical molar volume, which illustrates the deficits in the mathematical formulation of this equation of state at near critical conditions. For example, the critical conditions of pure CO_2 are 30.978°C, 7.3773 MPa and 94.118 cm^3 mol^{-1} (Span & Wagner 1996). A critical molar volume of 128.536 cm^3 mol^{-1} is calculated from the critical temperature and pressure according to Eqns (37) and (38).

HOMOGENIZATION CONDITIONS

Microthermometry is of major importance for the analyses of fluid inclusions. The homogenization conditions of liquid and vapour phases, also known as bubble point and dew point, in the inclusions can be directly used to calculate bulk-fluid densities and to define isochores and trapping conditions (e.g. Shepherd *et al.* 1985). Each equation of state can be used to perform these calculations; however, most equations have not been designed for these types of analyses. Thermodynamically, and for calculation, homogenization is defined as the point at which the fugacities of each component in both phases are equal (e.g. Prausnitz *et al.* 1980; Bakker 2003) (Eqn 39).

$$f_i^{\text{vap}} = f_i^{\text{liq}} \tag{39}$$

The fugacities in both phases are calculated with the same equation of state, according to Eqns (24) and (25). At equilibrium conditions, temperature and pressure of both phases are equal, whereas the molar volume of the liquid phase is clearly different from that of the vapour phase. The program *LonerW* allows the calculation of homogenization conditions (Fig. 6) with *WeoS*. Usually, homogenization temperatures are measured, which can be input directly in the procedure window *Bubble-Dew Point* (Fig. 6). In addition, homogenization pressure can also be input for experimental mathematical analyses. Fluid inclusions may homogenize into the liquid phase (at the bubble curve) or in to the vapour phase (at the dew curve), which has to be specified in the program, i.e. the *mode* of homogenization (Fig. 6). Critical homogenization is best analysed by selecting the calculation procedure *Critical Point*. The next step in the procedure is to calculate a *first approach*, because the complexity of mathematical model-



Select

● Homogenization temperature 10 °C

○ Homogenization pressure MPa

○ in K
● in °C

Mode

○ Vapour
● Liquid

First Approach

Homogenization Pressure 6.4 MPa

Composition

Phase X		Phase Y	
CO_2	*0.9*	CO_2	*0.5575634*
CH_4	*0.1*	CH_4	*0.4424366*

* The values in "First Approach can be manually changed

Homogenization Pressure 6.430408 MPa

	Phase X		Phase Y	
Molar Volume	92.71645		190.5827	
Density	0.4445068		0.2108824	
Composition	CO_2 CH_4	*0.9* *0.1*	CO_2 CH_4	*0.8634369* *0.1365631*
Fugacity (MPa)	CO_2 CH_4	*3.773309* *0.8284189*	CO_2 CH_4	*3.773309* *0.8284189*

Solution after 34 iterations

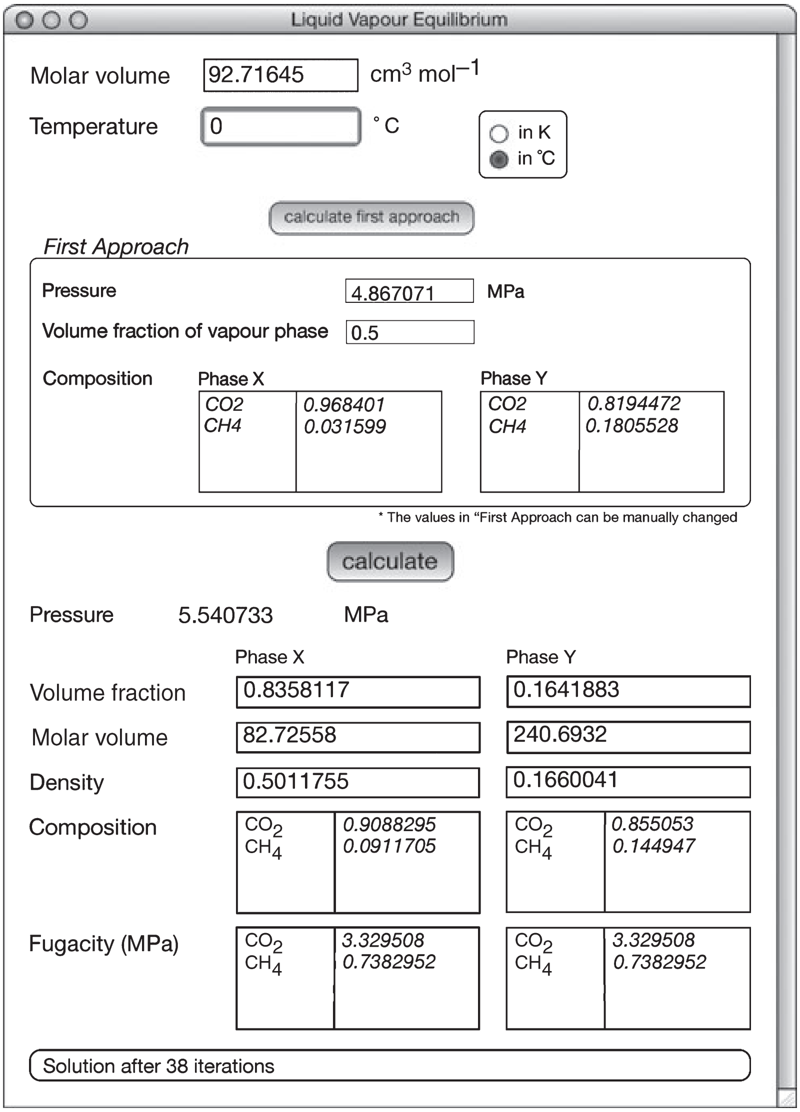
Fig. 6. The calculation procedure *Bubble-Dew Point* from the program *LonerW*, to calculate homogenization conditions of a binary CO_2–CH_4 fluid mixture with the bulk $x(CO_2) = 0.9$. See text for further details.

ling does not allow a simple straightforward solution. It is necessary to introduce a first *guess* close to the homogenization conditions. The *first approach* calculates phase equilibrium conditions according to Raoult's law (e.g. Prausnitz *et al.* 1986). The saturation pressure of individual gases above their critical point is arbitrarily defined along the critical isochore to allow application of Raoult's law at higher temperatures. The *first guess* of the homogenization pressure is calculated from the arithmetic average of saturation pressures of all gases (c.f. Eqn 5) in the mixture. Calculated amount-of-substances fractions of all components are then normalized to a sum of 1. This *first approach* can be directly used to calculate the phase equilibrium at homogenization conditions (the button *calculate* in Fig. 6). The results of the calculations are given in two columns, i.e. one for *phase X* (liquid) and the other for *phase Υ* (vapour), with its fluid properties (molar volume, density, composition and fugacity). Occasionally, the program may give a *trivial* solution, which is illustrated by near-equal fluid properties of both phases, that does not correspond to critical conditions. It is illustrated with a warning at the bottom line (Fig. 6). After a *trivial* solution, the numbers for pressure or composition in the *first approach* have to be changed, and, subsequently, the calculation has to be repeated. At a true mathematical solution, the program indicates the amount of performed iterations before the solution was estimated, and molar volume, density and composition of both phases must be distinctively different, whereas the fugacities of the components in both phases are equal. At near-critical conditions, it is common for the calculation to reach a *trivial* solution, and the *first approach* has to be very close to the real solution. In addition, the procedure *Critical Point* can be used to estimate those near-critical conditions that have to be introduced in the *first approach*.

All possible homogenization conditions of a binary H_2O–CO_2 fluid mixture with $x(CO_2) = 0.1$, also known is an *isopleth* are illustrated in Fig. 5. Within the shaded envelope, indicated with *bin* (Fig. 5), this fluid is unmixed in coexisting vapour and liquid phases. The figure shows an isochore calculated for a homogeneous mixture with a molar volume of 60.8013 $cm^3\ mol^{-1}$. An inclusion with these liquid-like fluid properties must nucleate a vapour bubble (phase separation) on entering into the envelope at 290°C (*hom* in Fig. 5). However, nucleation can be inhibited before the spinodal curve is intersected by this isochore. Consequently, the fluid inclusion can cool along this isochore down to 238.78°C and 2.183 MPa (*nuc* in Fig. 5) without the formation of a vapour bubble. At nucleation, the fluid system changes abruptly into a stable phase assemblage, at higher pressures (11.029 MPa) and within the isopleth.

LIQUID–VAPOUR EQUILIBRIA

Fluid inclusions, which contain a vapour bubble in a liquid phase, are thermodynamically considered at liquid–vapour equilibrium conditions. The properties of both phases are calculated according the fugacity equalities from Eqn (39) in the procedure *Liquid-Vapour Equilibrium* in the program *LonerW* (Fig. 7). The fluid properties of inclusions with known bulk composition and molar volume (density), as obtained from e.g. homogenization conditions from the procedure *Bubble-Dew Point* (see previous paragraph), can be calculated below their homogenization conditions. The



Molar volume 92.71645 $cm^3\ mol^{-1}$

Temperature 0 °C

○ in K
● in °C

First Approach

Pressure 4.867071 MPa

Volume fraction of vapour phase 0.5

Composition

	Phase X	Phase Y
CO2	0.968401	0.8194472
CH4	0.031599	0.1805528

* The values in "First Approach can be manually changed

Pressure 5.540733 MPa

	Phase X	Phase Y
Volume fraction	0.8358117	0.1641883
Molar volume	82.72558	240.6932
Density	0.5011755	0.1660041
Composition CO_2	0.9088295	0.855053
Composition CH_4	0.0911705	0.144947
Fugacity (MPa) CO_2	3.329508	3.329508
Fugacity (MPa) CH_4	0.7382952	0.7382952

Solution after 38 iterations

Fig. 7. The calculation procedure *Liquid-Vapour Equilibrium* from the program *LonerW*, to calculate the properties of coexisting liquid and vapour phase at 0°C, the bulk fluid (i.e. of a homogeneous fluid) is a binary CO_2–CH_4 mixture with $x(CO_2) = 0.9$ and a molar volume of 92.71645 $cm^3\ mol^{-1}$. See text for further details.

program calculates volume fractions of the coexisting phases, in addition to molar volume, density, composition and fugacity of the liquid and vapour phase at equilibrium conditions (Fig. 7). Consequently, the program permits the calculation of the continuation of *bulk* isochores of fluid mixtures in inclusions below homogenization conditions. Similar to the procedure *Bubble-Dew Point*, the calculations have to start with a *first approach* (Fig. 7), in which pressure, volume fractions and composition can be manually varied to obtain a mathematical solution.

Figure 5 illustrates the isochore calculated with *LonerW* within the phase-separation field (*isoc′* in Fig. 5) of the $x(CO_2) = 0.1$, $H_2O–CO_2$ fluid mixture, which ends at the bubble curve (homogenization conditions). Per definition, this isochore cannot be traced outside this field of immiscibility towards lower temperatures. Along this curve, the volume fraction of the vapour bubble and the properties of both liquid and vapour phase vary with decreasing temperature. For example, the volume fraction of the vapour bubble is 0.214 at the nucleation temperature 238.78°C and 11.029 MPa (Fig. 5). The fluid properties of the vapour are 268.94 $cm^3\ mol^{-1}$ and $x(CO_2) = 0.2222$, and those of the liquid are 50.22 $cm^3\ mol^{-1}$ and $x(CO_2) = 0.0668$.

CONCLUSIONS

The program group *Loners* from the computer package FLUIDS (Bakker 2003) have been revised and furnished with a new user interface (Graphical User Interface, REALBasic 2007). The equation of state according to van der Waals (1873) has been added to the list of programs in the *Loners* group with the name *LonerW*. This equation of state is used to illustrate all possible calculation procedures to obtain thermodynamic properties of fluid mixtures, including: (i) molar volume; (ii) pressure; (iii) temperature; (iv) fugacity; (v) activity; (vi) homogenization conditions; (vii) liquid–vapour equilibrium; (viii) spinodal; (ix) critical point; (x) internal energy; (xi) enthalpy; (xii) entropy; (xiii) Helmholtz energy; (xiv) Gibbs energy; (xv) chemical potentials. This type of revision will be applied to all the equations of state included in the group *Loners*.

Experimental mathematical calculations can be performed with the program *LonerW* to obtain the fluid properties of hypothetical systems. It can also be used to interpret microthermometric data from fluid inclusions and to interpret general pore fluid properties. The validity of this equation of state can be tested by direct comparison with experimental data for many thermodynamic parameters.

The program has been compiled for three different computer operating systems: Mac Os X (PowerPC and Intel), Microsoft Windows (2000, XP and Vista), and Linux (GTK+ 2.x), and it can be downloaded from the website: http://fluids.unileoben.ac.at/Computer.html

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APPENDIX

The partial derivatives of the Helmholtz energy in respect to total volume and amount of substance, as obtained from the *WeoS*.

$$A_V = \left(\frac{\partial A}{\partial V}\right)_{n_i,n_j,\ldots} = \frac{n_T^2 a}{V^2} - \frac{n_T RT}{V - n_T b} = -p \tag{A1}$$

$$\begin{aligned} A_{n_i} = \left(\frac{\partial A}{\partial n_i}\right)_{V,n_j} &= (u_i^0 - Ts_i^0) - \frac{2}{V}\sum_j n_j a_{ij} - RT\ln\left(\frac{V - n_T b}{V}\right) \\ &\quad + n_T RT\frac{b_i}{V - n_T b} - RT\left[\ln\left(\frac{V}{n_i RT}\right) - 1\right] \\ &= \mu_i \end{aligned} \tag{A2}$$

$$A_{VV} = \left(\frac{\partial^2 A}{\partial V^2}\right)_{n_i,n_j\ldots} = -2\frac{n_T^2 a}{V^3} + \frac{n_T RT}{(V - n_T b)^2} \tag{A3}$$

$$\begin{aligned} A_{n_i n_i} = \left(\frac{\partial^2 A}{\partial n_i^2}\right)_{V,n_j} &= -\frac{2}{V}a_{ii} + 2RT\frac{b_i}{V - n_T b} \\ &\quad + n_T RT\frac{b_i^2}{(V - n_T b)^2} + \frac{RT}{n_i} \end{aligned} \tag{A4}$$

$$\begin{aligned} A_{n_i n_j} = \left(\frac{\partial^2 A}{\partial n_i n_j}\right)_V &= -\frac{2}{V}a_{ij} + RT\frac{(b_i + b_j)}{V - n_T b} \\ &\quad + n_T RT\frac{b_i b_j}{(V - n_T b)^2} \end{aligned} \tag{A5}$$

$$\begin{aligned} A_{Vn_i} = \left(\frac{\partial^2 A}{\partial V \partial n_i}\right)_{n_j} &= \frac{2}{V^2}\sum_j n_j a_{ij} - \frac{RT}{V - n_T b} \\ &\quad - n_T RT\frac{b_i}{(V - n_T b)^2} \end{aligned} \tag{A6}$$

$$A_{VVV} = \left(\frac{\partial^3 A}{\partial V^3}\right)_n = 6\frac{n_T^2 a}{V^4} - 2n_T RT\frac{1}{(V - n_T b)^3} \tag{A7}$$

$$\begin{aligned} A_{n_i n_i n_i} = \left(\frac{\partial^3 A}{\partial n_i^3}\right)_{V,n_j} &= 2RT\frac{b_i^2}{(V - n_T b)^2} \\ &\quad + 2n_T RT\frac{b_i^3}{(V - n_T b)^3} - \frac{RT}{n_i^2} \end{aligned} \tag{A8}$$

$$\begin{aligned} A_{n_i n_j n_k} = \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial n_k}\right)_V &= RT\frac{(b_i + b_j)b_k}{(V - n_T b)^2} \\ &\quad + 2n_T RT\frac{b_i b_j b_k}{(V - n_T b)^3} \end{aligned} \tag{A9}$$

$$\begin{aligned} A_{n_i VV} &= \left(\frac{\partial^3 A}{\partial n_i \partial V^2}\right) \\ &= -\frac{4}{V^3}\sum_j n_j a_{ij} + RT\frac{1}{(V - n_T b)^2} \\ &\quad + 2n_T RT\frac{b_i}{(V - n_T b)^3} \end{aligned} \tag{A10}$$

$$\begin{aligned} A_{n_i n_i V} &= \left(\frac{\partial^3 A}{\partial n_i^2 \partial V}\right) \\ &= \frac{2}{V^2}a_{ii} - RT\frac{2b_i}{(V - n_T b)^2} \\ &\quad - 2n_T RT\frac{b_i^2}{(V - n_T b)^3} \end{aligned} \tag{A11}$$

$$\begin{aligned} A_{n_i n_j V} &= \left(\frac{\partial^3 A}{\partial n_i \partial n_j \partial V}\right) \\ &= \frac{2}{V^2}a_{ij} - RT\frac{(b_i + b_j)}{(V - n_T b)^2} \\ &\quad - 2n_T RT\frac{b_i b_j}{(V - n_T b)^3} \end{aligned} \tag{A12}$$