
Thermodynamic Properties and Applications of Modified van-der-Waals Equations of State

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1. Introduction

Physical and chemical properties of natural fluids are used to understand geological processes in crustal and mantle rock. The fluid phase plays an important role in processes in diagenesis, metamorphism, deformation, magmatism, and ore formation. The environment of these processes reaches depths of maximally 5 km in oceanic crusts, and 65 km in continental crusts, e.g. [1, 2], which corresponds to pressures and temperatures up to 2 GPa and 1000 °C, respectively. Although in deep environments the low porosity in solid rock does not allow the presence of large amounts of fluid phases, fluids may be entrapped in crystals as fluid inclusions, i.e. nm to μm sized cavities, e.g. [3], and fluid components may be present within the crystal lattice, e.g. [4]. The properties of the fluid phase can be approximated with equations of state (Eq. 1), which are mathematical formula that describe the relation between intensive properties of the fluid phase, such as pressure (p), temperature (T), composition (x), and molar volume (V_m).

$$p(T, V_m, x) \quad (1)$$

This pressure equation can be transformed according to thermodynamic principles [5], to calculate a variety of extensive properties, such as entropy, internal energy, enthalpy, Helmholtz energy, Gibbs energy, et al., as well as liquid-vapour equilibria and homogenization conditions of fluid inclusions, i.e. dew point curve, bubble point curve, and critical points, e.g. [6]. The partial derivative of Eq. 1 with respect to temperature is used to calculate total entropy change (dS in Eq. 2) and total internal energy change (dU in Eq. 3), according to the Maxwell's relations [5].

$$dS = \left(\frac{\partial p}{\partial T} \right)_{V, n_T} dV \quad (2)$$

$$dU = \left[T \cdot \left(\frac{\partial p}{\partial T} \right)_{V, n_T} - p \right] dV \quad (3)$$

where n_T is the total amount of substance in the system. The enthalpy (H) can be directly obtained from the internal energy and the product of pressure and volume according to Eq. 4.

$$H = U + p \cdot V \quad (4)$$

The Helmholtz energy (A) can be calculated by combining the internal energy and entropy (Eq. 5), or by a direct integration of pressure (Eq. 1) in terms of total volume (Eq. 6).

$$A = U - TS \quad (5)$$

$$dA = -pdV \quad (6)$$

The Gibbs energy (G) is calculated in a similar procedure according to its definition in Eq. 7.

$$G = U + p \cdot V - T \cdot S \quad (7)$$

The chemical potential (μ_i) of a specific fluid component (i) in a gas mixture or pure gas (Eq. 8) is obtained from the partial derivative of the Helmholtz energy (Eq. 5) with respect to the amount of substance of this component (n_i).

$$\mu_i = \left(\frac{\partial A}{\partial n_i} \right)_{T, V, n_j} \quad (8)$$

The fugacity (f) can be directly obtained from chemical potentials (Eq. 9) and from the definition of the fugacity coefficient (ϕ) with independent variables V and T (Eq. 10).

$$RT \ln \left(\frac{f_i}{f_i^0} \right) = \mu_i - \mu_i^0 \quad (9)$$

where μ_i^0 and f_i^0 are the chemical potential and fugacity, respectively, of component i at standard conditions (0.1 MPa).

$$RT \ln \phi_i = \int_V^\infty \left[\left(\frac{\partial p}{\partial n_i} \right)_{T, V, n_j} - \frac{RT}{V} \right] dV - RT \ln z \quad (10)$$

where ϕ and z (compressibility factor) are defined according to Eq. 11 and 12, respectively.

$$\phi_i = \frac{f_i}{x_i \cdot p} \quad (11)$$

$$z = \frac{pV}{n_T RT} \quad (12)$$

2. Two-constant cubic equation of state

The general formulation that summarizes two-constant cubic equations of state according to van der Waals [7], Redlich and Kwong [8], Soave [9], and Peng and Robinson [10] is illustrated in Eq. 13 and 14, see also [11]. In the following paragraphs, these equations are abbreviated with *Weos*, *RKeos*, *Seos*, and *PReos*.

$$p = \frac{RT}{V_m - \zeta_1} - \frac{\zeta_2}{V_m \cdot (V_m + \zeta_3) + \zeta_4 \cdot (V_m - \zeta_4)} \quad (13)$$

$$p = \frac{n_T RT}{V - n_T \zeta_1} - \frac{n_T^2 \zeta_2}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \quad (14)$$

where p is pressure (in MPa), T is temperature (in Kelvin), R is the gas constant (8.3144621 J·mol⁻¹K⁻¹), V is volume (in cm³), V_m is molar volume (in cm³·mol⁻¹), n_T is the total amount of substance (in mol). The parameters ζ_1 , ζ_2 , ζ_3 , and ζ_4 are defined according to the specific equations of state (Table 1), and are assigned specific values of the two constants a and b , as originally designed by Waals [7]. The a parameter reflects attractive forces between molecules, whereas the b parameter reflects the volume of molecules.

	W	RK	S	PR
ζ_1	b	b	b	b
ζ_2	a	$a \cdot T^{-0.5}$	a	a
ζ_3	-	b	b	b
ζ_4	-	-	-	b

Table 1. Definitions of ζ_1 , ζ_2 , ζ_3 , and ζ_4 according to van der Waals (W), Redlich and Kwong (RK), Soave (S) and Peng and Robinson (PR).

This type of equation of state can be transformed in the form of a cubic equation to define volume (Eq. 15) and compressibility factor (Eq. 16).

$$a_0 V^3 + a_1 V^2 + a_2 V + a_3 = 0 \quad (15)$$

$$b_0 z^3 + b_1 z^2 + b_2 z + b_3 = 0 \quad (16)$$

where a_0 , a_1 , a_2 , and a_3 are defined in Eq. 17, 18, 19, and 20, respectively; b_0 , b_1 , b_2 , and b_3 are defined in Eq. 21, 22, 23, and 24, respectively.

$$a_0 = p \quad (17)$$

$$a_1 = n_T p \cdot (\zeta_3 + \zeta_4 - \zeta_1) - n_T RT \quad (18)$$

$$a_2 = -n_T^2 p \cdot (\zeta_4^2 + \zeta_1 \zeta_3 + \zeta_1 \zeta_4) - n_T^2 RT \cdot (\zeta_3 + \zeta_4) + n_T^2 \zeta_2 \quad (19)$$

$$a_3 = n_T^3 p \cdot \zeta_1 \zeta_4^2 + n_T^3 RT \cdot \zeta_4^2 - n_T^3 \cdot \zeta_1 \zeta_2 \quad (20)$$

$$b_0 = \left(\frac{RT}{p} \right)^3 \quad (21)$$

$$b_1 = \left(\frac{RT}{p} \right)^2 \cdot \left(\zeta_3 + \zeta_4 - \zeta_1 - \frac{RT}{p} \right) \quad (22)$$

$$b_2 = \left(\frac{RT}{p} \right) \cdot \left(-\zeta_4^2 - (\zeta_3 + \zeta_4) \cdot \left(\zeta_1 + \frac{RT}{p} \right) + \frac{\zeta_2}{p} \right) \quad (23)$$

$$b_3 = \left(\zeta_1 + \frac{RT}{p} \right) \cdot \zeta_4^2 - \frac{\zeta_1 \zeta_2}{p} \quad (24)$$

The advantage of a cubic equation is the possibility to have multiple solutions (maximally three) for volume at specific temperature and pressure conditions, which may reflect coexisting liquid and vapour phases. Liquid-vapour equilibria can only be calculated from the same equation of state if multiple solution of volume can be calculated at the same temperature and pressure. The calculation of thermodynamic properties with this type of equation of state is based on splitting Eq. 14 in two parts (Eq. 25), i.e. an ideal pressure (from the ideal gas law) and a departure (or residual) pressure, see also [6].

$$p = p_{ideal} + p_{residual} \quad (25)$$

where

$$p_{ideal} = \frac{n_T RT}{V} \quad (26)$$

The residual pressure ($p_{residual}$) can be defined as the difference (Δp , Eq. 27) between ideal pressure and real pressure as expressed in Eq. 14 .

$$\Delta p = p_{residual} = -\frac{n_T RT}{V} + \frac{n_T RT}{V - n_T \zeta_1} - \frac{n_T^2 \zeta_2}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \quad (27)$$

The partial derivative of pressure with respect to temperature (Eq. 28) is the main equation to estimate the thermodynamic properties of fluids (see Eqs. 2 and 3).

$$\frac{\partial p}{\partial T} = \frac{\partial p_{ideal}}{\partial T} + \frac{\partial \Delta p}{\partial T} \quad (28)$$

where

$$\begin{aligned} \frac{\partial \Delta p}{\partial T} = & -\frac{n_T R}{V} + \frac{n_T R}{V - n_T \zeta_1} + \frac{n_T R T}{(V - n_T \zeta_1)^2} \cdot \frac{\partial(n_T \zeta_1)}{\partial T} \\ & - \frac{1}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \cdot \frac{\partial(n_T^2 \zeta_2)}{\partial T} \\ & + \frac{n_T^2 \zeta_2}{(V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2)^2} \cdot \frac{\partial(n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2)}{\partial T} \end{aligned} \quad (29)$$

The parameters ζ_1 , ζ_3 , and ζ_4 are usually independent of temperature, compare with the b parameter (Table 1). This reduces Eq. 29 to Eq. 30.

$$\frac{\partial \Delta p}{\partial T} = -\frac{n_T R}{V} + \frac{n_T R}{V - n_T \zeta_1} - \frac{1}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \cdot \frac{\partial(n_T^2 \zeta_2)}{\partial T} \quad (30)$$

Other important equations to calculate thermodynamic properties of fluids are partial derivatives of pressure with respect to volume (Eq. 31 and 32).

$$\frac{\partial p}{\partial V} = -\frac{n_T R T}{(V - n_T \zeta_1)^2} + \frac{n_T^2 \zeta_2}{(V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2)^2} \cdot (2V + n_T \zeta_3 + n_T \zeta_4) \quad (31)$$

$$\begin{aligned} \frac{\partial^2 p}{\partial V^2} = & \frac{2n_T R T}{(V - n_T \zeta_1)^3} - \frac{2n_T^2 \zeta_2}{(V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2)^3} \cdot (2V + n_T \zeta_3 + n_T \zeta_4)^2 \\ & + \frac{2n_T^2 \zeta_2}{(V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2)^2} \end{aligned} \quad (32)$$

Eqs. 31 and 32 already include the assumption that the parameters ζ_1 , ζ_2 , ζ_3 , and ζ_4 are independent of volume. Finally, the partial derivative of pressure in respect to the amount of substance of a specific component in the fluid mixture (n_i) is also used to characterize thermodynamic properties of fluid mixtures (Eq. 33).

$$\begin{aligned} \frac{\partial p}{\partial n_i} = & \frac{RT}{V - n_T \zeta_1} + \frac{n_T R T}{(V - n_T \zeta_1)^2} \cdot \frac{\partial(n_T \zeta_1)}{\partial n_i} \\ & - \frac{1}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \cdot \frac{\partial(n_T^2 \zeta_2)}{\partial n_i} \\ & + \frac{n_T^2 \zeta_2}{(V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2)^2} \cdot \left[\left(\frac{\partial(n_T \zeta_3)}{\partial n_i} + \frac{\partial(n_T \zeta_4)}{\partial n_i} \right) \cdot V - 2n_T \zeta_4 \frac{\partial(n_T \zeta_4)}{\partial n_i} \right] \end{aligned} \quad (33)$$

3. Thermodynamic parameters

The entropy (S) is obtained from the integration defined in Eq. 2 at constant temperature (Eqs. 34 and 35).

$$\int_{S_0}^{S_1} dS = \int_{V_0}^{V_1} \left(\frac{\partial p}{\partial T} \right)_{V, n_T} dV \quad (34)$$

$$S_1 = S_0 + \int_{V_0}^{V_1} \left(\frac{\partial p_{ideal}}{\partial T} + \frac{\partial \Delta p}{\partial T} \right) dV \quad (35)$$

The limits of integration are defined as a reference ideal gas at S_0 and V_0 , and a real gas at S_1 and V_1 . This integration can be split into two parts, according to the ideal pressure and residual pressure definition (Eqs. 25, 26, and 27). The integral has different solutions dependent on the values of ζ_3 and ζ_4 : Eq. 36 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eqs. 37 and 38 for $\zeta_3 > 0$.

$$S_1 = S_0 + n_T R \ln \left(\frac{V_1}{V_0} \right) + n_T R \ln \left(\frac{V_1 - n_T \zeta_1}{V_0 - n_T \zeta_1} \cdot \frac{V_0}{V_1} \right) + \left(\frac{1}{V_1} - \frac{1}{V_0} \right) \cdot \frac{\partial(n_T^2 \zeta_2)}{\partial T} \quad (36)$$

$$S_1 = S_0 + n_T R \ln \left(\frac{V_1}{V_0} \right) + n_T R \ln \left(\frac{V_1 - n_T \zeta_1}{V_0 - n_T \zeta_1} \cdot \frac{V_0}{V_1} \right) - \frac{1}{q} \cdot \frac{\partial(n_T^2 \zeta_2)}{\partial T} \cdot \ln \left(\frac{2V_1 + n_T(\zeta_3 + \zeta_4) - q}{2V_1 + n_T(\zeta_3 + \zeta_4) + q} \right) + \frac{1}{q} \cdot \frac{\partial(n_T^2 \zeta_2)}{\partial T} \cdot \ln \left(\frac{2V_0 + n_T(\zeta_3 + \zeta_4) - q}{2V_0 + n_T(\zeta_3 + \zeta_4) + q} \right) \quad (37)$$

where

$$q = n_T \sqrt{4\zeta_4^2 + (\zeta_3 + \zeta_4)^2} \quad (38)$$

The *RKeos* and *Seos* define q as $n_T b$, whereas in the *PREos* q is equal to $n_T b \sqrt{8}$, according to the values for ζ_3 and ζ_4 listed in Table 1. Eqs. 36 and 37 can be simplified by assuming that the lower limit of the integration corresponds to a large number of V_0 . As a consequence, part of the natural logarithms in Eqs. 36 and 37 can be replaced by the unit value 1 or 0 (Eqs. 39, 40, and 41).

$$\lim_{V_0 \rightarrow \infty} \left(\frac{V_0}{V_0 - n_T \zeta_1} \right) = 1 \quad (39)$$

$$\lim_{V_0 \rightarrow \infty} \left(\frac{1}{V_0} \right) = 0 \quad (40)$$

$$\lim_{V_0 \rightarrow \infty} \left(\frac{2V_0 + n_T(\zeta_3 + \zeta_4) - q}{2V_0 + n_T(\zeta_3 + \zeta_4) + q} \right) = 1 \quad (41)$$

The entropy change that is caused by a volume change of ideal gases corresponds to the second term on the right-hand side of Eqs. 36 and 37. This term can be used to express the behaviour of an ideal mixture of perfected gases. Each individual gas in a mixture expands from their partial volume (v_i) to the total volume at a pressure of 0.1 MPa, which results in a new expression for this term (Eq. 42)

$$n_T R \ln \left(\frac{V_1}{V_0} \right)_{ideal.mix} = \sum_i \left[n_i R \ln \left(\frac{V_1}{v_i} \right) \right] \quad (42)$$

where n_i is the amount of substance of component i in the fluid mixture. In addition, the partial volume of an ideal gas is related to the standard pressure p_0 (0.1 MPa) according to the ideal gas law (Eq. 43, compare with Eq. 26).

$$v_i = \frac{n_i R T}{p_0} \quad (43)$$

Finally, the entropy of fluid phases containing gas mixtures at any temperature and total volume according to the two-constant cubic equation of state is given by Eq. 44 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 45 for $\zeta_3 > 0$.

$$S = S_0 + \sum_i \left[n_i R \ln \left(\frac{p_0 V}{n_i R T} \right) \right] + n_T R \ln \left(\frac{V - n_T \zeta_1}{V} \right) + \frac{1}{V} \cdot \frac{\partial (n_T^2 \zeta_2)}{\partial T} \quad (44)$$

$$S = S_0 + \sum_i \left[n_i R \ln \left(\frac{p_0 V}{n_i R T} \right) \right] + n_T R \ln \left(\frac{V - n_T \zeta_1}{V} \right) - \frac{1}{q} \cdot \frac{\partial (n_T^2 \zeta_2)}{\partial T} \cdot \ln \left(\frac{2V + n_T (\zeta_3 + \zeta_4) - q}{2V + n_T (\zeta_3 + \zeta_4) + q} \right) \quad (45)$$

The subscripts "1" for the upper limit of integration is eliminated to present a pronounced equation. The standard state entropy (S_0) of a mixture of ideal gases is defined according to the arithmetic average principle (Eq. 46).

$$S_0 = \sum_i n_i \cdot s_i^0 \quad (46)$$

where s_i^0 is the molar entropy of a pure component i in an ideal gas mixture at temperature T .

The internal energy (U , see Eq. 3) is obtained from the pressure equation (Eq. 14) and its partial derivative with respect to temperature (Eqs. 28 and 30):

$$\int_{U_0}^{U_1} dU = \int_{V_0}^{V_1} \left(T \cdot \frac{\partial p}{\partial T} - p \right) dV \quad (47)$$

$$U_1 = U_0 + \int_{V_0}^{V_1} \left(\frac{1}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \cdot \left(n_T^2 \zeta_2 - T \frac{\partial (n_T^2 \zeta_2)}{\partial T} \right) \right) dV \quad (48)$$

Similar to the integral in the entropy definition (see Eqs. 44 and 45), Eq. 48 has different solutions dependent on the values of ζ_3 and ζ_4 : Eq. 49 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 50 for $\zeta_3 > 0$.

$$U = U_0 - \frac{1}{V} \cdot \left(n_T^2 \zeta_2 - T \frac{\partial(n_T^2 \zeta_2)}{\partial T} \right) \quad (49)$$

$$U = U_0 + \frac{1}{q} \cdot \left(n_T^2 \zeta_2 - T \frac{\partial(n_T^2 \zeta_2)}{\partial T} \right) \cdot \ln \left(\frac{2V + n_T(\zeta_3 + \zeta_4) - q}{2V + n_T(\zeta_3 + \zeta_4) + q} \right) \quad (50)$$

The definition of q is given in Eq. 38. The standard state internal energy (U_0) of a mixture of ideal gases is defined according to the arithmetic average principle (Eq. 51).

$$U_0 = \sum_i n_i \cdot u_i^0 \quad (51)$$

where u_i^0 is the molar internal energy of a pure component i in an ideal gas mixture at temperature T .

Enthalpy (Eq. 52 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 53 for $\zeta_3 > 0$), Helmholtz energy (Eq. 55 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 56 for $\zeta_3 > 0$), and Gibbs energy (Eq. 58 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 59 for $\zeta_3 > 0$) can be obtained from the definitions of pressure, entropy and internal energy according to standard thermodynamic relations, as illustrated in Eq. 4, 5, and 7. Standard state enthalpy (H_0), standard state Helmholtz energy (A_0), and standard state Gibbs energy (G_0) of an ideal gas mixture at 0.1 MPa and temperature T are defined in Eqs. 54, 57, and 60, respectively.

$$H = U_0 + \frac{n_T RTV}{V - n_T \zeta_1} - \frac{1}{V} \cdot \left(2n_T^2 \zeta_2 - T \frac{\partial(n_T^2 \zeta_2)}{\partial T} \right) \quad (52)$$

$$H = U_0 + \frac{n_T RTV}{V - n_T \zeta_1} - \frac{n_T^2 \zeta_2 V}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} + \frac{1}{q} \cdot \left(n_T^2 \zeta_2 - T \frac{\partial(n_T^2 \zeta_2)}{\partial T} \right) \cdot \ln \left(\frac{2V + n_T(\zeta_3 + \zeta_4) - q}{2V + n_T(\zeta_3 + \zeta_4) + q} \right) \quad (53)$$

$$H_0 = U_0 + n_T RT \quad (54)$$

$$A = U_0 - TS_0 - \sum_i \left[n_i RT \ln \left(\frac{p_0 V}{n_i RT} \right) \right] - n_T RT \ln \left(\frac{V - n_T \zeta_1}{V} \right) - \frac{n_T^2 \zeta_2}{V} \quad (55)$$

$$A = U_0 - TS_0 - \sum_i \left[n_i RT \ln \left(\frac{p_0 V}{n_i RT} \right) \right] - n_T RT \ln \left(\frac{V - n_T \zeta_1}{V} \right) + \frac{n_T^2 \zeta_2}{q} \cdot \ln \left(\frac{2V + n_T(\zeta_3 + \zeta_4) - q}{2V + n_T(\zeta_3 + \zeta_4) + q} \right) \quad (56)$$

$$A_0 = U_0 - TS_0 \quad (57)$$

$$G = U_0 - TS_0 - RT \sum_i \left[n_i \ln \left(\frac{p_0 V}{n_i RT} \right) \right] - n_T RT \ln \left(\frac{V - n_T \zeta_1}{V} \right) + \frac{n_T RT V}{V - n_T \zeta_1} - \frac{2n_T^2 \zeta_2}{V} \quad (58)$$

$$G = U_0 - TS_0 - RT \sum_i \left[n_i \ln \left(\frac{p_0 V}{n_i RT} \right) \right] - n_T RT \ln \left(\frac{V - n_T \zeta_1}{V} \right) + \frac{n_T RT V}{V - n_T \zeta_1} + \frac{n_T^2 \zeta_2}{q} \cdot \ln \left(\frac{2V + n_T(\zeta_3 + \zeta_4) - q}{2V + n_T(\zeta_3 + \zeta_4) + q} \right) - \frac{n_T^2 \zeta_2 V}{V^2 + n_T \zeta_3 V + n_T \zeta_4 V - n_T^2 \zeta_4^2} \quad (59)$$

$$G_0 = U_0 - TS_0 + n_T RT \quad (60)$$

The Helmholtz energy equation (Eqs. 55, 56, and 57) is used for the definition of chemical potential (μ) of a component in either vapour or liquid phase gas mixtures (compare with Eq. 8), Eq. 61 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 62 for $\zeta_3 > 0$, calculated with two-constant cubic equations of state.

$$\mu_i = \frac{\partial U_0}{\partial n_i} - T \frac{\partial S_0}{\partial n_i} - RT \ln \left(\frac{p_0 V}{n_i RT} \right) + RT - RT \ln \left(\frac{V - n_T \zeta_1}{V} \right) + \frac{n_T RT}{V - n_T \zeta_1} \cdot \frac{\partial(n_T \zeta_1)}{\partial n_i} - \frac{1}{V} \cdot \frac{\partial n_T^2 \zeta_2}{\partial n_i} \quad (61)$$

$$\begin{aligned} \mu_i = & \frac{\partial U_0}{\partial n_i} - T \frac{\partial S_0}{\partial n_i} - RT \ln \left(\frac{p_0 V}{n_i RT} \right) + RT - RT \ln \left(\frac{V - n_T \zeta_1}{V} \right) + \frac{n_T RT}{V - n_T \zeta_1} \cdot \frac{\partial(n_T \zeta_1)}{\partial n_i} \\ & + \left(\frac{\partial n_T^2 \zeta_2}{\partial n_i} \cdot \frac{1}{q} - \frac{n_T^2 \zeta_2}{q^2} \cdot \frac{\partial q}{\partial n_i} \right) \cdot \ln \left(\frac{2V + n_T(\zeta_3 + \zeta_4) - q}{2V + n_T(\zeta_3 + \zeta_4) + q} \right) \\ & + \frac{n_T^2 \zeta_2}{q} \cdot \frac{1}{2V + n_T(\zeta_3 + \zeta_4) - q} \cdot \left(\frac{\partial n_T \zeta_3}{\partial n_i} + \frac{\partial n_T \zeta_4}{\partial n_i} - \frac{\partial q}{\partial n_i} \right) \\ & - \frac{n_T^2 \zeta_2}{q} \cdot \frac{1}{2V + n_T(\zeta_3 + \zeta_4) + q} \cdot \left(\frac{\partial n_T \zeta_3}{\partial n_i} + \frac{\partial n_T \zeta_4}{\partial n_i} + \frac{\partial q}{\partial n_i} \right) \end{aligned} \quad (62)$$

where

$$\frac{\partial q}{\partial n_i} = \frac{1}{q} \left[4n_T \zeta_4 \frac{\partial n_T \zeta_4}{\partial n_i} + n_T(\zeta_3 + \zeta_4) \cdot \left(\frac{\partial n_T \zeta_3}{\partial n_i} + \frac{\partial n_T \zeta_4}{\partial n_i} \right) \right] \quad (63)$$

The definitions of the partial derivative of q in respect to amount of substance (Eq. 63) according to $\zeta_3 = b$ and $\zeta_4 = 0$ [8, 9] is illustrated in Eq. 64, and $\zeta_3 = b$ and $\zeta_4 = b$ [10] in Eq. 65.

$$\frac{\partial q}{\partial n_i} = \frac{\partial(n_T b)}{\partial n_i} \quad (64)$$

$$\frac{\partial q}{\partial n_i} = \sqrt{8} \cdot \frac{\partial(n_T b)}{\partial n_i} \quad (65)$$

The fugacity coefficient (φ) is defined according to Eqs. 9 and 10 from the difference between the chemical potential of a real gas mixture and an ideal gas mixture at standard conditions (0.1 MPa), see Eq. 66 for $\zeta_3 = 0$ and $\zeta_4 = 0$, and Eq. 67 for $\zeta_3 > 0$. Fugacity coefficient defined in Eq. 66 is applied to *Weos* and Eq. 67 is applied to *RKeos*, *Seos*, and *PREos*.

$$RT \ln(\varphi_i) = -RT \ln\left(\frac{pV}{n_T RT}\right) - RT \ln\left(\frac{V - n_T \zeta_1}{V}\right) + \frac{n_T RT}{V - n_T \zeta_1} \cdot \frac{\partial(n_T \zeta_1)}{\partial n_i} - \frac{1}{V} \cdot \frac{\partial n_T^2 \zeta_2}{\partial n_i} \quad (66)$$

$$\begin{aligned} RT \ln(\varphi_i) = & -RT \ln\left(\frac{pV}{n_T RT}\right) - RT \ln\left(\frac{V - n_T \zeta_1}{V}\right) + \frac{n_T RT}{V - n_T \zeta_1} \cdot \frac{\partial(n_T \zeta_1)}{\partial n_i} \\ & + \left(\frac{\partial n_T^2 \zeta_2}{\partial n_i} \cdot \frac{1}{q} - \frac{n_T^2 \zeta_2}{q^2} \cdot \frac{\partial q}{\partial n_i}\right) \cdot \ln\left(\frac{2V + n_T(\zeta_3 + \zeta_4) - q}{2V + n_T(\zeta_3 + \zeta_4) + q}\right) \\ & + \frac{n_T^2 \zeta_2}{q} \cdot \frac{1}{2V + n_T(\zeta_3 + \zeta_4) - q} \cdot \left(\frac{\partial n_T \zeta_3}{\partial n_i} + \frac{\partial n_T \zeta_4}{\partial n_i} - \frac{\partial q}{\partial n_i}\right) \\ & - \frac{n_T^2 \zeta_2}{q} \cdot \frac{1}{2V + n_T(\zeta_3 + \zeta_4) + q} \cdot \left(\frac{\partial n_T \zeta_3}{\partial n_i} + \frac{\partial n_T \zeta_4}{\partial n_i} + \frac{\partial q}{\partial n_i}\right) \end{aligned} \quad (67)$$

4. Spinodal

The stability limit of a fluid mixture can be calculated with two-constant cubic equations of state, e.g. see [6]. This limit is defined by the spinodal line, i.e. the locus of points on the surface of the Helmholtz energy or Gibbs energy functions that are inflection points, e.g. see [12] and references therein. The stability limit occurs at conditions where phase separation into a liquid and vapour phase should take place, which is defined by the binodal. Metastability is directly related to spinodal conditions, for example, nucleation of a vapour bubble in a cooling liquid phase within small constant volume cavities, such as fluid inclusions in minerals (< 100 μm diameter) occurs at conditions well below homogenization conditions of these phases in a heating experiment. The maximum temperature difference of nucleation and homogenization is defined by the spinodal. In multi-component fluid systems, 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 (Eq. 68) at spinodal conditions.

$$D_{spin} = \begin{vmatrix} A_{VV} & A_{n_1 V} & A_{n_2 V} & \cdots \\ A_{V n_1} & A_{n_1 n_1} & A_{n_2 n_1} & \cdots \\ A_{V n_2} & A_{n_1 n_2} & A_{n_2 n_2} & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} = 0 \quad (68)$$

This matrix is square and contains a specific number of columns that is defined by the number of differentiation variables, i.e. volume and number of components in the fluid mixture minus 1. The individual components of this matrix are defined according to Eqs. 69, 70, 71, 72, 73, and 74. The exact definition of these components according to two-constant cubic equations of state can be obtained from the web site <http://fluids.unileoben.ac.at> (see also [6]).

$$A_{VV} = \left(\frac{\partial^2 A}{\partial V^2} \right)_{n_1, n_2, \dots} \quad (69)$$

$$A_{n_1 n_1} = \left(\frac{\partial^2 A}{\partial n_1^2} \right)_{n_2, V, \dots} \quad (70)$$

$$A_{n_2 n_2} = \left(\frac{\partial^2 A}{\partial n_2^2} \right)_{n_1, V, \dots} \quad (71)$$

$$A_{n_1 V} = \left(\frac{\partial^2 A}{\partial n_1 \partial V} \right)_{n_2, \dots} = A_{V n_1} \quad (72)$$

$$A_{n_2 V} = \left(\frac{\partial^2 A}{\partial n_2 \partial V} \right)_{n_1, \dots} = A_{V n_2} \quad (73)$$

$$A_{n_1 n_2} = \left(\frac{\partial^2 A}{\partial n_1 \partial n_2} \right)_{V, \dots} = A_{n_2 n_1} \quad (74)$$

The determinant in Eq. 68 is calculated with the Laplacian expansion that contains "*minors*" and "*cofactors*", e.g. see [13]. The mathematical computation time increases exponential with increasing number of components. Therefore, the *LU* decomposition [14] can be applied in computer programming to reduce this time.

The spinodal curve, binodal curve and critical point of a binary CO₂-CH₄ mixture with $x(\text{CO}_2) = 0.9$ are illustrated in Figure 1, which are calculated with the *PR*eos [10]. The spinodal has a small loop near the critical point, and may reach negative pressures at lower temperatures. The binodal remains within the positive pressure part at all temperatures. The binodal is obtained from equality of fugacity (Eq. 66 and 67) of each component in both

liquid and vapour phase, and marks the boundary between a homogeneous fluid mixture and fluid immiscibility [6, 15].

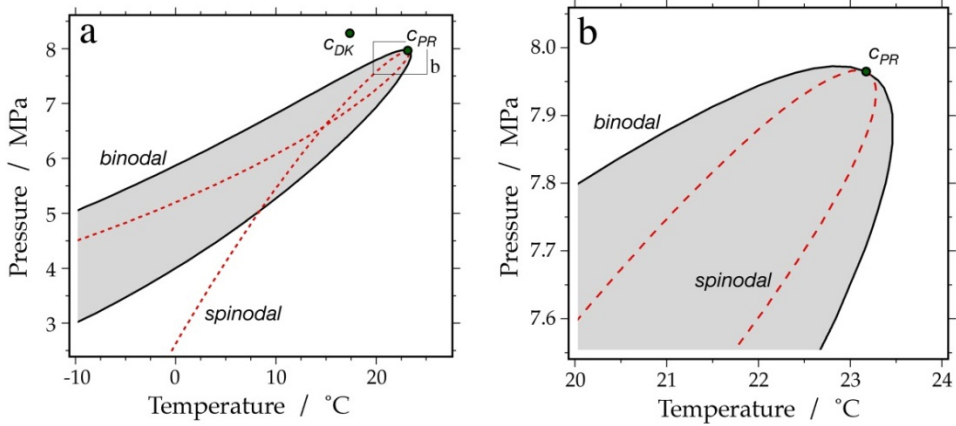


Figure 1. (a) Temperature-pressure diagram of a binary CO₂-CH₄ fluid mixture, with $x(\text{CO}_2) = 0.9$. The shaded area illustrates T - p condition of immiscibility of a CO₂-rich liquid phase and a CH₄-rich vapour phase (the binodal). The red dashed line is the spinodal. All lines are calculated with the equation of state according to *PR**eos* [10]. The calculated critical point is indicated with C_{PR} . C_{DK} is the interpolated critical point from experimental data [16]. (b) enlargement of (a) indicated with the square in thin lines.

5. Pseudo critical point

The pseudo critical point is defined according to the first and second partial derivatives of pressure with respect to volume (Eqs. 31 and 32). This point is defined in a p - V diagram where the inflection point and extremum coincide at a specific temperature, i.e. Eqs. 31 and 32 are equal to 0. The pseudo critical point is equal to the critical point for pure gas fluids, however, the critical point in mixtures cannot be obtained from Eqs. 31 and 32. The pseudo critical point estimation is used to define the two-constants (a and b) for pure gas fluids in cubic equations of state according to the following procedure. The molar volume of the pseudo critical point that is derived from Eqs 31 and 32 is presented in the form of a cubic equation (Eq. 75).

$$0 = V_m^3 - 3\zeta_1 \cdot V_m^2 + [3\zeta_4^2 - 3\zeta_1 \cdot (\zeta_3 + \zeta_4)] \cdot V_m - \zeta_1 \cdot [\zeta_4^2 + (\zeta_3 + \zeta_4)^2] + \zeta_4^2 \cdot (\zeta_3 + \zeta_4) \quad (75)$$

The solution of this cubic equation can be obtained from its reduced form, see page 9 in [15]:

$$x^3 + f \cdot x + g = 0 \quad (76)$$

where

$$f = 3 \cdot [\zeta_4^2 - \zeta_1 \cdot (\zeta_1 + \zeta_3 + \zeta_4)] \quad (77)$$

$$g = -2\zeta_1^3 + \zeta_1 \cdot \left[2\zeta_4^2 - (\zeta_3 + \zeta_4)^2 \right] + (\zeta_3 + \zeta_4) \cdot \left[\zeta_4^2 - 3\zeta_1^2 \right] \quad (78)$$

$$V_m = x + \zeta_1 \quad (79)$$

The values of f and g in terms of the b parameters for the individual two-constant cubic equations of state are given in Table 2. The molar volume at pseudo critical conditions is directly related to the b parameter in each equation of state: *Weos* Eq. 80; *RKeos* Eq. 81; *Seos* also Eq. 81; and *PREos* Eq. 82.

$$\text{Weos: } V_m^{pc} = 3 \cdot b \quad (80)$$

$$\text{RKeos: } V_m^{pc} = \frac{b}{\sqrt[3]{2} - 1} \approx 3.847322 \cdot b \quad (81)$$

$$\text{PREos: } V_m^{pc} = [1 + Q] \cdot b \approx 3.951373 \cdot b \quad (82)$$

where Q is defined according to Eq. 83, the superscript "pc" is the abbreviation for "pseudo critical".

$$Q = \left(4 + \sqrt{8} \right)^{\frac{1}{3}} + \left(4 - \sqrt{8} \right)^{\frac{1}{3}} \quad (83)$$

Equation of state	f	g	b in Eqs. 80-82	b in Eqs. 94-96	difference
van der Waals [7]	$-3b^2$	$-2b^3$	31.3727	42.8453	37 %
Redlich and Kwong [8]	$-6b^2$	$-6b^3$	24.4633	29.6971	21 %
Soave [9]	$-6b^2$	$-6b^3$	24.4633	29.6971	21 %
Peng and Robinson [10]	$-6b^2$	$-8b^3$	23.8191	26.6656	12 %

Table 2. Definitions of f and g according to Eq. 77 and 78, respectively. The values of b are calculated for the critical conditions of pure CO₂: $V_{m,c} = 94.118 \text{ cm}^3 \cdot \text{mol}^{-1}$, $T_c = 304.128 \text{ K}$ and $p_c = 7.3773 \text{ MPa}$ [18]. The last column gives the percentage of difference between the values of b (Eqs. 80-82 and 94-96).

The temperature at pseudo critical conditions is obtained from the combination of Eqs. 80-82 and the first partial derivative of pressure with respect to volume (Eq. 31).

$$\text{Weos: } T^{pc} = \frac{8}{27} \cdot \frac{\zeta_2}{bR} \approx 0.29629630 \cdot \frac{\zeta_2}{bR} \quad (84)$$

$$\text{RKeos: } T^{pc} = \left(\sqrt[3]{2} - 1 \right)^2 \cdot \left(\frac{3\zeta_2}{bR} \right) \approx 0.20267686 \cdot \frac{\zeta_2}{bR} \quad (85)$$

$$\text{PREos: } T^{pc} = \frac{2Q + 4}{\left(Q + 4 + \frac{2}{Q} \right)^2} \cdot \left(\frac{3\zeta_2}{bR} \right) \approx 0.17014442 \cdot \frac{\zeta_2}{bR} \quad (86)$$

where Q is defined according to Eq. 83. The order of equations (84, 85, 86) is according to the order of equations of state in Eq. 80, 81, and 82. The parameter ζ_2 is used in Eqs. 84, 85 and, 86 instead of the constant a (see Table 1). Eq. 87 illustrates the transformation of Eq. 85 for the *RKeos* [8] by substitution of ζ_2 according to its value given in Table 1.

$$T^{pc} = \left(\sqrt[3]{2} - 1\right)^{4/3} \cdot \left(\frac{3a}{bR}\right)^{2/3} \quad (87)$$

Any temperature dependency of the a constant has an effect on the definition of the pseudo critical temperature. The pressure at pseudo critical condition (Eqs. 88-90) is obtained from a combination of the pressure equation (Eq.14), pseudo critical temperature (Eqs. 84-87) and pseudo critical molar volume (Eqs. 80-82).

$$\text{Weos: } p^{pc} = \frac{1}{27} \cdot \frac{\zeta_2}{b^2} \approx 0.03703704 \cdot \frac{\zeta_2}{b^2} \quad (88)$$

$$\text{RKeos: } p^{pc} = \left(\sqrt[3]{2} - 1\right)^3 \cdot \frac{\zeta_2}{b^2} \approx 0.01755999 \cdot \frac{\zeta_2}{b^2} \quad (89)$$

$$\text{PREos: } p^{pc} = \frac{Q^2 - 2}{(Q^2 + 4Q + 2)^2} \cdot \frac{\zeta_2}{b^2} \approx 0.01227198 \cdot \frac{\zeta_2}{b^2} \quad (90)$$

where Q is defined according to Eq. 83. The order of equations (88, 89, and 90) is according to the order of equations of state in Eqs. 80, 81, and 82. These equations define the relation between the a and b constant in two-constant cubic equations of state and critical conditions, i.e. temperature, pressure, and molar volume of pure gas fluids. Therefore, knowledge of these conditions from experimental data can be used to determine the values of a (or ζ_2) and b , which can be defined as a function of only temperature and pressure (Eqs. 91-93, and 94-96, respectively).

$$\text{Weos: } \zeta_2 = \frac{27}{64} \cdot \frac{R^2 T_C^2}{p_C} = 0.421875 \cdot \frac{R^2 T_C^2}{p_C} \quad (91)$$

$$\text{RKeos: } \zeta_2 = \frac{1}{9 \cdot (\sqrt[3]{2} - 1)} \cdot \frac{R^2 T_C^2}{p_C} \approx 0.42748024 \cdot \frac{R^2 T_C^2}{p_C} \quad (92)$$

$$\text{PREos: } \zeta_2 = \frac{(Q^2 + 4Q + 2)^2 \cdot (Q^2 - 2)}{4Q^2 \cdot (Q + 2)^2} \cdot \frac{R^2 T_C^2}{p_C} \approx 0.45723553 \cdot \frac{R^2 T_C^2}{p_C} \quad (93)$$

$$\text{Weos: } b = \frac{1}{8} \cdot \frac{RT_C}{p_C} = 0.125 \cdot \frac{RT_C}{p_C} \quad (94)$$

$$RKeos: \quad b = \frac{(\sqrt[3]{2}-1)}{3} \cdot \frac{RT_C}{p_C} \approx 0.08664035 \cdot \frac{RT_C}{p_C} \quad (95)$$

$$PReos: \quad b = \frac{(Q^2-2)}{2Q^2 \cdot (Q+2)} \cdot \frac{RT_C}{p_C} \approx 0.07779607 \cdot \frac{RT_C}{p_C} \quad (96)$$

where T_C and p_C are the critical temperature and critical pressure, and Q is defined according to Eq. 83. The order of equations (91-93, and 94-96) is according to the order of equations of state in Eqs. 80-82. Comparison of the value of b calculated with experimental critical volume (Eqs. 80, 81 and 82) and critical temperature and pressure (Eqs. 94, 95, and 96) is illustrated in Table 2. The difference indicates the ability of a specific equation of state to reproduce fluid properties of pure gases. A large difference indicates that the geometry or morphology of the selected equation of state in the p - V - T - x parameter space is not exactly reproducing fluid properties of pure gases. The empirical modifications of the van-der-Waals equation of state according to Peng and Robinson [10] result in the most accurate equation in Table 2 (11% for pure CO₂).

6. Critical point and curve

The critical point is the highest temperature and pressure in a pure gas system where boiling may occur, i.e. where a distinction can be made between a liquid and vapour phase at constant temperature and pressure. At temperatures and pressures higher than the critical point the pure fluid is in a homogeneous supercritical state. The critical point of pure gases and multi-component fluid mixtures can be calculated exactly with the Helmholtz energy equation (Eqs. 55-57) that is obtained from two-constant cubic equations of state, e.g. see [17, 18], and it marks that part of the surface described with a Helmholtz energy function where two inflection points of the spinodal coincide. Therefore, the conditions of the spinodal are also applied to the critical point. In addition, the critical curve is defined by the determinant (D_{crit}) of the matrix illustrated in Eq. 97, see also [6].

$$D_{crit} = \begin{vmatrix} A_{VV} & A_{n_1 V} & A_{n_2 V} & \cdots \\ A_{V n_1} & A_{n_1 n_1} & A_{n_2 n_1} & \cdots \\ \vdots & \vdots & \vdots & \vdots \\ D_V & D_{n_1} & D_{n_2} & \ddots \end{vmatrix} = 0 \quad (97)$$

The number of rows in Eq.97 is defined by the differentiation variables volume and number of components minus 2. The last row is reserved for the partial derivatives of the determinant D_{spin} from Eq. 68:

$$D_V = \frac{\partial D_{spin}}{\partial V} \quad (98)$$

$$D_{n_1} = \frac{\partial D_{spin}}{\partial n_1} \tag{99}$$

$$D_{n_2} = \frac{\partial D_{spin}}{\partial n_2} \tag{100}$$

The derivatives of the spinodal determinant (Eqs. 98-100) are calculated from the sum of the element-by-element products of the matrix of "cofactors" (or adjoint matrix) of the spinodal (Eq. 101) and the matrix of the third derivatives of the Helmholtz energy function (Eq. 102).

$$\begin{vmatrix} C_{VV} & C_{n_1 V} & C_{n_2 V} & \dots \\ C_{V n_1} & C_{n_1 n_1} & C_{n_2 n_1} & \dots \\ C_{V n_2} & C_{n_1 n_2} & C_{n_2 n_2} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \tag{101}$$

$$\begin{vmatrix} A_{VV K} & A_{n_1 V K} & A_{n_2 V K} & \dots \\ A_{V n_1 K} & A_{n_1 n_1 K} & A_{n_2 n_1 K} & \dots \\ A_{V n_2 K} & A_{n_1 n_2 K} & A_{n_2 n_2 K} & \dots \\ \vdots & \vdots & \vdots & \ddots \end{vmatrix} \tag{102}$$

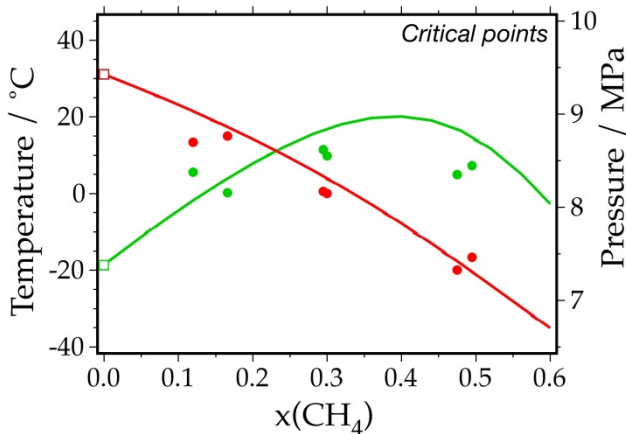


Figure 2. Calculated critical points of binary CO₂-CH₄ fluid mixtures in terms of temperature (red line) and pressure (green line), obtained from the *PREos* [10]. Solid circles are experimental data [16, 19]. The open squares are the critical point of pure CO₂ [20].

where C_{xy} are the individual elements in the matrix of "cofactors", as obtained from the Laplacian expansion. The subscript K refers to the variable that is used in the third differentiation (volume, amount of substance of the components 1 and 2. To reduce computation time in software that uses this calculation method, the *LU* decomposition has

been used to calculate the determinant in Eq. 97. The determinants in Eqs. 68 and 97 are both used to calculate exactly the critical point of any fluid mixture and pure gases, based on two-constant cubic equations of state that define the Helmholtz energy function.

An example of a calculated critical curve, i.e. critical points for a variety of compositions in a binary fluid system, is illustrated in Figure 2. The prediction of critical temperatures of fluid mixtures corresponds to experimental data [16, 19], whereas calculated critical pressures are slightly overestimated at higher fraction of CH₄. This example illustrates that the *PR*eos [10] is a favourable modification that can be used to calculate sub-critical conditions of CO₂-CH₄ fluid mixtures.

7. Mixing rules and definitions of ζ_1 and ζ_2

All modifications of the van-der-Waals two-constant cubic equation of state [7] have an empirical character. The main modifications are defined by Redlich and Kwong, Soave and Peng and Robinson (see Table 1), and all modification can be summarized by specific adaptations of the values of ζ_1 , ζ_2 , ζ_3 , and ζ_4 to fit experimental data. The original definition [7] of ζ_1 (b) and ζ_2 (a) for pure gases is obtained from the pseudo critical conditions (Eqs. 91-93, and 94-96). This principle is adapted in most modifications of the van-der-Waals equation of state, e.g. *RK*eos [8]. Soave [9] and Peng and Robinson [10] adjusted the definition of ζ_2 with a temperature dependent correction parameter α (Eqs. 103-105).

$$\zeta_2 = a_c \cdot \alpha \quad (103)$$

$$\alpha = \left[1 + m \left(1 - \sqrt{\frac{T}{T_c}} \right) \right]^2 \quad (104)$$

$$m = \sum_{i=0,1,2} m_i \cdot \omega^i \quad (105)$$

where a_c is defined by the pseudo critical conditions (Eqs. 91-93), and ω is the acentric factor. The summation in Eq. 105 does not exceed $i = 2$ for Soave [9] and Peng and Robinson [10]. The definition of the acentric factor is arbitrary and chosen for convenience [5] and is a purely empirical modification. These two equations of state have different definitions of pseudo critical conditions (see Eqs. 91-93 and 94-96), therefore, the values of m_i must be different for each equation (Table 3).

	<i>Soave</i> [9]	<i>Peng and Robinson</i> [10]
m_0	0.480	0.37464
m_1	1.574	1.54266
m_2	-0.176	-0.26992

Table 3. Values of the constant m_i in Eq. 105.

The two-constant cubic equation of state can be applied to determine the properties of fluid mixtures by using "mixing rules" for the parameters ζ_1 and ζ_2 which are defined for individual pure gases according to pseudo critical conditions. These mixing rules are based on simplified molecular behaviour of each component (i and j) in mixtures [21, 22] that describe the interaction between two molecules:

$$\zeta_1^{mix} = \sum_i \sum_j x_i \cdot \zeta_1(i) \quad (106)$$

$$\zeta_2^{mix} = \sum_i \sum_j x_i x_j \cdot \zeta_2(i, j) \quad (107)$$

where

$$\zeta_2(i, j) = \sqrt{\zeta_2(i) \cdot \zeta_2(j)} \quad (108)$$

These mixing rules have been subject to a variety of modifications, in order to predict fluid properties of newly available experimental data of mixtures. Soave [9] and Peng and Robinson [10] modified Eq. 108 by adding an extra correction factor (Eq. 109).

$$\zeta_2(i, j) = (1 - \delta_{ij}) \cdot \sqrt{\zeta_2(i) \cdot \zeta_2(j)} \quad (109)$$

where δ_{ij} has a constant value dependent on the nature of component i and j .

8. Experimental data

As mentioned before, modifications of two-constant cubic equation of state was mainly performed to obtain a better fit with experimental data for a multitude of possible gas mixtures and pure gases. Two types of experimental data of fluid properties were used: 1. homogeneous fluid mixtures at supercritical conditions; and 2. immiscible two-fluid systems at subcritical conditions (mainly in petroleum fluid research). The experimental data consist mainly of pressure, temperature, density (or molar volume) and compositional data, but can also include less parameters. Figure 3 gives an example of the misfit between the first type of experimental data for binary CO₂-CH₄ mixtures [19] and calculated fluid properties with *RKeos* [8] at a constant temperature (15 °C). The *RKeos* uses the pseudo critical defined parameters ζ_1 and ζ_2 (Eqs. 92 and 95) and mixing rules according to Eqs. 106-108 and is only approximately reproducing the fluid properties of CO₂-CH₄ mixtures at subcritical conditions

Experimental data of homogeneous supercritical gas mixtures in the ternary CO₂-CH₄-N₂ system [23] are compared with the two-constant cubic equations of state in Table 4. The *Weos* [7] clearly overestimates (up to 14.1 %) experimentally determined molar volumes at 100 MPa and 200 °C. The *Seos* [9] is the most accurate model in Table 4, but still reach deviations of up to 2.3 % for CO₂-rich gas mixtures. The *PReos* [10] gives highly underestimated molar volumes at these conditions.

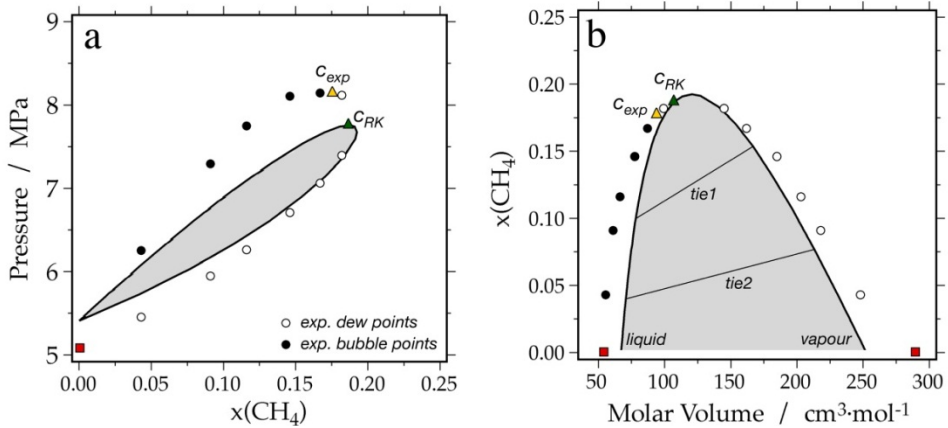


Figure 3. Modelled immiscibility of binary CO₂-CH₄ gas mixtures (shaded areas) in a pressure - amount CH₄ fraction diagram (a) and amount CH₄ fraction - molar volume diagram (b) at 15 °C. The solid and open circles are experimental data [16]. The red squares are the properties of pure CO₂ [20]. The yellow triangle (C_{exp}) is the interpolated critical point for experimental data, and the green triangle (C_{RK}) is the calculated critical point [8]. *tie1* and *tie2* in (b) are calculated tie-lines between two phases at constant pressures 6.891 and 6.036 MPa, respectively.

composition			$V_m(exp)$ $cm^3 \cdot mol^{-1}$	W	RK	S	PR
CO ₂	CH ₄	N ₂					
0.8	0.1	0.1	56.64	64.61 (14.1%)	54.90 (-3.1%)	57.94 (2.3%)	53.59 (-5.4%)
0.8	0.2	0.2	58.92	65.81 (11.7%)	56.61 (-3.9%)	59.61 (1.2%)	56.93 (-6.1%)
0.4	0.3	0.3	61.08	67.08 (9.6%)	58.27 (-4.6%)	61.12 (0.1%)	56.93 (-6.8%)
0.2	0.4	0.4	62.90	68.28 (8.6%)	59.83 (-4.9%)	62.42 (-0.8%)	58.28 (-7.3%)

Table 4. Comparison of supercritical experimental molar volumes [23] at 100 MPa and 200 °C with two-constant cubic equations of state (abbreviations see Table 1). The percentage of deviation from experimentally obtained molar volumes is indicated in brackets.

Figure 3 and Table 4 illustrate that these modified two-constant cubic equations of state still need to be modified again to obtain a better model to reproduce fluid properties at sub- and supercritical conditions.

9. Modifications of modified equations of state

The number of publications that have modified the previously mentioned two-constant cubic equations of state are numerous, see also [11], and they developed highly complex, but purely empirical equations to define the parameters ζ_1 and ζ_2 . A few examples are illustrated in the following paragraphs.

9.1. Chueh and Prausnitz [24]

The constant values in the definition of ζ_1 and ζ_2 (Eqs. 92 and 95) are modified for individual gases by Chueh and Prausnitz [24]. This equation is an arbitrary modification of the *RKees*

[8]. Consequently, the calculation of the value of ζ_1 and ζ_2 is not any more defined by pseudo critical conditions, which give exact mathematical definition of these constants. Although the prediction of fluid properties of a variety of gas mixtures was improved by these modifications, the morphology of the Helmholtz energy equation in the p - V - T - x parameter space is not any more related to observed fluid properties. The theory of pseudo critical conditions is violated according to these modifications.

The mixing rules in Eqs. 106-108 were further refined by arbitrary definitions of critical temperature, pressure, volume and compressibility for fluid mixtures.

$$\zeta_2(i,j) = \frac{\Omega_i + \Omega_j}{2} \cdot \frac{R^2 T_{Cij}^2}{p_{Cij}} \quad (110)$$

$$a_{ij} = \frac{\Omega_i + \Omega_j}{2} \cdot \frac{R^2 T_{Cij}^{2.5}}{p_{Cij}} \quad (111)$$

where Ω and Ω_j are the newly defined constant values of component i and j , and T_{Cij} and p_{Cij} are defined according to complex mixing rules [see 24]. The values of T_{Cij} and p_{Cij} are not related to true critical temperatures and pressures of specific binary gas mixtures.

The prediction of the properties of homogeneous fluids at supercritical conditions (Table 5) is only slightly improved compared to *RKeos* [10], but it is not exceeding the accuracy of the *Seos* [11]. At sub-critical condition (Figure 4), the Chueh-Prausnitz equation is less accurate than the Redlich-Kwong equation (compare Figure 3) in the binary CO₂-CH₄ fluid mixture at 15 °C.

composition			$V_m(exp)$ $cm^3 \cdot mol^{-1}$	CP	H	B1	B2
CO ₂	CH ₄	N ₂					
0.8	0.1	0.1	56.64	56.42 (-0.4%)	55.96 (-0.6%)	56.84 (0.4%)	56.53 (-0.2%)
0.8	0.2	0.2	58.92	57.85 (-1.8%)	57.68 (-2.1%)	59.43 (0.9%)	58.81 (-0.2%)
0.4	0.3	0.3	61.08	59.21 (-3.1%)	59.17 (-3.1%)	61.67 (1.0%)	60.79 (-0.5%)
0.2	0.4	0.4	62.90	60.44 (-3.9%)	60.38 (-4.0%)	63.45 (0.9%)	62.40 (-0.8%)

Table 5. The same experimental molar volumes as in Table 4 compared with two-constant equations of state according to Chueh and Prausnitz [24] (CP), Holloway [25, 26] (H), Bakker [27] [B1], and Bakker [28] (B2). The percentage of deviation from experimentally obtained molar volumes is indicated in brackets.

9.2. Holloway [25, 26] and Bakker [27]

The equation of Holloway [25, 26] is another modification of the *RKeos* [8]. The modification is mainly based on the improvement of predictions of homogenous fluid properties of H₂O and CO₂ mixtures, using calculated experimental data [29]. The value for ζ_1 and ζ_3 (both b) of H₂O is arbitrarily selected at 14.6 $cm^3 \cdot mol^{-1}$, whereas other pure gases are defined according to pseudo critical conditions. The definition of ζ_2 (i.e. a) for H₂O as a function of

temperature was subjected to a variety of best-fit procedures [25, 26]. The fitting was improved from four experimental data points [25] to six [26] (Figure 5), but was restricted to temperatures above 350 °C. Bakker [27] improved the best-fit equation by including the entire data set [29], down to 50 °C (Eq. 112).

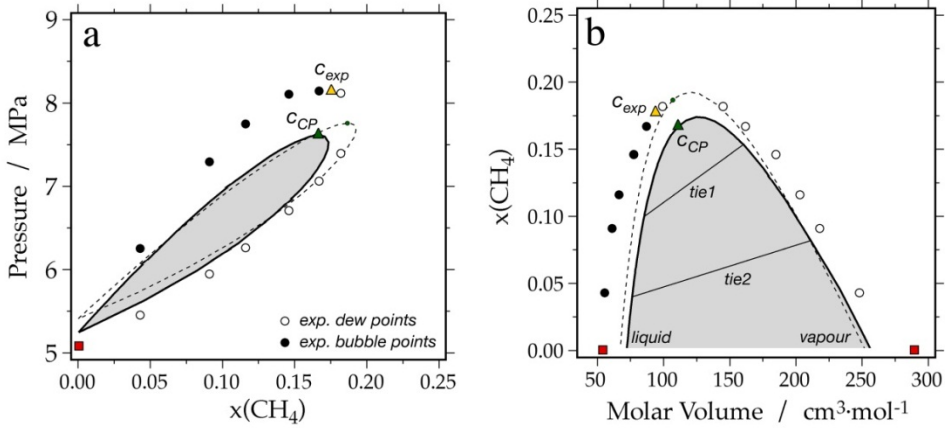


Figure 4. See Figure 3 for details. The RK_{EoS} is indicated by dashed lines in (a) and (b). The shaded areas are immiscibility conditions calculated with the Chueh-Prausnitz equation. $tie1$ and $tie2$ in (b) are calculated tie-lines between two phases at constant pressures 6.944 and 5.984 MPa, respectively.

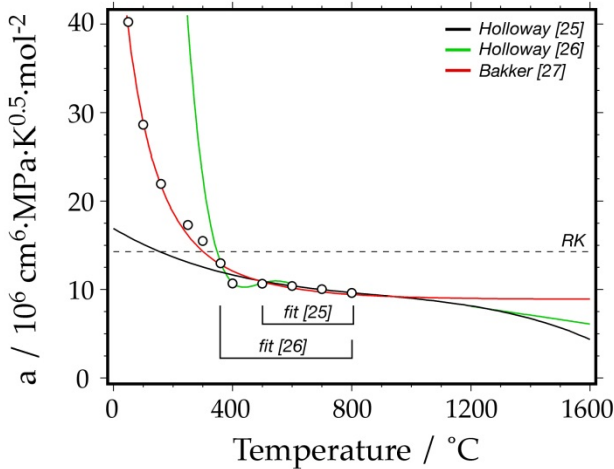


Figure 5. Temperature dependence of the a constant for pure H_2O in the modified cubic equation of state [25, 26]. The open circles are calculated experimental data [29]. $fit [25]$ is the range of fitting in the definition of Holloway [25], and $fit [26]$ of Holloway [26]. RK illustrates the constant value calculated from pseudo critical condition [8].

$$a_{H_2O} = \left(9.4654 - \frac{2.0246 \cdot 10^3}{T} + \frac{1.4928 \cdot 10^6}{T^2} + \frac{7.57 \cdot 10^8}{T^3} \right) \cdot 10^6 \quad (112)$$

where T is temperature in Kelvin, and the dimension of a is $\text{cm}^6 \cdot \text{MPa} \cdot \text{K}^{0.5} \cdot \text{mol}^{-2}$. The properties of homogeneous pure CO_2 , CH_4 and N_2 fluids [27] were also used to obtain a temperature dependent a constant (Eqs. 113, 114, and 115, respectively).

$$a_{\text{CO}_2} = \left(-1.2887 + \frac{5.9363 \cdot 10^3}{T} - \frac{1.4124 \cdot 10^6}{T^2} + \frac{1.1767 \cdot 10^8}{T^3} \right) \cdot 10^6 \quad (113)$$

$$a_{\text{CH}_4} = \left(-1.1764 + \frac{3.5216 \cdot 10^3}{T} - \frac{1.155 \cdot 10^6}{T^2} + \frac{1.1767 \cdot 10^8}{T^3} \right) \cdot 10^6 \quad (114)$$

$$a_{\text{N}_2} = \left(0.060191 - \frac{0.20059 \cdot 10^3}{T} + \frac{0.15386 \cdot 10^6}{T^2} \right) \cdot 10^6 \quad (115)$$

The a_{ij} value of fluid mixtures with a H_2O and CO_2 component (as in Eqs. 106-108 and 110-111) is not defined by the value of pure H_2O and CO_2 (Eqs. 112 and 113), but from a temperature independent constant value (Eqs. 116 and 117, respectively). In addition, a correction factor is used only for binary H_2O - CO_2 mixtures, see [25, 29].

$$a_0(\text{H}_2\text{O}) = 3.5464 \cdot 10^6 \text{ MPa} \cdot \text{cm}^6 \cdot \text{K}^{0.5} \cdot \text{mol}^2 \quad (116)$$

$$a_0(\text{CO}_2) = 4.661 \cdot 10^6 \text{ MPa} \cdot \text{cm}^6 \cdot \text{K}^{0.5} \cdot \text{mol}^2 \quad (117)$$

Table 5 illustrates that the equation of Holloway [25] is not improving the accuracy of predicted properties of supercritical CO_2 - CH_4 - N_2 fluids, compared to Chueh-Prausnitz [24] or *Seos* [9], and it is only a small improvement compared to the *RKeos* [8]. The accuracy of this equation is highly improved by using the definitions of a constants according to Bakker [27] (see Eqs. 112-115), and result in a maximum deviation of only 1% from experimental data in Table 5.

Experimental data, including molar volumes of binary H_2O - CO_2 fluid mixtures at supercritical conditions [30, 31, 32] are used to estimate fugacities of H_2O and CO_2 according to Eq. 118 (compare Eq. 10).

$$RT \ln \varphi_i = \int_0^p [V_{m,i} - V_m^{ideal}] dp \quad (118)$$

where $V_{m,i} - V_m^{ideal}$ is the difference between the partial molar volume of component i and the molar volume of an ideal gas (see also Eq. 43). The difference between Eqs. 118 and 10 is the

mathematical formulation and the use of different independent variables, which are temperature and pressure in Eq. 118. The integration to calculate the fugacity coefficient can be graphically obtained by measuring the surface of a diagram of the difference between the ideal molar volume and the partial molar volume (i.e. $V_{m,i} - V_{m,i}^{\text{ideal}}$) as a function of pressure (Figure 6). The surface obtained from experimental data can be directly compared to calculated curves from equations of state, according to Eq. 10 (Table 6).

The dashed line in Figure 6 is calculated with another type of equation of state: a modification of the Lee-Kesler equation of state [33] that is not treated in this manuscript because it is not a two-constant cubic equation of state. Fugacity estimations of H_2O are similar according to both equations, and reveal only a minor improvement for the two-constant cubic equation of state [27]. The experimental data to determine fugacity of CO_2 in this fluid mixture is inconsistent at relative low pressures (< 100 MPa). The calculated fugacity [27] is approximately compatible with the experimental data from [31, 32].

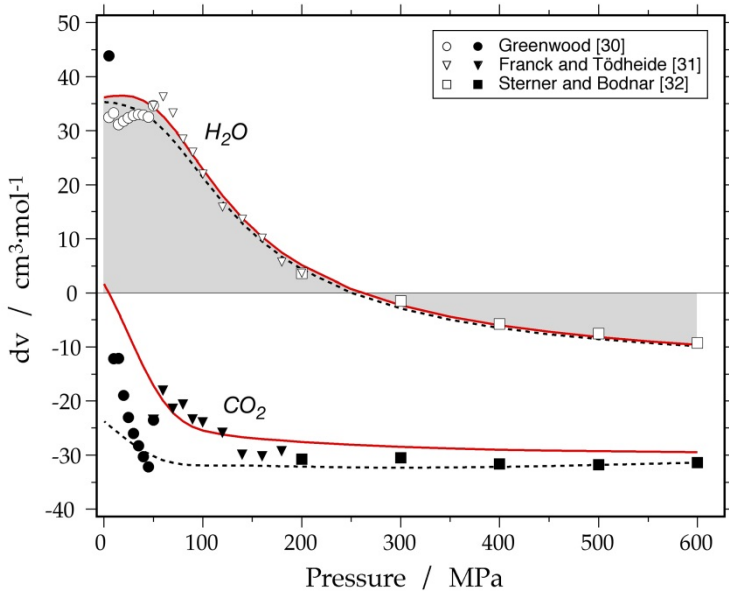


Figure 6. Fugacity estimation in a pressure - dv diagram at 873 K and a composition of $x(\text{CO}_2) = 0.3$ in the binary $\text{H}_2\text{O}-\text{CO}_2$ system, where dv is the molar volume difference of an ideal gas and the partial molar volume of either H_2O or CO_2 in binary mixtures. Experimental data are illustrated with circles, triangles and squares (solid for CO_2 and open for H_2O). The red lines are calculated with Bakker [27], and the shaded area is a measure for the fugacity coefficient of H_2O (Eq. 118).

<i>Pressure (MPa)</i>	<i>Exp. fugacity (MPa)</i>	<i>B1 fugacity (MPa)</i>
10	6.692	6.659 (-0.5%)
50	27.962	27.3061 (-2.3%)
100	45.341	44.6971 (-1.4%)
200	77.278	75.0515 (-2.9%)
300	114.221	111.072 (-2.8%)
400	160.105	157.145 (-1.8%)
500	219.252	216.817 (-1.1%)
600	295.350	294.216 (-04%)

Table 6. Fugacities of H₂O in H₂O-CO₂ fluid mixtures, $x(\text{CO}_2) = 0.3$, at 873.15 K and variable pressures. B1 fugacity is calculated with Bakker [27]. The deviation (in %) is illustrated in brackets.

9.3. Bowers and Helgeson [34] and Bakker [28]

Most natural occurring fluid phases in rock contain variable amounts of NaCl, which have an important influence on the fluid properties. Bowers and Helgeson [34] modified the *RKeos* [8] to be able to reproduce the properties of homogeneous supercritical fluids in the H₂O-CO₂-NaCl system, but only up to 35 mass% NaCl. The model is originally restricted between 350 and 600 °C and pressures above 50 MPa, according to the experimental data [35] that was used to design this equation. This model was modified by Bakker [28] including CH₄, N₂, and additionally any gas with *a* (ζ_2) and *b* (ζ_1) constants defined by the pseudo critical conditions (Eqs. 91-93 and 94-96). Experimental data in this multi-component fluid system with NaCl can be accurately reproduced up to 1000 MPa and 1300 K. Table 5 illustrates that this modification results in the best estimated molar volumes in the ternary CO₂-CH₄-N₂ fluid system at 100 MPa and 673 K. Similar to all modifications of the *RKeos* [8], this model cannot be used in and near the immiscibility conditions and critical points (i.e. sub-critical conditions).

10. Application to fluid inclusion research

Knowledge of the properties of fluid phases is of major importance in geological sciences. The interaction between rock and a fluid phase plays a role in many geological processes, such as development of magma [36], metamorphic reactions [37] and ore formation processes [38]. The fluid that is involved in these processes can be entrapped within single crystal of many minerals (e.g. quartz), which may be preserved over millions of years. The information obtained from fluid inclusions includes 1. fluid composition; 2. fluid density; 3. temperature and pressure condition of entrapment; and 4. a temporal evolution of the rock can be reconstructed from presence of various generation of fluid inclusions. An equation of state of fluid phases is the major tool to obtain this information. Microthermometry [39] is an

analytical technique that directly uses equations of state to obtain fluid composition and density of fluid inclusions. For example, cooling and heating experiment may reveal fluid phase changes at specific temperatures, such as dissolution and homogenization, which can be transformed in composition and density by using the proper equations of state.

The calculation method of fluid properties is extensive and is susceptible to errors, which is obvious from the mathematics presented in the previous paragraphs. The computer package FLUIDS [6, 40, 41] was developed to facilitate calculations of fluid properties in fluid inclusions, and fluids in general. This package includes the group "Loners" that handles a large variety of equations of state according to individual publications. This group allows researchers to perform mathematical experiments with equations of state and to test the accuracy by comparison with experimental data.

The equations of state handled in this study can be downloaded from the web site <http://fluids.unileoben.ac.at> and include 1. "LonerW" [7]; 2. "LonerRK" [8]; 3. "LonerS" [9]; 4. "LonerPR" [10]; 5. "LonerCP" [24]; 6. "LonerH" [25, 26, 27]; and 7. "LonerB" [28, 34]. Each program has to possibility to calculate a variety of fluid properties, including pressure, temperature, molar volume, fugacity, activity, liquid-vapour equilibria, homogenization conditions, spinodal, critical point, entropy, internal energy, enthalpy, Helmholtz energy, Gibbs energy, chemical potentials of pure gases and fluid mixtures. In addition, isochores can be calculated and exported in a text file. The diagrams and tables presented in this study are all calculated with these programs.

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