

Adaptation of the Bowers and Helgeson (1983) equation of state to the $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2-\text{NaCl}$ system

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Abstract

The equation of state developed by Bowers and Helgeson ([Bowers, T.S., Helgeson, H.C., 1983. Calculation of the thermodynamic and geochemical consequences of nonideal mixing in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ on phase relations in geological systems: equation of state for $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ fluids at high pressures and temperatures. *Geochim. Cosmochim. Acta*, 47, 1247–1275.] and [Bowers, T.S., Helgeson, H.C., 1985. Fortran programs for generating fluid inclusion isochores and fugacity coefficients for the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ at high pressures and temperatures. *Computers and Geosciences*, 11, 203–213.]), which was originally designed for $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ fluids, has been extended to CH_4 and N_2 bearing fluids. Available experimental $P-V-T-X$ data in the $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2-\text{NaCl}$ fluid system are accurately reproduced by this equation of state, and, therefore, isochores and fugacity coefficients can be accurately calculated up to 1000 MPa and 1300 K. This equation of state cannot be used in and near immiscibility regions and critical points, like any modified Redlich–Kwong equation of state. The empirical modifications allow isochore construction for realistic geological fluid systems which are often found in fluid inclusions, and which involve several gases and salts. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Equation of state; Isochore; Fugacity; Fluid inclusions

1. Introduction

One of the most important aims of fluid inclusion studies is to investigate the ancient environment of the studied rock, including temperature–pressure conditions and the characteristics of the fluid present in its pores. Isochore construction is therefore an important tool to constrain possible trapping conditions. Although, many equations of state that are used for isochore construction are based on theoretic

cal considerations, their predictability of natural fluid systems is obtained from an empirical best-fit to experimental data. The quality of extrapolations is firstly dependent on a fundamental understanding of molecular interactions. The elementary form of the mathematical formulas to describe the nature of these fluids is of major importance for the reliability of calculations beyond measurable conditions.

Gases and liquids were originally studied separately, until van der Waals (1873) described the continuity between these phases. His equation of state is purely theoretical and it is based on the

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kinetic theory of gases. The equation of state from van der Waals (1873) has been frequently modified (e.g., Redlich and Kwong, 1949) because it was unable to describe a fluid system over a larger temperature–pressure range. These modifications are in general purely empirical and based on one phase analysis, despite the continuity theorem of van der Waals (1873). For example, the equations of state according to Redlich and Kwong (1949) and Soave (1972) are designed for vapour-like fluids, and are unable to describe liquid-like systems at relative low pressures. This type of equation of state has the advantage that fluid mixtures can be described with relatively simple mixing rules, which are in turn purely arbitrary. Recently, equations of state have been generally accepted to describe all measurable properties of vapours and liquids, i.e., heat capacity, viscosity, volumetric data, and liquid–vapour equilibria (e.g., Hill, 1990). These equations are based on a unified Helmholtz function, and are only available for pure fluid systems. Recently, Anderko and Pitzer (1993) and Duan et al. (1995) have developed comprehensive equations of state for the H₂O–NaCl system and H₂O–CO₂–NaCl system, respectively, which are able to reproduce vapour–liquid equilibria and volumetric data. However, the effects of dissolved salts on complex fluid systems have been poorly described in the literature, and there is insufficient *P–V–T–X* data available for these salt-bearing systems.

In fluid inclusion studies one often finds several gas species and salts in the aqueous solution. Most equations of state that are used for isochore construction for these fluids do not include any salt species, because an equation of state is not available for these complex systems. Therefore, a modified Redlich–Kwong equation of state according to Bowers and Helgeson (1983, 1985) is re-examined carefully with new experimental data in this study for adaptation to complex fluid mixtures of H₂O, CO₂, CH₄, N₂, and NaCl, in order to be able to construct accurate isochores and to calculate fugacity coefficients.

2. The equation of state

The equation of state according to Bowers and Helgeson (1983, 1985) (hereafter referred to as the

‘BH-equation’) was originally designed to fit experimental data of Gehrig (1980) for H₂O–CO₂–NaCl fluids at pressures above 50 MPa and temperatures from 623 to 873 K for salinities from 0 to 35 wt.% in the one-phase region of this ternary system. The equation is related to the Redlich–Kwong equation of state:

$$P = \frac{RT}{(v - b)} - \frac{a}{v(v + b)\sqrt{T}} \quad (1)$$

where *P*, *T*, and *v* are pressure, temperature, and molar volume, respectively; *R* is the gas-constant; and *a* and *b* are constants similar to those from van der Waals (1873), which represent attractive molecular forces and molecular size, respectively. Redlich and Kwong (1949) related these constant values to critical properties of the gases:

$$a = \frac{\Omega_A \cdot R^2 \cdot (T_{\text{Crit}})^{2.5}}{P_{\text{Crit}}} \quad (2a)$$

$$b = \frac{\Omega_B \cdot R \cdot T_{\text{Crit}}}{P_{\text{Crit}}} \quad (2b)$$

where Ω_A and Ω_B are constants defined as:

$$\Omega_A = \frac{1}{9 \cdot (2^{1/3} - 1)} \approx 0.427482 \quad (3a)$$

$$\Omega_B = \frac{2^{1/3} - 1}{3} \approx 0.08664 \quad (3b)$$

According to these definitions the equation of state is exact at the critical point of pure fluids. However, it is very inaccurate near the critical point but then quite good again further away for vapour like fluids. There are many types of intermolecular attractive forces which can be specified as a summation in the *a* parameter:

$$a^{\text{total}} = a^{\text{permanent}} + a^{\text{induction}} + a^{\text{dispersion}} + a^{\text{chemical}} \quad (4)$$

where $a^{\text{permanent}}$ represents electrostatic forces between permanent dipoles, quadrupoles and higher multipoles; $a^{\text{induction}}$ are induction forces between a permanent dipole and an induced dipole; $a^{\text{dispersion}}$ are dispersion forces as a result of the oscillations of

electrons about the nucleus which are sufficient to cause a temporary dipole moment, even in so-called nonpolar molecules; and a^{chemical} are specific forces leading to association and complex formation (e.g., hydrogen bonds). London (1937) illustrated that induction forces and dispersion forces may account for 20% of the total potential energy for strongly polar substances, like H₂O. Santis et al. (1974) combined the $a^{\text{permanent}}$ and $a^{\text{induction}}$ terms of Eq. (4) for polar gases in one temperature dependent constant $a(1)$, and dispersion forces were expressed in a constant $a(0)$. The $a(1)$ term decreases as temperature rises, and polar and non-polar gases become similar at higher temperatures. In mixtures, the a parameter is expressed as the average over binary interactions, using the geometric-mean assumption (Berthelot, 1879):

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (5a)$$

$$a_{ij} = \sqrt{a_i a_j} \quad (5b)$$

where x_i is the mole fraction of component i , and a_{ij} represents binary interactions between component i and j in the fluid mixture. For polar–nonpolar molecular interactions, only the dispersion part $a(0)$ of polar molecules is active, since simple gases have no permanent dipole moment, and, therefore, they cannot induce any polarisation.

Holloway (1977) estimated simple purely empirical polynomes for the temperature dependence of the attractive term for H₂O, which were fitted to six data points from Santis et al. (1974) between 400 and 800°C. Later, Holloway (1981) adjusted his polynome to temperatures exceeding 1200°C, including the rest of the data given by Santis et al. (1974). For CO₂, Holloway (1977) obtained a temperature dependent polynome between 0 and 800°C for data from, again, Santis et al. (1974). In these studies, polynomes were only estimated for a^{total} and for $a(0)$, while $a(1)$ should be deduced from these functions. Bowers and Helgeson (1983) used a similar modification of the Redlich–Kwong equation of state, and they assumed that the presence of salt effects the parameters for H₂O due to the strong interaction between these molecules. The interactions between NaCl and CO₂ molecules were neglected. Parameters $a(0)$, a^{total} and b for H₂O were expressed as a

smooth empirical function of weight% NaCl and temperature:

$$a(0)_{\text{H}_2\text{O}} = 10^6 \cdot \exp(a_0 + a_1 \cdot w + a_2 \cdot w^2 + a_3 \cdot w^3) \quad (6a)$$

$$a_0 = 4.881243 + 1.823047 \cdot 10^{-3} \cdot T - 1.712269 \cdot 10^{-5} \cdot T^2 + 6.479419 \cdot 10^{-9} T^3$$

$$a_1 = 0.02636494 - 5.36994 \cdot 10^{-4} \cdot T + 2.687074 \cdot 10^{-6} \cdot T^2 - 4.321741 \cdot 10^{-9} \cdot T^3$$

$$a_2 = 6.802827 \cdot 10^{-3} - 9.48023 \cdot 10^{-5} \cdot T + 3.770339 \cdot 10^{-7} \cdot T^2 - 5.075318 \cdot 10^{-10} \cdot T^3$$

$$a_3 = 5.235827 \cdot 10^{-5} - 3.505272 \cdot 10^{-8} \cdot T$$

$$a_{\text{H}_2\text{O}}^{\text{total}} = 10^6 \cdot (a_0' + a_1' \cdot w) \quad (6b)$$

$$a_0' = 111.3057 + 50.70033 \cdot \exp(-9.82646 \cdot 10^{-3} \cdot T)$$

$$a_1' = -8.05658 \cdot \exp(-9.82646 \cdot 10^{-3} \cdot T)$$

$$b_{\text{H}_2\text{O}} (\text{cm}^3/\text{mol}) = 14.6 - 0.04420283 \cdot w \quad (6c)$$

where w is the salinity in wt.%; and T is temperature in °C. It should be noted that these a parameters are given in atm K^{0.5} cm⁶ mol⁻², which is multiplied by a factor 0.101325 to obtain MPa K^{0.5} cm⁶ mol⁻². The greek symbols in the original equations are replaced to avoid confusion with symbols for physical and chemical intensive variables. Apparently, the temperature independence of dispersion forces was abandoned by Bowers and Helgeson (1983). The a and b values for CO₂ were obtained from Holloway (1977). Complex forming between H₂O and CO₂ in the gas phase is expressed in an additional a^{chemical} for their cross-coefficient, according to Santis et al. (1974). The functional forms of the polynomes chosen to represent the a and b parameters (Eqs. (6a), (6b) and (6c)) were constrained to be consistent with the limits of the miscibility gap in the ternary system H₂O–CO₂–NaCl.

3. Pure N₂ and CH₄ fluids

The BH-equation can be easily extended to other gas components, according to the corresponding state principle as suggested by Redlich and Kwong (1949).

As mentioned before, NaCl only effects the parameters for H₂O, and not those for CO₂. Therefore, a similar approach can be used for gases like CH₄ and N₂, assuming that their *a* and *b* parameters are not affected by the presence of salts. The *b* parameters for N₂ and CH₄ (Table 1), which account for the volume occupied by the molecules in a fluid, have been calculated from critical properties (Eq. (2b)) according to Redlich and Kwong (1949). The *b* parameter is assumed to remain constant, and it is similar to that calculated by Holloway (1981). This assumption allows a bestfit estimation for values of the *a* parameter in Eq. (1), which accounts for the attractive potential between molecules. Calculated *PTV*-data for pure CH₄ and N₂ are obtained from the IUPAC equations (Angus et al., 1978, 1979) and Duan et al. (1992a). These calculated data are substituted in Eq. (1) to obtain optimum values for the *a* parameter (Fig. 1). The isobars in Fig. 1 illustrate that the *a* parameter decreases for higher temperatures. However, an obvious temperature dependent equation is difficult to estimate because the isobars cover a small range of *a* values for any given temperature, indicating that pressure or molar volume should be included in the mathematical description for *a* values. This effect might be an artefact, indicating that the *b* parameter is sensitive to pressure. The *a* parameter for N₂ becomes negative at higher temperatures, implying that attractive forces become repulsive, which is physically impossible. Furthermore, negative *a* values for gas mixtures including N₂ lead to mathematical problems in the geometric mixing rule (Eqs. (5a) and (5b)). Therefore, in the mathematical approach of this study *a* parameters in gas mixtures with negative values are set to zero, whereas, in a pure N₂ fluid these negative values remain valid. Consequently, N₂-rich gas mixtures with a negative *a* parameter mix ideally

Table 1

a(0) and *b* values for pure CH₄ and N₂ according to Redlich and Kwong (1949)

	<i>a</i> (0)	<i>b</i>
	(MPa √K cm ⁶ mol ⁻²)	(cm ³ mol ⁻¹)
CH ₄	3.222 · 10 ⁶	29.8
N ₂	1.5689 · 10 ⁶	27.0

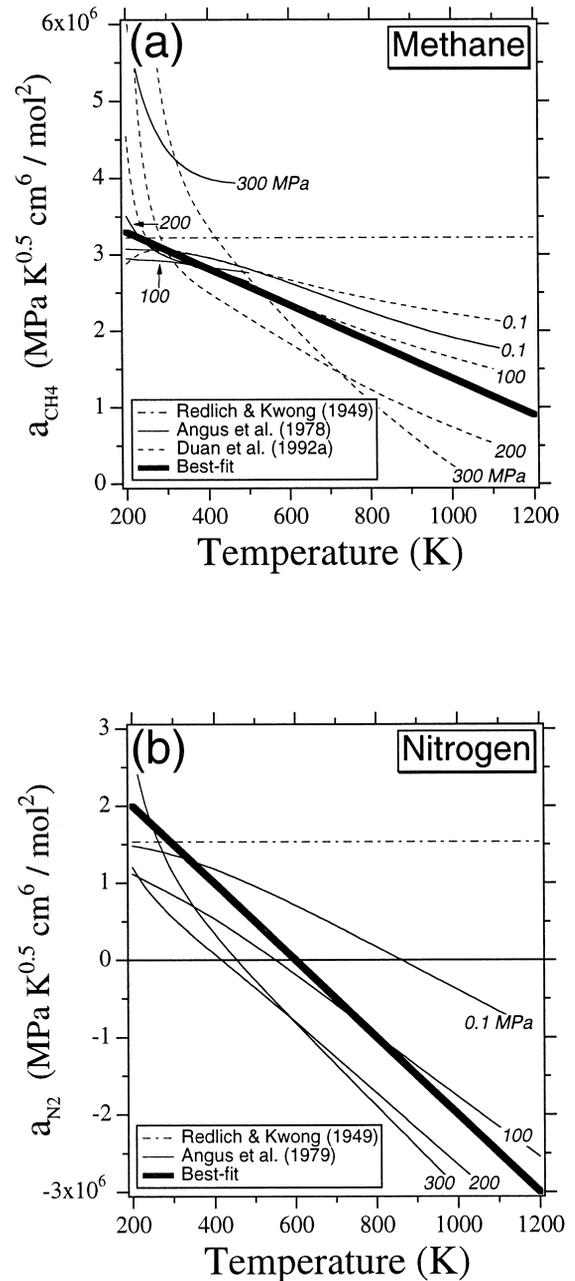


Fig. 1. Temperature dependence of the *a* parameter for methane (a) and nitrogen (b). The best-fit (thick solid line) is roughly optimizing calculated values obtained from Angus et al. (1978, 1979) and Duan et al. (1992a).

according to this mathematical restriction. The variation in optimized *a* values using several equations of state for pure CH₄, i.e., Angus et al. (1978) and

Duan et al. (1992a) is evident from Fig. 1a. These discrepancies impede an irrefutable estimation of the temperature dependence of a values. Nevertheless, an average temperature dependence has been chosen for both CH_4 and N_2 which is roughly an optimalization of the a parameters up to 1200 K and up to at least 300 MPa:

$$a_{\text{CH}_4}^{\text{total}} = 3.1244 \cdot 10^6 - 2.4 \cdot 10^3 \cdot T \quad (7a)$$

$$a_{\text{N}_2}^{\text{total}} = 1.6343 \cdot 10^6 - 5.0 \cdot 10^3 \cdot T \quad (7b)$$

where T is temperature in $^\circ\text{C}$; and a values are expressed in $\text{MPa K}^{0.5} \text{ cm}^6 \text{ mol}^{-2}$. The choice of these lines is purely arbitrary. Santis et al. (1974) assumed for these simple gases that $a(1) = 0$ and $a(0)$ is obtained from critical data (see Table 1). These constant values lead to large deviations at higher temperatures and pressures (see Fig. 1). The a^{total} values in Eqs. (7a) and (7b) are assumed to represent temperature dependent dispersion forces for CH_4 and N_2 , which are equivalent to $a(0)$ values according to Santis et al. (1974).

4. Comparison to experimental data

Recently, Brown and Lamb (1989) and Duan et al. (1995) have compared the BH-equation to experimental data and other equations of state to demonstrate its accuracy in isochore calculations. Brown and Lamb (1989) concluded that the BH-equation does not work well for high-density $\text{H}_2\text{O}-\text{NaCl}$ and $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ mixtures, which is consistent with the temperature–pressure limit indications from Bowers and Helgeson (1985). Additionally, these conclusions were reinforced by Duan et al. (1995) who illustrated large errors for the BH-equation for $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ mixtures. However, Duan et al. (1995) had completely misinterpreted the BH-equation of state (notice the wrongly calculated values in Table 6 from Duan et al., 1995), and they have used results from the BH-equation outside its temperature–pressure limits, i.e., lower than 50 MPa between 703 and 763 K, to illustrate the superiority of their equations. These unsubstantiated conclusions justify a re-examination of the BH-equation of state.

4.1. $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ fluid system

First, the BH-equation is compared to the pure H_2O fluid system (Fig. 2) as defined by the steam tables (Haar et al., 1984), and it appears to give a good fit up to 1000 MPa and 1300 K, with a maximum deviation in calculated densities of 5–6%. Near the critical point and the saturation curve deviations may exceed 10% (Fig. 2b), illustrating the incompetence of modified Redlich–Kwong equations of state to predict PTV -properties of liquid-like fluids and saturation properties at relative low pressures. In addition, within this PT region more than one solution is present for calculated molar volumes from a given temperature and pressure (Fig. 2b), which demonstrates mathematical problems in find-

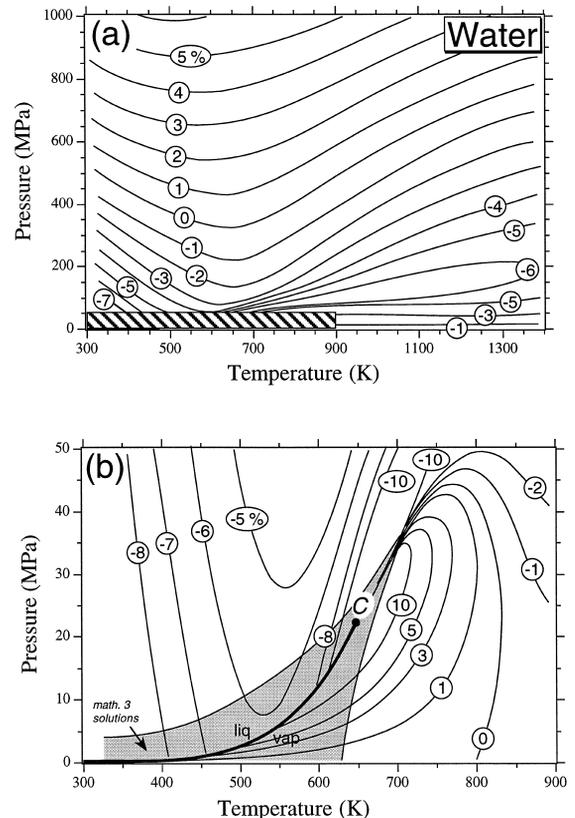


Fig. 2. Contours of deviation in molar volumes (in percentages) between the BH-equation and Haar et al. (1984) for pure H_2O , in the temperature–pressure range up to 1373 K and 1000 MPa (a), and in the near critical region (b). The shaded area indicate PT conditions, which have three mathematical solutions for calculated molar volumes.

ing single solutions for homogeneous phases. Most deviations within the PT -range illustrated in Fig. 2 are much smaller than 5%, which is usually a limiting error indication for studied natural fluids. Consequently, the BH-equation can correctly construct isochores for pure H_2O up to 1000 MPa and 1300 K.

Second, data from the H_2O –NaCl fluid system are compared to the BH-equation. Originally, Bowers and Helgeson (1983) used the data from Gehrig (1980) to develop their equations. Some of these data for 6 and 10 wt.% NaCl are plotted in Fig. 3 to

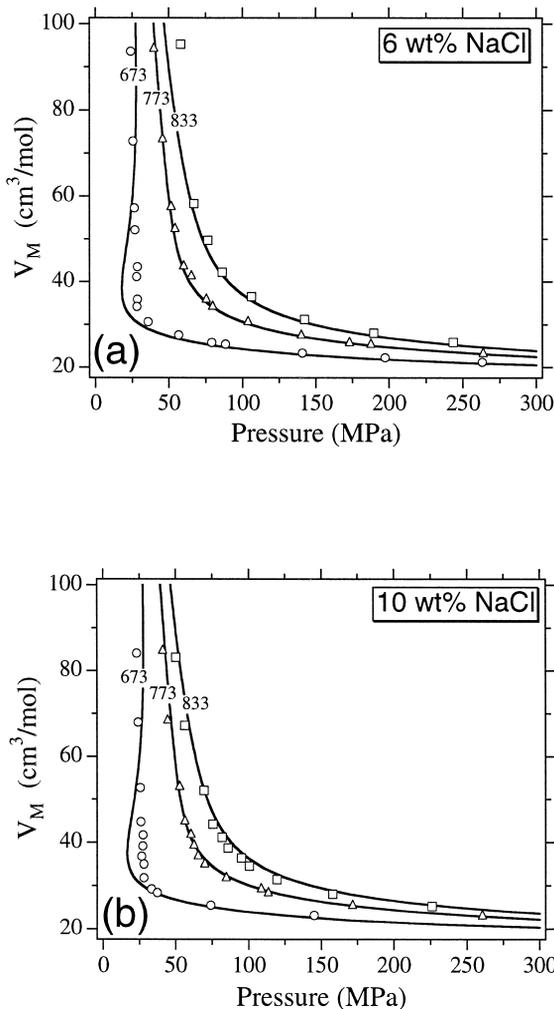


Fig. 3. Isotherms (673, 773, and 833 K) in PV diagrams for comparison between experimental data from Gehrig (1980) and the BH-equation, for 6 wt.% NaCl solutions (a) and 10 wt.% NaCl solutions (b).

Table 2

Experimental data for the H_2O –NaCl fluid system from Zhang and Frantz (1987) at 300 MPa and selected salinities in comparison to BH-equation of state

wt.% NaCl	T_{EXP} (K)	V_{EXP} (cm^3/mol)	V_{CAL} (cm^3/mol)	dev%
2.839	623	20.1	19.812	–1.43
	673	20.9	20.688	–1.01
	723	22.1	21.648	–2.05
	775	23.4	22.740	–2.82
	883	26.2	25.320	–3.36
	977	29.5	27.892	–5.45
10.465	624	20.1	19.389	–3.54
	671	20.8	20.165	–3.05
	725	21.6	21.155	–2.06
	776	22.5	22.191	–1.37
	897	24.8	25.052	1.02
	993	27.2	27.700	1.84
20.822	627	20.5	18.832	–8.14
	681	21.2	19.660	–7.26
	730	21.9	20.514	–6.33
	784	22.7	21.571	–4.97
	884	24.0	23.850	–0.06
	977	25.8	26.329	2.05

illustrate real deviations in density calculation. The 773 K and 833 K isotherms have excellent fits to experimental data, however, the differences increase for lower temperatures (673 K), near the miscibility gap in this fluid system. These differences occur evidently at PT conditions similar to the previously mentioned large deviations for pure H_2O fluids, which shows again the incompetence of this type of equation of state near the immiscibility region. These conclusions are consistent with the results from Brown and Lamb (1989). However, these problems are irrelevant for isochore constructions to much higher temperatures and pressures. The BH-equation is also compared to experimental data from Zhang and Frantz (1987) at 300 MPa, which is based on synthetic fluid inclusions studies (Table 2). The fit up to 10.465 wt.% NaCl solutions is very good, and deviations are in general much better than 5%. Deviations increase up to 8% for a 20.822 wt.% NaCl solution and relative low temperatures (< 733 K), however, the fit for this NaCl solution is much better at higher temperatures. This comparison illustrates that data obtained from synthetic fluid inclusions also have an excellent fit to the BH-equation.

Third, experimental data for the H₂O–CO₂ fluid system from Zakirov (1984) and Sterner and Bodnar (1991) are compared to the BH-equation. Near the miscibility gap in this system experimental molar volumes from Zakirov (1984) exceed between 4 and 8% calculated values, with the highest deviations near critical conditions. Again, these results are consistent with the previously mentioned deficiency of the BH-equation. Other equations of state (e.g., Duan et al., 1992b, 1996) have a similar accuracy for molar volumes in H₂O-rich fluids within this *PT* region. Only a part of the data from Sterner and Bodnar (1991) are plotted in Fig. 4, which shows a good fit to the BH-equation at 773 K and between 200 to 600 MPa. Error indications of individual measurements, which are not illustrated in Fig. 4, result in a nearly perfect fit. Calculated molar volumes from Sterner and Bodnar (1991) are not taken into account to allow a comparison based purely on measured values. The deviations of experimental data at 673, 873, and 973 K are similar to those for 773 K, and they do not exceed 4%, while most values are within 2%. These results indicate that the BH-equation can be used to at least 973 K and 600 MPa in the H₂O–CO₂ fluid system.

Fourth, the BH-equation is compared to experimental data in the H₂O–CO₂–NaCl fluid system. Again, a part of the data from Gehrig (1980) is selected to illustrate the excellent fit in calculated densities between the BH-equation and data (Table 3). The largest deviation appears for nearly pure H₂O fluids in near critical conditions, which is

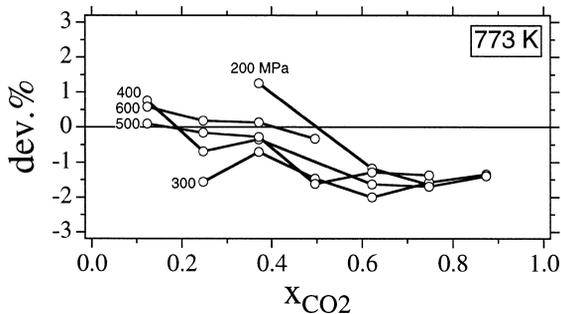


Fig. 4. Deviations (in percentages) of calculated molar volumes in the H₂O–CO₂ fluid mixtures to experimental data from Sterner and Bodnar (1991) at 773 K and selected pressures of 200, 300, 400, 500, and 600 MPa. These isobars are indicated with solid lines.

Table 3

Experimental data for the H₂O–CO₂–NaCl fluid system from Gehrig (1980), for 6 wt.% NaCl at 773 K, in comparison with the BH-equation

mol%		P_{EXP}	V_{EXP}	V_{CAL}	dev.%
H ₂ O	CO ₂	(MPa)	(cm ³ /mol)	(cm ³ /mol)	
97.9	0.18	51.7	61.325	55.713	–9.15
		56.2	51.104	47.406	–7.24
		64.5	40.883	39.968	–2.24
		103.0	30.662	30.416	–0.80
		184.4	25.552	25.286	–1.04
88.75	9.69	52.3	76.656	77.801	1.49
		62.0	61.325	61.466	2.30
		79.8	45.994	46.762	1.67
		94.6	39.861	40.990	2.83
		115.5	35.773	36.381	1.70
77.47	21.01	297.0	25.552	25.767	0.84
		51.0	95.053	95.466	0.43
		61.9	76.656	76.377	–0.36
		76.7	61.325	61.247	–0.13
		94.6	51.104	51.172	0.12
65.91	32.80	116.2	43.949	44.333	0.87
		142.5	38.839	39.451	1.58
		171.5	35.773	36.076	0.85
		242.1	30.662	31.459	2.60
		58.5	93.009	92.198	–0.87
50.79	48.21	70.6	76.656	76.675	0.02
		91.6	61.325	61.193	–0.22
		117.8	51.104	51.037	–0.13
		153.0	43.949	43.723	–0.51
		84.1	75.981	75.012	–1.28
28.50	70.94	110.3	61.560	61.322	–0.39
		175.1	45.994	46.621	1.36
		211.5	42.927	42.587	–0.79
		265.6	38.839	38.700	–0.36
		139.0	61.325	61.108	–0.35
4.45	95.46	197.2	51.104	50.718	–0.76
		277.7	43.949	43.702	–0.56
		37.7	177.198	182.246	2.85
		41.2	165.577	168.382	1.69
		48.0	143.091	147.411	3.02
		65.2	112.429	114.546	1.88
		101.0	81.766	83.249	1.81
		153.0	61.325	64.723	5.54

consistent with similar deviations as illustrated in Fig. 2b for pure H₂O. These large deviations have been stressed by Duan et al. (1995) to illustrate the incompetence of the BH-equation. However, Table 3 shows that most values are less than 1%. Johnson (1992) used synthetic fluid inclusions to estimate some experimental data in this fluid system at higher pressures and temperatures. His data are reinter-

Table 4

Experimental data for the H₂O–CO₂–NaCl fluid system from Johnson (1992), compared to the BH-equation

	Mole fractions			wt.% NaCl	Experimental conditions			V _{CAL} (cm ³ /mol)
	H ₂ O	CO ₂	NaCl		T (K)	P (MPa)	V (cm ³ /mol)	
ET-71	0.777(±0.02)	0.177(±0.02)	0.046(±0.002)	16.16	1211(±5)	745.8(±5)	25.24(±1.0)	26.88(±0.6)
ET-60	0.693(±0.03)	0.270(±0.03)	0.037(±0.002)	14.93	1203(±14)	660(±7)	28.38(±1.5)	30.10(±1.0)
ET-68	0.467(±0.07)	0.507(±0.07)	0.026(±0.003)	15.04	1197(±10)	680(±5)	35.00(±3.0)	34.61(±1.6)
ET-85	0.626(±0.03)	0.313(±0.03)	0.061(±0.003)	23.90	1213(±21)	740(±5)	28.61(±1.5)	29.61(±1.0)

preted (Table 4) using computer program Q2 from Bakker et al. (1996) and Bakker (1997). This program allows calculation of the composition and density of the total fluid inclusion from the clathrate melting temperature, homogenisation temperature of the CO₂ phases, and volume fraction estimates. These calculations are purely based on the analysis of the fluid actually present in inclusions, and it does not include any pre- and post-experiment information of the fluid present in the experimental capsules. Johnson (1992) has illustrated the difference for salinity estimations, but ignored any effects on the H₂O–CO₂ ratio. Although the average molar volumes may differ up to 6% from the BH-equation (Table 4), the error indication in individual measurements result in an almost perfect fit, which is similar to the conclusions of Johnson (1992). This fit is better than that obtained from the equation according to Duan et al. (1995). The isochores calculated with the BH-equation reproduce the trapping pressure and temperature well for the experiments of Johnson (1992) for fluids

with less than 50 mol% CO₂ and up to 23.9 wt.% NaCl.

4.2. CO₂–CH₄–N₂ fluid system

Applications of the suggested modifications of the BH-equation are illustrated for binary and ternary mixtures in the CO₂–CH₄–N₂ fluid system at 473 K and 100 MPa from Seitz et al. (1994). Experimental data in binary mixtures, i.e., CO₂–CH₄, CH₄–N₂, and N₂–CO₂ (Fig. 5) have an excellent fit to the modified BH-equation, and deviations in calculated densities do not exceed 1.7%. The ternary fluid system (Table 5) has deviations less 1.3%, which, again, illustrates the excellent accuracy of the modified BH-equation. Comparison with higher pressure and temperature data (Table 6), obtained from molecular dynamics simulations (Duan et al., 1996), indicates deviations less than 3% up to 1200 K and

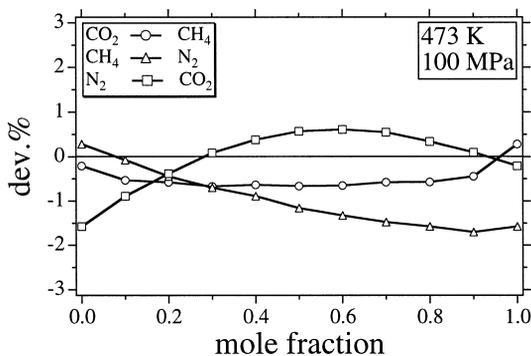


Fig. 5. Deviations (in percentages) in molar volumes for binary fluid mixtures in the CO₂–CH₄–N₂ system at 473 K and 100 MPa between the modified BH-equation and experimental data from Seitz et al. (1994).

Table 5

Experimental data for the ternary CO₂–CH₄–N₂ fluid system from Seitz et al. (1994) at 473 K and 100 MPa, compared to the modified BH-equation

Composition			V _{EXP} (cm ³ /mol)	V _{CAL} (cm ³ /mol)	dev. %
CO ₂	CH ₄	N ₂			
80	10	10	56.64	56.574	–0.12
60	20	20	58.92	58.870	–0.08
40	30	30	61.08	60.869	–0.34
20	40	40	62.9	62.491	–0.65
10	80	10	62.21	62.101	–0.18
20	60	20	62.22	61.875	–0.56
30	40	30	61.8	61.573	–0.37
40	20	40	61.27	61.193	–0.13
10	10	80	64.71	63.900	–1.25
20	20	60	63.43	63.022	–0.64
30	30	40	62.07	61.885	–0.30
40	40	20	60.7	60.529	–0.28

Table 6

Experimental data for the ternary CO₂–CH₄–N₂ fluid system from Duan et al. (1996), compared to the modified BH-equation

Mole fractions			Molecular dynamics simulation			V _{CAL} (cm ³ /mol)	dev. %
CH ₄	CO ₂	N ₂	T (K)	P (MPa)	V (cm ³ /mol)		
0.3906	0.3906	0.2188	291.0(±3)	67.32(±2.8)	50	48.73(±1.4)	–2.55
			383.1(±4)	120.14(±5.4)	50	48.46(±1.0)	–3.09
			484.0(±6)	171.12(±6.6)	50	48.70(±1.0)	–2.60
			562.9(±5)	201.94(±6.5)	50	49.57(±0.9)	–0.85
			722.8(±9)	281.63(±10.2)	50	49.17(±1.0)	–1.67
0.3906	0.3906	0.2188	973.4(±8)	390.51(±12.0)	50	49.26(±0.8)	–1.49
			973.0(±11)	2985.91(±33.3)	25	31.83(±0.07)	27.34
			470.4(±5)	2126.31(±29.7)	25	30.93(±0.04)	23.71
0.375	0.3125	0.3125	302.2(±7)	79.43(±2.5)	50	48.51(±1.2)	–2.98
			362.5(±3)	112.82(±4.1)	50	48.45(±0.8)	–3.09
			461.6(±5)	162.8(±5.5)	50	48.67(±1.0)	–2.66
			602(±7)	227.27(±8.8)	50	49.38(±1.1)	–1.23
			1201(±12)	484.08(±12.5)	50	49.34(±0.8)	–1.31

500 MPa. The fit appears to be nearly perfect if the error in individual temperature and pressure estimates is taken into account. At extreme high pressures (2126 and 2985 MPa in Table 6) the modified

BH-equation is unable to predict experimental estimated densities, and calculated molar volumes are more than 20% overestimated.

4.3. H₂O–CH₄–NaCl fluid system

Experimental *P–T–V–X* data in the H₂O–CH₄–NaCl fluid system is only available for the boundary of the immiscibility field (e.g., Krader and Franck, 1987; Lamb et al., 1996). As mentioned before, modified Redlich–Kwong equations of state are unable to calculate this boundary and very large deviation are present near critical conditions. Table 7 illustrates this large difference for the H₂O–CH₄–NaCl fluid system, which may exceed a deviation of 20% in calculated densities. The experimental data in Table 7 is obtained from Krader and Franck (1987). Although the fit is much better for CH₄-richer fluids, the modified BH-equation is not suitable for these *PT* conditions in this fluid system. However, it is expected that the constructed isochores give accurate results at higher temperatures and pressures, similar to the results for the H₂O–CO₂–NaCl fluid system.

Table 7

Experimental data for the ternary system H₂O–CH₄–NaCl from Krader and Franck (1987), for 8.0 wt.% NaCl, compared to the modified BH-equation

mol%		Experimental conditions			V _{CAL} (cm ³ /mol)	dev.%
H ₂ O	CH ₄	P (MPa)	T (K)	V (cm ³ /mol)		
88.73	8.90	50.0	698	51.2	61.19	19.52
		61.4	686	41.1	43.64	6.18
		82.0	685	33.3	35.88	7.76
		124.5	687	28.9	30.37	5.08
		154.0	688	27.4	28.42	3.72
47.14	51.60	225.0	691	25.2	25.73	2.09
		68.0	793	99.9	108.46	8.57
		75.6	773	86.5	96.54	11.61
		101.0	755	70.3	75.09	6.82
		120.0	753	59.6	66.25	11.17
		142.0	751	54.3	59.14	8.91
		169.0	754	49.1	53.41	8.77
29.80	69.40	219.0	758	44.5	46.57	4.64
		73.5	713	95.1	97.60	2.63
		85.5	706	84.0	86.20	2.62
		110.5	701	65.2	71.57	9.77
		151.8	700	55.0	58.76	6.84
		220.0	701	47.5	48.48	2.07
		250.0	703	45.7	45.82	0.27

5. Fugacity coefficients

The fugacity coefficient of a component in the H₂O–CO₂–CH₄–N₂–NaCl fluid system is calcu-

lated according to the theoretical consideration of Prausnitz et al. (1986). The method of calculation has been extensively described by Bowers and Helgeson (1983, 1985) for the H₂O–CO₂–NaCl system. Their equations (Eqs. 8–18 in Bowers and Helgeson, 1985) have been adopted in this study and extended to include CH₄ and N₂. First, it is important to give definitions of the relative amounts of components in the fluid system:

$$n_T = n_{\text{H}_2\text{O}}^* + n_{\text{CO}_2} + n_{\text{CH}_4} + n_{\text{N}_2} \quad (8a)$$

$$n_{\text{H}_2\text{O}}^* = n_{\text{H}_2\text{O}} + n_{\text{NaCl}} \quad (8b)$$

$$\text{Weight\%} = 100\% \times \frac{\text{MW}_{\text{NaCl}} n_{\text{NaCl}}}{\text{MW}_{\text{H}_2\text{O}} n_{\text{H}_2\text{O}} + \text{MW}_{\text{NaCl}} n_{\text{NaCl}}} \quad (9)$$

where n_T is the total amount of matter in the system, n_i the amount of individual components; MW_{NaCl} and $\text{MW}_{\text{H}_2\text{O}}$ are the mole-weight of NaCl and H₂O, respectively; and Weight% is the salinity of the aqueous solution, relative to only H₂O. The amount of NaCl is added to that of H₂O (Eq. (8b)) for calculation of partial properties. Consequently, this arrangement of the mass-equation (Eq. (8a)) implies a failure to describe NaCl-rich fluids, because the a and b parameters for NaCl are not included. Similar to Eqs. 12–14 from Bowers and Helgeson (1985) the partial derivative of the b parameter for CH₄ and N₂ is obtained from:

$$\left(\frac{\partial(n_T b)}{\partial n_{\text{CH}_4}} \right)_{T,V,n_j} = b_{\text{CH}_4} \quad (10a)$$

$$\left(\frac{\partial(n_T b)}{\partial n_{\text{N}_2}} \right)_{T,V,n_j} = b_{\text{N}_2} \quad (10b)$$

The partial derivative of the a parameter in Eqs. 15–18 from Bowers and Helgeson (1985) has been extended to include the CH₄ and N₂ components in binary interactions:

$$\left(\frac{\partial(n_T^2 a)}{\partial n_i} \right)_{T,V,n_j} = 2 \sum_j n_j a_{ij} \quad (11)$$

where i stands for CO₂, CH₄, or N₂, and j includes additionally H₂O. NaCl is not included in the sum-

mation over j gas components, but $n_{\text{H}_2\text{O}}$ is defined according to Eq. (8b), and should be replaced by $n_{\text{H}_2\text{O}}^*$. The partial derivative for H₂O and NaCl are defined according to:

$$\left(\frac{\partial(n_T^2 a)}{\partial n_{\text{H}_2\text{O}}} \right)_{T,V,n_j} = 2 \sum_j n_j (a_{\text{H}_2\text{O}-j}) + n_{\text{H}_2\text{O}}^* n_j \frac{\partial(a_{\text{H}_2\text{O}-j})}{\partial n_{\text{H}_2\text{O}}} \quad (12a)$$

$$\left(\frac{\partial(n_T^2 a)}{\partial n_{\text{NaCl}}} \right)_{T,V,n_j} = 2 \sum_j n_j (a_{\text{H}_2\text{O}-j}) + n_{\text{H}_2\text{O}} n_j \frac{\partial(a_{\text{H}_2\text{O}-j})}{\partial n_{\text{NaCl}}} \quad (12b)$$

The calculation of fugacity coefficients is similar to the method described in Bowers and Helgeson (1985). Fugacities are not directly measurable properties of gas mixtures, but deduced from volumetric measurements. Only those equations of state that are able to reproduce accurately PTV data over the entire pressure interval from 0 to the pressure of interest can be used to calculate fugacities, unless reference values are known at a selected pressure. Consequently, accurate fugacity estimations from the BH-equation are directly related to the previously mentioned molar volume calculations.

6. Computer program

Program GASWET has been developed using Turbo C++ version 3.0 (Borland, 1992) to calculate molar volume at selected PT conditions, or pressure at selected VT conditions for a known chemical composition of the fluid system. The program allows comparison with experimental data. Furthermore, fugacity coefficients and fugacities are calculated for each component in the fluid mixture at selected PTV values. The program can run on a PC and a Macintosh, and it is readily available on request.

7. Conclusions

The equation of state according to Bowers and Helgeson (1983, 1985) is eminently useful in the construction of isochores in the $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ fluid system, despite recently published statements. The relative simple mathematical form of the equations allows easy adaptation to more complex fluid systems. The van der Waals a parameter for pure CH_4 and N_2 fluids are described by simple temperature dependent polynomials, assuming that the van der Waals b parameters are constant and defined by their critical temperature and pressure. These parameters are added to the mixing equation for complex fluid system. Experimental data on volumetric properties of CH_4 - and N_2 -bearing mixtures are accurately reproduced using this modified Bowers–Helgeson equation of state. In general, volumetric properties and fugacity coefficients in the $\text{H}_2\text{O}-\text{CO}_2-\text{CH}_4-\text{N}_2-\text{NaCl}$ fluid system can be accurately reproduced by this modification up to 1000 MPa and 1300 K. At relatively low pressures and temperatures for liquid-like fluids, near the immiscibility field, this equation of state is not accurate, like any modified Redlich–Kwong equation of state, and it should not be used to extend isochores in this PT region. Similarly, this equation of state cannot be used to predict phase equilibria. The modified BH-equation of state should be regarded as an empirical attempt to construct isochores for realistic geological fluid systems that are often found in fluid inclusions, and which involve several gases and salts.

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