SIMPLE EQUATION OF STATE
FOR WATER, CARBON DIOXIDE, METHANE, AND THEIR MIXTURES

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ABSTRACT

The PVT data of H_2O (0-800°C, up to 60 kbar), CO_2 (0÷800°C, up to 30 kbar) and CH_4 (-110÷350°C, up to 10 kbar) were approximated by equation

$$P, bar = RTm\{1 + Am - Bm/(1 + \beta m) - Cm^2\{1 - (1 - (Am)^2)exp(-(Am)^2)\} + Dm^3\}$$

Here R is gas constant (0.0831441 $dm^3 \times bar \times mol^{-1} \times K^{-1}$), T is absolute temperature, m is molarity of gas (moles per dm^3), A, B, β, C, D are model parameters (below q = 298.15/T):

$A_{H_2O} = 0.022699 + 0.0049722q/(1+0.539q^{12})$
$B_{H_2O} = 1.0629q \times exp\{2.768(q-1)\}$
$\beta_{H_2O} = 0.060225q^{1.9} + 0.20051q^{3.5} + 0.0035436q^{14}$
$C_{H_2O} = 0.017461q^{2.9}/(1+6.701q^{2.3}) + 0.0016763q^{2.4}/(1+1.993q^{8.3})$
$D_{H_2O} = 0.000057006q + 0.000022393q/(1+1.54q^9)$

$A_{CO_2} = 0.053736/(1 + 0.2497q)$
$B_{CO_2} = 0.16508q \times exp\{0.673(q-1)\}$
$\beta_{CO_2} = 0.016222q^{3.4}$
$C_{CO_2} = 0.030447q^{3.1}/(1+6.015q^{2.7}) + 0.0071431q^{2.3}$
$D_{CO_2} = 0.00061996q$

$A_{CH_4} = 0.049878/(1+0.03094q)$
$B_{CH_4} = 0.088477q \times exp\{0.2873(q-1)\}$
$\beta_{CH_4} = 0.0041616q^3$
$C_{CH_4} = 0.008267q^{2.9}/(1+2.267q^{2.2}) + 0.0025764q^2$
$D_{CH_4} = 0.00040808q$

The properties of H_2O-CO_2-CH_4 mixtures (0-700°C, up to 6 kbar) are consistent with
$A_x = \sum A_i X_i$
$B_x = B_x^o - 2k_{CO_2H_2O}(B_{CO_2}B_{H_2O})^{0.5}X_{CO_2}X_{H_2O} - 2k_{CH_4H_2O}(B_{CH_4}B_{H_2O})^{0.5}X_{CH_4}X_{H_2O}$
$\qquad B_x^o = (\sum B_i^{1/2}X_i)^2; \qquad k_{CO_2H_2O} = 0.2286 - 0.6123q^5 + 0.6888q^7 - 0.256q^9$
$\qquad \quad k_{CH_4H_2O} = 0.3595 -1.653q^5 + 2.037q^7 -0.731q^9; \qquad (k_{CH_4CO_2} = 0)$
$\beta_x = \sum \beta_i X_i$
$C_x = \{\sum C_i^{1/3}X_i\}^3$
$D_x = \{\sum D_i^{1/4}X_i\}^4$

The fugacity of gas in the H_2O-CO_2-CH_4 mixture may be found from $f_i = RTm_iY_i$ and

$$\ln Y_i = (A_i + A_x)m - \{2B_i^{0.5}(B_x^{o\,0.5} - \sum_j k_{ij}B_j^{0.5}X_j) - B_x(\beta_i/\beta_x)\}\ln(1 + \beta_x m)/\beta_x - B_x(\beta_i/\beta_x)m/(1 + \beta_x m)$$
$$- 1.5(C_iC_x^2)^{1/3}m^2[1 - exp\{-(A_xm)^2\}] - C_xm^4A_iA_xexp\{-(A_xm)^2\} + (4/3)(D_iD_x^3)^{1/4}m^3$$

INTRODUCTION

The equation of state is a very useful tool for understanding of various geological phenomena. Since the geology deals with complex mixtures of fluids at high parameters, high accuracy of calculations seems to be inaccessible. Because of this, multiparametric and, potentially exact approaches are weakly applicable, since they are not efficient and even senseless (e.g., negative volume) above the experimental range. Thus, less accurate, but simpler approaches, having ability for more or less successful extrapolation, and which may be easily extended to complex gas mixtures, are more relevant. The aim of present study is a creation of equation of state, which is 1) simple and convenient 2) more or less accurate 3) applicable to complex mixtures 4) applicable from low up to extreme T-P conditions. This study is focused on most important system H_2O-CO_2. However, both these fluid components are rather peculiar substances, and the model was also tested on PVT data for methane.

METHODS

The PVT data for methane were taken from equation of state of Setzmann and Wagner (1991; 90-620 K, up to 10 kbar), and finally were used up to 2 kbar in the range 160-400 K and up to 0.5 kbar at 500-600 K. Above 2 kbar, the model was fitted to experimental data from Robertson and Babb (1969; 35÷200°C, to 10 kbar) and Morris (1984; -20÷150°C, to 6.9 kbar). Data from Kortbeek and Schouten (1990; 25°C, to 10 kbar) were not used because of small inconsistence with data from Robertson and Babb (1969), which were preferred due to large temperature range covered by experiment. Data from Tsiklis (1971a; 50-400°C, to 8.5 kbar) were not used because of systematic deviation from other studies by 0.6 percent.

The PVT data for water at 0-800°C up to 1 kbar were taken from Rivkin and Aleksandrov (1984) steam tables. Above 1 kbar, model was fitted to the volumetric data from Bridgman (1912; 0÷80°C, to 12 kbar), Grindley and Lind (1971; 25÷150°C, to 8 kbar), Hilbert et al. (1981; 20÷600°C, to 4 kbar), and values deduced from sound velocity measurements: Wiryana et al. (1998; 80÷200°C, 2.5-35 kbar), Abramson and Brown (2004; 100÷400°C, 10÷60 kbar). The data from Burnham et al. (1969; 20÷900°C, to 8.9 kbar) were not used because of systematic deviation from other studies (at 8 kbar and 20÷400°C, the density is underestimated by 0.6 %), except excellent agreement with data from Bridgman 1935 (0÷100°C, to 12 kbar), which also were rejected. The data from Bridgman (1942; 25-175°C, up to melting curve, 36.56 kbar in maximum) were not used because these data were measured as increments in volume between 5 kbar and higher pressure (thus, "true" value for density at 5 kbar should be selected arbitrarily). The data from Von Köster and Frank (1969; 25÷600°C, to 10 kbar) are in excellent agreement with results of other studies up to 150°C, but at higher temperatures and highest pressures they seems to be in error (at 8 kbar and 600°C, disagreement with data from Burnham et al., 1969, is 1.9 %; at 10 kbar and 400°C, disagreement with data from Abramson and Brown, 2004, is 1.2 %). The same is probably true for the data from Von Maier and Frank (1966; 200÷850°C, up to 6 kbar; at 6 kbar and 800°C, disagreement with data from Burnham et al., 1969, is 3 %). Data from fluid inclusion studies: Brodholt and Wood (1994; 900÷1600°C, 9.5-25 kbar), Withers et al. (2000; 710÷1100°C, 14÷40 kbar), Frost and Wood (1997; 1000÷1400°C, 14.5 kbar) also were not considered because of small inconsistence with data from Abramson and Brown (2004) which were preferred. The values tabulated by Rice and Walsh (1957) were not used because it is prognostic equation of state.

In case of carbon dioxide, the model was fitted to volumetric data from Michels and Michels (1935; 0-150°C, to 0.25 kbar) Michels et al., (1935; 0÷150°C, up to 3.1 kbar), Vukalovich et al. (1962, 1963; 40÷750°C, up to 0.6 kbar), Kennedy (1954; 0-1000°C, up to 1.4 kbar), Jůza et al. (1965; 50-475°C, up to 4 kbar), Tsiklis et al. (1971b; 50-400°C up to 7 kbar), Shmonov and Shmulovich (1974; 408.2-707.5°C, up to 8 kbar), and data deduced from sound velocity measurements: Giordano et at. (2006; 27-427°C, up to 80 kbar). There is large (up to 4.4 %) discrepancy among various data, and construction of self-consistent calibration dataset is a problem, which has no unique solution. The following data were rejected from

final calibration dataset: from Kennedy (1954) above 800°C, from Tsiklis et al. (1971b) above 5 kbar, from Shmonov and Shmulovich (1974) above 5 kbar and all data at 707.5^{o}C, from Giordano et al. (2006) above 200°C.

The selected data were used for construction of isotherms at round temperatures. Above 1 kbar, data were used with large increments (1 or 2 kbar to 10 kbar, 5 kbar to 20 kbar and then 10 kbar). If necessary, experimental data were interpolated (or, slightly extrapolated) to round temperatures and pressures with use of approximations:

$$V = V(t_r^oC) + a(t-t_r) + b(t-t_r)^2 \tag{1}$$
$$\rho = \rho(P_r, bar) + c(P-P_r)/(1+d(P-P_r)) \tag{2}$$

Here t_r and P_r are round temperature and pressure, a, b, c, and d are adjusting parameters.

The isotherms were converted into "second virial function", $(Z-1)/\rho$, where ρ is density in g/cm^3, and $Z = PV/RT$ is compressibility factor. Further the best fit values of parameters were determined at each round temperature, and initial approximation was found for each parameter. Then the completely parameterized equation was optimized with use of all selected data. In case of carbon dioxide and methane, the data on saturation pressure were not used, and thus, the model was applied solely for the range above ~ 0.9T_{cr}. In case of water, temperature dependence of parameters was optimized for the range 200-800°C, whereas in the range 0-150°C the best fit parameters at each round temperature were found with use of values of fugacity at saturation (this gives independent relation between parameters). Then the equation (for range 200-800°C) and best fit values (in the range 0-150°C) for the most stable parameter were approximated with general equation. This equation was fixed, and procedure was repeated until the general approximation for the last parameter was found.

RESULTS AND DISCUSSION

The following equation was found more or less applicable:

$$P, bar = RTm\{1 + Am - Bm/(1+ \beta m) - Cm^2\{1 - (1 -(Am)^2)exp(-(Am)^2)\} + Dm^3\} \tag{3}$$

Here R is gas constant (0.0831441 dm^3×bar×mol^{-1}×K^{-1}), T is absolute temperature, m is molarity of gas (moles per dm^3; M_{H_2O} = 18.0152 g/mol, M_{CO_2} = 44.0098 g/mol, M_{CH_4} = 16.043 g/mol), A, B, β, C, D – are model parameters (below q = 298.15/T):

$$A_{H_2O} = 0.022699 + 0.0049722q/(1+0.539q^{12}) \tag{4}$$
$$B_{H_2O} = 1.0629q×exp\{2.768(q-1)\} \tag{5}$$
$$\beta_{H_2O} = 0.060225q^{1.9} + 0.20051q^{3.5} + 0.0035436q^{14} \tag{6}$$
$$C_{H_2O} = 0.017461q^{2.9}/(1+6.701q^{2.3}) + 0.0016763q^{2.4}/(1+1.993q^{8.3}) \tag{7}$$
$$D_{H_2O} = 0.000057006q + 0.000022393q/(1+1.54q^9) \tag{8}$$

$$A_{CO_2} = 0.053736/(1 + 0.2497q) \tag{9}$$
$$B_{CO_2} = 0.16508q×exp\{0.673(q-1)\} \tag{10}$$
$$\beta_{CO_2} = 0.016222q^{3.4} \tag{11}$$
$$C_{CO_2} = 0.030447q^{3.1}/(1+6.015q^{2.7}) + 0.0071431q^{2.3} \tag{12}$$
$$D_{CO_2} = 0.00061996q \tag{13}$$

$$A_{CH_4} = 0.049878/(1+0.03094q) \tag{14}$$
$$B_{CH_4} = 0.088477q×exp\{0.2873(q-1)\} \tag{15}$$
$$\beta_{CH_4} = 0.0041616q^3 \tag{16}$$
$$C_{CH_4} = 0.008267q^{2.9}/(1+2.267q^{2.2}) + 0.0025764q^2 \tag{17}$$
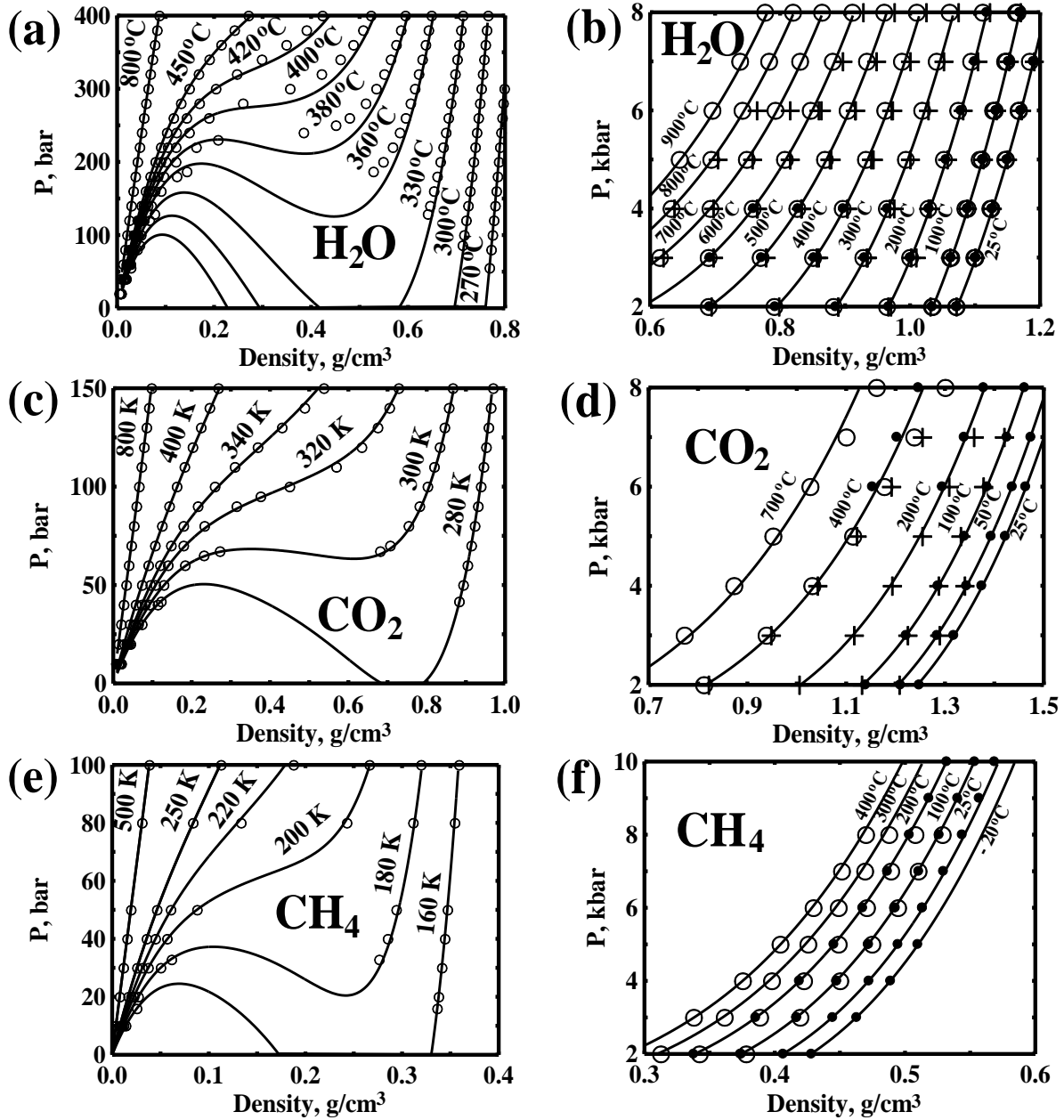$$D_{CH_4} = 0.00040808q \tag{18}$$

Fig. 1. Density of water (a, b) carbon dioxide (c, d) and methane (e, f) in the critical region and at elevated pressures (some data were adjusted to round t and P):

a) water: data from Rivkin and Alexandrov (1984);

b) water: closed circles − data from Bridgman (1912), Grindley and Lind (1971), Hilbert et al. (1981), Wiryana et al. (1998); open circles − data from Bridgman (1935), Burnham et al. (1969); crosses − data from Von Maier and Frank (1966), Von Köster and Frank (1969);

c) carbon dioxide: data from Altunin (1975);

d) carbon dioxide: closed circles − data from Giordano et al. (2006); open circles − data from Shmonov and Smulovich (1974); crosses − data from Tsiklis et al. (1971a);

e) methane: data from Setzmann and Wagner (1991);

f) methane: closed circles − data from Robertson and Babb, (1969), Morris, (1984), Kortbeek and Schouten (1990); open circles: data from Tsiklis et al. (1971b).

Parameter A was used twice: as an offset of second virial coefficient (second virial coefficient at infinite temperature) and as an exponential factor, which is similar to that in Benedict-Webb-Rubin equation (Benedict et al., 1940). This is artificial, and probably,

senseless correlation, but this simplification was found more or less applicable. The pre-exponential factor $(1-(Am)^2)$ may be omitted, and recalibration of the model gives approximately similar quality of description. However, this factor simplifies calculation of fugacity.

Fig. 1 shows behavior of Eq. (3) in the critical region and at elevated pressures. The modeled critical temperatures are 394.5, 31.6, and -81.4°C for water, carbon dioxide and methane (experimental values are 374.1, 31.1, and -82.6°C), i.e. the model of water is most inaccurate. The accuracy of the model with respect to selected data is generally better than 0.3 % in molar volume, except critical region (deviations in pressure up to 10 % for water, and up to 3 % for carbon dioxide and methane).
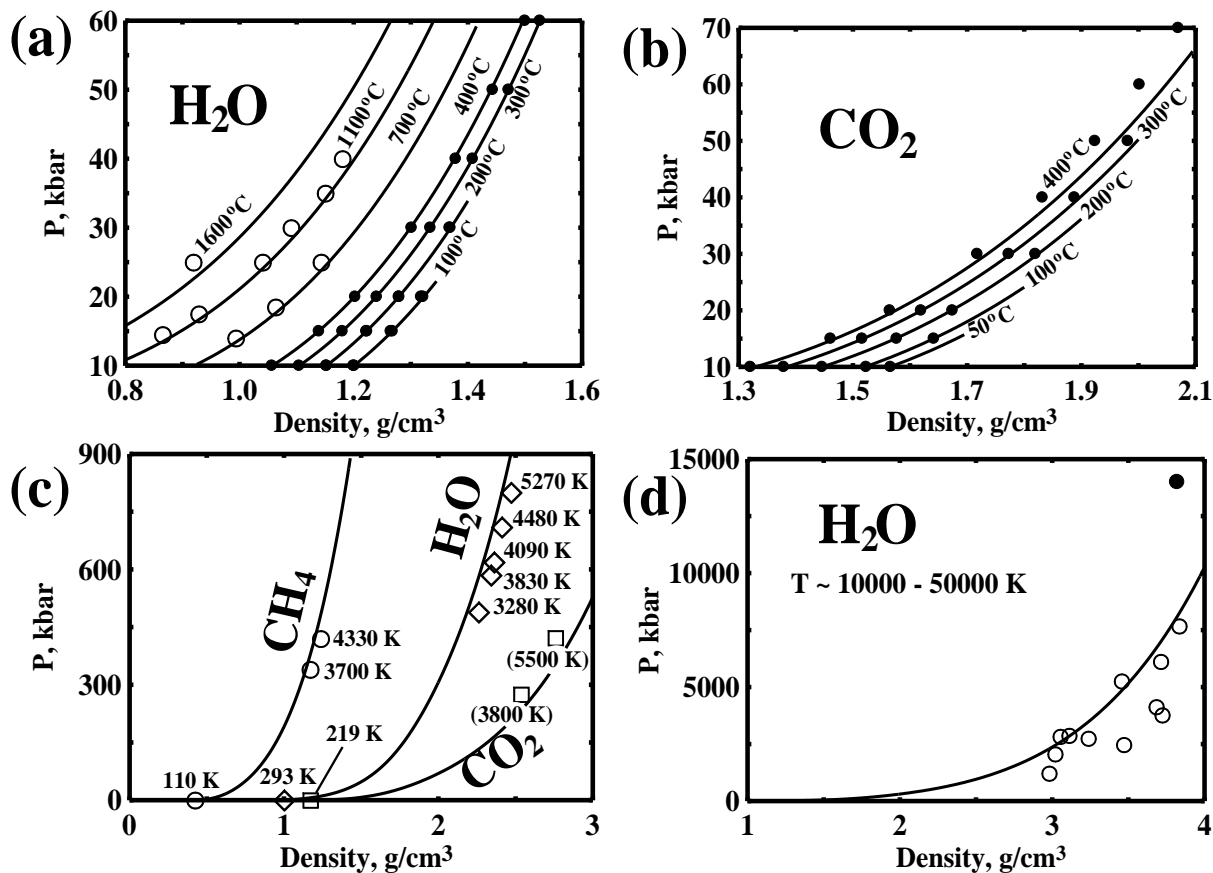

Fig. 2. Density of water, carbon dioxide and methane at high pressures (some data were adjusted to round t and P):

a) water: closed circles − data from Wiryana et al. (1998), Abramson and Brown (2004); open circles − data from Brodholt and Wood (1993), Frost and Wood (1997), Withers et al. (2000);

b) carbon dioxide: data from Giordano et al. (2006);

c) density of shock-compressed methane (circles: Radousky et al., 1990), water (diamonds: Lysenga et al., 1982), and carbon dioxide (boxes: Nellis et al., 1991). Experimental or, in brackets, theoretical temperatures are indicated near each point. Solid curves were calculated with use of approximations: $T = T_o + a(\rho-\rho_o)^b$, where a and b are adjusting parameters.

d) density of shock-compressed water in the dense plasma region; data from Celliers et al. (2004, open circles) and from Podurets et al. (1972, solid circle); solid curve is the same as in Fig. 2c.

In Fig. 2, the model calculations are compared with experimental data at high pressures. Within the present approach, the values of density of water from fluid inclusion studies (Fig. 2a, open circles) are slightly inconsistent with values obtained from sound velocity measurements (Fig. 2a, closed circles). In the range 700-1100°C, the model deviates from results of fluid inclusion studies by 1-2 %, which is experimental uncertainty of these measurements.

As may be seen in Fig. 2b, the model deviates by 2.7 % in maximum from values deduced from sound velocity by Giordano et al. (2006). The 400°C data seem to be inconsistent with lower temperature data (the best fit parameters, optimized for each isotherm and plotted against temperature, exhibit large step between 300 and 400°C). It should be noted, that the values above 50 kbar were not really measured: for the measurements of sound velocity in the diamond anvil, it is necessary to know the values of refractive index; these values were measured up to 48 kbar and extrapolated to higher pressures. Thus, the values of sound velocity as well as density above 48 kbar should be considered as extrapolated ones. Up to 50 kbar, the present model is consistent with these data within the experimental error, 2 %, as estimated by Giordano et al. (2006).

Within 2-4 % the model agrees with Hugoniot data up to 800 kbar (Fig. 2c) and gives, at least, not senseless results for the dense plasma region (>2000 kbar; Fig. 2d).

The common mixing rules may be guessed on basis of common sense. For instance, the equation of state of water at very high pressure is simply

$$P \sim RT \times D_{H_2O}m^4 \qquad\qquad (19)$$

One may imagine that the compressed water consists of monomeric and dimeric molecules:

$$P \sim RT \times D_{H_2O}(m_1 + 2m_2)^4 = RT(D_1^{1/4}m_1 + D_2^{1/4}m_2)^4 \qquad\qquad (20)$$

Here m_1 and m_2 are molarities of monomeric and dimeric molecules, $D_1 = D_{H_2O}$ and $D_2 = 16D_{H_2O}$ are model parameters for monomeric and dimeric water. So on, the mixture of components "1" and "2" may be modeled with use of the following mixing rule:

$$D_x = (D_1^{1/4}X_1 + D_2^{1/4}X_2)^4 \qquad\qquad (21)$$

Similar considerations give general mixing rule, which is referred below as "n+1 rule":

$$N_x = (\Sigma N_i^{1/(n+1)}X_i)^{n+1} \qquad\qquad (22)$$

Here N is model parameter, and n is power factor of molarity in the equation of state, $Z = PV/RT = f(m)$. As it was found by Benedict et al. (1942), similar relation is consistent with behavior of mixtures of hydrocarbons.

Another semi-empirical rule may be deduced from Van der Waals equation:

$$P = RT/(V-b) - a/V^2 = RT(m + bm^2 + cm^3 + dm^4.....) - am^2 \qquad\qquad (23)$$

Here $c = b^2$, $d = b^3$, etc. As it was suggested by Van der Waals (1881), parameter b of mixture ("uncompressible volume") is additive function of composition:

$$b_x = \Sigma X_i b_i \qquad\qquad (24)$$

Based on this relation, one may obtain the common mixing rule for parameters b, $c = b^2$, $d = b^3$, etc (see Eq. 23):

$$N_x = (\Sigma N_i^{1/n} X_i)^n \tag{25}$$

As above, N is model parameter, and n is power factor of molarity in the equation of state $Z = PV/RT = f(m)$. This relation is referred below as "n rule".

As it was suggested by Van der Waals (1881), parameter "a" in the Eq (23) is consistent with "n + 1 rule" (Eq . 22). For binary mixture of "inert components", it is:

$$a_x = (\Sigma a_i^{0.5} X_i)^2 = X_1^2 a_1 + X_2^2 a_2 + 2(a_1 a_2)^{0.5} X_1 X_2 \tag{26}$$

If the specific interaction of component is significant, the additional parameter is necessary:

$$a_x = X_1^2 a_1 + X_2^2 a_2 + 2(1-k_{12})(a_1 a_2)^{0.5} X_1 X_2 = (\Sigma a_i^{0.5} X_i)^2 - 2k_{12}(a_1 a_2)^{0.5} X_1 X_2 \tag{27}$$

Here k_{12} is so called "coupling parameter". The value $k_{12} > 0$ indicates repulsive interaction, whereas $k_{12} < 0$ corresponds to attractive interaction. If to suggest, that the parameter "a" is formation constant of dimeric molecules, the value $2(1-k_{12})(a_1 a_2)^{0.5}$ is formation constant of dimer, composed of two components.
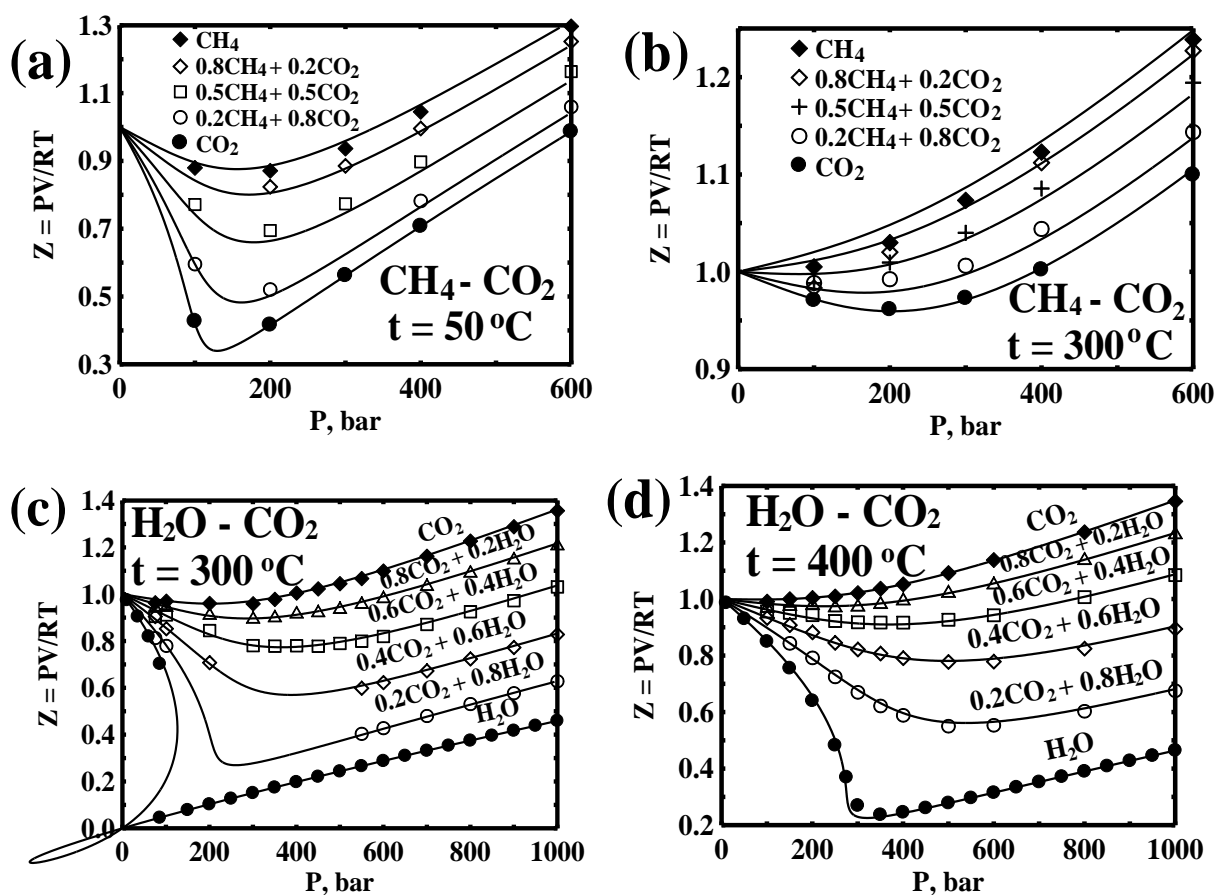
Fig. 3. Compressibility factor, $Z=PV/RT$, of CO_2-CH_4 (a, b) and CO_2-H_2O (c, d) mixtures. Data (a, b) from Seitz et al (1996); data (c, d) from Blencoe et al. (2001) and Seitz and Blencoe (1999), correspondingly, except these for pure water (Rivkin and Aleksandrov, 1984). Solid curves were calculated in accordance with Eqs (28-36).
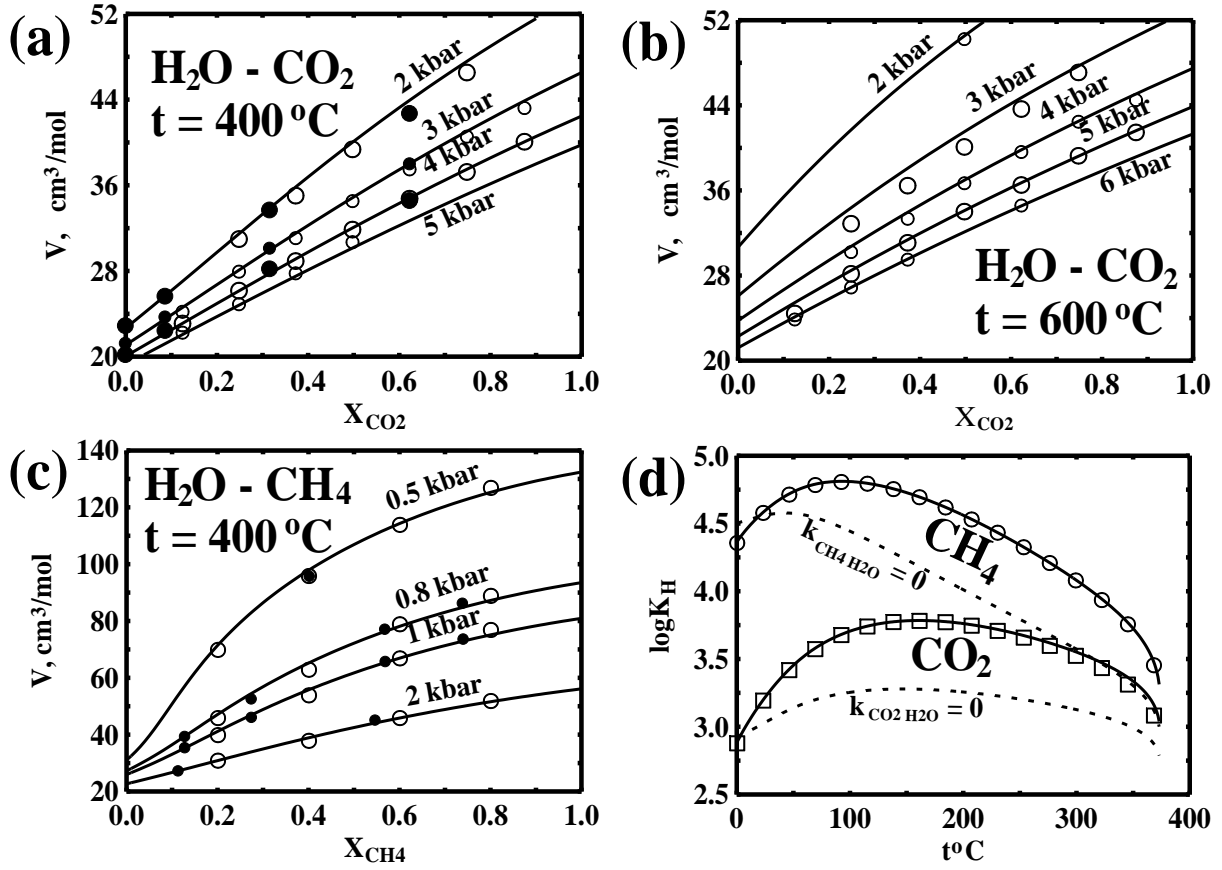
Fig. 4 Molar volume of CO_2-H_2O (a,b) and CH_4-H_2O (c) mixtures and Henry constant (d) of carbon dioxide and methane in water: data (a, b) from Sterner and Bodnar (1991, open circles) and from Shmulovich et al. (1980, solid circles); data (c) from Shmonov et al. (1993, open circles) and from Sretenskaya et al. (1986, solid circles); data (d) from Fernández-Prini et al. (2003); solid curves were calculated in accordance with Eqs (28-36); dashed curves (d) were calculated with k_{ij} = 0.

By tries and errors, the following relations were found to be applicable for H_2O-CO_2-CH_4 mixtures (see Figs 3 and 4):

$$A_x = \sum A_i X_i \tag{28}$$
$$B_x = B^o_x - 2k_{CO_2 H_2O}\{B_{CO_2}B_{H_2O}\}^{1/2}X_{CO_2}X_{H_2O} - 2k_{CH_4 H_2O}\{B_{CH_4}B_{H_2O}\}^{1/2}X_{CH_4}X_{H_2O} \tag{29}$$
$$B^o_x = \{\sum B_i^{1/2}X_i\}^2 \tag{30}$$
$$\beta_x = \sum \beta_i X_i \tag{31}$$
$$C_x = \{\sum C_i^{1/3}X_i\}^3 \tag{32}$$
$$D_x = \{\sum D_i^{1/4}X_i\}^4 \tag{33}$$
$$k_{CO_2 H_2O} = 0.2286 - 0.6123q^5 + 0.6888q^7 - 0.256q^9 \tag{34}$$
$$k_{CH_4 H_2O} = 0.3595 - 1.653q^5 + 2.037q^7 - 0.731q^9 \tag{35}$$
$$(k_{CO_2 CH_4} = 0) \tag{36}$$

Here, as above, q is 298.15/T. The mixing rule for parameters A_x and β_x was found close to "n rule" (Eq. 25), whereas parameters B_x, C_x and D_x are consistent (or almost consistent) with "n+1 rule" (Eq. 22). In case of aqueous mixtures, there is small repulsive ("hydrophobic") interaction, which is distinctive at low pressures, but fast decreases with density. Such behavior may be simulated solely via adjustment of term $Bm/(1+\beta m)$.

To obtain the approximations for the coupling parameters (Eqs 34 and 35), the values of Henry constant (see Fig. 4d) were simply converted into coupling parameters, and these values were approximated (all volumetric data for mixtures were ignored). The values of Henry constant for carbon dioxide above 200°C and for methane above 300°C were found inconsistent with the model and were rejected (perhaps, this is due to uncertainty of the model in the critical region). In general, specific interaction is small: the prediction based on properties of pure components overestimates solubility of gases at 100-370°C by 2-3 times (dashed curves in Fig 4d; below 100°C, the model of water is overparameterized and thus, behavior of coupling parameter in this range has no deep sense). It should be noted that this deviation is likely a specific property of water (tendency to form clusters) rather than real specific interaction. The model was tested also on data for helium (not shown here), and absolutely identical deviation from solubility curve was obtained. In case of CH_4-CO_2 mixtures, the coupling parameter is slightly positive ($\sim$ 0-0.1). However, this effect is comparable with experimental error, and coupling parameter was set to zero (see Fig 3ab).

The fugacity may be calculated with use of the following relations between the compressibility factor $Z=P/mRT$ and thermodynamic potentials:

$$dA^{ex}/RT = \{(Z-1)/m\}dm \tag{37}$$
$$dG^{ex}/RT = (1/m)d(Z-1)m \tag{38}$$
$$G^{ex}/RT = A^{ex}/RT + md(A^{ex}/RT)/dm = A^{ex}/RT + Z - 1 \tag{39}$$
$$Z = 1 + A_xm - B_xm/(1+\beta_xm) - C_xm^2[1-\{1-(A_xm)^2\}\exp(-(A_xm)^2)] + D_xm^3 \tag{40}$$
$$A^{ex}/RT = A_xm - B_x\ln(1+\beta_xm)/\beta_x - 0.5C_xm^2[1-\exp(-(A_xm)^2)] + (1/3)D_xm^3 \tag{41}$$

Here G^{ex} and A^{ex} are Gibbs and Helmholtz excess energies, m is total molarity of the mixture. For pure component, the fugacity f may be calculated from

$$f = RTmY \tag{42}$$
$$Y = \exp(G^{ex}/RT) \tag{43}$$

Here Y is "absolute activity coefficient". For the mixture, the absolute activity coefficient of component, Y_i is related with its mole fraction X_i:

$$\ln Y_i = G^{ex}/RT + (1-X_i)\{d(A^{ex}/RT)/dX_i\}_{m, X_j/X_k = const} \tag{44}$$

The Eq. (44) is convenient for numerical differentiation. However, the Eq (41) is relatively simple, and the absolute activity coefficient may be calculated analytically. The result is:

$$\ln Y_i = (A_i + A_x)m - \{2B_i^{0.5}(B_x^{o\,0.5} - \sum_j k_{ij}B_j^{0.5}X_j) - B_x(\beta_i/\beta_x)\}\ln(1+\beta_xm)/\beta_x - B_x(\beta_i/\beta_x)m/(1+\beta_xm)$$
$$- 1.5(C_iC_x^2)^{1/3}m^2[1 - \exp\{-(A_xm)^2\}] - C_xm^4A_iA_x\exp\{-(A_xm)^2\} + (4/3)(D_iD_x^3)^{1/4}m^3 \tag{45}$$

Here $\sum_j$ is sum for components other than "i". With use of this relation, the Henry constant (Fig. 4d) may be calculated from:

$$K_H = f_2/X_2 \text{ (at } f_2 \rightarrow 0) = RTm_2Y_2/\{m_2/m\} = RTmY_2 \tag{46}$$

Here f_2, x_2, m_2, Y_2 – are fugacity, mole fraction, molarity, and absolute activity coefficient of dissolved gas, m is total molarity (here, molarity of pure water at saturation).

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CONCLUDING REMARKS

In spite of strong non-ideality of fluid mixtures, the specific interaction of fluid components is weak and may be accounted for via adjustment of terms related to second virial coefficient. The contribution of specific interactions at high pressures is negligible. Compressibility of substance at very high pressures is consistent with $P \sim \rho^4$, and thus, the repulsive branch of Lennard-Jones potential is close to $\sim \rho^3$, or $1/r^9$.

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