Thermodynamic Description of Equilibria in Mixed Fluids (H₂O–Nonpolar Gas) in a Wide Range of Temperatures (25–700°C) and Pressures (1–5000 bar)

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Abstract—A new method is proposed for calculating equilibria in mixed multicomponent systems H₂O–nonpolar gas at high temperatures and pressures. The method is based on calculation of electrostatic interactions between a solute component and surrounding molecules of a solvent (H₂O). The SUPCRT98 database and the Helgeson–Kirkham–Flowers equation of state for components of an aqueous solution were used for computer realization of the method. The thermodynamic properties of solute gases at elevated temperatures and pressures are calculated by the Redlich–Kwong equation. The dielectric properties of a mixed solvent are determined using the modified Kirkwood equation. The proposed method was approved in description of the available set of experimental data on constants of H₂O and NaCl dissociation, as well as data on solubility of both covalent and ionic crystals [SiO₂, AgCl, Ag₂SO₄, Ca(OH)₂, CaCO₃] in mixed solvents H₂O–nonpolar component [1,4-dioxane (C₄H₄O₂), Ar, CO₂]. The calculation and experimental data agree in a wide range of *PTx* conditions (temperatures up to 500°C, pressures up to 5000 bar, and mole fractions (*x*) of a nonpolar component in fluid up to 0.3). The proposed approach can be used for assessing the Born parameters of solute components. The calculation algorithm developed allows us not only to consider separate reactions but also to study equilibria in hydrothermal systems as a whole. Hence, the proposed approach can be used for constructing thermodynamic models of evolution of fluids rich in volatile components and vital to natural processes of mineral formation.

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INTRODUCTION

Being of primary importance in the formation of ore deposits, natural hydrothermal fluids contain, in addition to water, solute gases (CO₂, CH₄, N₂), the concentration of which varies within a wide range and might reach tens of mole percent. Volatile-rich fluids differ greatly in physicochemical properties from aqueous solutions. The study of fluid inclusions (Drummond and Ohmoto, 1985; Robert and Kelly, 1987; Dubessi *et al.*, 1987; Naden and Shepherd, 1989; Prokof'ev, 2000; Matthäi *et al.*, 1995; Yardley, 1996; Wilkinson and Johnston, 1996) shows that the cause of metal deposition from such fluids is a change in the fluid composition (acidity, ligand concentration, H₂O activity) on volatile degassing. There is one more standpoint at present, according to which a change in the dielectric permeability of a fluid (ε) related to volatile removal may be a significant complementary factor of ore deposition (Walther, 1986; Walther and Schott, 1988; Dubessy *et al.*, 1989; Bowers, 1991). Estimates made in (Walther and Schott, 1988; Dandurand and Schott, 1992; Gibert *et al.*, 1992; Akinfiev, 1994, 1998; Kolonin *et al.*, 1994) for different systems showed the validity of such a standpoint: a decrease in ε of a solvent due to the presence of solute nonpolar gas may result in a cardinal change in components of the solution and a decrease in mineral solubility by orders of magnitude.

Thermodynamic description of mixed fluids such as H₂O–nonpolar gas at high temperatures and pressures is a challenging problem. Obviously, consideration of the equilibria of individual reactions is insufficient for describing the equilibrium in the system as a whole. The purpose of this work is to propose a general method allowing the study of equilibria in multi-systems over mixed fluid. The method uses the Helgeson–Kirkham–Flowers (HKF) electrostatic equation of state for aqueous components (Tanger and Helgeson, 1988) and can be regarded as an extension of this equation to the case of mixed fluids H₂O–volatile. The extensive thermodynamic database SUPCRT98 (Johnson *et al.*, 1992; Sverjensky *et al.*, 1997; Shock *et al.*, 1997), used along with the Gibbs universal minimization program BALANCE (Akinfiev, 1986, 1993), permits not only consideration of individual reactions but also study of equilibria in such hydrothermal systems as a whole.

KEY RELATIONSHIPS

To predict the behavior of components in a solution at high temperatures and pressures, so-called electro-

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static models are used (Fuoss, 1958; Ryzhenko, 1981; Helgeson and Kirkham, 1976; Tanger and Helgeson, 1988). According to these models, the "solvate" constituent of the ion chemical potential ($\mu_{j,s}^0$), which reflects the contribution of electrostatic interaction between the ion and the solvent, plays a large role at elevated temperatures. In such a case, the chemical potential of the aqueous component j (μ_j^0) is described as the sum of two constituents, the so-called structural nonsolvate constituent $\mu_{j,n}^0$ and the solvate constituent $\mu_{j,s}^0$,

$$\mu_j^0 = \mu_{j,n}^0 + \mu_{j,s}^0. \tag{1}$$

The solvate constituent of the chemical potential represents the energy of ion hydration in the solvent and is determined by the Born equation (Born, 1920; Helgeson and Kirkham, 1976):

$$\mu_{j,s}^0 = \omega_j^{abs}\left(\frac{1}{\varepsilon} - 1\right), \tag{2}$$

where ε is the dielectric permeability of the solvent and ω_j^{abs} is the absolute value of the Born parameter of the component j (cal mol^{-1}):

$$\omega_j^{abs} = 1.66027 \times 10^5 \frac{Q_j^2}{r_{e,j}}. \tag{3}$$

Here, Q_j is the ion charge (in elementary charge units) and $r_{e,j}$ is its effective electrostatic radius in Å. Using the agreement for the Born parameter, which is accepted in (Tanger and Helgeson, 1988) and the SUPCRT98 database (Johnson *et al.*, 1992; Sverjensky *et al.*, 1997; Shock *et al.*, 1997), Eq. (2) should be presented as

$$\mu_{j,s}^0 = \omega_j\left(\frac{1}{\varepsilon} - 1\right), \tag{4}$$

where $\omega_j \equiv \omega_j^{abs} - Q\omega_{H^+}^{abs}$ and $\omega_{H^+}^{abs} = 0.5387 \times 10^5$ cal mol^{-1} is the absolute value of the Born parameter of hydroxonium ion (H$^+$).

The dielectric permeability of the mixed fluid (H$_2$O–nonpolar gas) is lower than that of the pure solvent (H$_2$O), and this reduces the hydration energy of the solute component. The corresponding change in the chemical potential of this component ($\Delta\mu_j^0$) according to (4) is determined by the change in the dielectric permeability of the mixed solvent (ε) compared with the pure solvent (ε_{H_2O}):

$$\Delta\mu_j^0 = \omega_j\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{H_2O}}\right). \tag{5}$$

For the equilibrium constant of the reaction with aqueous solution components, we may write

$$\Delta\log K = -\Delta_r\omega\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{H_2O}}\right)\frac{1}{2.303RT}, \tag{6}$$

where $\Delta\log K$ is the change in the logarithm of the equilibrium constant in the mixture compared to the equilibrium constant in pure water; $\Delta_r\omega$ is a change in the Born parameter of aqueous solution components of the reaction; $R = 1.9872$ cal mol^{-1} K^{-1} is the univeral gas constant; and T is temperature, K. Introducing for the convenience further analysis the value of the *dielectric correction factor* (θ)

$$\theta \equiv \left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{H_2O}}\right)\frac{1}{1.303RT}, \tag{7}$$

Eq. (6) can be represented as

$$\Delta\log K = -\Delta_r\omega\theta. \tag{8}$$

The value θ characterizes the degree of variation in hydration energy in the component of the solution and/or the reaction during a change in the dielectric permeability of the solvent. The value θ is a composite function of the solvent temperature, pressure, and density and the volatile concentration, with an increase in which the function steadily grows.

Sometimes it is convenient to use the dimensionless quantity of the *reduced* chemical potential of the component

$$z_j \equiv \frac{\mu_j}{2.303RT}. \tag{9}$$

Then Eq. (5) will take the form

$$\Delta z_j = \omega_j\theta. \tag{10}$$

DETERMINATION OF THE STANDARD STATE

An activity equal to 1 generally corresponds to the standard state of pure solid phases and a solvent (H$_2$O). The activity of H$_2$O in a mixed solvent is assumed equal to its mole fraction. As the solid-phase solubility in a pure volatile component (for instance, CO$_2$) is low compared to pure water, the solubility in a mixed solvent is always calculated relative to H$_2$O and expressed in mol (kg H$_2$O)$^{-1}$ regardless of the concentration of a nonpolar component in a fluid. Moreover, the method that we have used assumes that the presence of a nonpolar component *changes the physicochemical properties of a solvent* (i.e., its ε). Thus, the description of a solute component should take into account changes in solvent properties and, hence, the standard state of this component should be modified. In this connection, assumed as the standard state for an aqueous component is the state of a hypothetical, infinitely diluted solution of unit molality but *possessing properties of a mixed solvent* (ε and density). Hence, the solute stan-

Table 1. Parameters of the Redlich–Kwong equation of pure gases accepted in this work

Gas	b_{gas}, cm^3 mol^{-1}	$a_{gas} \times 10^6$, cm^6 bar^{-1} K$^{0.5}$ mol^{-2}	Source
CO_2	29.70	$73.03 - 0.0714T[°C] + 2.157 \times 10^{-5}T^2[°C]$	Holloway, 1981
H_2	15.15	3.56	Holloway, 1981
Ar	22.35	16.95	$T_c = 150.65$ K, $P_c = 48.6$ bar (*Physical Quantities...*, 1991)

dard state depends on the nonpolar gas mole fraction (x_{gas}) in a fluid and the relationship between the "traditional" standard state and that accepted in this work is determined by Eq. (5).

CALCULATION OF ACTIVITY COEFFICIENTS

Ionic activity coefficients (γ) were calculated by the Debye–Hückel equation (Helgeson *et al.*, 1981)

$$\log\gamma = \frac{-AQ^2 I^{0.5}}{1 + BrI^{0.5}} - \log(1 + 0.018m), \quad (11)$$

where I is the solution ionic strength, mol kg^{-1}; m is the total molality of solute components, nonpolar gas included; Q is the ion charge; $r = 4.5$ Å (Rafal'skii, 1973) is the distance of closest approach of ions; and A and B are the Debye–Hückel coefficients for the mixed solvent with dielectric permeability ε and molar volume V, cm^3 mol^{-1} (Helgeson *et al.*, 1981):

$$A = \frac{7.74538 \times 10^6}{V^{0.5}\varepsilon^{1.5}T^{1.5}}; \quad B = \frac{213.4597}{V^{0.5}\varepsilon^{0.5}T^{0.5}}. \quad (12)$$

Activity coefficients of neutral molecules were taken as equal to 1.

BULK PROPERTIES

Bulk properties of the mixed fluid H_2O–nonpolar gas were calculated by the Redlich–Kwong equation (Ferri and Baumgartner, 1992):

$$P = \frac{\tilde{R}T}{V - b} - \frac{a}{T^{0.5}V(V + b)}, \quad (13)$$

where P is pressure, bar; T is temperature, K; and $\tilde{R} = 83.1441$ cm^3 bar K^{-1} mol^{-1} is the absolute gas constant in "volume" units. The Redlich–Kwong parameters a and b of the mixed fluid of the composition x_{H_2O} and $x_{gas} \equiv 1 - x_{H_2O}$ were calculated according to the van der Waals mixture rule (Ferri and Baumgartner, 1992):

$$b = b_{H_2O}x_{H_2O} + b_{gas}x_{gas}, \quad (14a)$$

$$a = a_{H_2O}x_{H_2O}^2 + 2a_{H_2O-gas}x_{H_2O}x_{gas} + a_{gas}x_{gas}^2, \quad (14b)$$

$$a_{H_2O-gas} = (a_{H_2O}a_{gas})^{0.5}. \quad (14c)$$

Here, a_{H_2O}, b_{H_2O} and a_{gas}, b_{gas} are the Redlich–Kwong parameters of the pure components H_2O and gas, respectively. The parameter a_{H_2O} at each PT point was calculated by Eq. (13) and the V_{H_2O} value found according to the Hill equation (Hill, 1990); the parameter b_{H_2O} was taken as constant and equal to 14.6 cm^3 mol^{-1} (Ferri and Baumgartner, 1992).

The Redlich–Kwong parameters in pure gases were taken either directly from the literature (Table 1) or calculated using known values of critical parameters (T_c and P_c) of these gases (Ferri and Baumgartner, 1992):

$$a_{gas} = 0.4278\frac{\tilde{R}^2 T_c^{2.5}}{P_c}, \quad (15)$$

$$b_{gas} = 0.0867\frac{\tilde{R}T_c}{P_c}. \quad (16)$$

The Redlich–Kwong equation of state allows calculation of the activity coefficient of the component i in the mixture γ_i at T (K), P (bar), and x_i (Akinfiev, 1997):

$$\ln\gamma_i = -\ln P + \ln\frac{RT}{V - b} + \frac{b_i}{V - b}$$
$$- \frac{2\Sigma x_i a_{ij}}{RT^{3/2}b}\ln\frac{V + b}{V} + \frac{ab_i}{RT^{3/2}b^2}\left(\ln\frac{V + b}{V} - \frac{b}{V + b}\right), \quad (17)$$

where the index-free parameters correspond to the mixture, b_i is the excluded volume of the pure component i, and a_j is the mixed parameter of intermolecular interaction (Eq. (14c)). At infinite dilution, $x_i \longrightarrow 0$, $V \longrightarrow V_{H_2O}$, $b \longrightarrow b_{H_2O}$, and the last equation transforms into the equation for the solute fugacity coefficient at infinite dilution:

$$\ln\gamma^\infty = -\ln P + \ln\frac{RT}{V_{H_2O} - b_{H_2O}} + \frac{b_{gas}}{V_{H_2O} - b_{H_2O}}$$
$$- \frac{2a_{H_2O-gas}}{RT^{3/2}b_{H_2O}}\ln\frac{V_{H_2O} + b_{H_2O}}{V_{H_2O}}$$
$$+ \frac{a_{H_2O}b_{gas}}{RT^{3/2}b_{H_2O}^2}\left(\ln\frac{V_{H_2O} + b_{H_2O}}{V_{H_2O}} - \frac{b_{H_2O}}{V_{H_2O} + b_{H_2O}}\right). \quad (18)$$
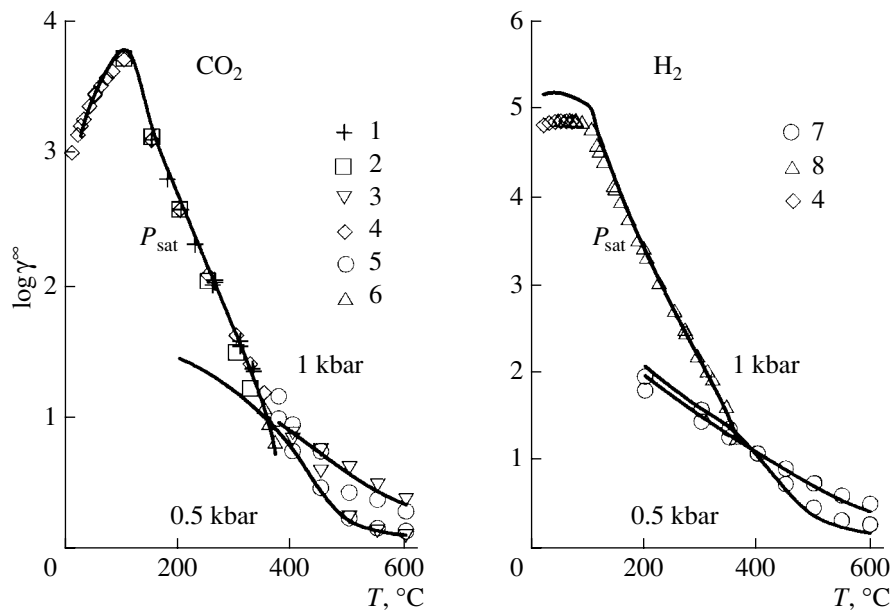
Fig. 1. Temperature dependence of logarithmic fugacity coefficients for CO_2 and H_2 at infinite dilution for different pressures. P_{sat} corresponds to the pressure of saturated H_2O vapor at a temperature exceeding 100°C and a pressure of 1 bar at lower temperatures. (1) Ellis and Golding, 1963; (2) Malinin, 1979; (3) Bowers and Helgeson, 1983; (4) Namiot, 1991; (5) Plyasunov and Zakirov, 1991; (6) Crovetto and Wood, 1992; (7) Kishima and Sakai, 1984; (8) Alvarez *et al.*, 1988; lines designate the calculation based on the Redlich–Kwong equation used in this work.

The partial molal volume of the solute component is equal to

$$V_{gas} \equiv V + x_{H_2O} \frac{\partial V}{\partial x_{gas}} \bigg|_{P,T} \qquad (18a)$$

and also can be calculated by the Redlich–Kwong equation (13). Differentiating (13) for x_{gas} at constant pressure and temperature and applying the mixture rule (in Eq. (14)), we have

$$\frac{\partial b}{\partial x_{gas}} = b_{gas} - b_{H_2O},$$

$$\frac{\partial a}{\partial x_{gas}} = 2a_{gas}x_{gas} + 2a_{H_2O-gas}(x_{gas} - x_{H_2O}) - 2a_{H_2O}x_{H_2O}, \qquad (18b)$$

$$\frac{\partial V}{\partial x_{gas}} = \frac{\dfrac{RT}{(V-b)^2}\dfrac{\partial b}{\partial x_{gas}} + \dfrac{aV}{T^{1/2}V^2(V+b)^2}\dfrac{\partial b}{\partial x_{gas}} - \dfrac{1}{T^{1/2}V(V+b)}\dfrac{\partial a}{\partial x_{gas}}}{\dfrac{RT}{(V-b)^2} - \dfrac{a(2V+b)}{T^{1/2}V^2(V+b)^2}}.$$

Then, the expression for the excess mixture volume will be

$$V^E = V - x_{gas}V_{gas} - x_{H_2O}V_{H_2O}. \qquad (18c)$$

We tested the applicability of this approach for predicting thermodynamic properties of water–gas mixtures, including activity coefficients and excess volumes of the gas component in a wide range of state parameters (Fig. 1). From this figure, we notice that, with increasing temperature, the calculated γ^∞ values

asymptotically tend to 1 in accordance with the system transition to the state of the ideal mixture of gases.

The approach we have used is applicable even to calculating excess partial volumes of a mixture in a transcritical area of H_2O. Figures 2 and 3 show the quantitative agreement between the model calculation and the experiment. Hence, the Redlich–Kwong equation as modified by us allows calculation of different thermodynamic properties of mixed fluids H_2O–gas in a wide range of compositions of the solute gas ($x_{gas} \leq 0.6$).
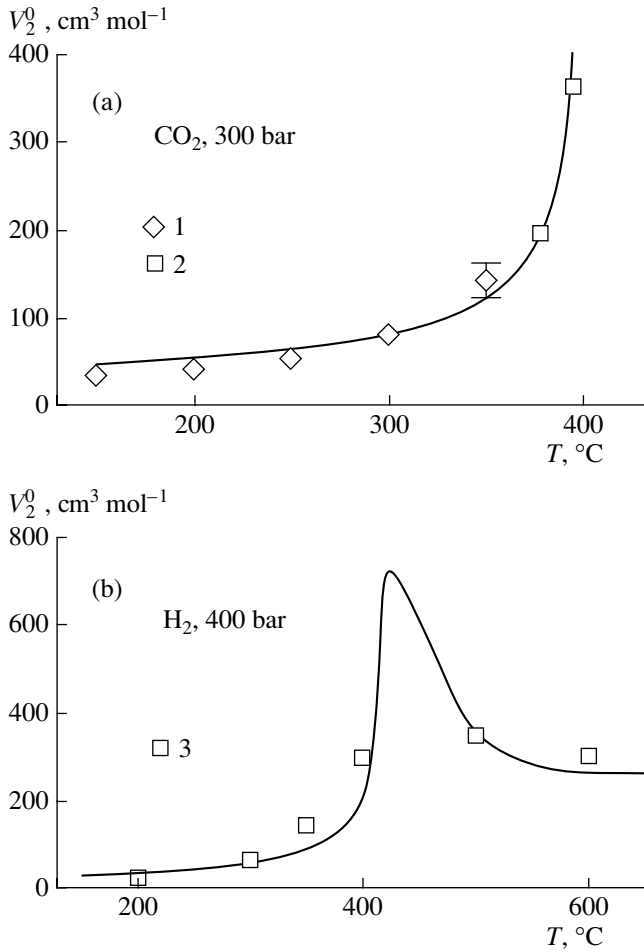
Fig. 2. Temperature dependence of solute gas V_2^0 at infinite dilution: CO_2 at 300 bar (a) and H_2 at 400 bar (b). (1) Malinin, 1979; (2) Crovetto and Wood, 1991; (3) Kishima and Sakai, 1984; lines designate the calculation based on the modified Redlich–Kwong equation.
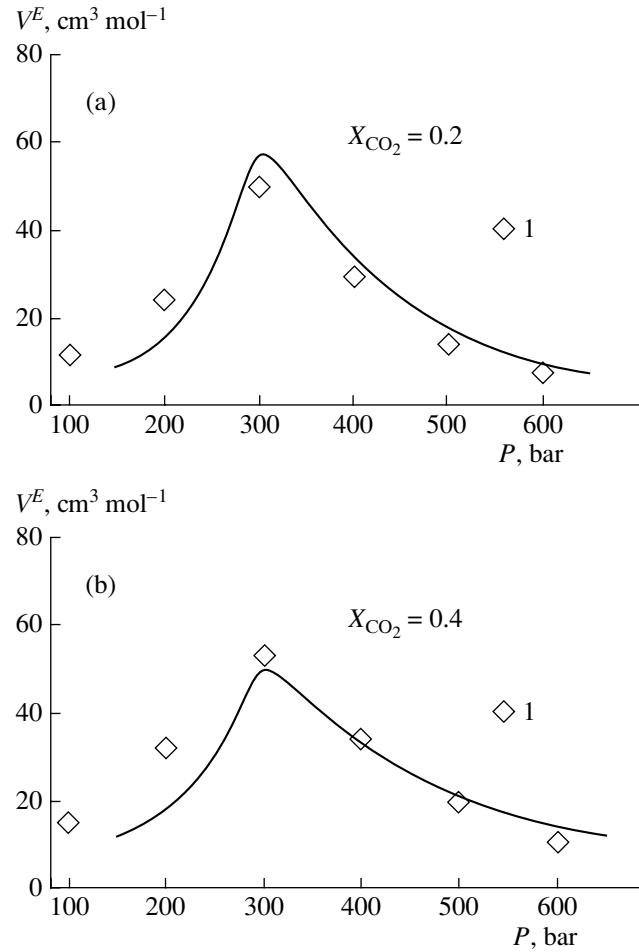
Fig. 3. Dependence of excess mixing volume V^E for H_2O–CO_2 mixtures at 400°C and different mole fractions of CO_2 in the mixture: $x_{CO_2} = 0.2$ (a) and $x_{CO_2} = 0.4$ (b). (1) Plyasunov and Zakirov, 1991; lines designate the calculation based on the modified Redlich–Kwong equation.

A detailed description of the approach is given in (Akinfiev, 1997).

CALCULATION OF DIELECTRIC PERMEABILITY

The dielectric permeability of pure gases (ε_{gas}) was calculated by the Kirkwood equation (Kirkwood, 1939):

$$\frac{(2\varepsilon_{gas} + 1)(\varepsilon_{gas} - 1)}{3\varepsilon_{gas}} = 4\pi\frac{N_A}{V_{gas}}\alpha_{gas}, \qquad (19)$$

where α_{gas} is the average polarizability of a gas molecule and $N_A = 6.022 \times 10^{23}$ mol^{-1} is Avogadro's constant. Values α_{gas} accepted in this work are shown in Table 2. Gas mole volumes at given T and P were calculated by (13) based on the modified Redlich–Kwong equation. The dielectric permeability of pure H_2O was calculated according to (Archer and Wang, 1990).

Values of ε for mixtures were determined proceeding from the assumption on additivity of the contributions of the polar and the nonpolar fluid components to the polarizability (Orlov and Smirnov, 1994)

$$\frac{(2\varepsilon + 1)(\varepsilon - 1)}{3\varepsilon}$$
$$= 4\pi\frac{N_A}{V}\left[x_{gas}\alpha_{gas} + x_{H_2O}\left(\alpha_{H_2O} + \frac{2.4143 \times 10^{-21}d_{H_2O}^2 g}{T}\right)\right], \qquad (20)$$

where V is the mole volume of the mixture; $\alpha_{H_2O} = 1.27 \times 10^{-24}$ cm^3 is the polarizability (Murphy, 1977), $d_{H_2O} = 1.857$ D is the dipole moment of a H_2O molecule (Clongh *et al.*, 1973); and g is the Kirkwood cor-

Table 2. Polarizabilities (α) of nonpolar components of aqueous fluids accepted in this work (*Handbook for Chemists*, 1966)

Component	$\alpha \times 10^{24}$, cm^3
Benzene	10.4
Dioxane	18.4
Ar	1.63
CO$_2$	2.65

relation factor, which reflects the mutual orientation of neighboring H_2O molecules in a liquid. The value of g was calculated by the equation from (Archer and Wang, 1990) using the total volume of the mixture V (but not the *partial* volume V_{H_2O}). It should be pointed out that such an approach can be used only for mixtures in which electrostatic interaction between different molecules may be neglected, and the H_2O–nonpolar gas mixtures of interest to us meet this requirement since $\varepsilon_{gas} \approx 1$. We approved the applicability of Eq. (20) for the description of the not numerous experimental data on ε of mixtures: H_2O–1,4-dioxane at $T = 0$–80°C (Akhadov, 1981) and H_2O–benzene at 300–400°C and $P = 100$–2800 bar (Deul and Frank, 1991). The ε values of pure benzene and 1,4-dioxane were calculated by

Eq. (19) with data from Table 2. The volumes of H_2O–benzene mixtures were taken directly from an experimental work by Deul and Frank (1991), and we assumed ideal miscibility of H_2O–1,4-dioxane mixtures when calculating their bulk properties. The calculated ε values are in good agreement with experimental data (Figs. 4, 5).

It is a customary practice for calculating ε values in the geochemical literature to use the Looyenga equation (Looyenga, 1965):

$$\varepsilon^{1/3} = \Phi_{H_2O}\varepsilon_{H_2O}^{1/3} + \Phi_{gas}\varepsilon_{gas}^{1/3}, \qquad (21)$$

where Φ_{H_2O} and Φ_{gas} are the volume fractions of H_2O and gas in the mixture. It should be noted that the equation was obtained proceeding from the assumption that the ε values of the mixture components are close to each other (Landau and Lifshitz, 1982; Looyenga, 1965). It is for this reason that the Looyenga equation, in the strict sense, cannot be used for predicting ε values of mixtures with a volatile having $\varepsilon_{gas} \approx 1$. Despite quite a good agreement of ε values of mixtures calculated by Eq. (21) with experimental data, especially at elevated temperatures, we will use hereinafter the Kirkwood modified equation (20). The equation contains no restrictions on ε values of mixture components and theoretically is more well-grounded.
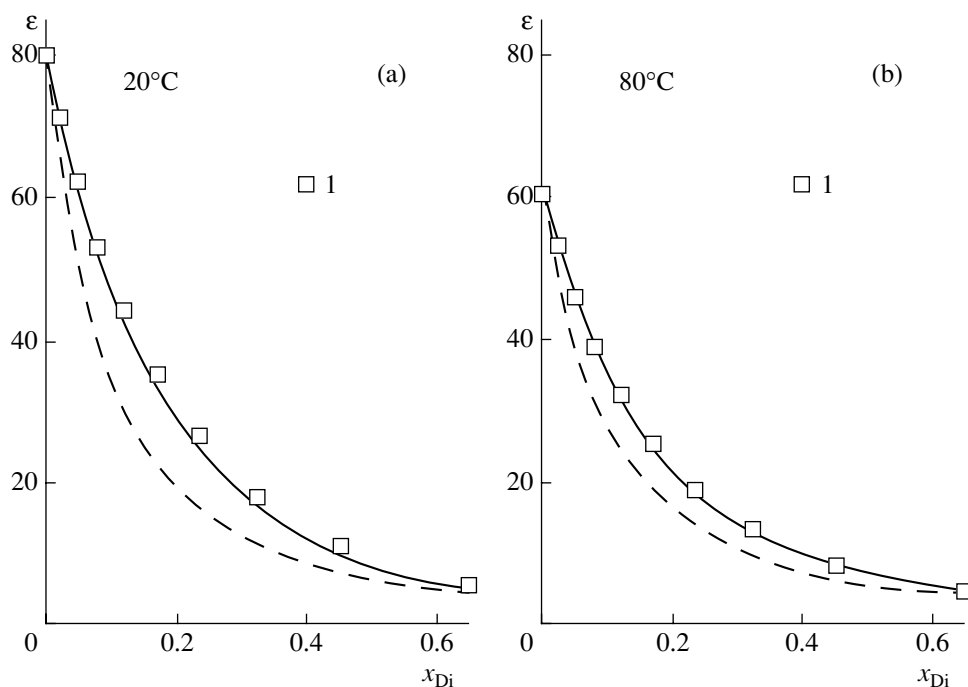

Fig. 4. Dielectric permeability of water–dioxane mixed solution (ε) at temperatures of 20 (a) and 80°C (b) and a pressure of 1 bar as a function of the dioxane mole fraction (x_{Di}) in the mixture. (1) Akhadov, 1981; solid lines designate the calculation based on Eq. (20) of this work; dotted lines, on the Looyenga equation (21) (Looyenga, 1965).
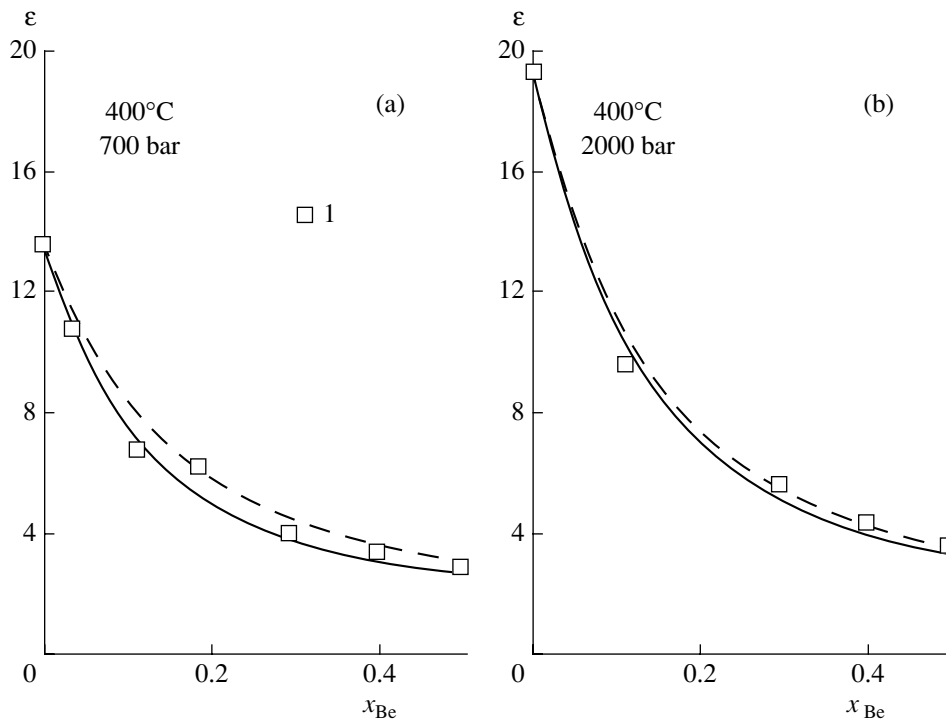
Fig. 5. Dielectric permeability of water–benzene mixtures (x_{Di}) at $P = 700$ (a) and 2000 bar (b) and $T = 400°C$ as a function of the benzene mole fraction (x_{Be}) in the mixture. (1) Deul and Frank, 1991; solid lines designate the calculation based on Eq. (20) of this work; dotted lines, on the Looyenga equation (21) (Looyenga, 1965).

CALCULATION METHODS AND THERMODYNAMIC DATA

Solubility and dissociation of components were determined using a modified version of the BALANCE code (Akinfiev, 1986, 1993), intended for calculating equilibria in multi systems. The SUPCRT92 software package (Johnson *et al.*, 1992), for calculating the thermodynamic properties of components by the HKF model, was attached to the calculation algorithm as an external subprogram. Hence, thermodynamic data for most of the substances were taken directly from the SUPCRT92 database (Johnson *et al.*, 1992) and its supplements (Sverjensky *et al.*, 1997; Shock *et al.*, 1997). The chemical potential of hydroxide ion (OH⁻) in pure water at each *PT* point was calculated using the equation from (Marshall and Frank, 1981) for the water dissociation constant:

$$\log K_w = -4.098 - \frac{3245.2}{T} + \frac{2.2362 \times 10^5}{T^2}$$
$$-\frac{3.984 \times 10^7}{T^3} + \left(13.957 - \frac{1262.3}{T} + \frac{8.5641 \times 10^5}{T^2}\right)\log\rho_w, \quad (22)$$

where T is temperature, K, and ρ_w is the density of pure H_2O, g cm⁻³. Such a calculation method differs from the method accepted in SUPCRT92. It should be noted that the use of data for H_2O and OH⁻ generated by SUPCRT92 results in a substantial disagreement with

experimental data (Marshall and Frank, 1981) in the supercritical H_2O area. It is this condition that made us reject the SUPCRT92 package and apply Eq. (22) when calculating the thermodynamic properties of OH⁻.

The calculation procedure at each *PTx* point involved the following steps:

1. Calculation of volumetric properties of the mixture by Eqs. (13) and (14).

2. Calculation of ε of the mixed fluid by Eq. (20) using the known volume V of the mixture (step 1), as well as calculation of θ according to Eq. (7).

3. Calculation of coefficients A and B of the Debye–Hückel equation for the mixed fluid by Eqs. (12) and (13) using the known values ε and V (steps 1 and 2).

4. Calculation of modified values of the standard chemical potentials for all aqueous components by Eq. (10). The values of the Born parameters (ω) were assumed as constant and equal to their tabular values at 25°C and 1 bar.

5. Calculation of equilibrium in the studied system by the method of minimization of the Gibbs function of the system (the BALANCE code) based on modified values of the standard chemical potentials of aqueous components (step 4) and their activity coefficients by Eq. (11) using the "new" values of the Debye–Hückel parameters (step 4).
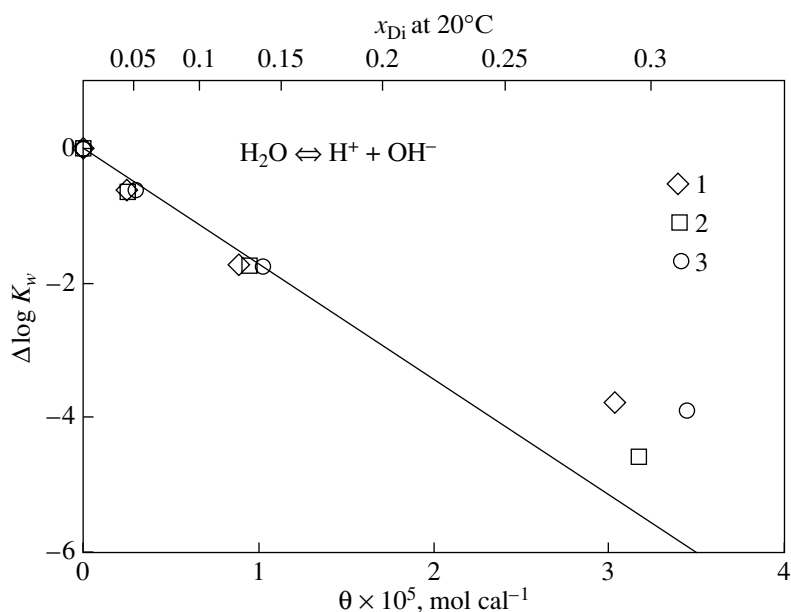
Fig. 6. Variation of the logarithmic constant of H_2O dissociation ($\log K_w$) at 0 (1), 20 (2), and 50°C (3) depending on θ (Eq. (7)) in water–dioxane mixtures. (1–3) Experimental data (Harned and Fallon, 1939); lines correspond to theoretical slopes with the Born parameter $\omega_{OH^-} = 1.7246 \times 10^5$ cal mol^{-1} (Johnson *et al.*, 1992).

CALCULATION RESULTS

O–H System

It is convenient to begin checking the application of the proposed approach with the description of the H_2O dissociation constant (K_w) in the mixed fluid. Experimental data available in the literature comprise both $\log K_w$ values for H_2O–1,4-dioxane mixtures (Harned and Fallon, 1939) and corresponding ε values for mixtures (Akhadov, 1981). Application of Eq. (8) for a change of the logarithmic H_2O dissociation constant ($\log K_w$) in the mixed fluid relative to the corresponding value in pure H_2O gives

$$\Delta \log K_w = -\Delta_w \omega \theta, \qquad (23)$$

where $\Delta_w \omega = \omega_{OH^-} + \omega_{H^+}$ is the change in the Born parameter of the dissociation reaction. Since, as was mentioned above, the value ω_{H^+} is assumed to be equal to 0 at all the state parameters, we finally have

$$\Delta \log K_w = -\omega_{OH^-} \theta. \qquad (24)$$

Figure 6 represents experimental values of $\log K_w$ (Harned and Fallon, 1939) as a function of θ calculated on the basis of (Akhadov, 1981). The line in the figure corresponds to Eq. (24) with $\omega_{OH^-} = 1.7246 \times 10^5$ cal mol^{-1} from the SUPCRT92 database. From this figure, we notice that, at small dioxane concentrations ($x_{H_2O} > 0.8$), the linear dependence (24) precisely

reproduces the experiment at all temperatures. A slight deviation from the experiment shows up only at high dioxane concentrations in the mixture ($x_{H_2O} < 0.7$, $\theta > 3 \times 10^{-5}$ mol cal^{-1}).

Na–Cl–O–H System

The same procedure was used for describing experimental data (Dunn and Marshall, 1969) on NaCl dissociation in H_2O–1,4-dioxane mixtures at 100°C. The dielectric properties of the mixtures were calculated by Eq. (24). They happened to be close to values extrapolated by the authors (Dunn and Marshall, 1969). The values of the dissociation constant of the reaction

$$NaCl_{aq} \Leftrightarrow Na^+ + Cl^- \qquad (25)$$

in mixtures of different composition can be represented as a function of θ in terms of

$$\log K_d = \log K_d^0 + \Delta_d \omega \theta, \qquad (26)$$

where K_d^0 is the dissociation constant of reaction (25) in pure H_2O,[1] and $\Delta_d \omega = \omega_{Na^+} + \omega_{Cl^-} - \omega_{NaCl_{aq}}$ is the change in the Born parameter of reaction (25). In this work, we assumed $\Delta_d \omega = 1.8246 \times 10^5$ cal mol^{-1} according to data from SUPCRT92. The comparison of calcu-

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[1] The superscript [0] hereinafter corresponds to the thermodynamic value in pure water. The same symbol without a superscript designates the corresponding value in the mixed solvent.
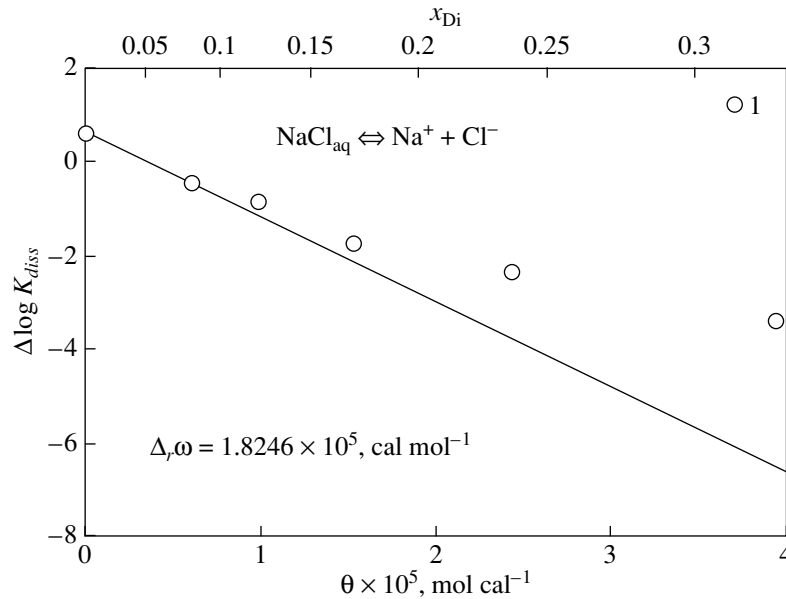
Fig. 7. Dependence of the logarithmic constant of NaCl dissociation in water–dioxane mixtures at $T = 100°C$ on θ (Eq. (7)). (1) Experimental data (Dunn and Marshall, 1969); lines correspond to the theoretical slope with data for reaction components from the database (Johnson *et al.*, 1992).

lated and experimental (Dunn and Marshall, 1969) results is illustrated in Fig. 7. The proposed model is seen to give correct predictions right up to $\theta \leq 2 \times 10^{-5}$ mol cal^{-1}, which corresponds to mole fractions of dioxane $x_{Di} < 0.2$. At higher x_{Di} values, the deviation increases similarly to K_w (Fig. 6). The deviation is likely to be caused by the fact that the method used does not take into account changes introduced by short-range interactions between dioxane molecules and surrounding H_2O molecules on a change in the fluid composition.

Ag_2SO_4–O–H System

Experimental data (Davis *et al.*, 1939) on the solubility of crystalline Ag_2SO_4 in the mixed fluid H_2O–1,4-dioxane at 25°C were processed according to the method proposed above. Only ions Ag^+ and SO_4^{2-} were taken into consideration, and their thermodynamic data were borrowed from SUPCRT92. The comparison of experimental and calculation data is shown in Fig. 8. The theoretical slope of the solubility curve corresponds to a change in the Born parameter of the reaction

$$Ag_2SO_{4\,(cr)} \Leftrightarrow 2Ag^+ + SO_4^{2-}, \qquad (27)$$
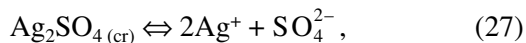
and this change makes up $\Delta_r\omega_{27} = 2\omega_{Ag^+} + \omega_{SO_4^{2-}} = (2 \times 0.2160 + 3.1463) \times 10^5 = 3.5783 \times 10^5$ cal mol^{-1}. The calculation is seen to correspond exactly to the experiment at $x_{Di} < 0.17$ (Fig. 8). In addition to the short-range interactions mentioned above, ionic association may become apparent with increasing x_{Di}. For instance, taking

into account silver sulfate complex, the solution reaction can be written as

$$Ag_2SO_{4\,(cr)} \Leftrightarrow Ag^+ + AgSO_4^-. \qquad (28)$$

The components of the reaction are only monovalent ions; therefore, a change in the Born parameter $\Delta_r\omega_{28}$ will be lower than for reaction (27) with participation of the divalent ion SO_4^{2-}. This means that the contribution of reaction (28) to the total solubility of salt will result in a decrease in the solubility curve slope. Unfortunately, the lack of experimental data gives no way of providing a qualitative assessment of this effect.

Si–O–H System

Silica solubility in aqueous species was studied in both the subcritical and the supercritical areas of water (Walther and Helgeson, 1977; Pokrovskii and Helgeson, 1991). Walther and Helgeson (1977) wrote the dissolution reaction as

$$SiO_{2(quartz)} \Leftrightarrow SiO_{2(aq)}$$
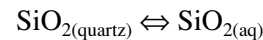
and assigned the positive value of the Born parameter $\omega_{SiO_{2(aq)}} = 0.1291 \times 10^5$ cal mol^{-1} to solute silica ($SiO_{2(aq)}$) for describing experimental data. The same value $\omega_{SiO_{2(aq)}}$ was accepted by Shock *et al.* (1989) when including $SiO_{2(aq)}$ into the SUPCRT92 thermodynamic database, using the HKF equation format. A positive value of the Born parameter of an electroneutral molecule is indicative of a nonzero dipole (multidipole) moment. This means that the behavior of such a com-
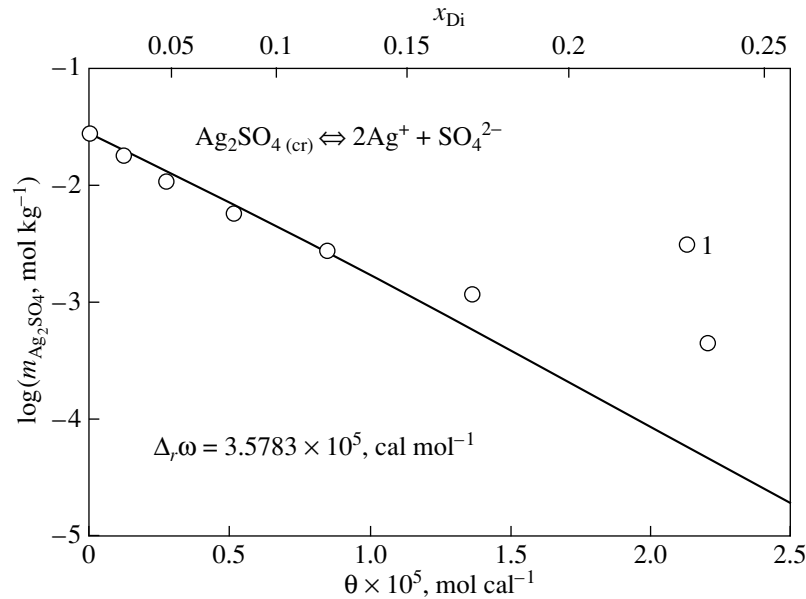
Fig. 8. Dependence of solubility of crystalline Ag_2SO_4 at 25°C in water–dioxane mixtures on θ (Eq. (7)). (1) Davis *et al.*, 1939; the line corresponds to the theoretical slope for reaction (27) with data for Ag^+ and SO_4^{2-} from the database (Johnson *et al.*, 1992).
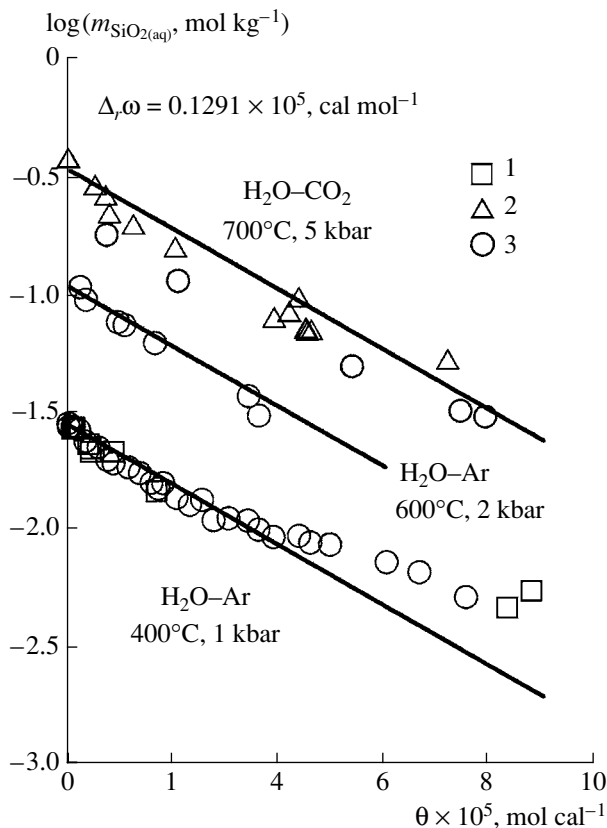

Fig. 9. Logarithm of the molal concentration of dissolved silica $SiO_{2(aq)}$ in equilibrium with quartz as a function of θ of H_2O–Ar and H_2O–CO_2 mixtures for 400–700°C and 1–5 kbar. (1) Sommerfeld, 1967; (2) Novgorodov, 1975; (3) Walther and Orville, 1983; lines correspond to the theoretical slope with the Born parameter (Johnson *et al.*, 1992).

ponent of the solution will be sensitive to changing ε of the solvent. Assuming an ideal behavior of $SiO_{2(aq)}$ in aqueous solution, the expression for the constant of silica solution in the mixed solvent, according to (6), can be written as

$$\log K = \log m_{SiO_2} = \log K^0 - \omega_{SiO_2}\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_{H_2O}}\right)\frac{1}{2.303RT}$$

$$= \log m_{SiO_2}^0 - \omega_{SiO_2}\theta, \qquad (29)$$

where $\log K^0 = \log m_{SiO_2}^0$ is the logarithmic molal solubility of quartz in pure water at the same T and P and θ, as previously, is the correction dielectric factor (Eq. (7)). Figure 9 illustrates a similar-to-linear decay of solubility $\log m_{SiO_2}$ from calculated θ values for H_2O–Ar and H_2O–CO_2 fluid mixtures at 400–700°C and 1–5 kbar. The lines in the figure show calculated values of solubility with regard to the value $\omega_{SiO_{2(aq)}} = 0.1291 \times 10^5$ cal mol^{-1} accepted in SUPCRT92. It is evident that a close agreement between the calculation and the experiment is observed up to $\theta \leq 4 \times 10^{-5}$ mol cal^{-1}, which corresponds to $x_{gas} \leq 0.3$. It should be emphasized once again that the value $\omega_{SiO_{2(aq)}} = 0.1291 \times 10^5$ cal mol^{-1} used in this work was obtained only from experimental data on quartz solubility in pure water (Walther and Helgeson, 1977). The agreement of our calculation based on the same value $\omega_{SiO_{2(aq)}}$ with the experiment in mixed solvents testifies that the approach

Table 3. Standard thermodynamic properties and parameters of the HKF equation for components of aqueous fluid accepted in this work

Thermodynamic property		$AgCl^0$ (Akinfiev and Zotov, 2001)	$AgCl_2^-$ (Tagirov et al., 1997)	HCl^0 (Tagirov et al., 1997)	$CaOH^+$ (this work)	$CaHCO_3^+$ (this work)
$\Delta_f G_{298}^0$	cal mol^{-1}	-17399	-51350	-30411	-171490	-273720
S_{298}^0	cal mol^{-1} K^{-1}	32.067	49.78	0.421	-5.346	8.003
$C_{p,\,298}^0$	cal mol^{-1} K^{-1}	-5.328	-16.60	35.74	15.59	67.408
V_{298}^0	cm^3 mol^{-1}	21.631	37.10	22.75	-29.4	4.764
$a_1 \times 10$	cal mol^{-1} bar^{-1}	4.2750	7.1327	16.1573	-2.2875	2.448
$a_2 \times 10^{-2}$	cal mol^{-1}	3.7555	9.8065	-11.4311	-13.3704	-1.826
a_3	cal K mol^{-1} bar^{-1}	4.2739	1.8947	-46.1866	11.0053	6.468
$a_4 \times 10^{-4}$	cal K mol^{-1}	-2.9343	-3.1844	-2.304	-2.2263	-2.7035
c_1	cal mol^{-1} K^{-1}	3.0441	4.8953	46.4716	14.5527	55.5203
$c_2 \times 10^{-4}$	cal K mol^{-1}	-4.1199	-6.7789	-5.2811	0.1431	6.1746
$\omega \times 10^{-5}$	cal mol^{-1}	0.0	0.6667	0.0	-0.082	0.0723

we have proposed requires no supplementary adjusting parameters.

Low-temperature experiments on amorphous silica solubility in aqueous mixed solvents (polar organic component) (Schott and Dandurand, 1987) at 25°C yield a higher value of $\omega_{SiO_{2(aq)}} = 0.4422 \times 10^5$ cal mol^{-1}. Nevertheless, these authors report a decrease in $\omega_{SiO_{2(aq)}}$ with increasing temperature. Their estimate of $\omega_{SiO_{2(aq)}}$ at 200°C amounts to 0.1013×10^5 cal mol^{-1}, which is very close to the value accepted in the SUPCRT92 database. Such a behavior of $\omega_{SiO_{2(aq)}}$ may result from the temperature dependence between hydrogen bonds of the $SiO_{2(aq)}$ molecule and surrounding H_2O molecules.

Chlorargyrite (AgCl$_{cr}$) Solubility

Akinfiev et al. (1998) experimentally studied chlorargyrite solubility in H_2O–$NaCl$–CO_2 solutions in fluid with a NaCl concentration of 0.2 mol kg^{-1} and a CO_2 mole fraction x_{CO_2} up to 0.3 at 400°C and $P = 400$ and 600 bar. The Ag(I)–Na–Cl–C(IV)–O–H system is more complicated than those discussed above since chlorargyrite solubility is not described by the equilibrium of one reaction. However, the advantage of this system is that AgCl$_{cr}$ solubility in pure water has been thoroughly studied in a wide range of temperatures (0–450°C) and pressures (1–1500 bar) (Seward, 1976; Zotov et al., 1986; Levin, 1992; Zotov et al., 1995; Tagirov et al., 1997). The results obtained in these works give grounds to assess the applicability of the proposed calculation

model. When performing model calculations, the following components of the aqueous solution were taken into account: Ag^+, $AgCl^0$, $AgCl_2^-$, Na^+, $NaCl^0$, CO_2^0, HCO_3^-, CO_3^{2-}, Cl^-, OH^-, H^+, and HCl^0. The thermodynamic properties of most of the aqueous components were taken from SUPCRT92 (Johnson et al., 1992), for $AgCl_2^-$ and HCl^0, from (Tagirov et al., 1997), and those for $AgCl^0$, from (Akinfiev and Zotov, 2001). For the convenience of the reader, the parameters of the last three components are given in Table 3.

The calculation of AgCl$_{cr}$ solubility was performed by the algorithm cited above, and the comparison of the calculation results with the experiment is shown in Fig. 10. The significant decrease in AgCl$_{cr}$ solubility on an increase in x_{CO_2} to 0.15–0.2 can be quantitatively accounted for within the framework of our approach. Since $AgCl_2^-$ is the prevailing form of silver in aqueous fluids under the conditions of the experiment (Seward, 1976; Zotov et al., 1986; Levin, 1992; Tagirov et al., 1997), chlorargyrite solubility can be described by the reaction

$$AgCl_{cr} + Cl^- \Leftrightarrow AgCl_2^-. \qquad (30)$$

The change in the Born parameter of this reaction is negative, $\Delta_r\omega_{(30)} = \omega_{AgCl_2^-} - \omega_{Cl^-} = [0.6743 - 1.4560] \times 10^5 = -0.783 \times 10^5$ cal. In this case, a decrease in ε of the solvent with increasing x_{CO_2} will promote a shift to the right of the equilibrium and result in an increase in
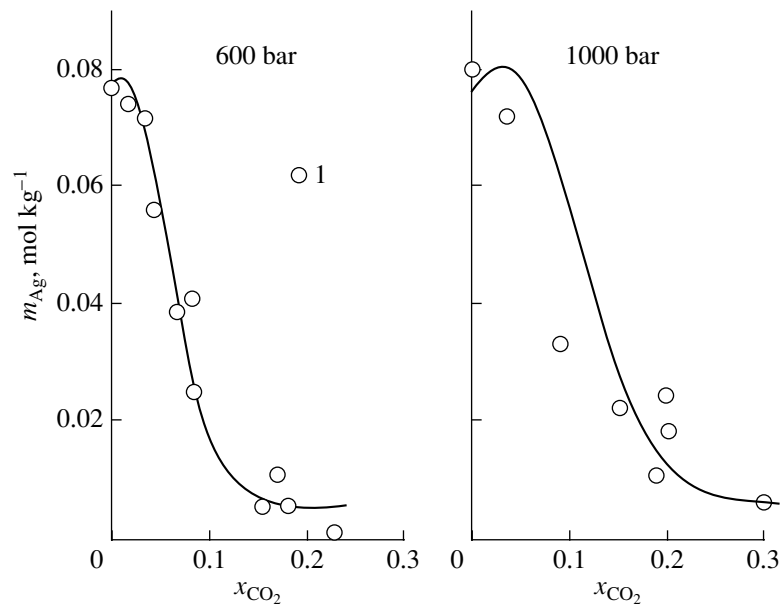
Fig. 10. Dependence of chlorargyrite solubility in H_2O–CO_2–NaCl fluid on the mole fraction of CO_2 (x_{CO_2}) at $T = 400°C$ and $P = 600$ and 1000 bar. The total NaCl concentration is 0.2 mol kg^{-1}. (1) Akinfiev *et al.*, 1998; lines signify the theoretical model.

$AgCl_{cr}$ solubility. However, it should be taken into consideration that a decrease in ε will simultaneously reduce the concentration of free Cl^- due to association in $NaCl^0$. The value $\Delta_r\omega$ of the association reaction is also negative, amounting to -1.8246×10^5 cal. The total effect of "resistance" can be presented as the reaction

$$AgCl_{cr} + NaCl^0 \Leftrightarrow AgCl_2^- + Na^+, \qquad (31)$$

for which a change in the Born parameter $\Delta_r\omega_{(31)} = +1.0429 \times 10^5$ cal is positive as well. Hence, a decrease in ε of mixed fluid due to the presence of a nonpolar volatile component in it will result in decreasing chlorargyrite solubility.

The good agreement of experimental data on $AgCl_{cr}$ solubility with calculation data (Fig. 10) confirms the capabilities of the proposed algorithm of predicting equilibria in multi component systems in the presence of a mixed fluid. It should be pointed out that the value of the Born parameter $\omega_{AgCl_2^-} = 0.6667 \times 10^5$ cal mol^{-1} accepted in the calculation model was obtained by (Tagirov *et al.*, 1997) based on $AgCl_{cr}$ solubility in the Ag–Na–Cl–O–H system in the absence of a nonpolar component. The use of the value $\omega_{AgCl_2^-} = 0.9169 \times 10^5$ cal mol^{-1} included in the SUPCRT92 database and based on correlation ratios (Sverjensky *et al.*, 1997) worsens the description.

Portlandite Ca(OH)$_{2, cr}$ Solubility

Portlandite solubility in supercritical fluids was studied by Walther (1986) at T up to 600°C and P 1–3 kbar. Portlandite solubility in H_2O–Ar mixed fluid ($x_{Ar} = 0$–0.33) at 400–620°C and pressures up to 2 kbar was examined by Fein and Walther (1989). Only "free" Ca^{2+} ion was involved in model descriptions of experiment in these works. We, when describing available experimental data, assumed $CaOH^+$ and $Ca(OH)_2^0$ to exist at elevated temperatures.

Portlandite thermodynamic properties were taken according to (*Thermodynamic...*, 1981): $\Delta_fG_{298}^0 = -214684$ cal mol^{-1}, $S_{298}^0 = 19.933$ cal mol^{-1} K^{-1}, $V^0 = 33.056$ cm^3 mol^{-1}, and the Mayer–Kelley equation for heat capacity in cal mol^{-1} K^{-1} as $C_p^0 = 21.3346 + 7.9140 \times 10^{-3}T - 2.4749 \times 10^5/T^2$. The thermodynamic properties of Ca^{2+} ion were taken from SUPCRT92.

Preliminary calculations of portlandite solubility in pure water showed that the free Ca^{2+} ion concentration does not exceed 10% of the total solubility of the mineral according to experimental data (Walther, 1986). Moreover, due to a high value of the Born parameter in the reaction

$$Ca(OH)_{2, cr} \Leftrightarrow Ca^{2+} + 2OH^-, \qquad (32)$$
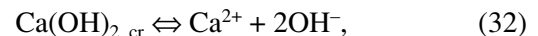
$\Delta_r\omega_{(32)} = 4.6858 \times 10^5$ cal mol^{-1}, the addition of the nonpolar component Ar should be accompanied by a very strong shift to the right of the equilibrium in reaction (32), thus decreasing the concentration of Ca^{2+}. It is for this reason that two reactions
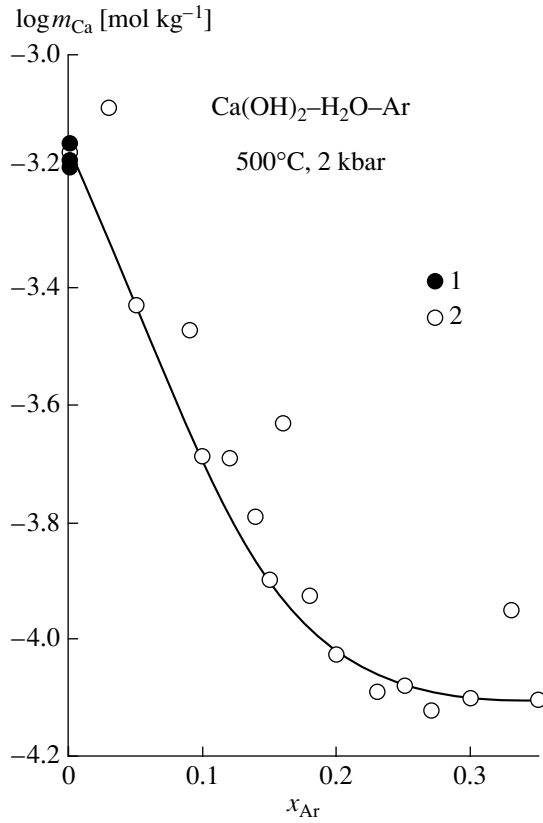
$$Ca(OH)_{2, cr} \Leftrightarrow CaOH^+ + OH^- \qquad (33)$$
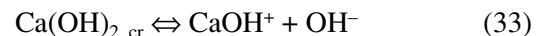
Fig. 11. Dependence of portlandite $Ca(OH)_{2,cr}$ solubility in H_2O–Ar mixtures on the mole fraction of Ar (x_{Ar}) in a fluid at $T = 500°C$ and $P = 2$ kbar. (1) Walther, 1986; (2) Fein and Walther, 1989; lines signify the theoretical model.
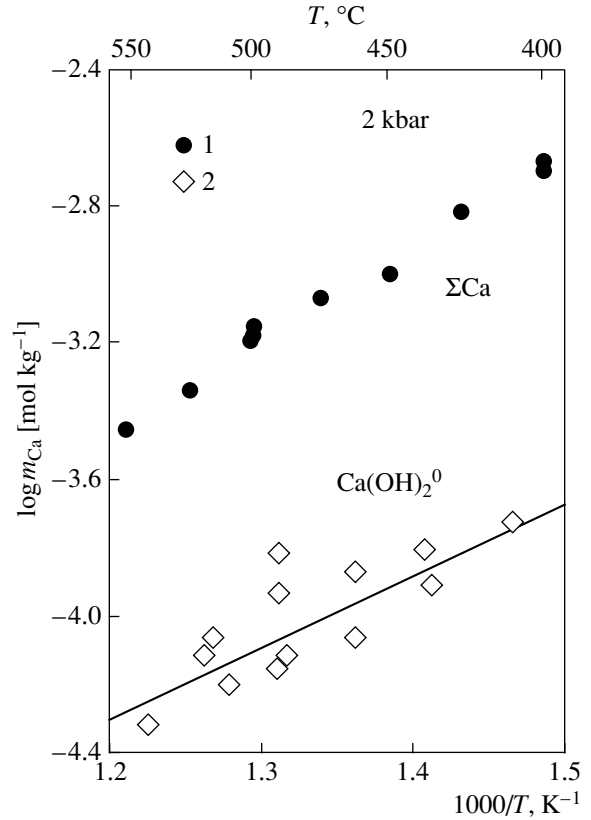

Fig. 12. Temperature dependence of the logarithm of portlandite solubility (1) in pure H_2O at $P = 2$ kbar (Walther, 1986) and corresponding calculated values of the molal concentration of $Ca(OH)_2^0$ (2). The line corresponds to a linear approximation of $Ca(OH)_2^0$ concentration on inverse temperature (see text).

and

$$Ca(OH)_{2,cr} \Leftrightarrow Ca(OH)_2^0 \qquad (34)$$

were assumed to be key reactions determining portlandite solubility in H_2O–Ar fluid mixtures.

The equilibrium of reaction (33) depends on the dielectric permeability of fluid since the reaction is not isocharging. According to Eq. (8)

$$\log K_{(33)} \approx \log[CaOH^+] \cdot [OH^-]$$
$$= \log K_{(33)}^0 - \Delta_r \omega_{(33)} \theta \qquad (34a)$$

and, therefore,

$$\log[CaOH^+] = \log[OH^-] = \frac{1}{2}(\log K_{(33)}^0 - \Delta_r \omega_{(33)} \theta). \qquad (35)$$

The equilibrium of reaction (34) does not depend on the dielectric permeability of fluid, as the reaction product is an electroneutral molecule. Hence, the overall change in the Born parameter of the reaction is $\Delta_r \omega_{(34)} \cong 0$, and consequently, $\log K_{(34)} = \log K_{(34)}^0$, where, as previously, K and K^0 correspond to the constants of reaction equilibrium in the mixed fluid and pure water, respectively.

Figure 11 illustrates the change in prevailing forms of Ca in the mixed solvent at a temperature of 500°C and a total pressure of 2 kbar. At up to $x_{Ar} \leq 0.15$, the first Ca hydrocomplex $CaOH^+$ prevails, while, at $x_{Ar} > 0.2$, when solubility stops depending on x_{Ar}, the second Ca hydrocomplex $Ca(OH)_2^0$ becomes prevailing. The dependence of portlandite solubility on the Ar mole fraction in fluid at different temperatures and pressures served as the basis for optimization of the Born parameter of $CaOH^+$ and calculation of the thermodynamic properties of the first and second hydrocomplexes of calcium. The optimization results are presented in Fig. 12. The linear dependence $\log K_{(34)}$ on the inverse temperature at $P = 2$ kbar corresponds to the equation

$$\log K_{(34)} \cong \log[Ca(OH)_2^0] = -6.7963 + \frac{2078}{T(K)}. \qquad (36)$$
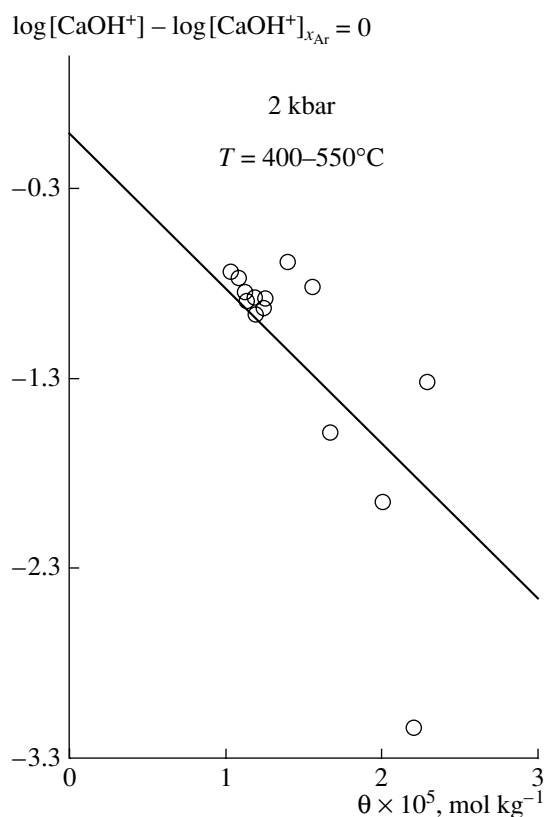
Fig. 13. Difference between logarithms of $CaOH^+$ molal concentration in H_2O–Ar mixtures and pure water in equilibrium with portlandite depending on θ. (1) Fein and Walther, 1989; the line designates the calculation based on the model, and its slope corresponds to one-half of the variation of the Born parameter of reaction (33) $0.5\Delta_r\omega = 0.8213 \times 10^5$ cal mol^{-1}.

Fig. 14. Dependence of portlandite $Ca(OH)_{2, cr}$ solubility in pure water on the temperature at pressures of saturated water vapor of 0.5, 1.0, 2.0, and 3.0 kbar. (1) *Handbook for Chemists*, 1964; (2) Walther, 1986; (3) Seewald and Seyfried, 1991; lines designate the calculation with data for $CaOH^+$ from Table 3.

The average ω value of reaction (33) in this case amounts to $\Delta_r\omega_{(33)} = 1.6426 \times 10^5$ cal (Fig. 13). Then, assuming $\omega_{OH^-} = 1.7246 \times 10^5$ cal mol^{-1} according to SUPCRT92, we have $\omega_{CaOH^+} = -0.082 \times 10^5$ cal mol^{-1}.

The obtained values $K_{(34)}$ and ω_{CaOH^+} can be used for predicting $Ca(OH)_{2, cr}$ solubility under different *PT* conditions. Figure 11 demonstrates a good agreement between the experiment and the calculation.

The parameters of the HKF model for $CaOH^+$ presented in Table 3 are based on the ω_{CaOH^+} value of this work (see above); the value $\Delta_f G^0_{298} = -171490$ cal mol^{-1} was taken from collected data (Högfeldt, 1982); data on portlandite solubility were borrowed from (Walther, 1986) and (Seewald and Seyfried, 1991). The values of entropy (S^0_{298}) and heat capacity (C^0_{P298}) and the mole volume of this complex were determined by the least-squares method using the UT-HEL code (Yu.V. Shvarov, 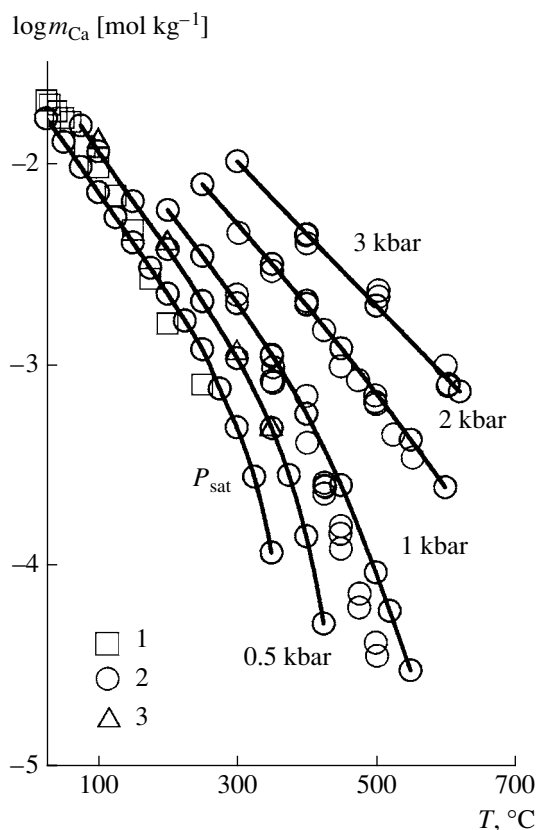1995). The HKF parameters ($a_1...a_4, c_1, c_2$) were calculated by correlation dependences (Shock and Helgeson, 1988).

The comparison between experimental and theoretical portlandite solubility with accepted values of the thermodynamic properties of $CaOH^+$ is presented in Fig. 14. As is evident from the figure, the model description exactly reproduces the experiment for the whole range of temperatures (100–600°C) and pressures ($P_{sat} = 3$ kbar). It should be pointed out that, in describing portlandite solubility, the calculation model took into account the possibility of existence of the whole set of Ca-bearing ions and molecules (Ca^{2+}, $CaOH^+$, and $Ca(OH)_2^0$), $CaOH^+$ being the prevailing form under the given *PT* conditions.

Calcite (CaCO$_{3, cr}$) Solubility

Calcite solubility in supercritical CO_2–H_2O fluids was studied by Fein and Walther (1987) at 300–600°C and $P = 1$ and 2 kbar. In contrast to other experimental works represented in a review by Holland and Malinin

(1979), the study by Fein and Walther (1987) involved a wider range of CO_2 concentrations up to $x_{CO_2} = 0.15$. The authors established that, with increasing x_{CO_2} (up to 0.05), the solubility of calcite first increases and then begins to decrease, decreasing by nearly an order of magnitude at $x_{CO_2} = 0.15$. This behavior of $CaCO_{3, cr}$ solubility received no explanation in the cited work.

Preliminary calculations of calcite solubility in the $Ca–CO_2–H_2O$ system with data from SUPCRT92 showed that the main contribution to the solubility should be assigned to the reaction

$$CaCO_{3, cr} + CO_2^0 + H_2O \Leftrightarrow CaHCO_3^+ + HCO_3^- \quad (37)$$
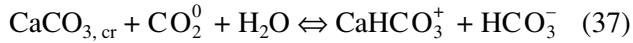
with participation of $CaHCO_3^+$ complex. However, the thermodynamic properties of this complex presented in SUPCRT92 are based only on low-temperature experimental data ($T < 100°C$) and are unfit for our case.

The procedure of obtaining the thermodynamic parameters for $CaHCO_3^+$ was similar to that for $CaOH^+$ described above. First, values of the reduced chemical potential of $CaHCO_3^+$ ($z_{CaHCO_3^+}$) were calculated from data on Ca solubility in the $Ca–CO_2–H_2O$ system for each PTx_{CO_2} experimental point. The thermodynamic properties of "basic" ions (Ca^{2+}, HCO_3^-, CO_3^{2-}) were taken from SUPCRT92. The thermodynamic properties of dissolved carbon dioxide CO_2^0 were calculated based on the Redlich–Kwong equation (Eqs. (13)–(16)), and its activity ratio, on Eq. (17). As was mentioned above, such an approach ensures a greater accuracy in describing neutral aqueous components under supercritical conditions than the standard method accepted in the HKF model (Shock *et al.*, 1989).

The calculation of the Born parameter of $CaHCO_3^+$ ($\omega_{CaHCO_3^+}$) was carried out by the iteration method with the use of experimental data at $P = 2$ kbar since these data cover the largest range of CO_2 concentrations ($x_{CO_2} = 0–0.15$). The value 0.3084×10^5 cal mol^{-1} from SUPCRT92 was used as an initial approximation. The value $\omega_{CaHCO_3^+}$ obtained as a result of a successive iteration was used for transformation of the whole set of $z_{CaHCO_3^+}$ values in experimental PTx_{CO_2} points into $z_{CaHCO_3^+}^0$ values at the same P and T but at $x_{CO_2} = 0$ according to Eq. (10):

$$z_{CaHCO_3^+}^0(P, T) = z_{CaHCO_3^+}(P, T, x_{CO_2}) - \omega_{CaHCO_3^+}\theta. \quad (38)$$

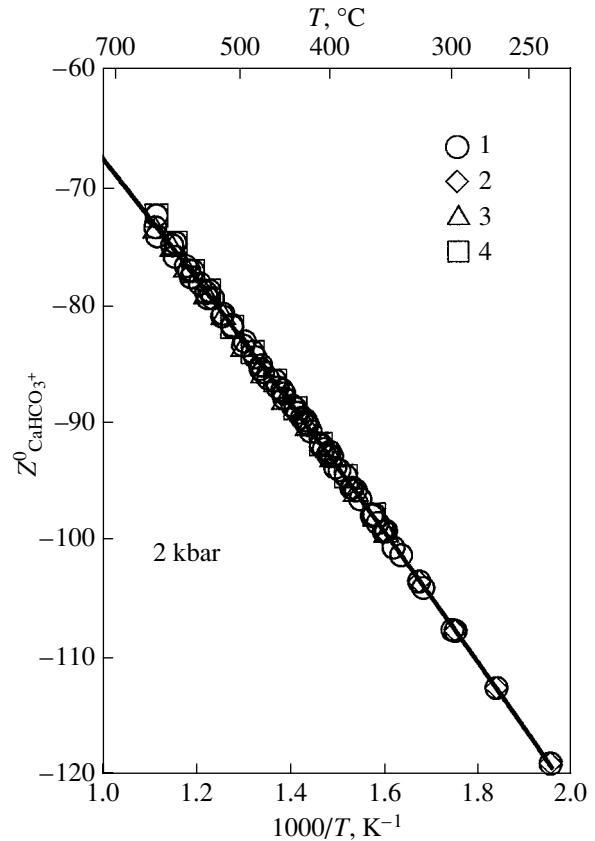**Fig. 15.** Temperature dependence of the reduced chemical potential of $CaHCO_3^+$ ($z_{CaHCO_3^+}^0$) corrected to a pure water fluid ($x_{CO_2} = 0$). (1–4) Experimental data (Fein and Walther, 1987) with $x_{CO_2} = 0.02, 0.05, 0.07,$ and 0.15, respectively; the line is a smoothed temperature dependence (see text).

The dependence of $z_{CaHCO_3^+}^0$ on the inverse temperature (Fig. 15) was approximated by a linear dependence for obtaining smoothed values of the reduced chemical potential of $CaHCO_3^+$ ($z_{CaHCO_3^+}^{0, smoothed}$). Later on, variations of the current value $z_{CaHCO_3^+}$ from its smoothed value

$$\Delta z = z_{CaHCO_3^+} - z_{CaHCO_3^+}^{0, smoothed}, \quad (39)$$

depending on θ were used to obtain a successive approximation of $\omega_{CaHCO_3^+}$ (Fig. 16). Iterations rapidly converge and the obtained value $\omega_{CaHCO_3^+}$ amounts to 0.0723×10^5 cal mol^{-1}.

The thermodynamic properties of $CaHCO_3^+$ under standard conditions ($\Delta_f G_{298}^0$, S_{298}^0, $C_{p, 298}^0$, and $V_{2, 298}^0$)
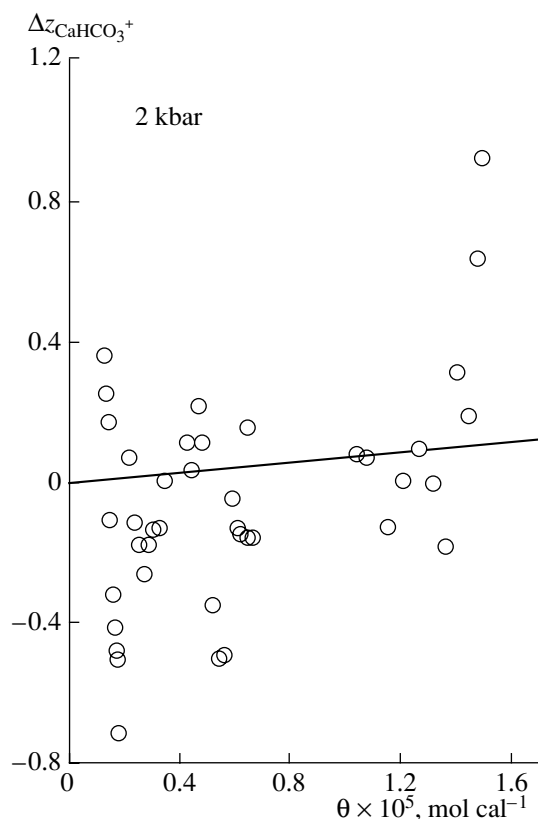
Fig. 16. Deviation of the reduced chemical potential of $CaHCO_3^+$ in an H_2O–CO_2 fluid from a smoothed value in pure water ($\Delta z = z_{CaHCO_3^+} - z_{CaHCO_3^+}^0$) depending on θ at P = 2 kbar and T = 250–600°C based on experimental data (Fein and Walther, 1987). The linear approximation corresponds to the Born parameter of $CaHCO_3^+$ $\omega_{CaHCO_3^+} = 0.0723 \times 10^5$ cal mol^{-1}.

were calculated proceeding from low-temperature data on calcite solubility (Plummer and Busenberg, 1982) and the set of smoothed values $z_{CaHCO_3^+}^{0,\,smoothed}$ in experimental PT points on the basis of the accepted value $\omega_{CaHCO_3^+}$ using the UT-HEL optimization code. The parameters of the HKF equation ($a_1...a_4$, c_1, c_2) of this complex were determined by correlation (Shock and Helgeson, 1988). The full set of the obtained thermodynamic parameters of $CaHCO_3^+$ is presented in Table 3.

A comparison between the calculated and the experimental calcite solubilities in H_2O–CO_2 fluids is given in Figs. 17 and 18. As is seen from the figures, there is in general a good agreement of the calculation with the experiments for the whole range of temperatures, pressures, and CO_2 concentrations in the fluid. The data of

Malinin (1979) at 300°C and $x_{CO_2} > 0.05$ are in conflict with the data from Fein and Walther (1987) and seem to be overvalued. The appearance of a maximum of calcite solubility with an isothermic growth of x_{CO_2} is determined by the effect of two opposite factors. First, an increase in CO_2^0 concentration shifts the equilibrium of reaction (37) to the right and solubilizes calcite. With a further increase in x_{CO_2} (>0.05), a decrease in dielectric permeability of the fluid becomes apparent that shifts the equilibrium of reaction (37) to the left, towards uncharged reagents.

INACCURACIES AND CONSTRAINTS OF THE METHOD

The method proposed for calculating equilibria in mixed fluids H_2O–nonpolar gas has three sources of inaccuracy.

The first source is errors in values of the Born parameters of aqueous solution components, which are, as a rule, assessed in the HKF model on the basis of correlation dependences (Shock and Helgeson, 1988; Shock *et al.*, 1989). To minimize this source of errors, an experimental determination of these parameters would be preferable. It was shown above how the proposed calculation method allows processing of experimental data on solubility of minerals in mixed fluids for obtaining values of the Born parameters for ions. Moreover, reliable ω values can be obtained from experiments in purely aqueous fluids under transcritical conditions, when the effect of electrostatic interactions is governing. The value of the Born parameter ($\omega_{SiO_{2(aq)}}$) was obtained by Walther and Helgeson (1977) from data on quartz solubility in pure water at 350–450°C and, as was shown above, can be used for predicting quartz solubility in mixed solutions H_2O–nonpolar gas.

The second source of errors is related to the inference that the value of the Born parameter for an ion is constant and does not depend on temperature and pressure. The authors of the modified version of the HKF model (Tanger and Helgeson, 1988) at elevated temperatures and low densities of the solvent use a special correction (Shock *et al.*, 1992) for ω. However, in the case of relatively dense fluids ($\rho_{H_2O} > 0.6$ g cm^{-3}), such a correction is not too large and, as a rule, is less than experimental errors. For instance, the value of the Born parameter $\omega_{AgCl_2^-}$ calculated by the HKF model at 400°C and 600 bar (ρ_{H_2O} = 0.612 g cm^{-3}) amounts to 0.6706×10^5 cal mol^{-1} and is close to the corresponding value under standard conditions (25°C, 1 bar), 0.6667×10^5 cal mol^{-1}. At a lower fluid density, a relevant correction can be realized by introducing an additional procedure for calculating $\omega(P, T)$ at a given
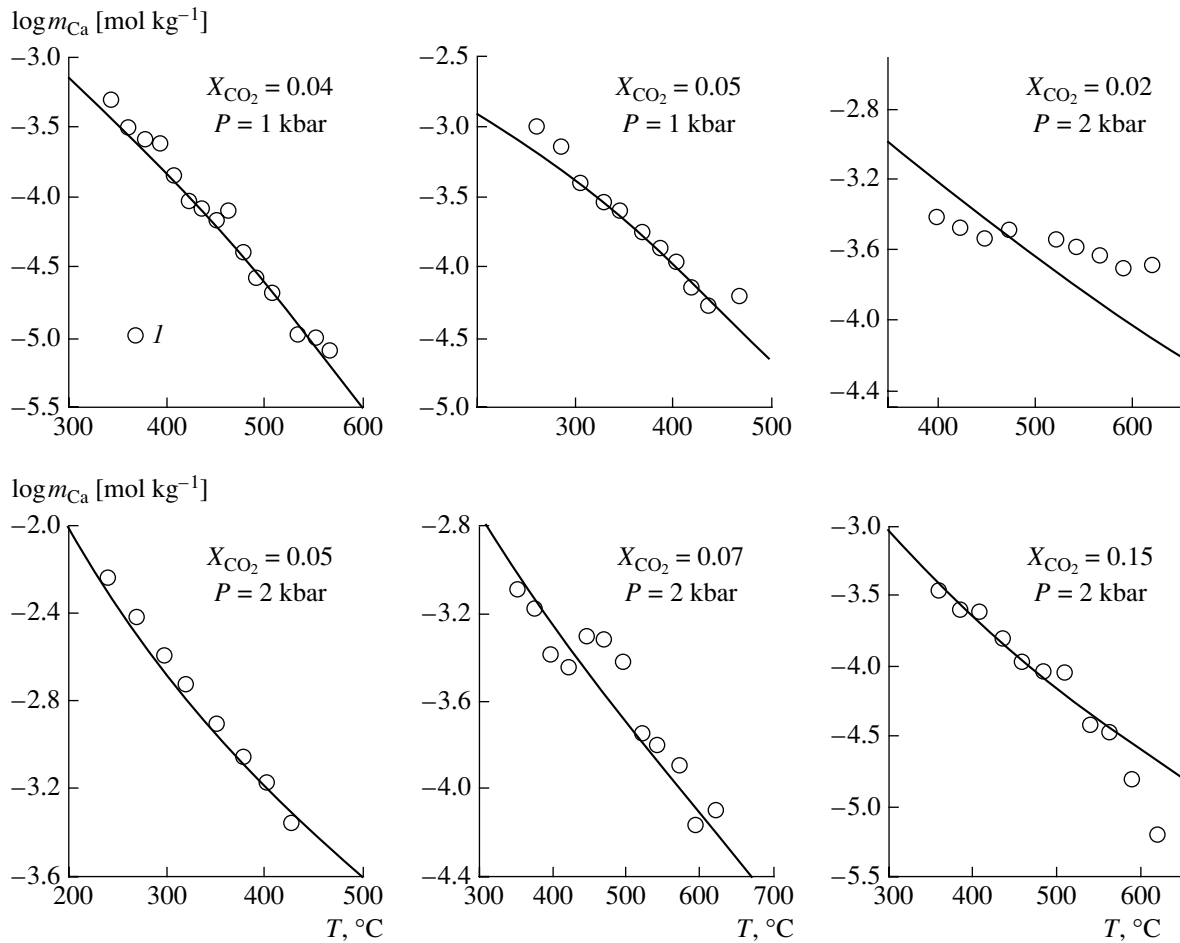
Fig. 17. Dependence of calcite solubility on temperature at $P = 1$ and 2 kbar and different x_{CO_2} in a fluid. (1) Fein and Walther, 1987; lines signify the model calculation with data for $CaHCO_3^+$ from Table 3.

PT point according to Shock *et al.* (1992). The dependence $\omega(x_{gas})$ is unclear due to insufficient experimental information.

The third source of possible errors is directly related to the calculation algorithm. The proposed approach is based on an assumption on the electrostatic nature of hydration of components of an aqueous solution. This suggests that short-range interactions between dissolved and nonpolar components of the solution are negligible and their effect may be disregarded. The nature of such interactions is unpredictable in a general way; nevertheless, it is apparent that their contribution should increase with increasing x_{gas}. Applicability of the proposed "electrostatic" algorithm can be tested by the linearity of experimental values of equilibrium constants $\log K$ with the participation of ions from θ (ratio (7)). Figs. 6–11, 17, and 18 testify that our approach is valid up to $x_{gas} = 0.15$ at low temperatures ($T < 100°C$) and up to $x_{gas} = 0.30$ at higher temperatures ($T > 300°C$). Such an extension of the approach appli-

cability accords with the idea on the prevalence of electrostatic interactions at high temperatures (Ryzhenko, 1981; Helgeson *et al.*, 1981).

The activity of water in mixed fluids was assumed to be equal to its mole fraction; i.e., the behavior of H_2O was described by Raoult's law for ideal solutions. This sort of simplification does not seem to be a source of appreciable errors since, other than the dissociation reaction

$$H_2O \Rightarrow H^+ + OH^-, \qquad (40)$$
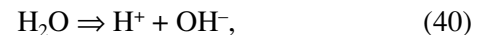
the activity of water does not appear in the expressions for the equilibrium constants of the reactions studied above. For reaction (40), the change in the Born parameter $\Delta_w\omega = \omega_{OH^-} + \omega_{H^+} = 1.7246 \times 10^5$ cal is so high that the "dielectric" factor prevails and changes introduced by the imperfection of H_2O behavior represent corrections of the second order of smallness.
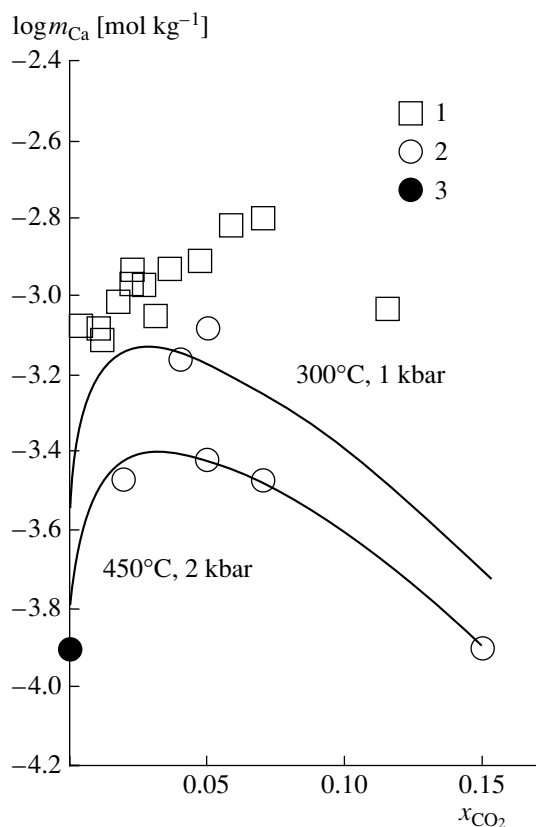
logm_{Ca} [mol kg^{-1}]

Fig. 18. Dependence of calcite solubility on x_{CO_2} in a fluid at T = 300°C, P = 1 kbar and T = 450°C, P = 2 kbar. (1) Malinin, 1979; (2) Fein and Walther, 1987; (3) Walther and Long, 1986; lines designate the calculation based on the proposed model.

CONCLUSIONS

The good agreement between calculation and experiment testifies that the proposed approach can be used for calculating multicomponent heterogeneous equilibria in mixed fluids in a wide range of PTx_{gas} conditions. Hence, a new tool is suggested for studying the role of fluids rich in volatiles during ore deposition. The calculated algorithm is applicable for fluids with a mole fraction of volatiles up to 0.3, which covers almost the entire spectrum of natural hydrothermal geochemically important fluids.

It was also shown that the proposed method can be used for calculating the Born parameters of solution components, thus, facilitating the refinement of the thermodynamic description of these components at elevated parameters of state.

Computer calculation codes (MIX-FL for calculation of the bulk and dielectric properties of mixed fluids and BALANCE, a universal program of calculating equilibria in multisystems) are available free of charge and can be supplied by the authors by request (akinfiev@igem.ru).

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