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GEOCHEMISTRY

Equations of State for NaCl and $CaCl_2$ Solutions of Arbitrary Concentration at Temperatures 423.15–623.15 K and Pressures up to 5 kbar[1]

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Abstract—Equations of state valid for all possible salt concentrations in solution are obtained for binary fluids H_2O—NaCl and H_2O—$CaCl_2$. The equations are based on the empirical form of the Gibbs free energy for salt solutions of arbitrary concentration, developed earlier. Based on experimental data on the *PVTx* properties the obtained earlier thermodynamic description of H_2O—NaCl and H_2O—$CaCl_2$ solutions at saturated vapor pressure is extended towards higher pressures. For H_2O—NaCl pressures are up to 5 kbar. For H_2O—$CaCl_2$ pressures cover the range of available experimental data up to 0.7 kbar. The equations allow precise calculation of the whole set of thermodynamic parameters of the discussed salt solutions in the temperature ranges 423.15–573.15 K and 423.15–623.15 K, corresponding to low temperature hydrothermal ore deposits, that could be relevant for thermodynamic modeling of ore-bearing fluids at such deposits.

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In the work [1] we proposed an empirical model for the concentration dependence of the Gibbs free energy for solutions of chlorides of alkaline and alkaline earth metals in water. Using the model, we obtained equations of state for water solutions of NaCl and $CaCl_2$ at water vapor pressure in the temperature ranges 423.15–573.15 K and 423.15–623.15 K. The aim of the present work is to extend this thermodynamic model towards higher pressures.

Experimental basis for such extension of the empirical model [1] is constituted by the existing data on the density of NaCl and $CaCl_2$ water solutions. After thorough analysis we used the experimental data provided in [2–7] for the system H_2O—$CaCl_2$. For the well studied system H_2O—NaCl we confined to the results [8, 9] without conducting analysis of the existing experimental data.

Expressed through the density of solution the molar volume V relates to the Gibbs free energy G as follows

$$V = \left(\frac{\partial G}{\partial P}\right)_{T,x_i} = V^{\text{ex}} + x_1 V_1^0 + x_2 V_2^0, \tag{1a}$$

where

$$V^{\text{ex}} = \left(\frac{\partial G^{\text{mix}}}{\partial P}\right)_{T,x_i}, \tag{1b}$$

V_1^0 and V_2^0 are mole volumes of pure water and pure dissolved salt at the given temperature T and pressure P; $x_1 = x_{H_2O}$ is mole fraction of water, x_2 is mole fraction of dissolved salt ($x_2 = x_{NaCl}$ or $x_2 = x_{CaCl_2}$).

Since $G^{\text{mix}} = G^{\text{config}} + G^{\text{ex}}$ and the values of G^{config} in the formulas for the Gibbs free energy [1] are independent on pressure, we have

$$V^{\text{ex}} = \left(\frac{\partial G^{\text{ex}}}{\partial P}\right)_{T,x_i} = \sum_{i=1}^{3} g_i \frac{\partial W_i(T,P)}{\partial P} = \sum_{i=1}^{3} g_i V_i^{\text{ex}}, \tag{1c}$$

(see Eqs. (4)–(6) in [1]). Temperature dependencies for the parameters $W_i(T,P) = W_{iT}(T)$ were obtained at water vapor saturation pressures (Eqs. (7)–(10) in [1]). Parameter P is not included in these formulas. Because the range of vapor saturation pressures is rather small compared to the range of several kilobars of experimental measurements of NaCl and $CaCl_2$ solutions density, we have retained the expressions $W_{iT}(T)$, with correspondently changed coefficients, as

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independent on pressure terms in the formulas for $W_i(T,P)$

$$W_i(T,P) = W_{iT}(T) + W_{iP}(T,P). \tag{2}$$

In the result

$$V^{\text{ex}}(x_2,T,P) = g_1(x_2)V_1^{\text{ex}}(T,P) + g_2(x_2)V_2^{\text{ex}}(T,P) + g_3(x_2)V_3^{\text{ex}}(T,P), \tag{3}$$

where

$$V_i^{\text{ex}} = \frac{\partial W_{iP}(T,P)}{\partial P}.$$

Formulas for $g_i(x_2)$ are introduced in [1].

Within the range of temperatures we consider here, the dependence of the integral excess molar volume on pressure can be approximated with a high accuracy by the expression

$$V^{\text{ex}}(T,P) = v_1 + (v_2 + v_3P)\exp(-v_0P), \tag{4a}$$

with the coefficients v_0, ..., v_3 dependent on the temperature. Correspondently, for partial molar volumes V_i^{ex} the pressure dependence is set as

$$V_i^{\text{ex}}(T,P) = v_{i1} + (v_{i2} + v_{i3}P)\exp(-v_{i0}P). \tag{4b}$$

The temperature dependence of coefficients v_{ij} is established in the form

$$v_{ij} = q_{1ij} + q_{2ij}\exp(q_{3i}T). \tag{5}$$

According to expression (4b) for $V_i^{\text{ex}}(T,P)$ the components of coefficients W_i dependent on pressure look like

$$W_{iP}(P,T) = B_i + v_{i1}P - (B_i + A_iP)\exp(-v_{i0}P), \tag{6}$$

where $A_i = \frac{v_{i3}}{v_{i0}}$, $B_i = \frac{v_{i2} + v_{i3}}{v_{i0}}$.

According to the equation (1a), the values V_1^0 and V_2^0 should be known to enable calculations of V^{ex} based on the data on the total volumes of solutions. Values of V_1^0 are easily obtained from the current standard equation of state for pure water IAPWS-95 [10]. On the other hand, obtaining V_2^0 values dependent on the temperature and pressure in our range of *TP* parameters is associated with considerable difficulties, namely with the extrapolation of the temperature dependence of the molar volume of molten salt towards a region of sufficiently lower temperatures. At the same time, both the total density of the solution ρ and the total molar volume *V*, linked to it, are values directly obtained from the experimental data. In our approach, we prefer obtaining the dependencies $V_2^0(T,P)$ together with V_i^{ex} in the same calculation. Possible inaccuracies in evaluation of V_2^0 and consequently $V^{\text{ex}}(x_2,P,T)$ are compensated in the reverse transition to $V(x_2,P,T)$ and do not change the final result. Values of $V_2^0(T,P)$ obtained in such calculation belong only to the present thermodynamic model and have pure formal meaning. Linear approximation of temperature and pressure dependencies was applied for values of V_2^0

$$V_2^0(T,P) = v_0 + v_TT + v_PP. \tag{7}$$

Parameters of our model for H_2O–NaCl and H_2O–$CaCl_2$ solutions obtained on the basis of the available experimental data are presented in Table 1. For both of these solutions, the parameters were determined from the condition of minimizing the sum of squared deviations of the calculated values of the molar volume and the osmotic coefficient from the corresponding base/experimental values. The sets of experimental data for the osmotic coefficient coincided with those used in [1]. The resulting model dependences for the osmotic coefficient at saturated vapor pressure practically do not differ from those presented in [1]. As mentioned above, for the H_2O–NaCl solution we did not carry out our own analysis of experimental data for molar volume dependence on the temperature and pressure and used the available sufficiently accurate numerical approximation [8]. For the purposes of compatibility with the equation of state of pure water IAPWS-95 the primary data for our fitting were obtained from a modification of the formulas [8] carried out in [9]. In the temperature range 423.15–573.15 K and pressure up to $P = 5$ kbar our formulas together with the parameters of Table 1 precisely reproduce the data of [9]. Both results for the density of the H_2O–NaCl solution are compared in Fig. 1.

The number of reliable experimental data on the density of H_2O–$CaCl_2$ solutions is essentially smaller than those for the solutions with NaCl. In particular, the available experimental data are confined by pressures up to $P = 0.7$ kbar. For higher pressures there are only two experimental points for $P = 1.5$ kbar at $CaCl_2$ molality $m = 1$ mol/kg H_2O [11]. Rather accurate results [2] refer to two pressures 0.07 and 0.41 kbar, temperatures up to 523 K and $CaCl_2$ mole fraction in the solution up to $x_2 = x_{CaCl_2} = 0.1$ (*m* up to 6.15). The works [3, 4] show results obtained for low pressures about 0.02 kbar, temperatures up to 473.15 K, and $M <$ 6.5. Data for temperatures up to 473 K and pressures up to 0.68 kbar have been obtained recently [6] for three values of $m = 1, 3, 6$. In our calculations we used data from [6] only for $m = 1$, $m = 3$.The data for $m = 6$ are not consistent with the results of other studies and have been omitted. The disagreement between the results [2] and [6] relating to the same temperature, but different pressure is seen in Fig. 2. We used also the data [5] for 400 K ≤ T ≤ 548 K. These data cover the range of pressures up to 0.37 kbar and $CaCl_2$ concentrations up to $m = 6.42$. All the mentioned above experimental studies of $CaCl_2$ water solutions were carried out for the solutions of relatively low concentration $m < 6.5$. However, in the range of temperatures up to 623.15 K the mole fraction of $CaCl_2$ in water solution may exceed 0.35 ($m > 30$). It is known, that aqueous fluids with high $CaCl_2$ concentrations of are quite common in nature, and their properties are of great interest for geological studies [12]. Currently, the work [7] is the only one known investigation of density of concentrated $CaCl_2$ solutions. It presents the measured values of density of $CaCl_2$ solutions at temperatures from 511 K up to 611 K, pressures up to 0.6 kbar, and molality of solutions up to $m = 27.1$ ($x_{CaCl_2} \leq 0.328$). The accuracy of the results [7] is lower than that of [2–6]. Comparing the results from [7] for the specific volume of pure water with the values given by IAPWS95, it is possible to estimate the measurement errors of [7] being about 2%. Nevertheless, the data [7] are necessary for obtaining a realistic thermodynamic description of $CaCl_2$ solutions with $m > 6.5$. Therefore, the data [7] were used for refinement the parameters of our model with a less weight, compared with the data [2–6]. Values of the parameters are presented in Table 1. Comparison of our results on density of $H_2O–CaCl_2$ solutions with some experimental data (Fig. 2) shows that the calculations reproduce with high accuracy the results [2–5], [6] at $m = 1$, 3, and correspond to the course of dependencies $\rho(x_2)$ in [7].

The most effective of the modern models of *PVTx* properties of $H_2O–CaCl_2$ solutions was introduced in [13] for temperatures up to 523 K, pressures up to 0.6 kbar, and $m \leq 6$. Figure 3 compares the discrepancy between the experimental values of density [2] and its calculated values by our model and [13]. Our model provides a more accurate agreement with experimental data, especially at high concentrations of $CaCl_2$. The experimental data, we employed in our calculations, refer mainly to $CaCl_2$ concentrations up to $m < 6.5$, pressures up to 0.7 kbar, and $423.15\text{ K} \leq T \leq 623.15\text{ K}$. In this range of the parameters, our model provides the values of density of $H_2O–CaCl_2$ solution with the average error not higher than 0.5%. With a certain decrease in the accuracy, we consider it possible to extrapolate our dependencies to $P = 0.8–0.9$ kbar. For solutions with concentration $m > 6.5$ possible errors of our model are caused by the errors of experimental data [7] and can amount to several units of per cent in calculations of density ρ.

An advantage of our thermodynamic description of $H_2O–NaCl$ and $H_2O–CaCl_2$ saline solutions in comparison to the models of *PVTx* properties proposed in [8, 9, 13] is the possibility of direct calculation of activities of solution components and related parameters.- Equations for *V* do not include terms in the Gibbs free

Table 1. Numerical parameters of the proposed thermodynamic model. Dimension of the parameters is determined by SI (m^3, Pa, mol, kg, J, K)

	$H_2O–NaCl$	$H_2O–CaCl_2$
u_{10}	6.11627667E+01	4.18160711E+01
$u_{\varepsilon 0}$	9.68157997E−02	−1.12841581E−02
$u_{\varepsilon 1}$	5.10709740E+02	1.52069633E+03
$u_{\varepsilon 2}$	−2.75373438E−09	2.13269485E−10
u_{20}	−7.91677960E+03	−2.77399803E+04
u_{21}	5.22658560E+02	5.46161426E+02
u_{22}	−2.28926628E−04	−5.79250053E−05
u_{30}	1.51621022E+04	8.09733813E+03
u_{31}	4.98831378E+02	7.04689481E+02
u_{32}	−3.07088546E−04	1.89241835E−04
q_{31}	1.45284650E−02	6.71020628E−03
q_{32}	1.46942341E−02	9.73979946E−03
q_{33}	1.13458316E−02	3.39416869E−04
q_{110}	1.32545020E−08	1.05731791E−08
q_{210}	1.31880667E−12	−9.55965544E−11
q_{120}	7.10745593E−09	1.80854630E−09
q_{220}	2.25661567E−13	3.83297037E−11
q_{130}	−3.50842105E−11	8.65142170E−10
q_{230}	2.88446898E−13	5.01564252E−09
q_{111}	3.11258565E−07	1.02298394E−05
q_{211}	−8.95514764E−11	−1.14936868E−06
q_{121}	1.64260467E−04	−3.41773998E−05
q_{221}	3.94967342E−10	1.36039949E−07
q_{131}	−4.34382696E−08	1.66709238E−03
q_{231}	−3.97991083E−07	−1.40160863E−03
q_{112}	1.46868503E−06	2.73473941E−06
q_{212}	−4.19148362E−09	1.34234695E−07
q_{122}	−5.00400585E−07	7.84832149E−06
q_{222}	1.21607231E−09	−5.45122183E−08
q_{132}	2.32234552E−04	8.93044285E−05
q_{232}	4.82317690E−07	−3.61853829E−05
q_{113}	1.03556433E−15	−1.54792534E−14
q_{213}	−3.75275017E−19	5.80785776E−15
q_{123}	3.51285849E−14	1.11553097E−13
q_{223}	−5.14301200E−17	−3.57549828E−17
q_{133}	−5.70663019E−14	6.88636444E−12
q_{233}	4.41084058E−17	−6.62930245E−12
v_0	−1.45755285E−04	−2.22175118E−05
v_T	−8.19797872E−09	1.71368016E−07
v_P	1.72897637E−14	3.70271807E−15

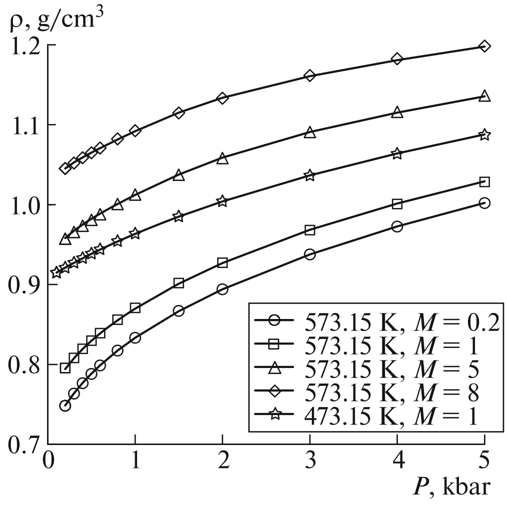

Fig. 1. Density of NaCl water solution dependent on pressure by [9] (symbols) and our calculations (curves).

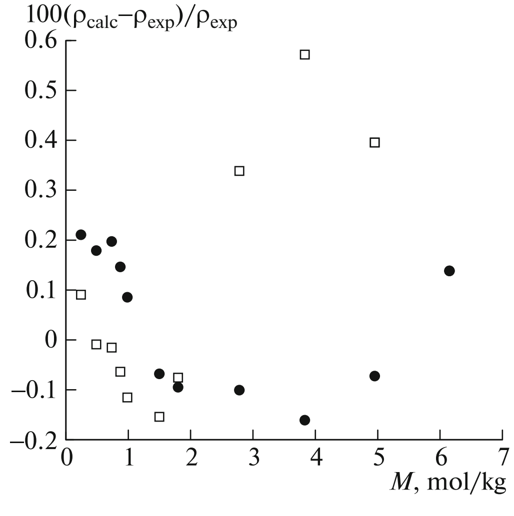

Fig. 3. Correlation of experimental data [2] for density of the H_2O–$CaCl_2$ solution at 523.15 K, 0.41 kbar (ρ_{exp}) and calculations (ρ_{calc}). This study ρ_{calc} (●) and [13] (□).

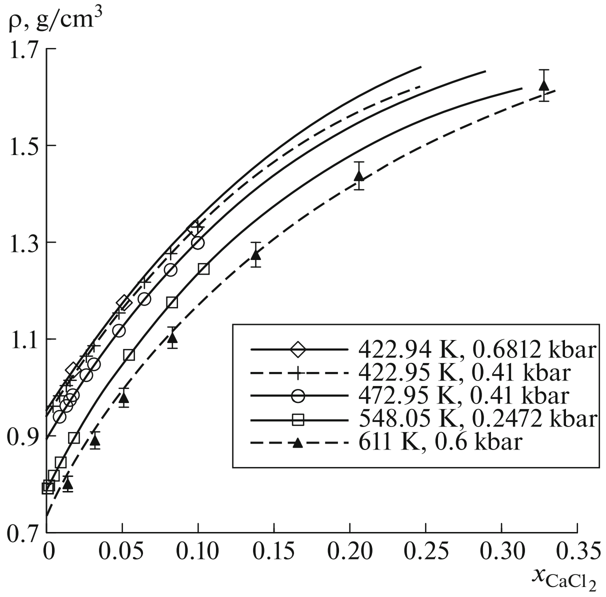

Fig. 2. Density of water solution dependent on mole fraction of $CaCl_2$ by our calculations (curves) and experimental data [2] (422.95 K, 0.41 kbar; 472.95 K, 0.41 kbar), [6] (422.94 K, 0.6812 kbar), [5] (548.05 K, 0.2472 kbar), and [7] (611 K, 0.6 kbar).

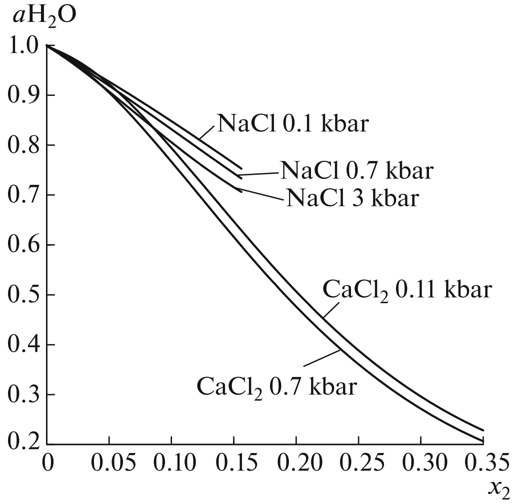

Fig. 4. Water activity at different pressures and 573.15 K as the function of salt mole fraction in H_2O–NaCl and H_2O–$CaCl_2$ solutions.

energy independent on pressure. In the analytical form these terms are given in [1], their values for the solutions H_2O–NaCl and H_2O–$CaCl_2$ are determined by numerical parameters u_{ij} (Table 1). These components play a crucial role in determining activities of the components of the solutions considered here. An example of the activity of water in both of considered systems dependent on the concentration of the solutions at 573.15 K for several pressure values is given in Fig. 4. It is seen, that a moderate increase in pressure has a relatively small effect on the value of water activity, which is largely determined by the independent on pressure terms in the Gibbs free energy, defined in [1]. It results, in particular, that in our model the activity of the components in the system H_2O–$CaCl_2$ at high concentrations of $CaCl_2$ can be determined with significantly greater accuracy than the molar volumes and densities of the solution.

For the system H_2O–NaCl our results on molar volumes and densities are close to those on [9], but the presence of terms like $g_i(x_2)W_{iT}(T)$ in our equation for the Gibbs free energy enables reliable calculation the activities and some other thermodynamic parameters, which is impossible on the basis of *PVTx* properties only. The same relates to the comparison of our results for the system $H_2O-CaCl_2$ with the *PVTx* results of [13]. Furthermore, compared to [13] our model for $H_2O-CaCl_2$ has no restrictions on the concentration of the solution and shows a better agreement with the experimental results. The studied temperature intervals 423.15–573.15 K and 423.15–623.15 K correspond to epi- and mesothermal hydrothermal ore deposits and parameters of brines calculated by the proposed models can be relevant for thermodynamic modeling of ore bearing fluids at such objects.

On request, the authors provide the computer program performing the calculations according to the proposed above thermodynamic model.

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