Thermodynamic properties of minerals and fluids

Ivanov M.V. Thermodynamic model of fluid water-carbon dioxide for temperatures 50-350°C and pressures 0.2-3.5 kbar based on the Van Laar equation. *UDC* 550.41+536.7

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Abstract. At temperatures below the critical point of water and moderate high pressures, the miscibility of neutral gases with water is, as a rule, limited. As a result, for a wide range of *P*-*T* conditions, the water-neutral gas system can consist of two coexisting phases which do not mix with each other. The composition of these phases can be determined experimentally. The Van Laar equation, widely used in the thermodynamics of such systems, contains two parameters A_{12} and A_{21} . The presence for a certain combination of P-T of two experimentally determined numbers characterizing the characterizing the compositions of coexisting phases makes it possible to unambiguously determine the parameters A_{12} and A_{21} . Experimental data for a set of *P*-*T* combinations make it possible to reduce the construction of a thermodynamic model to a numerical approximation of the dependencies $A_{12}(P,T)$, $A_{21}(P,T)$. This approach for the H₂O-CO₂ system made it possible to obtain a highly accurate numerical thermodynamic model for temperatures of 50-350°C and pressures of 0.2-3.5 kbar.

Keywords: high pressure, elevated temperature, watercarbon dioxide fluid, equation of state

Knowledge of the thermodynamics of aqueous fluids in the P-T conditions of the upper crust is important both for understanding and studying hydrothermal processes, including the deposition of ore matter, and also has practical significance in the technology of drilling oil and gas wells. Technical applications require fairly high accuracy in determining the parameters of fluids, especially the conditions of phase transitions, such as the separation of a fluid into coexisting phases. One of the most common components of geological fluids is CO₂. The goal of this work was to develop a numerical thermodynamic model of the H₂O-CO₂ system that describes experimental data with sufficient accuracy for temperatures below the critical point of water and moderately high pressures above 200 bar.

Currently, there is a significant amount of experimental works on the properties of the H_2O-CO_2 system, primarily on its phase state and the compositions of coexisting phases. Most of these works, such as, for example, (Malinin, Savelyeva, 1972; Malinin, Kurovskaya, 1975; Hou et al, 2013; Zhao et al, 2015), refer to temperatures and pressures lower than the region of interest to us. A significant number of references to other experimental works are given in (Sun, Dubessy, 2010; Zhao, Lvov, 2016). Among the works related to the range of

temperatures and pressures we selected, we were primarily interested in works containing data on the composition of both, liquid and gas, coexisting phases. The presence of such information greatly simplifies the construction of the equation of state. The most detailed of these studies are (Malinin, Tödheide. Franck. 1963: Takenouchi. 1959 Kennedy, 1964). The results on the composition of the aqueous phase obtained in these works are in good agreement with each other. However, data on the composition of the gas phase obtained by (Tödheide, Franck, 1963) and (Malinin, 1959; Takenouchi, Kennedy, 1964) differ markedly. In this work, following the arguments of (Zhao, Lvov, 2016), we relied on experimental results (Tödheide, Franck, 1963). The construction of a numerical model, similar to the presented below, on the basis of data (Malinin, 1959; Takenouchi, Kennedy, 1964) seems quite possible, but is beyond the scope of this work.

The presented numerical thermodynamic model of H_2O-CO_2 is based on the equation of state expressed in terms of the excess Gibbs free energy of mixing G^{ex} . This quantity consists of entropy and energy terms

$$G^{\text{ex}} = RT(x_1 \ln x_1 + x_2 \ln x_2) + G_{\text{wg}}$$
(1)

Here x_1 and x_2 are the mole fractions of H₂O and CO₂ in the mixture, *T* is the temperature in Kelvins. The energy term in this model was taken in the form of the Van Laar equation. This equation is widely used to describe liquid-gas equilibrium for mixtures of substances. For the excess Gibbs free energy of mixing two substances, the equation has the form

$$G_{\rm wg} = RT \frac{A_{12}x_1 A_{21}x_2}{A_{12}x_1 + A_{21}x_2}, \qquad (2)$$

where A_{12} and A_{21} are parameters determined on the basis of experimental data. The known compositions of the coexisting liquid and gas phases of two substances make it possible to unambiguously determine the parameters A_{12} and A_{21} . The values of A_{12} and A_{21} are determined for a large number of liquid pairs (see references in (Peng, 2010)). A numerical thermodynamic description of supercritical fluids H₂O-CO₂, H₂O-N₂, H₂O-H₂, H₂O-CH₄, H₂O-CO, H₂O-H₂S, H₂O-O₂, H₂O-Ar, H₂O-NH₃ using the simplified Van Laar equation was obtained in works (Aranovich et al., 2010; Aranovich, 2013).



In Fig. 1, the dots stay for the compositions of the coexisting phases obtained in (Tödheide, Franck, 1963). For each combination of temperature and pressure, there is a pair of dots corresponding to the compositions of the liquid (left) and gas (right) phases. Parameters A_{12} and A_{21} were determined for each of these pairs so that the equation of state (1)-(2) ensures the decomposition of the system into two phases with compositions coinciding with those obtained in the experiment. An example of G^{ex} the dependent on the mole fraction of CO₂ with parameters A_{12} and A_{21} selected for a temperature of 250°C and a pressure of 1 kbar is given in Fig.2. In Fig. 3, the dots represent the values of A_{12} and A_{21} obtained for experimental points at 200°C and

pressures from 0.2 to 3.5 kbar.

After an array of A_{12} and A_{21} values has been obtained for all experimental points used (these are all compositions of coexisting phases obtained (Tödheide, Franck, 1963)), the task of constructing a working numerical thermodynamic model is reduced to creating approximating formulas or an algorithm for obtaining free energy values Gibbs over the entire range of temperatures and pressures studied in the experiment. This is a purely mathematical problem and it is much simpler than constructing an equation of state from scratch. For the values of A_{12} and A_{21} , the same formulas were used with separate arrays of values of the fitting parameters (r_k , s_k , u_k) for A_{12} and A_{21} :

$$A_{ij} = (r_{a} + r_{b} / V_{1} + r_{c} / V_{2} + r_{d} / (V_{1}V_{2}) + r_{e} / V_{2}^{4} + r_{f} / V_{1}^{4} + r_{g} / V_{1}^{5}V_{2} + r_{h} / (V_{1}^{5}V_{2}^{5})) / T + (s_{a} + s_{b} / V_{1} + s_{c} / V_{2} + s_{d} / (V_{1}V_{2}) + s_{e} / V_{2}^{4} + s_{f} / V_{1}^{4} + s_{g} / V_{1}^{5}V_{2} + s_{h} / (V_{1}^{5}V_{2}^{5})) + (u_{a} + u_{b} / V_{1} + u_{c} / V_{2} + u_{d} / (V_{1}V_{2}) + u_{e} / V_{2}^{4} + u_{f} / V_{1}^{4} + u_{g} / V_{1}^{5}V_{2} + u_{h} / (V_{1}^{5}V_{2}^{5})) / T^{2}$$
(3)

where V_1 and V_2 in (3) are the molar volumes of water and CO₂ at the corresponding temperatures and pressures, calculated using the IAPWS95 equations of state (Wagner, Pruß, 2002) for water and (Span, Wagner, 1996) for CO₂.



Fig. 2. Excess Gibbs free energy as a function of CO_2 mole fraction at values of parameters A_{12} μ A_{21} , reproducing experimental results at 250°C and 1 kbar pressure.



Fig. 3. Parameters A_{12} and A_{21} obtained from experimental results (Tödheide, Frank, 1963) for temperature 200°C (dots). Lines are their approximations by equations (3).

The results of applying formulas (3) to the approximation of A_{12} and A_{21} at a temperature of 200°C (T = 473.15 K) are shown by lines in Fig. 3. The results for the compositions of coexisting fluid phases given by our numerical thermodynamic model, that is, the equations for the excess Gibbs free energy of mixing of H_2O and CO_2 (1)-(2) with parameters A12 and A21 given by equations (3), are shown by the lines in Fig. 1. Comparison with existing rather complex models, for example (Sun, Dubessy, 2010; Zhao, Lvov; 2016) shows the significant superiority of the presented and, thermodynamic model thus. its better applicability both for direct practical use and for constructing thermodynamic models of more complex systems. It must be emphasized that the presented model is not an approximation of experimental data on phase decomposition, but provides the obtaining of G^{ex} , which, together with the equations of state for pure substances, allows obtaining complete thermodynamic information about the system, such as the activity of components, density and compressibility of the fluid, and so on. As for the large number of parameters in formulas (3), the equations of state of pure substances also contain a large number of empirical parameters. In both cases, this is a reflection of the complex nature of molecular interactions in a real system. A computer program that allows building of $G^{ex}(x_2)$ dependencies similar to those presented in Fig. 2 is public available in the domain https://www.dropbox.com/scl/fi/d7zzg3jws7rimqb4z 9y09/Gex H2OCO2.zip?rlkey=hq7wbzdeq17jhfnedy m11mqag&st=zkcxg2tm&dl=0.

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Ivanov M.V. Thermodynamic models of ternary fluid systems H₂O-CO₂-NaCl and H₂O-CO₂-CaCl₂ for temperatures 150-350°C and pressures 0.2-1.4 kbar. UDC 550.41+536.7

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Abstract. Numerical thermodynamics models of ternary fluid systems H_2O-CO_2 -NaCl and H_2O-CO_2 -CaCl₂ are developed fot temperatures below the critical point of water and pressures from 0.2 to 1.4 kbar. The models are

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formulated in terms of Gibbs free energy. For the edge system H_2O-CO_2 , a thermodynamic model based on the Van Laar equation has been developed. The description of the binary boundary systems H_2O -NaCl and H_2O -CaCl₂ is based on previously obtained (Ivanov, Bushmin, Aranovich, 2018a, 2018b) equations of state, which accurately reproduce the thermodynamics of H_2O -NaCl and H_2O -CaCl₂ at temperatures from 150°C to 350°C, pressures up to 5 kbar and arbitrary salt concentrations. This feature is a distinctive characteristic of the presented models. The additional terms in the free energy equation describing the interaction of carbon dioxide with salt were determined on the basis of experimental data on the solubility of CO_2 in the corresponding brine.

Keywords: high pressure, fluid, phase splitting, upper crust, CO_2, NaCl, CaCl_2

Development of numerical thermodynamic models of low-temperature fluids of the amphibolite and greenschist facies is one of the prerequisites for identifying the factors and conditions contributing to the formation of medium-low temperature metamorphogenic ore deposits. This paper presents the results of the development of such models for two three-component fluid systems H_2O-CO_2 -NaCl and H_2O-CO_2 -CaCl₂.

Equation of state. The excess Gibbs free energy of mixing G^{ex} of the considered ternary systems (per one mole) has the form

$$G^{\rm ex} = G_{\rm S} + G_{\rm ws} + G_{\rm wg} + G_{\rm sg} \tag{1}$$

Thus, the value G^{ex} is considered as consisting of the contribution of the entropy of mixing G_{S} and the energy contributions of pair interactions: water and salt G_{ws} , water and carbon dioxide G_{wg} , salt and carbon dioxide G_{sg} . These thermodynamic quantities will be expressed in terms of the mole fractions of the fluid components $x_1 = x_{\text{H}_2\text{O}}$, $x_2 = x_{\text{CO}_2}$, $x_3 = x_{\text{NaCl}}$ or

 $x_3 = x_{CaCl_2}; x_1 + x_2 + x_3 = 1.$

The entropy contribution to the free energy has the form

$$G_{\rm S} = RT \left\{ x_1 \ln x_1 + x_2 \ln x_2 + x_3 (1 + \alpha_3) \ln[(1 + \alpha_3)x_3] - x_{\rm all} \ln x_{\rm all} \right\},$$
(2)

where $x_{all} = x_1 + x_2 + (1+\alpha)x_3 = 1+\alpha x_3 \alpha$ is the number of additional particles formed from one salt molecule during its dissociation. At $x_2 = 0$ the value of G_S given by eq. (2) coincides with the entropy contribution to the excess free Gibbs energy of mixing according to the formulas of (Ivanov et al., 2018a). Numerical thermodynamic models for H₂O-NaCl and H₂O-CaCl₂ (Ivanov et al., 2018a, 2018b) assumed complete dissociation of the strong electrolytes NaCl and $CaCl_2$, that is, for NaCl and $CaCl_2$.

Water-salt system. The water-salt interaction energy G_{ws} obtained in (Ivanov et al., 2018a) consists of three terms

$$G_{\rm ws} = g_1 W_1 + x_1 x_3 W_2 + x_1 x_3^2 W_3 \tag{3}$$

The second and third terms in this formula are terms of the Margules type with coefficients W_2 and W_3 depending on temperature and pressure. The first of the terms in (3) provides an empirical description of the contribution to the Gibbs free energy from the electrostatic interaction of ions, which is most significant for dilute solutions. The quantity g_1 in this term has the form

$$g_1 = x_3^{1/2} \ln(1 + x_3^{1/2} / \varepsilon) - x_3 \ln(1 + 1 / \varepsilon)$$
(4)

Parameters W_1 and ε also depend on temperature and pressure.

Water-carbon dioxide system. For the binary system H_2O-CO_2 , the energy term in the excess free Gibbs energy of mixing was obtained by us earlier (Ivanov, 2024) in the form of the Van Laar equation

$$G_{\rm wg} = RT \frac{A_{12}x_1 A_{21}x_2}{A_{12}x_1 + A_{21}x_2}$$
(5)

with temperature and pressure dependent parameters A_{12} and A_{21} . For a system that includes components additional to H₂O and CO₂, this term is modified as

$$G_{\rm wg} = RT \frac{A_{12}x_1A_{21}x_2}{A_{12}x_1 + A_{21}x_2} (x_1 + x_2)$$
(6)



Fig. 1. Phase diagrams of H₂O–CÕ₂–NaCl the system. Curved lines are solvuses. To the left of solvus the is homogeneous liquid phase, to the right are coexisting liquid and gas phases. Symbols ■ are experimental data bv Takenouchi and Kennedy (1965).

H₂O–CO₂–NaCl system For the terms in the free energy responsible for the interaction of carbon dioxide with NaCl, the expression was used:

$$G_{\rm sg} = W_{\rm sg1} x_2^4 x_3^3 + W_{\rm sg2} x_2^4 x_3 \tag{7}$$

When using this form for G_{sg} , by selecting the parameters W_{sg1} and W_{sg2} , it is possible to reproduce the experimental results from the minimum pressure P = 0.2 kbar to the maximum experimental value P = 1.4 kbar for a low temperature of 150°C and up to *P*-*T* parameters approaching the critical point of

the system H₂O–CO₂. Fig. 1 presents examples of experimental points of composition of the liquid phase in equilibrium with the gas phase (Takenouchi, Kennedy, 1965) and solvuses of the system, constructed according to the above equations with parameters W_{sg1} and W_{sg2} obtained by fitting experimental data.

For sets of W_{sg1} and W_{sg2} values obtained at temperatures of 150°C, 250°C and 350°C (for which data are available for two NaCl concentrations at one combination of temperature and pressure), approximating formulas were constructed:

$$W_{sg1} = (a_2t^2 + a_1t + a_0)P^{-2} + b_2t^2 + b_1t + b_0 , \qquad (8)$$

$$W_{sg2} = (c_1t + c_0)P^{-2} + (d_2t^2 + d_1t + d_0)P^{-1} + e_2t^2 + e_1t + e_0$$

where $a_0=2.37698E12$; $a_1=-1.15737E10$; $a_2=1.41648E7$; $b_0=1.36188E12; b_1=-1.16334E10; b_2=2.13839E7; c_0=-$ 7.04383E8; *c*₁=4.0096E6; *d*₀=9.38245E9; *d*₁=-6.55154E7; d_2 =106565; e_0 =-1/50277E9; e_1 =1.21754E7; e_2 =-21830.9.



constructed

(1965),

approximation

in comparison



H₂O-CO₂-CaCl₂ system. A similar approach was applied to the construction of a numerical thermodynamic model for the H₂O-CO₂-CaCl₂ fluid system. The numerical parameters were obtained based on experimental results by (Malinin, 1959). Since for each *P*-*T* combination in this work, the

composition of the aqueous phase coexisting with the gas phase was obtained for only one salt concentration, the representation of the salt-carbon dioxide interaction was limited to one term:

$$G_{\rm sg} = W_{\rm sg1} x_2^4 x_3^3$$



Fig. 3. Phase diagrams of the H₂O–CO₂–CaCl₂ system. Symbols \blacksquare are experimental data by (Malinin, 1959).

For the W_{sg1} values found for each *P*-*T* point, an approximating formula was obtained, expressing the W_{sg1} values in terms of temperature and molar volume of water at the corresponding temperature and pressure:

$$W_{\rm sg1} = a_0 + a_1 t + a_2 t^2 + (b_0 + b_1 t + b_2 t^2) V_1, \quad t \quad \text{is the}$$

temperature in °C, V_1 is the mole volume of water, $a_0 = 2.84909 e_{16}, a_1 = -2.84829 e_{14}, a_2 = 6.31087 e_{11},$ $b_0 = -1.13328e_{15}, b_1 = 1.17969e_{13}, b_2 = -2.66434e_{10}.$

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Korepanov Ya.I., Chareev D.A., Osadchii V.O., Osadchii E.G. Thermodynamic properties of AgPd₃Se determined by the solid-state EMF method in the temperature range 373 - 773 K. UDC 550.4.02

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Abstract. In the ternary Ag-Pd-Se system, the temperature dependence of the EMF in the solid state galvanic cell was determined with the solid electrolyte Ag- β alumina C|Ag|AgI|(Ag_rPd_{1-xr}AgPd_3Se, (Ag_{0.41}Pd_{0.59})_{22}Se_6)|C

Based on the experimental data and the literature one it was shown that it is possible to obtain:

1) thermodynamic properties for the AgPd $_3$ Se phase

2) the activity of silver in a silver-palladium alloy.

Keywords: Thermodynamics, silver, palladium, selenium, chalcogenides, EMF, electrochemistry.

The Ag-Pd-Se system (Korepanov Ya.I. et al., 2023) has a lot of compounds that have natural analogues - minerals. Minerals of the Ag-Pd-Se system are found in deposits of various genesis (magmatogenic, hydrothermal, epithermal, sedimentary), however, there are no thermodynamic data in this system or questions arise about their reliability. Studies of the thermodynamic properties of individual equilibria can be used both in physical-chemical analysis of ore formation conditions and in any work within the studied system.



Fig.1. Isothermal section of the three-component phase diagram Ag-Pd-Se at T=350°C.

Experiment. For the study, a composition (Ag-0.1835g, Pd-0.2534g, Se-0.0614g) was chosen, as indicated on the phase diagram taken from the article (Vymazalová A. et al., 2014). Powdered palladium (Aldrich Chem. Co., 99.95% purity), silver (Aldrich Chem. Co., 99.99% purity), and selenium (Aldrich Chem. Co., 99.99% purity) were used to prepare the sample. Synthesis was carried out in a horizontal furnace in a vacuum-sealed ampoule at a temperature of 450°C with two intermediate sample grindings in an agate mortar to homogenize the composition. Agβ-Alumina (Ionotec. Ltd) was used as the electrolyte.

An electrochemical cell with the sample system indicated in Fig.1 is placed in a quartz ampoule and evacuated, then placed in a vertical heating furnace for measuring the potential difference as a function of temperature. The EMF of the element (A) is determined by the difference in the chemical potentials of the element in the sample under study (the composition is indicated in the phase diagram Fig.1.) and the pure element.



Fig. 2. Cell scheme. 1- copper leads, 2- tube for evacuating the ampoule, 3- spring, 4- quartz tube, 5-graphite tablet, 6- sample system, 7- solid electrolyte β -alumina, 8- comparison system (Ag), 9- graphite tablet, 10- ceramic stopper, 11- thermocouple, 12- heating furnace, 13- quartz cell housing.

C|Ag| Ag-
$$\beta$$
 alumina |(Ag_xPd_{1-x},AgPd₃Se, (Ag_{0.41}Pd_{0.59})₂₂Se₆)|C
(A)
$$\mu_{Aa}^{\text{sample system}} - \mu_{Aa}^{\text{comparison system}} = RTln(a_{Aa}^{\text{sample system}}) = -z^{Ag}FE$$

where $a_{Ag}^{\text{sample system}}$ – effective silver concentration in the sample(also known as activity), μ - chemical potential, R-

universal gas constant, F- Faraday constant, E – measured EMF value, z^{Ag} - silver valence in the electrolyte.

The obtained dependency of the effective silver concentration in the sample system can be interpreted for determining the thermodynamic parameters of the alloy in equilibrium in the sample system and for calculating thermodynamic data from the reaction: $6AgPd_3Se + 8.33Ag = (Ag_{0.41}Pd_{0.59})_{22}Se_6 + 8.33(Ag_{0.64}Pd_{0.36})$, Where $\Delta G_r = -mz^{Ag}FE$, where m – number of moles of silver participating in the reaction.

Table.1.



Fig.3. Potential difference dependency of the cell (A). This potential difference dependency clearly shows that the dependency of the composition of the alloy in equilibrium in the sample system has a negative correlation with temperature (with an increase in temperature, the silver concentration in the Ag-Pd solid solution increases).

Furthermore, the coefficients of the reaction can be refined from the potential difference dependency, because the composition of the alloy depends on the temperature and the given reaction is only valid for T=350°C.

The available literature data and temperature dependence of the thermodynamic data for the Ag-Pd alloy do not allow to accurately calculate the alloy composition in the studied equilibrium.

Conclusions.

1 The negative slope of the EMF dependence indicates that with the increase in temperature, the concentration of silver in the equilibrium alloy increases.

2 The reaction from which thermodynamic data can be obtained has the form::

 $6AgPd_{3}Se + 8.33Ag = (Ag_{0.41}Pd_{0.59})_{22}Se_{6} + 8.33(Ag_{0.64}Pd_{0.36})_{3.}$

3 Existing EMF dependencies for the Ag-Pd alloy cannot be called reliable, as the data on EMF and alloy composition differ from those obtained in this study (See Table 1).

T / C	Molar fraction of Pd in Ag _x Pd _{1-x}	Molar fraction of Ag in Ag _x Pd _{1-x}	Molar fraction of Ag calculated using data from (Feng D., Taskinen P. 2014)	Measured EMF values EMF / mV	EMF calculated using data from (Feng D., Taskinen P. 2014)
350	0.37	0.63	0.46	75.21	46.65
427	0.347	0.653	0.52	72.87	46.15
527	0.323	0.677	0.59	71.33	45.82

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Misyura M.A., Bushmin S.A., Aleksandrovich O.V., Mamykina M.E., Savva E.V. Thermodynamic model of the H₂O–LiCl– NaCl system for fluid inclusions study: calculation using Pitzer's equations, comparison with experiments. *UDC 550.41*

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Abstract. A thermodynamic model of the ternary fluid system H₂O-LiCl-NaCl is proposed for the temperature range from -77 to +300°C. This model incorporates lowtemperature phase transitions of freezing products of water-salt inclusions. The model is based on the Pitzer equations using new interaction parameters of Na, Cl and the corresponding equilibrium constants of reactions involving solids and liquid phases. Basing on microthermometry data of fluid inclusions (T of phase transitions during heating after freezing), the model allows to determine the salt concentrations. Characteristics (7, wt% LiCl and NaCl) of the triple points with solid phases including the eutectic $E^{\,\prime\prime}(\text{ice}$ + LiCl·5H_2O + NaCl·2H_2O), peritectic $P_1^{\prime\prime}$ (LiCl·5H_2O + NaCl·2H_2O + NaCl) and $P_2^{\prime\prime}$ (LiCl \cdot 5H₂O + LiCl \cdot 3H₂O + NaCl) and cotectic, peritectic curves separating the phase fields (ice + L, NaCl·2H₂O + L, NaCl + L), as well as solubility isotherms of ice, hydrohalite and halite calculated by the model showed good agreement with experimental data. As an example of the application of the model to the natural object, we determined the salt contents in lithium-bearing brine inclusions in late quartz veins of the Bolshie Keivy area (Fennoscandian Shield).

Keywords: H₂O-LiCl-NaCl fluid system; Pitzer equations; microthermometry of fluid inclusions

Studing the properties of fluids using microthermometry and Raman spectroscopy of fluid inclusions in minerals of metamorphic and metasomatic rocks of the Bolshie Keivy area (Belomorian-Lapland orogen, Fennoscandian Shield), the fluid system of H₂O–CaCl₂–NaCl was identified in brine inclusions (Bushmin et al., 2024).

However, in several samples from the zones of later alterations at the contacts of quartz veins and in late quartz veins, the brine inclusions yielded very low melting temperatures of ice (from -74 to -58° C) and hydrohalite (from -59° C). These data and the presence of zabuyelite (Li₂CO₃, Raman spectroscopy) in the inclusions suggested the presence of an H₂O–LiCl–NaCl system in the brine inclusions (e.g., Dubois et al., 2010; Steele-MacInnis et al., 2016).

The previously proposed model (Dubois et al., 2010), based on the Pitzer equations, differs from ours by a smaller temperature range (from -50 to $+100^{\circ}$ C), which did not allow to make calculations for the position of the triple points (eutectics and peritectics) and phase field boundaries located in the lower temperature region, and compare them with the experimental data. Therefore, the aim of this work was to develop a thermodynamic model of the ternary fluid system H₂O–LiCl–NaCl over a wider temperature range from -77 to $+300^{\circ}$ C, including low-temperature phase transitions of frozen aqueous salt inclusion products.

The theoretical foundations of thermodynamic modeling using the Pitzer equations (Pitzer, 1973) are discussed in the works of (Felmy, Weare, 1986; Møller, 1988). In the Pitzer-based aqueous solution model, the maximum concentration is approximately 12 mol/kg (Monin et al., 2002), which is considered the upper concentration limit for our model.

In the proposed model of the H₂O–LiCl–NaCl system using the Pitzer equations, we used new interaction parameters for Na and Cl and their corresponding equilibrium constants for ice, halite, and hydrohalite in the temperature range from -73 to $+25^{\circ}$ C, as obtained in the work (Toner, Catling, 2017). In the halite field (halite + liquid phase), calculations were performed using the Pitzer parameters and equilibrium constants calibrated from +25 to $+250^{\circ}$ C (Møller, 1988). However, the Pitzer equations allowed us to obtain halite solubility isotherms up to a maximum temperature of $+300^{\circ}$ C.

Figure 1 shows the phase diagram for the ternary system H₂O–NaCl–LiCl, illustrating the equilibrium characteristics of the solid and liquid phases in our model. The right side of the diagram presents the calculated on the base of the model eutectic point E and peritectic point P for the H₂O–NaCl system, E' and P'₁ for H₂O–LiCl, μ E'', P''₁ and P''₂ for the ternary system, along with the cotectic and peritectic phase boundaries and the isotherms for the melting of ice, hydrohalite, and halite. The left side of the diagram shows an enlarged view of the region with the ternary system points E'', P''₁ and P''₂.



Fig. 1. Phase diagram of the H₂O-LiCl-NaCl system E'(-75.9°C) and P₁' (-65.4°C) – the calculated points for the binary H₂O-LiCl system, E(-21.2°C) and P (+0.2°C) – the points for the H₂O-NaCl system, and E'', P₁'' and P₂'' – the points for the ternary H₂O-NaCl-LiCl system (table.1), here and further: *ice* – *ice*, *hh* – hydrohalite, *h* – halite, L – liquid phase, isotherms in the *hh* field every 5°C.

Table 1 presents a comparison of the parameters (*T*, wt% NaCl μ LiCl) of the experimentally obtained ternary eutectic and peritectic points of the system (Akopov, 1963) with those calculated by our model. The points show good agreement with the experimental data, though not perfect, for example, the temperature of point P₁''. This non-ideal agreement is due to the lack of the Pitzer interaction parameters for Li and Cl ions at temperatures below -22° C. Also, the constant value of the pair interaction parameter Na–Li = 0.0029 and the triple interaction parameter Na–Li = 0 (Pitzer, 1991) play a negative role as well. Additionally, the

calculations of the points P_3'' and P_4'' are outside the limitations of the Pitzer equations.

Calculations using our model are also consistent with the data obtained from experiments with synthetic inclusions (table 2).

Table 3 presents another comparison, this time of the salt contents calculated based on different models from the microthermometry data of fluid inclusions from the study (Harlaux et al., 2017), which used the model by (Dubois et al, 2010).

Akopov, 1963			Calcul	ations based on	Solid phases in triple		
	T, ℃	NaCl, wt%	LiCl, wt%	Т, °С	NaCl, wt%	LiCl, wt%	points + L
E″	-77	1.2	23.0	-77.00	0.36	24.52	ice + hh + Li5 + L
$P_1^{\prime\prime}$	-73.2	1.4	24.6	-67.91	0.24	28.04	Li5 + hh + h + L
$P_2^{\prime\prime}$	-65.5	0.3	30.7	-66.08	0.16	29.10	Li5 + Li3 + h + L
				Beyo	ond the constrain Pitzer equation	nts of the	
$P_3^{\prime\prime}$	-18.5	0.25	38.5	-28.82	0.04	34.13	Li3 + Li2 + h + L
P4''	+17.5	0.2	44.8	+29.69	0.03	38.26	Li2 + Li1 + h + L

Table 1. Comparison of the parameters of the experimentally obtained ternary points with solid phases (eutectics andperitectics) for the H2O-LiCl-NaCl (Akopov, 1963) with the calculations based on our model.

Note. E and P – triple points, Li5 – LiCl·5H₂O, Li3 – LiCl·3H₂O, Li2 – LiCl·2H₂O, Li1 – LiCl·H₂O.

Table 2. Comparison of the ice and hydrohalite melting temperatures calculated based on our model with the experimental measurements of synthetic inclusions.

m _{NaCl} , mol/kg	m _{LiCl} , mol/kg	Dubois at al., 2010		Our n	nodel
		$T_{\mathrm{m},ice}, ^{\circ}\mathrm{C}$	$T_{\mathrm{m},hh}, ^{\mathrm{o}}\mathrm{C}$	$T_{\mathrm{m,ice}}, ^{\mathrm{o}}\mathrm{C}$	$T_{\mathrm{m},hh}, ^{\mathrm{o}}\mathrm{C}$
2.8038	2.8710		-16.9		-15.9
0.9105	6.0993		-23.7		-22.3
0.1060	0.6997	-3.2		-3.0	
0.3796	2.5051	-13.5		-13.5	
0.0466	0.9358	-4.9		-3.7	
0.1033	2.0759	-9.6		-9.5	

Note. Here and further: $T_{m,ice}$ – ice melting temperature, $T_{m,hh}$ – hydrohalite melting temperature.

Table 3. Comparison of the salt contents calculated from microthermometry data using our model and the model (Dubois et al, 2010), as used in the study by (Harlaux et al., 2017).

Harlaux et al., 2017		Model from Du	bois et al., 2010	Our model		
$T_{\mathrm{m},ice}, ^{\mathrm{o}}\mathrm{C}$	$T_{\mathrm{m},h}, ^{\circ}\mathrm{C}$	NaCl, wt%	LiCl, wt%	NaCl, wt%	LiCl, wt%	
-37.1	275	26.5	12.5	23.95	10.42	
-37.8	280	26.1	12.9	24.43	10.46	
-34.8	280	27.1	11.4	25.34	9.45	
-35.8	280	26.6	11.4	25.02	9.80	
-34	282	28.5	10.5	25.62	9.15	
-39.9	280	24.9	13.3	23.88	11.08	
-36.1	280	26.9	12.1	24.92	9.91	
-29.9	280	30.8	8.2	27.33	7.33	
-30	280	31.6	8.4	27.28	7.38	
-41.8	280	25.6	14.4	23.43	11.58	

Note. Here and further: $T_{m,h}$ – halite melting temperature.

Thus, the proposed model allows for the determination of salt concentrations based on microthermometry data of fluid inclusions (phase transition temperatures during heating after freezing). The characteristics (*T*, wt% LiCl and NaCl) of the triple points with solid phases eutectic E'' (ice + LiCl·5H₂O + NaCl·2H₂O), peritectic P₁'' (LiCl·5H₂O + NaCl·2H₂O) + NaCl) and P₂'' (LiCl·5H₂O + LiCl·3H₂O + NaCl) as well as the cotectic and peritectic curves separating the phase fields (ice + L,

 $NaCl \cdot 2H_2O + L$, NaCl + L), and the solubility isotherms for ice, hydrohalite, and halite calculated based on the model, showed good agreement with the experimental data.

As an example of applying the model to the study of a natural object, table 4 presents the salt contents in lithium-bearing brine inclusions from late quartz veins in the Bolshie Keivy area of the Fennoscandian Shield.

Table 4.	Salt contents	in brine	inclusions	from	quartz	veins i	n the	Bolshie	Keivy	area.
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Sample	Micro	othermometry	data	Calculations based on our model				
	$T_{\mathrm{m},ice},^{\circ}\mathrm{C}$	$T_{\mathrm{m},hh},^{\mathrm{o}}\mathrm{C}$	$T_{\mathrm{m},h}, ^{\mathrm{o}}\mathrm{C}$	NaCl, wt%	LiCl, wt%	NaCl + LiCl, wt%		
E3-1c		-20	180	12.86	17.15	30.01		
	-60		180	11.94	18.2	30.14		
Б880-7а		-32.5	152	8.06	21.35	29.41		
	-58		152	10.31	18.53	28.84		

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Shornikov S.I. Thermodynamic properties of the $Na_2O-P_4O_{10}$ melts

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Abstract. Within the framework of the developed semiempirical model, the thermodynamic properties of the $Na_2O-P_4O_{10}$ melts were calculated in the temperature region 600–1900 K. The obtained values of the partial pressures of vapor species as well as the oxide activities and the mixing energies of the melts are compared with available information.

Keywords: thermodynamic properties of oxide melts, the $Na_2O-P_4O_{10}$ system

The physicochemical properties of sodium phosphates and their melts are of considerable interest for metallurgy, materials science, medicine and other branches of modern industry, as well as due to their recent discovery in significant quantities in ocean water on Enceladus, that had not previously been observed outside the Earth (Postberg et al., 2023).

The presence of four sodium phosphates in the $Na_2O-P_4O_{10}$ system has been established, existing in various structural modifications depending on temperature. The NaPO₃ ($2Na_2O \cdot P_4O_{10}$), $Na_4P_2O_7$ ($4Na_2O \cdot P_4O_{10}$) \varkappa Na₃PO₄ ($6Na_2O \cdot P_4O_{10}$) compounds melt congruently at 901, 1252, and 1852 K, respectively. The Na₅P₃O₁₀ ($10Na_2O \cdot 3P_4O_{10}$) compound dissociates at 903 K. The Na₂O-P₄O₁₀ phase diagram according to the survey data (Xie et al., 2020) is shown in Fig. 1.

The available thermodynamic data on sodium phosphates are scarce. Low temperature heat capacities of compounds were determined in (Andon et al., 1967), high temperature ones for NaPO₃ and Na₄P₂O₇ (up to 620 K) were determined in (Ashcroft et al., 1969) and for Na₃PO₄ (up to 1000 K) in (Lazarev et al., 1985). The enthalpy of formation of sodium phosphates were obtained by the solution calorimetry methods by Irving & McKerrell (1967, 1967), the entropy of formation was determined in (Andon et al., 1967).

Measurements of the oxide activities (a_i) in the melts, obtained using the Knudsen effusion mass spectrometric (Steblevsky et al., 1978; Malheiros et al., 1993) and the e. m. f. methods (Yamaguchi & Goto, 1984; Huang & Lin, 1989; Kozhina & Shultz, 1997), do not correspond at 873–1673 K. (Fig. 2). In particular, despite the identity in the Na₂O and NaPO₃ activities (Fig. 2A, C), the differences in the P₄O₁₀ activities at 1673 K, determined by Malheiros et al. (1993) and Yamaguchi and Goto (1984), exceed 10 orders of magnitude (Fig. 2B), that in turn leads to significant discrepancies in the minimum mixing energy (ΔG^m) in the melts (Fig. 2D) more than 130 kJ/mol.



Fig. 1. The phase diagram of the Na₂O–P₄O₁₀ system (Xie et al., 2020): 1 – γ-Na₂O + α-Na₃PO₄; 2 – β-Na₂O + α-Na₃PO₄; 3 – α-Na₂O + liquid; 4 – α-Na₃PO₄ + liquid; 5 – β-Na₃PO₄ + liquid; 6 – α-Na₃PO₄ + α-Na₄P₂O₇; 7 – α-Na₃PO₄ + β-Na₄P₂O₇; 8 – α-Na₃PO₄ + γ-, δ-, ε-, ζ-Na₄P₂O₇; 9 – α-Na₄P₂O₇ + α-Na₅P₃O₁₀; 10 – β-Na₄P₂O₇ + α-Na₅P₃O₁₀; 11 – γ-, δ-, ε-, ζ-Na₄P₂O₇ + β-Na₅P₃O₁₀; 12 – ζ-Na₄P₂O₇ + liquid; 13 – α-Na₅P₃O₁₀ + α-Na₅P₃O₁₀ + liquid; 15 – β-Na₆O₃ + liquid; 16 – γ-NaPO₃ + liquid; 17 – α-NaPO₃ + P₄O₁₀; 18 – α-NaPO₃ + liquid; 19 – P₄O₁₀ + liquid; 20 – liquid.



Fig. 2. The activities of Na₂O (A), P_4O_{10} (B), NaPO₃ (C) and mixing energy (D) in the Na₂O– P_4O_{10} melts determined experimentally in (Kozhina & Shultz, 1997) (1), (Huang & Lin, 1989) (2), (Yamaguchi & Goto, 1984) (3), (Steblevsky et al., 1978) (4), (Malheiros et al., 1993) (5), as well as calculated in (Xie et al., 2020) (6, 7) and in the present study (8–11) at 1073 (1, 6, 8), 1173 (2, 9), 1573 (3), 1580 (4), 1673 (5, 7, 10) and 1873 (11) K.



Fig. 3. Temperature dependences of partial pressures of vapor species over NaPO₃ (A) and Na₃PO₄ (B), determined by the mass spectrometric method in (Steblevsky et al., 1974) (1, 6), (Alikhanyan et al., 1975) (2), (Steblevsky et al., 1978) (3, 10), (Ratkovsky et al., 1976) (4), (Malheiros et al., 1993) (5, 8, 11), (Steblevsky et al., 1977) (7), (Rudny et al., 1986) (9) and calculated in the present study (12–16). List of symbols: NaPO₃ (1–5, 12), Na₂P₂O₆ (6), Na (7, 8, 13), O₂ (9–11, 14), PO (15), PO₂ (16).

The studies on the evaporation of sodium phosphates and their melts from platinum, quartz and molybdenum effusion cells (Steblevsky et al., 1974, 1978; Alikhanyan et al., 1975; Ratkovsky et al., 1976; Rudny et al., 1986; Malheiros et al., 1993) showed a predominant content of NaPO₃ molecules in the gas phase (Fig. 3A), their amount decreases with an increase in the Na₂O content in the condensed phase (Fig. 2C). In addition to NaPO₃, its dissociation products (NaPO, NaPO₂ and Na₂P₂O₆) were found in the gas phase over the melts, as well as the vapor species corresponding to the evaporation of sodium oxide - Na and O₂ (Fig. 3B). No vapor species corresponding to the evaporation of P_4O_{10} phosphorus oxide contained in the melt were found, that greatly complicated both the direct determination of P₄O₁₀ activities and their calculation using the Gibbs-Duhem equation.

The theoretical calculations of thermodynamic properties of the Na₂O-P₄O₁₀ melts in the temperature range 600–1900 K were performed using a semi-empirical model (Shornikov, 2019). The model parameters were the values of standard Gibbs energies (ΔG°) calculated from experimental and theoretical data for the formation of simple oxides $(Na_2O \text{ and } P_4O_{10})$ and sodium phosphates $(NaPO_3,$ Na₄P₂O₇, Na₃PO₄ and Na₅P₃O₁₀). The initial values of the standard Gibbs energies of the formation of Na₂O and P_4O_{10} in the crystalline and liquid state, as well as information on possible equilibria in the gas phase over the melt involving atomic and molecular vapor species (Na, Na₂, NaO, Na₂O, Na₂O₂, P, P₂, P₃, P₄, PO, PO₂, P₂O₃, P₂O₄, P₂O₅, P₃O₆, P₄O₆, P₄O₇, P₄O₈, P₄O₉, P₄O₁₀, NaPO, NaPO₂, NaPO₃, Na₂P₂O₆, O, O₂, O₃ and O₄) were adopted on the reference data (Glushko et al., 1978–1982), as well as the results obtained by Alikhanyan et al. (1975) and Rudny et

al. (1986). The ΔG° values of condensed phases and vapor species over the melt were used to find equilibrium conditions for a given melt composition and temperature.

A comparison of the results of calculations of oxide activities and mixing energy in the Na₂O- P_4O_{10} melts obtained it the present study (Fig. 2) shows compliance with those performed by the e.m. f. method (Yamaguchi & Goto, 1984; Kozhina & Schultz, 1997). From Fig. 2A it is possible to notice a good coincidence with the values of Na₂O activities obtained in (Huang & Ling, 1989; Malheiros et al., 1993). The minimum value of the mixing energy in the Na₂O–P₄O₁₀ melt is observed in the concentration range close to the eutectic composition between NaPO₃ and Na₄P₂O₇. The observed discrepancies in the results obtained by the mass spectrometric method may have been caused by significant fragmentation of NaPO₃ and Na₂P₂O₆ vapor species under the action of an electron shock (45-70 eV), leading to errors in the decoding of mass spectra.

The results of calculations of the partial pressures of molecular oxygen over NaPO₃ and Na₃PO₄ (Fig. 3) correspond to experimental data obtained by the Knudsen effusion mass spectrometric method (Steblevsky et al., 1978; Rudny et al., 1986; Malheiros et al., 1993). The high value of the partial pressure of atomic Na over NaPO₃ (Fig. 3A, symbol 7), obtained by Steblevsky et al. (1977), does not correspond to the low activity of Na₂O in the melt of metaphosphate, determined by sodium them (Steblevsky et al., 1978). As follows from the calculation, the partial pressures of the predominant phosphate vapor species (PO and PO₂) over NaPO₃ (Fig. 3A) at 1100-1400 K are quite low for the capabilities of the equipment used in the above-listed mass spectrometric studies and do not exceed 10^{-8} atm.

Thus, the thermodynamic properties of the $Na_2O-P_4O_{10}$ melts at 600–1900 K are calculated in the present study. The calculated values of the partial pressures of the vapor species of the gas phase, as well as the activities of oxides and mixing energies in the melts correspond to the available experimental data.

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Shornikov S.I. Thermodynamic properties of the K₂O–P₄O₁₀ melts

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Abstract. Calculations of the thermodynamic properties of the $K_2O-P_4O_{10}$ melts in the temperature range of 600–1900 K were carried out within the framework of the developed semi-empirical model. The calculated values of the partial pressures of the vapor species over KPO₃ are compared with the available experimental information. The more negative values of the mixing energy in the $K_2O-P_4O_{10}$ melts compared with those for Na₂O–P₄O₁₀ melts are due to the K₂O lower activity compared with the Na₂O activity in the phosphate melt, since the P₄O₁₀ activity is approximately the same.

Keywords: thermodynamic properties of oxide melts, the $K_2O-P_4O_{10}$ system

The physicochemical properties of potassium phosphates and their melts are of considerable interest in connection with the discovery of phosphates in the Murchison meteorite (Cooper et al., 1992), as well as for technologies in food production.

The presence of four potassium phosphates has been established in the $K_2O-P_4O_{10}$ system. They exist in various structural modifications depending

on temperature. The KPO₃ $(2K_2O \cdot P_4O_{10})$, $K_4P_2O_7$ $(4K_2O \cdot P_4O_{10})$ and K_3PO_4 $(6K_2O \cdot P_4O_{10})$ compounds melt congruently at 1086, 1376, and 1892 K, respectively, although other data are

available (Markina and Voskresenskaya, 1969). The $K_5P_3O_{10}$ (10 $K_2O \cdot 3P_4O_{10}$) compound dissociates at 916 K. According to the data (Xie et al., 2020) the $K_2O-P_4O_{10}$ phase diagram is shown in Fig. 1.



Fig. 1. The phase diagram of the K₂O–P₄O₁₀ system (Xie et al., 2020): 1 – β-K₂O + α-K₃PO₄; 2 – α-K₂O + β-K₃PO₄; 3 – α-K₂O + liquid; 4 – β-K₃PO₄ + liquid; 5 – γ-K₃PO₄ + liquid; 6 – α-K₃PO₄ + α-K₄P₂O₇; 7 – α-K₃PO₄ + β-K₄P₂O₇; 8 – β-K₃PO₄ + β-K₄P₂O₇; 9 – β-K₃PO₄ + γ-K₄P₂O₇; 10 – α-K₄P₂O₇ + α-K₅P₃O₁₀; 11 – β-K₄P₂O₇ + β-K₅P₃O₁₀ + liquid; 13 – γ-K₄P₂O₇ + liquid; 14 – β-K₅P₃O₁₀ + β-KPO₃; 15 – β-KPO₃ + liquid; 16 – γ-KPO₃ + liquid; 17 – α-KPO₃ + P₄O₁₀; 18 – α-KPO₃ + liquid; 19 – β-KPO₃ + liquid; 20 – P₄O₁₀ + liquid; 21 – liquid.

The available thermodynamic data on potassium phosphates and their melts are very scarce and have often not been determined experimentally (Kogan, 1969, 1971; Barin, 1995). The low temperature heat capacities and enthalpy of formation of KPO₃ and $K_4P_2O_7$ were determined in (Egan & Wakefield, 1960; Luff & Reed, 1979) and (Egan & Wakefield, 1960: Rudko et al., 1974: Luff & Reed, 1979a). respectively. The melting enthalpy of potassium metaphosphate was determined by calorimetry in (Hassan et al., 1987). Studies of evaporation of potassium metaphosphate and their melt from platinum, quartz and molybdenum effusion cells (Alikhanyan et al., 1975; Ratkovsky et al., 1975, 1976; Steblevsky et al., 1977) showed a predominant content of KPO₃ molecules in the gas phase and the small amounts of (KPO₃)₂ dimer and atomic of K (Fig. 2). No vapor species corresponding to the evaporation of P₄O₁₀ phosphorus oxide contained in the melt were found.

The theoretical calculations of thermodynamic properties of the $K_2O-P_4O_{10}$ melts in the temperature range 600-1900 K were performed using a semiempirical model (Shornikov, 2019). The model parameters were the values of standard Gibbs energies (ΔG°) calculated from experimental and theoretical data for the formation of simple oxides $(K_2O \text{ and } P_4O_{10})$ and potassium phosphates $(KPO_3,$ $K_4P_2O_7$, K_3PO_4 and $K_5P_3O_{10}$). The initial values of the standard Gibbs energies of the formation of K₂O and P_4O_{10} in the crystalline and liquid state, as well as information on possible equilibria in the gas phase over the melt involving atomic and molecular vapor species (K, K₂, KO, K₂O, K₂O₂, P, P₂, P₃, P₄, PO, PO₂, P₂O₃, P₂O₄, P₂O₅, P₃O₆, P₄O₆, P₄O₇, P₄O₈, P₄O₉, P_4O_{10} , KPO_3 , $K_2P_2O_6$, O, O₂, O₃ and O₄) were adopted on the reference data (Glushko et al., 1978-1982), as well as the results obtained by Alikhanyan et al. (1975) and Rudny et al. (1986). The ΔG° values of condensed phases and vapor species over the melt were used to find equilibrium conditions for a given melt composition and temperature.



Fig. 3. The activities (A) of $K_2O(1)$, $Na_2O(2)$, $P_4O_{10}(3, 4)$ and the mixing energy (B) in the $K_2O-P_4O_{10}(1, 3, 5)$ and $Na_2O-P_4O_{10}(2, 4, 6)$ melts at 1673 K, calculated in the present study.

A comparison of the results obtained in the present study of calculations of oxide activities and mixing energy in the $K_2O-P_4O_{10}$ melts (Fig. 3) at 1673 K with those for the $Na_2O-P_4O_{10}$ melts shows their similarity. The minimum of mixing energy in the $K_2O-P_4O_{10}$ melt (as in the case of the Na₂O-P₄O₁₀ melts) is observed in the concentration range close to the eutectic composition between KPO₃ and $K_4P_2O_7$ (NaPO₃ and Na₄P₂O₇, respectively). Note that the more negative values of mixing energy in the $K_2O-P_4O_{10}$ melts compared with those for the Na₂O- P_4O_{10} melts (Fig. 3B) are due to the K₂O lower activity compared with the Na₂O activity in the phosphate melt (Fig. 3A, lines 1 and 2), since the P_4O_{10} activities are approximately the same (Fig. 3A, lines 3 and 4).

The PO₂ and O₂ partial pressures over the KPO₃ melt at 1300 K calculated in the present study do not exceed 10^{-6} atm (Fig. 2). The K partial pressure over the potassium metaphosphate at 1175 K is no more than 10^{-14} atm, which significantly differs from the results obtained by Steblevsky et al. (1977). The value determined by them is too high (Fig. 2, symbol

4) and cannot correspond to the K_2O low activity in the potassium metaphosphate melt (Fig. 3A). The probable reason for the observed deviation of the results of Steblevsky et al. (1978) from the calculated data obtained in the present study is the significant fragmentation of the KPO₃ molecular ion under the action of an electron impact, which could lead to errors in the decoding of mass spectra.

Thus, the thermodynamic properties of the $K_2O-P_4O_{10}$ melts in the temperature range 600–1900 K are calculated in the present study. The partial pressures of vapor species of the gas phase, as well as the oxide activities and mixing energies in the $K_2O-P_4O_{10}$ melts correlate with those for the Na₂O–P₄O₁₀ melts.

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Shornikov S. I. Thermodynamic properties of the FeO–P₄O₁₀ melts

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Abstract. Within the framework of the developed semiempirical model, the thermodynamic properties of the FeO–P₄O₁₀ melts were calculated in the temperature region 600–1700 K. The calculated values of the partial pressures of vapor species as well as the oxide activities and the mixing energies of melts are compared with available information.

Keywords: thermodynamic properties of oxide melts, the FeO- P_4O_{10} system

The physico-chemical data characterizing iron phosphates are of interest for the geochemistry of the Moon, due to the detection of phosphorus-containing olivines in lunar matter, as well as for the search for promising materials used in highly efficient lithiumion batteries.

It has been found the FeP_4O_{11} (FeO $\cdot P_4O_{10}$), FeP_2O_6 (2FeO · P_4O_{10}), $Fe_2P_2O_7$ (4FeO · P_4O_{10}) and $Fe_3P_2O_8$ (6FeO · P₄O₁₀) iron phosphates in the FeO- P_4O_{10} system, which melt congruently at 998±10 K (Weil & Glaum, 1998), 1218±8 K (Zhang, 2010), 1378±8 K (Zhang, 2010) and 1323±15 K (Tromel & Schwerdtfeger), respectively. The $Fe_5P_3O_{13}$ (20FeO · 3P₄O₁₀) compound is formed at 753±8 K (Khadhraoui et al., 2019) and dissociates at 1233±15 K (Tromel & Schwerdtfeger, 1963). Graftonite $(Fe_3P_2O_8)$ undergoes a phase transition from an olivine to a graftonite-like structure at 1013±10 K (Modaressi et al., 1983). Bouchdoug et al. (1982) were synthesized the $Fe_4(PO_4)_2O$ (8FeO $\cdot P_4O_{10}$) compound from mixtures of Fe₂O₃-FePO₄ or Fe₃PO₇–FePO₄ at 1173 K under reducing conditions. The phase diagram of the $FeO-P_4O_{10}$ system based on these data is presented in Fig. 1.



Thermodynamic information on iron phosphates and their melts is scarce (Teterevkov & Pechkovsky, 1974; Ong et al., 2008; Zhang, 2010; Schmitt, 2022). The low temperature heat capacity and enthalpy formation of Fe₂P₂O₇ were determined by Shi et al. (2013). The FeO activities in the FeO- P_4O_{10} melts were determined in the studies of heterogeneous equilibria involving a gas mixture of H₂ / H₂O (Banya & Watanabe, 1977), as well as the P_4O_{10} activities were determined in the studies of sample evaporation from alund effusion cells by mass spectrometric method (Kambayashi et al., 1985; Ohara et al., 1987) in the concentration range of $0-11 \text{ mol. } \% \text{ P}_4\text{O}_{10}$ and at 1643-1673 K (Fig. 2) The results of mass spectrometric studies of the evaporation of $Fe_2P_2O_7$ and Fe₃P₂O₈ from platinum effusion cells at 1300-1500 K (Lopatin, 1995) showed a predominant content of the PO₂ and PO molecules in the gas phase over the melts, respectively (Fig. 3). Stolyarova et al. (2004) studied the equilibriums:

$$FeO + PO_2 = FePO_3 \tag{1}$$

$$FeO + PO = FePO_2$$
 (2)

in the gas phase over the FeO and P₄O₁₀ mixtures

Fig. 1. The phase diagram of the FeO-P₄O₁₀ system: 1 - FeO + α -Fe₃P₂O₈; 2 - FeO + Fe₅P₃O₁₃; 3 - FeO + liquid; 4 - Fe₅P₃O₁₃ + α -Fe₃P₂O₈; 5 - Fe₅P₃O₁₃ + β -Fe₃P₂O₈; 6 -Fe₅P₃O₁₃ + liquid; 7 - β -Fe₃P₂O₈ + liquid; 8 - α -Fe₃P₂O₈ + Fe₂P₂O₇; 9 - β -Fe₃P₂O₈ + Fe₂P₂O₇; 10 - Fe₂P₂O₇ + liquid; 11 - Fe₂P₂O₇ + FeP₂O₆; 12 - FeP₂O₆ + liquid; 13 - FeP₂O₆ + FeP₄O₁₁; 14 - FeP₄O₁₁ + liquid; 15 -FeP₄O₁₁ + P₄O₁₀; 16 - P₄O₁₀ + liquid; 17 liquid.

using the Knudsen effusion mass spectrometry at 1724–1851 K.

The theoretical calculations of thermodynamic properties of the FeO– P_4O_{10} melts in the temperature range 600-1700 K were performed using a semiempirical model (Shornikov, 2019). The model parameters were the values of standard Gibbs energies (ΔG°) calculated from experimental and theoretical data for the formation of simple oxides (FeO and P_4O_{10}) and iron phosphates (FeP₄O₁₁, FeP_2O_6 , $Fe_2P_2O_7$, $Fe_3P_2O_8$ и $Fe_5P_3O_{13}$). The initial values of the standard Gibbs energies of the formation of FeO and P₄O₁₀ in the crystalline and liquid state, as well as information on possible equilibria in the gas phase over the melt involving atomic and molecular vapor species (Fe, Fe₂, FeO, FeO₂, P, P₂, P₃, P₄, PO, PO₂, P₂O₃, P₂O₄, P₂O₅, P₃O₆, P₄O₆, P₄O₇, P₄O₈, P₄O₉, P₄O₁₀, FePO₂, FePO₃, O, O₂, O_3 and O_4) were adopted on the reference data (Barin, 1995), as well as the results obtained by Stolvarova et al. (2004). The ΔG° values of condensed phases and vapor species over the melt were used to find equilibrium conditions for a given melt composition and temperature.



Fig. 2. The activities of FeO (A) and P_4O_{10} (B) in the FeO– P_4O_{10} melts at 1643–1673 K, determined in the studies of heterogeneous equilibria (Ban-ya & Watanabe, 1977) (1), by the mass spectrometric method (Kambayashi et al., 1985; Ohara et al., 1987) (3, 4), as well as calculated in the present study (2, 5).



Fig. 3. Temperature dependences of partial pressures of the vapor species over $Fe_2P_2O_7$ (A) and $Fe_3P_2O_8$ (B), determined by the mass spectrometric method by Lopatin (1995) (1, 2), as well as calculated in the present study (3–9). List of symbols: PO (1, 3), PO₂ (2, 4), P₂O₃ (5), P₂O₄ (6), P₄O₉ (7), O (8), O₂ (9).



Fig. 4. The partial pressures of the vapor species of the gas phase Fe (1), PO (2), PO₂ (3), P_4O_{10} (4), O (5) and O_2 (6), as well as the activities of FeO (7), P_4O_{10} (8) and mixing energy (9) in the FeO– P_4O_{10} melts at 1673 K, calculated in the present study.

As follows from Fig. 4, the concentration dependencies of the Fe and P₄O₁₀ partial vapor pressures correlate with those for the FeO and P_4O_{10} activities. A comparison of the results of calculations of the oxide activities in the FeO– P_4O_{10} melts at 1673 K with the experimental values obtained in (Ban-ya & Watanabe, 1977; Kambayashi et al., 1985; Ohara et al., 1987) shows their satisfactory correspondence (Fig. 2). The minimum mixing energy in the FeO- P_4O_{10} melts (Fig. 4) is observed, as in the case of the $K_2O - P_4O_{10}$ and $Na_2O-P_4O_{10}$ melts, in the concentration range close to the eutectic composition between Fe₂P₂O₇ and FeP₂O₆ (Fig. 1).

The results of calculations of the PO₂ partial pressures over the Fe₂P₂O₇ melt (Fig. 3A) and the PO partial pressures over the Fe₃P₂O₈ melt (Fig. 3B) are quite close to the experimental values obtained by Lopatin (1995), and it indicate the predominance of the vapor species containing phosphorus and oxygen in the gas phase over iron phosphate melts (PO, PO₂,

 P_2O_3 , P_2O_4 , P_4O_9 , O, O₂). The Fe partial vapor pressure (as well as gaseous iron phosphates FePO₂ and FePO₃) over the melts of these iron phosphates is quite low for experimental determination and does not exceed 10^{-12} atm in the temperature range under consideration (1275–1525 K).

Thus, the thermodynamic properties of the FeO– P_4O_{10} melts in the temperature range of 600–1700 K are calculated in the present study. It is shown that the results of calculations of thermodynamic properties of melts correspond to the available experimental data.

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