WIDE-RANGE EQUATIONS OF STATE OF GRANITE AND WATER WITH ALLOWANCE FOR EVAPORATION, DISSOCIATION, AND IONIZATION

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Semiempirical wide-range equations of state of granite and water based on resolution of the pressure and energy into a cold component and thermal electronic and nuclear components are presented. The thermal electronic component is calculated using the Thomas–Fermi model, which makes it possible to describe both thermal ionization and ionization by pressure. Evaporation and dissociation are allowed for by introducing the corresponding terms into the free energy. The condensed state is described within the framework of the Debye approximation. The cold isotherm is constructed with allowance for available experimental data.

Wide-range equations of state (ESs) that realistically describe thermodynamic characteristics of a substance in a wide region of a phase diagram containing segments of both the condensed and gaseous states and that allow for the processes of dissociation and ionization are required in numerical modeling of gas-dynamic problems of high-speed impact. They include problems associated with the creation of meteorite defense, the study of meteorite craters, the origin of planetary atmospheres, possible consequences of the fall of large nonterrestrial objects onto the earth, etc. In these processes, the substance goes through stages from the condensed state through evaporation, dissociation, and ionization to a rarefied gaseous state. The need for correct allowance for the interparticle interaction renders a successive theoretical description of the equation of state for the substance impossible. Therefore, in calculations, we have to consider semiempirical models containing reasonable functional dependences specified in advance for thermodynamic parameters and coefficients whose selection enables us to describe with a certain degree of accuracy the available experimental thermodynamic data. Models of equations of state of a substance are reviewed in detail in [1]. Among more recent models, we should note an ES for water that is adequate up to temperatures of 60,000 K and pressures of 4 GPa [2].

In the present work, use is made of an additive approximation developed for rocks in [3, 4] and for water in [5]. To construct the equation of state, we employ resolution of the pressure and energy into a cold component and thermal nuclear and electronic components:

\[ P(\rho, T) = P_{\text{cold}}(\rho) + P_k(\rho, T) + P_e(\rho, T), \]

\[ E(\rho, T) = E_{\text{cold}}(\rho) + E_k(\rho, T) + E_e(\rho, T). \]

To calculate \( P_e \) and \( E_e \), we use the results of calculations by the Thomas–Fermi model [6] for an average charge \( Z = 10 \) that is the same for both water and the main component of granite SiO\textsubscript{2}. In what follows, we will consider, as the ES of granite, the ES of its main component.

The free energy of the nuclear component of the substance is written as

\[ F_k = F_{\text{cond}} + N_kT \ln (1 + z_{\text{1}}^{n_1})^{1/n_1} - N_kT \ln (1 + z_{\text{2}}^{n_2})^{1/n_2}. \]

The second term corresponds to evaporation, and the third term to dissociation of the molecules. If \( T \) is such that the substance evaporated completely, then...
\[ F_{\text{vap}} = F_{\text{cond}} + NkT \ln z_1 \]  

(1)

on condition that \( z_1 \gg 1 \) in developed evaporation. Similarly to \( z_1 \), the expression for \( z_2 \) is determined from the relation

\[ F_{\text{dis}} = F_{\text{vap}} + NkT \ln z_2 , \]  

(2)

which corresponds to complete dissociation of the molecules of the substance.

In what follows, the ESs of SiO\(_2\) and water are considered separately.

Granite. The pressure on the cold isotherm for SiO\(_2\) when \( p < p_{0K} \) is specified in the form

\[ P_{\text{cold}} = A (\delta^m - \delta^n) , \quad \delta = \rho/\rho_{0K} . \]

The parameters \( A \) and \( m \) are determined from the relation

\[ \frac{d}{dp} P_{\text{cold}} (p_0) = c^2 \]

and the condition of equality of the work of compression from \( p = 0 \) to \( p = \rho_{0K} \) to the sublimation energy. We took \( 5/3 \) for \( n \). Then \( m = 3.115 \) and \( A = 2.48 \cdot 10^{10} \) Pa. For compressions that are larger than unity but smaller than three we used a cold isotherm that allows for the experimental data of [7], which for large compressions was joined to the cold isotherm of the Thomas–Fermi model with corrections calculated for the average charge \( Z = 10 \).

Since the critical temperature of SiO\(_2\) is almost an order of magnitude larger than the Debye temperature \( \theta_0 \) (\( \theta_0 = 600 \) K) under normal conditions, to determine \( z_1 \) from Eq. (1) the expression

\[ F_{\text{cond}} = - NkT \ln \left[ Z_{\text{SiO}_2} \left( \frac{T}{\theta_D} \right)^{9/4} \right] , \]

is used for \( F_{\text{cond}} \), which agrees with the Einstein model, which is a good approximation at high temperatures. Considering the vibrations and rotation of a molecule in the classical approximation, for the free energy of the vapor we obtain

\[ F_{\text{vap}} = - NkT \ln \left[ \left( \frac{2\pi M_{\text{SiO}_2} kT}{h^2 N_A} \right)^{3/2} \frac{eV}{8\pi^2 JT} \frac{T^4}{N} \frac{1}{2h^2} \frac{1}{\theta_1^2 \theta_2^2 \theta_3^2} Z_{\text{SiO}_2} \right] , \]

where \( \theta_1 = 1351 \) K; \( \theta_2 = 603 \) K; \( \theta_3 = 1780 \) K; \( M_{\text{SiO}_2} \) is the molecular weight; \( J = 1.28 \cdot 10^{-45} \) kg \cdot m\(^2\). If we assume

\[ \theta_D/\theta_0 = (V_0/V)^\gamma , \]

we obtain

\[ z_1 = \frac{26.6}{\theta_0 V^{\frac{9}{4} \gamma}} \theta_1^2 \theta_2^2 \theta_3 T^{5/2} V^\gamma - 1 . \]

Subsequently it is taken that \( \gamma = 2/3 \).

To determine \( z_2 \) from Eq. (2), we use the expression for the free energy of an ideal gas of silicon and oxygen atoms

\[ F_{\text{dis}} = - NkT \ln \left[ \left( \frac{2\pi M_{\text{Si}} kT}{h N_A} \right)^{3/2} \left( \frac{2\pi M_{\text{O}} kT}{h N_A} \right)^3 \frac{V^3}{4N^3} Z_{\text{Si}} Z_{\text{O}}^2 \right] . \]