

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

F. N. Borovik and G. S. Romanov

UDC 536.71

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:

$$P(\rho, T) = P_{\text{cold}}(\rho) + P_{\text{k}}(\rho, T) + P_{\text{e}}(\rho, T),$$

$$E(\rho, T) = E_{\text{cold}}(\rho) + E_{\text{k}}(\rho, T) + E_{\text{e}}(\rho, T).$$

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_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

$$F_{\text{k}} = F_{\text{cond}} + NkT \ln(1 + z_1^{n_1})^{1/n_1} - NkT \ln(1 + z_2^{n_2})^{1/n_2}.$$

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

Academic Scientific Complex "A. V. Luikov Heat and Mass Transfer Institute," National Academy of Sciences of Belarus, Minsk, Belarus. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 72, No. 6, pp. 1055-1061, November–December, 1999. Original article submitted April 13, 1999.

$$F_{\text{vap}} = F_{\text{cond}} + NkT \ln z_1 \quad (1)$$

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

$$F_{\text{dis}} = F_{\text{vap}} + NkT \ln z_2, \quad (2)$$

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

In what follows, the ESs of SiO₂ and water are considered separately.

Granite. The pressure on the cold isotherm for SiO₂ when $\rho < \rho_{0K}$ 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

$$\frac{d}{d\rho} P_{\text{cold}}(\rho_0) = c^2$$

and the condition of equality of the work of compression from $\rho = 0$ to $\rho = \rho_{0K}$ 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 SiO₂ is almost an order of magnitude larger than the Debye temperature θ_0 ($\theta_0 = 600$ K) under normal conditions, to determine z_1 from Eq. (1) the expression

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

is used for F_{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

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

where $\theta_1 = 1351$ K; $\theta_2 = 603$ K; $\theta_3 = 1780$ K; M_{SiO_2} is the molecular weight; $J = 1.28 \cdot 10^{-45}$ kg·m². If we assume

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

we obtain

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

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

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

Since

$$\frac{Z_{eSi} Z_{eO}^2}{Z_{eSiO_2}} = \frac{g_{0Si} g_{0O}^2}{g_{0SiO_2}} \exp\left(-\frac{Q_{dis} M_{SiO_2}}{RT}\right),$$

where Q_{dis} is the dissociation energy of an SiO_2 molecule, we obtain

$$z_2 = 1.336 \cdot 10^{-5} \theta_1 \theta_2^2 \theta_3 \frac{V^2}{T^2} \exp\left(-\frac{Q_{dis} M_{SiO_2}}{RT}\right).$$

When $T_2 = Q_{dis} M_{SiO_2} / RT$ the function z_2 has a maximum. Therefore, for $T > T_2$, z_2 was taken to be equal to a constant.

The approximations presented lead to the relations

$$P_k = \frac{9\gamma RT}{VM_{SiO_2}} - (9\gamma - 1) \frac{RT}{VM_{SiO_2}} \frac{z_1^{n_1}}{1 + z_1^{n_1}} + \frac{2RT}{VM_{SiO_2}} \frac{z_2^{n_2}}{1 + z_2^{n_2}},$$

$$E_k = \frac{9RT}{M_{SiO_2}} - \frac{5}{2} \frac{RT}{M_{SiO_2}} \frac{z_1^{n_1}}{1 + z_1^{n_1}} - \left(\frac{2RT}{M_{SiO_2}} - Q_{dis}\right) \frac{z_2^{n_2}}{1 + z_2^{n_2}}.$$

For a more relastic description, we use the following expression for the energy:

$$E_k = \frac{E_* + 6.5 \frac{RT}{M_{SiO_2}} z_1^{n_1}}{1 + z_1^{n_1}} - \left(\frac{2RT}{M_{SiO_2}} - Q_{dis}\right) \frac{z_2^{n_2}}{1 + z_2^{n_2}}.$$

Here

$$E_* = a_1 + a_2 T + a_3 T^2, \text{ if } T < T_*,$$

$$E_* = b_1 + b_2 T, \text{ if } T > T_*,$$

$$T_* = 680 \text{ K}, \quad a_1 = -8.36 \cdot 10^3 \text{ J/kg}, \quad a_2 = 66.9 \text{ J/(kg} \cdot \text{deg}^2),$$

$$a_3 = 118.5 \cdot 10^{-2} \text{ J/(kg} \cdot \text{deg}^2), \quad b_1 = -55.7 \text{ J/kg},$$

$$b_2 = 1.67 \cdot 10^3 \text{ J/(kg} \cdot \text{deg}^2).$$

For the best agreement with results of calculations in the region of an ideal gas we took $n_1 = 0.25$ and $n_2 = 0.2$.

Calculations based on the procedure presented above show that at temperatures lower than 5400 K and densities lower than 1 kg/dm^3 the isotherms are nonmonotonic, i.e., reveal a behavior characteristic of van der Waals isotherms, and have segments that correspond to thermodynamically unstable states. The isotherm with $T = 5386 \text{ K}$ has an inflection point (i.e., a critical point) at a specific volume of $1.33 \text{ dm}^3/\text{kg}$ and a pressure of 0.51 GPa . It should be noted that at temperatures lower than 4500 K the isotherms have segments of negative pressure. At higher temperatures, the thermal pressure already compensates for the negative pressure of the cold isotherm. As is known, the presence of van der Waals singularities indicates decomposition of the substance into two phases whose equilibrium thermodynamic parameters are determined according to Maxwell's rule at the specified

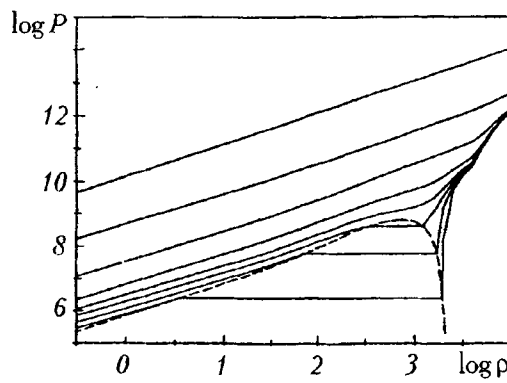


Fig. 1. Binodal curve (dashed line) and isotherms (solid lines) of granite for temperatures of 3160, 4000, 5000, 6300, 10,000, 32,000, 200,000, and 10^6 K. The isotherms are directed from the bottom upward as the temperature increases. P , Pa; ρ , kg/m^3 .

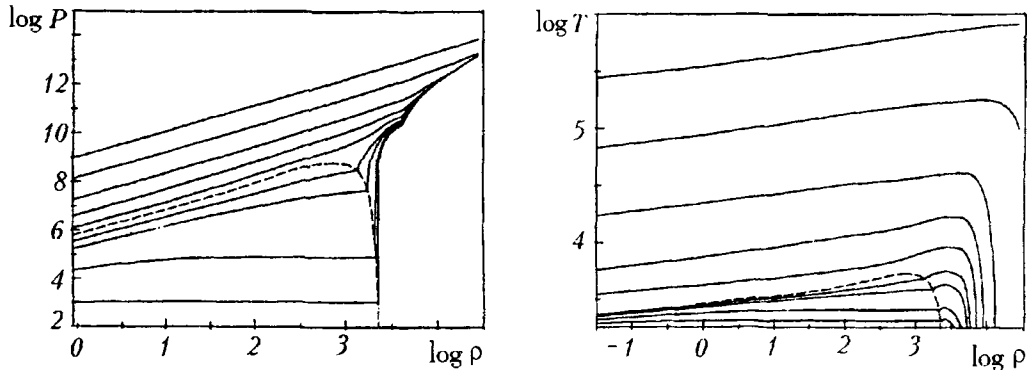


Fig. 2. Binodal curve (dashed line) and isoennergetic curves (solid lines) of granite for specific energies of 3, 4, 7, 10, 20, 40, 100, 600, and 4000 MJ/kg. The isoennergetic curves are directed from the bottom upward as the energy increases. T , K.

temperature. Maxwell's rule enables us to construct a curve (a binodal curve) that bounds the coexistence domain of the phases. Figure 1 shows isotherms for a number of temperatures that have horizontal segments within the region of two-phase states. The abrupt change in the slope of the isotherms at high densities is due to pressure ionization. The latter is caused by deformation of the energy levels with the compression since, in this case, the volume of the cell for one atom of the substance is decreased. The deformation of the levels is accompanied by pressing of them out into a continuous spectrum, i.e., by ionization. We note that in the vicinity of the critical point effects due to incipient dissociation already manifest themselves. Figure 2 shows isoennergetic curves of granite in the density-pressure and density-temperature planes. The presence of a maximum on the isoennergetic curves $T(\rho)$ is attributable to the fact that on the isotherms the energy first decreases with compression but subsequently begins to increase at increased densities as the zero isotherm is approached. This is associated with the Coulomb interaction growing in significance and deformation of the energy spectrum.

Water. To describe the cold isotherm, we employed experimental data from [8, 9] approximated by polynomials that were subsequently joined to the cold isotherm of the Thomas-Fermi model.

In turn, the indicated intervals of densities were broken down into smaller ones, for each its own set of coefficients being used. The cold-compression energy was determined from the relation

$$E_{\text{cold}} = \int_{\rho_{0\text{K}}}^{\rho} \frac{P_{\text{cold}}}{\rho^2} d\rho,$$

where $\rho_{0\text{K}} = 1.17229 \text{ kg}/\text{dm}^3$ at $T = 0 \text{ K}$.

Just for granite, the contribution of the thermal nuclear component was calculated based on its representation as a sum of terms that allow for the thermal motion of the nuclei in the condensed state and the processes of evaporation and dissociation. A correction for hydrogen bonds was allowed for.

Since for water the Debye temperature under normal conditions is approximately half the critical temperature, the pressure due to the thermal motion of the nuclei in the condensed state was calculated by the formula

$$P_k = \frac{RT}{MV} 5\gamma \frac{\theta_D}{T} \frac{\exp(-\theta_D/T)}{1 - \exp(-\theta_D/T)},$$

where the Debye temperature, which depends on the density, was determined as

$$\theta_D = \theta_0 \exp \left(\int_{\rho_0}^{\rho} \frac{\gamma}{\rho} d\rho \right).$$

Here $\theta_0 = 170$ K is the Debye temperature under normal conditions. For the Grüneisen coefficient we used the approximations

$$\gamma = 0.5 + \left(\frac{\rho}{3.886 - 4.153\rho + 1.8\rho^2} \right)^2, \quad \rho \geq 1.2;$$

$$\gamma = 0.0282 + 0.9305\rho, \quad 1 \leq \rho \leq 1.2;$$

$$\gamma = 0.3437 + 0.353(0.32 + \rho)^2, \quad 0.1 < \rho \leq 1;$$

$$\gamma = 0.4052 + 29.07(\rho - 0.949)^2, \quad 0 < \rho < 0.1 \text{ kg/dm}^3$$

with specially selected coefficients.

The quantities z_1 and z_2 were determined from Eqs. (1) and (2). For n_1 and n_2 we took values of 0.4 and 0.5, respectively.

The pressure component due to evaporation was calculated in the following manner:

$$P_{\text{vap}} = \frac{RT}{MV} \left[1 - 5\gamma \frac{\theta_D}{T} \frac{\exp(-\theta_D/T)}{1 - \exp(-\theta_D/T)} \right] \frac{z_1^{n_1}}{1 + z_1^{n_1}},$$

$$z_1 = \frac{2 \cdot 10^4}{VT^{5/2} (1 - \exp(-\theta_D/T))^5}.$$

For the pressure component due to dissociation, use was made of the expression

$$P_{\text{dis}} = 2 \frac{RT}{MV} \frac{z_2^{n_2}}{1 + z_2^{n_2}},$$

where

$$z_2 = \frac{8.6 \cdot 10^3 V^2}{T^{3/2}} \exp \left(- \frac{Q_{\text{dis}} M}{RT} \right), \quad T \leq 73\,760 \text{ K}.$$

At high temperatures the function z_2 was assumed to be equal to a constant. The correction to the pressure that allows for hydrogen bonds has the form

$$P_H = \varphi(V) f(T),$$

where

$$\begin{aligned} \varphi(V) = & -7.08 (V \cdot 10^{-3} - 0.84467) (V \cdot 10^{-3} - 1.90956) \times \\ & \times \exp(-1.94 (V \cdot 10^{-3} - 1)), \end{aligned}$$

$$f(T) = (85.793d^3 - 25.961d^2 + 1.040069d) \cdot 10^{10}, \quad T \leq 353 \text{ K};$$

$$f(T) = 8.0963 \cdot 10^{14} d^{12.23}, \quad T > 353 \text{ K}; \quad d = 100/T.$$

In calculating the contribution of vibrational motion in the molecules to the energy, we must allow for quantum effects since the temperatures at which the liquid phase exists are much lower than the characteristic temperatures of internal vibrations. Therefore for the energy that is due to the thermal motion of the nuclei in the condensed state we used the expression

$$E_k = \frac{RT}{M} \left[5 \frac{\theta_D}{T} \frac{\exp(-\theta_D/T)}{1 - \exp(-\theta_D/T)} + \frac{1}{2} + \sum_1^3 \frac{\theta_i}{T} \frac{\exp(-\theta_i/T)}{1 - \exp(-\theta_i/T)} \right].$$

Here M is the molecular weight of water; $\theta_1 = 2370 \text{ K}$; $\theta_2 = 5510 \text{ K}$; $\theta_3 = 5660 \text{ K}$.

The energy associated with the process of evaporation was calculated by the formula

$$E_{\text{vap}} = \frac{5 RT}{2 M} \left(1 - 2 \frac{\theta_D}{T} \frac{\exp(-\theta_D/T)}{1 - \exp(-\theta_D/T)} \right) \frac{z_1^{n_1}}{1 + z_1^{n_1}}.$$

For the energy due to the process of dissociation, we used the following expression:

$$E_{\text{dis}} = \left(Q_{\text{dis}} - \frac{3}{2} T \frac{R}{M} \right) \frac{z_2^{n_2}}{1 + z_2^{n_2}}.$$

The energy correction due to the hydrogen bonds has the form

$$E_H = \frac{R}{M} (-5.25 \cdot 10^{-3} T^2 + 6.8T - 2.2 \cdot 10^3) \frac{1}{1 + z_1^{n_1}}, \quad T \leq 647 \text{ K};$$

$$E_H = 0, \quad T > 647 \text{ K}.$$

Furthermore, we introduced another correction to the energy of the form

$$E_{\text{ad}} = 3.65 (V - 1) (V - 0.723) \exp(-1.94 (V - 1)) \psi(T);$$

$$\psi(T) = -1.323 \cdot 10^{-3} f(T), \quad T \geq 353 \text{ K};$$

$$\psi(T) = -3.4317416 \cdot 10^{11} d^3 + 7.78 \cdot 10^{10} d^2 - 2.081248 \cdot 10^9 d,$$

$$d = \frac{100}{T}, \quad T < 353 \text{ K}.$$

In all the above formulas, the specific volume V has dimensions of m^3/kg , P has dimensions of Pa, and $E - \text{J}/\text{kg}$.

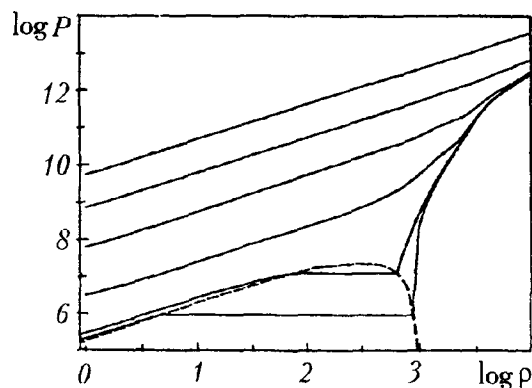


Fig. 3. Binodal curve (dashed line) and isotherms (solid lines) of water for temperatures of 400, 600, 4000, 30,000, 200,000, and 1,000,000 K. The isotherms are directed from the bottom upward as the temperature increases.

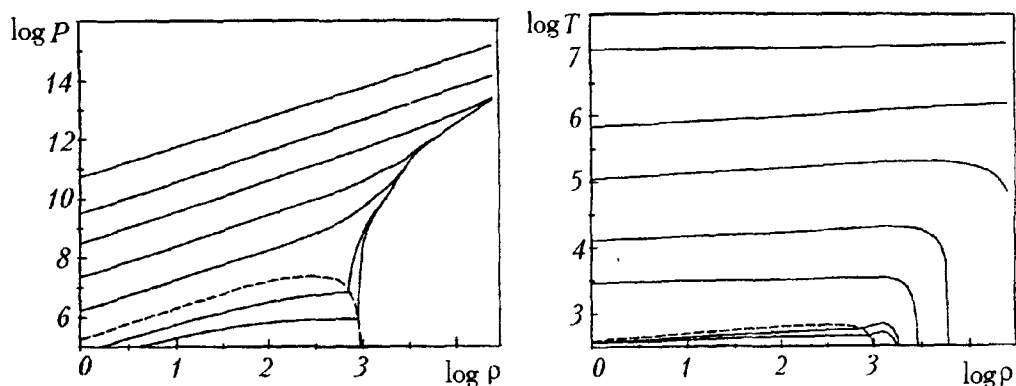


Fig. 4. Binodal curve (dashed line) and isoenergetic curves (solid lines) of water for specific energies of 1, 1.5, 10, 100, 1000, 10,000, and 100,000 MJ/kg. The isoenergetic curves are directed from the bottom upward as the energy increases.

Calculations based on the procedure presented show that, for temperatures lower than 652 K and densities lower than 1 kg/dm^3 , the isotherms are nonmonotonic, i.e., reveal behavior inherent in van der Waals isotherms, and have segments that correspond to thermodynamically unstable states. The isotherm with $T = 652 \text{ K}$ has an inflection point (i.e., a critical point) for a specific volume of $3.17 \text{ dm}^3/\text{kg}$ and a pressure of $2.35 \cdot 10^7 \text{ Pa}$, which corresponds to experimental values. At temperatures lower than 600 K, there are segments of negative pressure on the isotherms. At higher temperatures, the thermal pressure already compensates for the negative pressure of the cold isotherm. As in the case of granite, the curve of coexistence of the condensed and gaseous phases was determined according to Maxwell's rule at the specified temperature. Figure 3 shows isotherms for a number of temperatures that have horizontal segments within the region of two-phase states. The calculated boiling point and heat of evaporation under normal conditions are also in agreement with the experimental values. We note that, unlike granite, in the vicinity of the critical point of water dissociation effects are absent since the temperatures are still rather low. Since, to describe the thermal electronic components of the pressure and energy, we employ the Thomas-Fermi model, which describes ionization by pressure, the behavior of the isotherms as the zero isotherm is approached is similar to the situation for granite. Figure 4 shows isoenergetic curves of water in the density-pressure and density-temperature planes. We can note the presence of a maximum on the isoenergetic curves of water, which, as has already been discussed, is associated with the zero isotherm being approached and the nonideality growing in importance.

The work was carried out under the program of the International Science and Technology Center, project B23-96.

NOTATION

P , total pressure; P_{cold} , cold pressure, P_k , E_k , and F_k , pressure, energy, and free energy due to the thermal motion of the nuclei; P_e and E_e , thermal electronic pressure and energy; E , total specific energy; E_{cold} , cold energy; V , specific volume; ρ , density; T , temperature; Z , average charge; F_{cond} , free energy of the condensed state; k , Boltzmann constant; N , number of particles per gram of the substance; n_1 and n_2 , exponents in the expressions for the free energy; z_1 and z_2 , statistical sums involved in the expressions for the free energy; F_{vap} , free energy of an ideal gas comprised of molecules; F_{dis} , free energy of an ideal gas comprised of atoms; ρ_{0K} , density at the absolute zero of temperature; ρ_0 , density under normal conditions; V_0 , volume under normal conditions; δ , compression; c , velocity of sound; m , n , and A , constants; θ_0 , Debye temperature under normal conditions; θ_D , Debye temperature that depends on the volume; $Z_{e\text{SiO}_2}$, electron statistical sum of a molecule; h , Planck constant; N_A , Avogadro number; M , molecular or atomic weight; J , moment of inertia; θ_1 , θ_2 , and θ_3 , characteristic temperatures; γ , Grüneisen coefficient; $Z_{e\text{Si}}$, electron statistical sum of a silicon atom; Z_{eO} , electron statistical sum of an oxygen atom; g_0 , statistical weight of the ground state; Q_{dis} , dissociation energy; R , gas constant; T_2 , constant; E_* and T_* , constants in the expression for the thermal energy; a_0 , a_1 , a_2 , a_3 , a_4 , b_1 , and b_2 , constants in the approximation dependences; A_1 , B_1 , C_1 , A_2 , B_2 , A_3 , B_3 , and C_3 , constants in the expressions for the Grüneisen coefficient; P_H , pressure due to hydrogen bonds; φ and f , functions that describe the correction to the pressure; E_H , energy due to hydrogen bonds; E_{ad} , additional correction to the energy; ψ , function that describes the additional correction to the energy. Subscripts: k, nuclear; cold, cold; e, electron; cond, condensed; vap, vapor; dis, dissociated; H, hydrogen; ad, additional.

REFERENCES

1. A. V. Bushman and V. E. Fortov, *Usp. Fiz. Nauk*, **140**, Issue 2, 177-232 (1983).
2. A. M. Belyaev, V. S. Vorob'ev, and A. L. Khomkin, *Teplofiz. Vys. Temp.*, **28**, No. 3, 467-472 (1990).
3. S. V. Bobrovskii, V. M. Gogolev, B. V. Zamyshlyaev, et al., *Fiz. Tekh. Probl. Razrab. Polezn. Iskop.*, No. 2, 58-61 (1976).
4. S. V. Bobrovskii, V. M. Gogolev, B. V. Zamyshlyaev, et al., *Fiz. Tekh. Probl. Razrab. Polezn. Iskop.*, No. 3, 49-57 (1976).
5. S. V. Bobrovskii, V. M. Gogolev, M. G. Menzhulin, et al., *Prikl. Mekh. Tekh. Fiz.*, No. 5, 130-139 (1978).
6. N. N. Kalitkin and L. V. Kuz'mina, *Tables of Thermodynamic Functions of a Substance with a High Concentration of Energy*, Preprint No. 35 of the Institute of Applied Mathematics of the USSR Academy of Sciences [in Russian], Moscow (1975).
7. S. Clark (ed.), *Handbook of Physical Constants of Rocks* [Russian translation], Moscow (1969).
8. M. P. Vukalovich, *Thermophysical Properties of Water and Water Vapor* [in Russian], Moscow (1967).
9. A. A. Bakanova, V. V. Zubarev, and Yu. N. Sutulov, *Zh. Eksp. Teor. Fiz.*, **68**, Issue 3, 1600-1610 (1975).