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EQUILIBRIUM AND KINETIC PROPERTIES OF AN ATOMIC-MOLECULAR PLASMA*

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Using methods of chemical thermodynamics a model of a wide-range equation of state of a multicomponent plasma of different substances and a procedure to calculate the kinetic coefficients of completely and partially ionized plasmas on the basis of a solution of the Boltzmann kinetic equation are developed.

Investigation of the equilibrium and kinetic properties of nonideal low-temperature plasmas is gaining in importance owing to increased investigation in the physics of pulse actions on various media with a complex chemical composition and to development of different pulse technologies on this basis [1]. Determination of the thermodynamic potentials and kinetic coefficients of a plasma of a complicated composition is of independent interest attributable to the study of the physical properties of nonideal systems with many parameters of interparticle interaction.

We calculated thermodynamic parameters and transport coefficients of a nonideal plasma under conditions of strong interaction between particles of all species contained in it.

1. Equilibrium Properties of a Nonideal Plasma. A model of the equation of state of a plasma is constructed in an approximation of the paired correlations in the charged subsystem, and it takes into account the influence of the inner electron shells of the atomic and molecular ions and the weak degeneracy of the electron component. The interactions between neutral particles of all varieties (atom–atom, atom–molecule, atom–ion, etc.) are calculated with account for the paired and three-particle correlations. The equation of state of the plasma that relates the pressure P, temperature T, and particle concentrations n_k is as follows:

$$P = T \left\{ \sum_{i=1}^{M} n_i \left[\frac{1}{1 - \sum\limits_{j=1}^{M} n_j b_{ij}} - \frac{1}{T} \sum_{j=1}^{M} n_j a_{ij} + \pi \left(\frac{e^2}{T} \right)^2 z_i^2 \sum_{j=1}^{M} n_j z_j^2 r_{ij} \right] + \right.$$

$$+ \frac{n_e^2 \lambda_e^3}{2^{7/2}} + \sum_{i=1}^{M} n_i^3 C_{iii} + 3 \sum_{i=1}^{M} \sum_{j=i+1}^{M} n_i n_j^2 C_{ijj} +$$

$$\left. + 6 \sum_{i=1}^{M-2} \sum_{j=i+1}^{M-1} \sum_{k=j+1}^{M} n_i n_j n_k C_{ijk} - \frac{\sqrt{\pi}}{3} \left[\frac{e^2}{T} \sum_{i=1}^{M} n_i z_i^2 \right]^{3/2} \right\}. \tag{1}$$

A numerical calculation shows that at high particle densities of different species ($n_k > 10^{20}$ cm^{-3}) the representative values of the particle-particle interaction parameters such as $n_k b_{kl}$, $n_i n_j C_{ijk}$ are comparable to the

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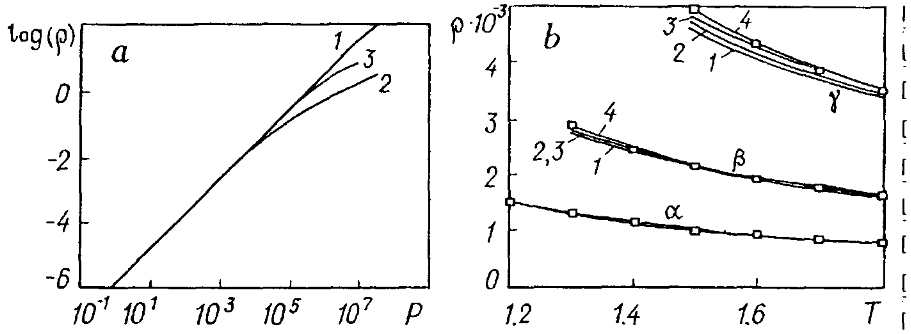

Fig. 1. Density of an atomic–molecular plasma: a) hydrogen (isotherm T = 7200 K): 1) ideal gas, 2) [2], 3) present work; b) sodium [isobars: α) $P = 5$ atm, β) $P = 10$ atm, γ) $P = 20$ atm, T = 1000 K]: 1) ideal gas, 2) [4], 3) present work, 4) [5]; points, experiment [6]. ρ, g/cm^3; P, atm.

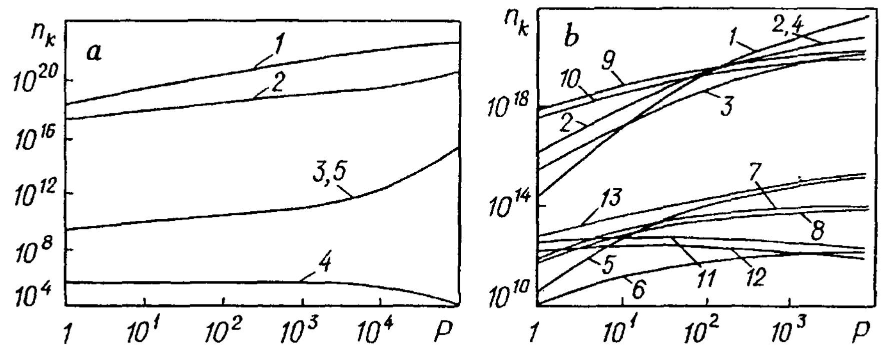

Fig. 2. Composition of a multicomponent plasma: a) oxygen (isotherm T = 3000 K): 1) O_2, 2) O, 3) O_2^+, 4) O^+, 5) e^-; b) water vapor (isotherm T = 5000 K): 1) H_2O, 2) H_2, 3) O_2, 4) OH, 5) H_2O^+, 6) H_2^+, 7) O_2^+, 8) OH^+, 9) H, 10) O, 11) H^+, 12) O^+, 13) e^-. n_k, cm^{-3}. The particle concentration of each species is denoted by the corresponding chemical symbol.

value of the Debye nonideality parameter $\Gamma = e^2/(r_D T)$. In this case, all the kinds of interparticle interactions are equally significant. For different classes of substances, inside which the atoms and molecules possess correspondingly close values of the ionization potentials and the dissociation energies, there are characteristic regions on the diagram of states where particle interactions of one or another type prevail.

We carried out extensive calculations of the thermodynamic functions and composition of the plasma of a wide class of pure substances: inert gases, hydrogen, oxygen, nitrogen, alkali vapor, aluminium, mercury, copper, etc. and water vapor. The results of the numerical calculations cover wide regions of the phase diagrams of these substances up to the stability limits of the thermodynamic model suggested. In some cases, for instance, for hydrogen, the calculations were made in the megabar pressure range. It should be noted that at elevated pressures $P > 10^2 - 10^4$ atm (depending on the kind of substance), along with thermal ionization and dissociation, ionization and dissociation by pressure play a significant role. The relationship between thermal ionization and dissociation and ionization and dissociation by pressure in a hydrogen plasma is discussed at length in [2, 3].

The results obtained using the suggested model of the equation of state were compared with existing experimental and theoretical data of other authors. As an example, Fig. 1 shows results of a density calculation for a hydrogen plasma (for comparison, data of [2] are shown) and a sodium plasma (here, results of theoretical calculations [4, 5] and an experiment [6] are given). Figure 2 shows composition data for oxygen and water vapor plasmas calculated by the suggested model.

2. Kinetic Properties of a Nonideal Plasma. To calculate the kinetic coefficients of a nonideal plasma, we solved the Boltzmann kinetic equation [7]

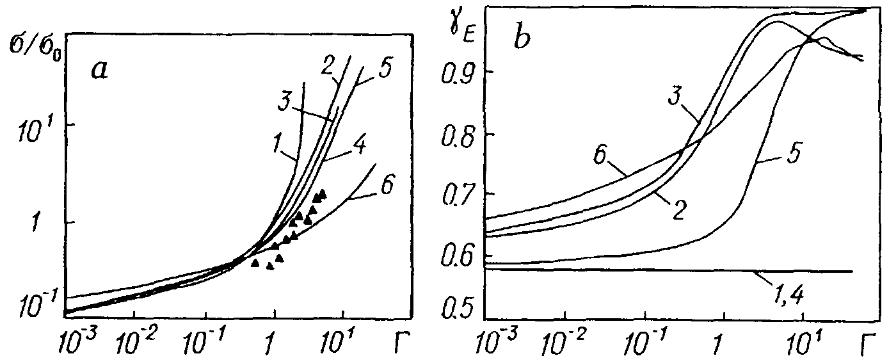

Fig. 3. Reduced electrical conductivity (a) and Spitzer factor (b) versus the nonideality parameter: 1) [9]; 2, 3) [11], without and with account for the off-logarithmic terms, respectively; 4, 5) the same, [10]; 6) [8]; 1-6) theory; points, experiment [12].

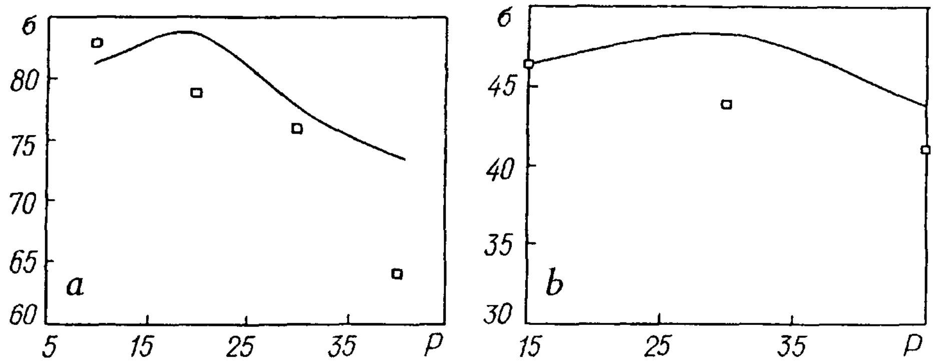

Fig. 4. Conductivity σ ($\Omega^{-1}\cdot\text{cm}^{-1}$) of a weakly nonideal plasma versus the pressure P (atm) along isotherms (curves, the present work; points, experiment [14]): a) argon, T = 16,400 K; b) xenon, T = 12,400 K.

$$\frac{\partial f_e}{\partial t} + (\mathbf{v}_e \nabla) f_e + \mathbf{F} \frac{\partial f_e}{\partial \mathbf{p}} = \mathrm{St}\,(f_e)\,. \tag{2}$$

The calculations were made for totally and partially ionized plasmas with allowance for electron–ion, electron–electron, and electron–atom collisions with the use of different calculation models of transport cross sections of scattering of charged particles. Kinetic equation (2) was solved by the Chapman–Enskog method with a 7th-order series expansion of the nonequilibrium correction to the distribution function f_e in Sonin polynomials for all species of colliding particles.

It was established that for a totally ionized plasma the Spitzer factor γ_e (being the ratio of the conductivities of a totally ionized plasma calculated with and without allowance for electron–electron collisions, respectively) is a function of the plasma nonideality parameter Γ for the majority of calculation models of transport cross sections. Introducing the notion of the reduced kinetic coefficient K^* (by analogy with the electrical conductivity σ^*), we can obtain a universal dependence $K^*(\Gamma)$ for all types of transport cross sections of scattering of charged particles, which was shown previously [8] for the short-range potential of the interaction between charges. Figure 3 shows the reduced conductivity and the Spitzer factor of a totally ionized plasma as a function of the nonideality parameter. We used different models of calculation of transport cross sections: our model from [8], data of theoretical calculations of other authors [9-11] and results [12] of experimental measurements of the Coulomb conductivity component. The calculations were made with and without account for the off-logarithm terms in the transport cross sections of electron–electron collisions of higher orders. Similar dependences exist for the remaining electron kinetic coefficients: α, λ, D, etc. Such calculations were also made for a multiply ionized charge-asymmetric plasma.

TABLE 1. Electrical Conductivity of a Singly Ionized Plasma

Pressure P, atm	Temperature T, K	Particle concentration, cm^{-3}			Γ	Conductivity σ, $\Omega^{-1}\cdot cm^{-1}$	
		n_a	n_i	n_e		experiment [12]	present work
Argon							
270	22,200	$3.0\cdot10^{19}$	$2.8\cdot10^{19}$	$2.8\cdot10^{19}$	0.55	185	224
700	20,300	$1.4\cdot10^{20}$	$5.5\cdot10^{19}$	$5.5\cdot10^{19}$	0.84	150	192
1550	19,300	$4.0\cdot10^{20}$	$8.1\cdot10^{19}$	$8.1\cdot10^{19}$	1.1	160	164
Xenon							
2000	30,100	$3.70\cdot10^{20}$	$2.5\cdot10^{21}$	$2.5\cdot10^{21}$	1.1	445	440
4400	27,500	$1.90\cdot10^{21}$	$5.9\cdot10^{21}$	$5.9\cdot10^{21}$	1.8	655	403

TABLE 2. Electrical Conductivity of a Doubly Ionized Xenon Plasma

Pressure P, atm	Temperature T, K	Particle concentration, cm^{-3}				Γ	Conductivity σ, $\Omega^{-1}\cdot m^{-1}$	
		n_a	n_i	n_i^{++}	n_e		experiment [13]	present work
4000	47,000	$3.0\cdot10^{19}$	$1.1\cdot10^{20}$	$1.9\cdot10^{20}$	$4.9\cdot10^{20}$	0.87	470	1140.0
7900	70,000	$2.9\cdot10^{19}$	$3.6\cdot10^{19}$	$2.6\cdot10^{20}$	$5.6\cdot10^{20}$	0.53	700	1860.8

In calculating the electron kinetic coefficients, calculation of the integral matrix elements of the electron–electron collision integral [7]

$$L_{rn}^{ee} = \frac{2}{n_e}\frac{m_e}{2T} \int\int \int\int f_e^0 f_{e_1}^0 v_e S_n^{3/2}\left(\frac{m_e v_e^2}{2T}\right) g_{ee_1} b \left|\frac{db}{d\chi}\right| d\chi\, d\varphi\, dv_e\, dv_{e_1} \times$$

$$\times \left[v_e' S_r^{3/2}\left(\frac{m_e v_e'^2}{2T}\right) - v_e S_r^{3/2}\left(\frac{m_e v_e^2}{2T}\right) + v_{e_1}' S_r^{3/2}\left(\frac{m_e v_{e_1}'^2}{2T}\right) - v_{e_1} S_r^{3/2}\left(\frac{m_e v_{e_1}^2}{2T}\right)\right], \quad (3)$$

is the most difficult task, and moreover the computational difficulties considerably increase with the numbers r, n of the expansion terms. To improve the accuracy of the calculation of the kinetic coefficients with account for higher approximations in the Sonin polynomials in the Chapman–Enskog method in expressions of the type (3) a special computer program in Pascal has been developed for analytical calculations. With its help we determined the contribution of electron–electron collisions to the kinetic coefficients of a completely ionized plasma with account for higher terms of the expansion up to the 7th order inclusive.

We also calculated the electrical conductivity of partially ionized argon and xenon plasmas in a wide region of the diagram of states for single and double ionization (Tables 1, 2); in the tables n_a, n_i, n_i^{++}, n_e are the concentrations of atoms, singly and doubly charged ions, and electrons, respectively. In the region of weak and moderate nonideality $\Gamma < 1$ the agreement of the calculated and experimental data can be considered to be satisfactory (Fig. 4, Table 1), and at $\Gamma > 1$ the calculated values are markedly smaller than the experimental ones. For a multiply charged partially ionized plasma the calculated conductivities are always considerably higher than the experimental ones (Table 2), and this is the case for all types of transport cross sections. The only exception is the case where the ideal-gas model is used to calculate the plasma composition, which is, however, not satisfactory from the viewpoint of performing the thermodynamic calculations.

Thus, we have suggested a rather universal model of a wide-range equation of state of a multicomponent nonideal plasma that allows calculation of the thermodynamic parameters of complex (including chemically reacting) systems with the use of particle-particle interaction parameters. A procedure is developed to calculate the electron kinetic coefficients of totally and partially ionized plasmas that is based on the solution of the Boltzmann equation for different types of the transport cross sections of scattering of charged particles. The results obtained are compared with existing experimental and theoretical data of other authors.

NOTATION

P, plasma pressure; T, plasma temperature; e, electron charge; z_i, particle charge of the species i in units of the electron charge; M, number of components; n_k, particle concentration of the k-th species; b_{kl}, a_{kl}, components of the second virial coefficient characterizing repulsion and attraction of particles of the species k and l, respectively; C_{ijk}, third virial coefficient; r_{ij}, sum of the radii of ion cores for particles of the corresponding species; $\lambda_e = (2\pi\hbar^2/m_e T)^{1/2}$, thermal de Broglie wavelength for an electron; m_e, electron mass; $\hbar$, Plank constant; Γ, nonideality parameter; r_D, Debye radius; f_e, electron distribution function; v_e, electron velocity; F, force acting on an electron from the side of the external field; ∇, gradient operator; p, electron momentum; $St(f_e)$, collision integral; γ_E, Spittzer factor; σ, plasma conductivity; K^*, reduced kinetic coefficient; σ^*, reduced conductivity; α, electron thermoelectromotive force; ρ, plasma density; λ, electron thermal conductivity; D, diffusion coefficient of electrons; subscript (superscript) e indicates the electron-component characteristic; $\mathbf{v}_e$, $\mathbf{v}_{e_1}$ and $\mathbf{v}'_e$, $\mathbf{v}'_{e_1}$, velocities of colliding electrons before and after a collision in the laboratory coordinate system; g_{ee_1}, relative velocity of colliding electrons; b, impact parameter; χ, angle of scattering; φ, polar angle; f_e^0, Maxwell distribution function; $S_r^{3/2}(x)$, Sonin polynomial of power r and order 3/2; L_{rn}^{ee}, determinant element of the electron–electron collision integral.

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