

The considerably greater prospects for applying systems of lines with distributed parameters as compared with the other schemes considered can be considered the general deduction from the estimates presented.

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EQUATION OF STATE OF HYDROGEN UP TO 10 MBAR

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The problem of calculating the equation of state of hydrogen in its exact formulation is insoluble by contemporary methods, and therefore it is necessary to resort to physical models or formal interpolations. One such model, the compressible covolume model (CCM), was formulated in [1] under another name.

The "covolume" V^o (a function of the pressure p) is a synonym for the "elastic volume" of [1]. In the present article the CCM is generalized to the case of a nonideal plasma, the covolumes of the molecular and atomic phases of hydrogen are constructed mainly on the basis of experimental data, and the complete equation of state of hydrogen up to a pressure of 10 Mbar is calculated in the temperature range T above 100°K for $p < 10$ kbar, and above the Debye temperature $\Theta(p)$ for $p > 10$ kbar.

Assuming the results and notation of [1], we note here only the generalization to the case of a plasma. There are five kinds of particles, differing in the index n : molecules H_2 ($n = m$), atoms H ($n = a$), ions H_2^+ ($n = i$), protons H^+ ($n = p$), and electrons e ($n = e$); the α_n are the concentrations of the particles, and the $V_n^o(p)$ are the covolumes. For molecules and atoms the covolumes are identified with the zero isotherms ($T = 0$) of the corresponding phases. According to estimates in [2] the Coulomb field of the charged particles is strongly self-screened, and can be neglected.

Electrons are formed as a result of the ionization of atoms or molecules. Strictly speaking, the very idea of ionization becomes indefinite when the particles are "close"; rather, one should speak of the excitation of electrons, of the removal of their degeneracy. On the other hand, when the temperature is lowered, the degeneracy of excited electrons shows up in the fact that they "sit" in orbits around protons or ions, forming neutral atoms or molecules. In accord with the fundamental idea of the additivity of free and elastic volumes [1], we add to the free volume $\alpha_p RT/p$ of electrons formed in the $\text{H} = \text{H}^+ + e$ reaction the elastic volume $\alpha_p V_a^o(p)$. At high temperatures there is no degeneracy, and only the first term is important; at low temperatures total degeneracy is approached, and only the second term is important. Similarly, for the $\text{H}_2 = \text{H}_2^+ + e$ reaction we add $\alpha_i V_m^o(p)$ to $\alpha_i RT/p$. From the law of conservation of charge $\alpha_p + \alpha_i = \alpha_e$.

We assume that in the equations from [1] an ideal electron gas (ionized or excited) has a Maxwell-Boltzmann distribution. Then the form of the CCM equations remains unchanged for a plasma if we formally supplement the definitions of the covolumes of charged particles: $V_p^o = V_a^o$, $V_i^o = V_m^o$, $V_e^o = 0$.

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We construct the zero isotherms of the molecular and atomic phases mainly on the basis of experimental data [3, 4] on an almost adiabatic compression of hydrogen in the 0.4-8-Mbar range in which the contribution to the pressure from heating is estimated as 20-30%.

The complete analytic form of the equation of state for the molecular phase is presented in [4], and the zero isotherm is separated out. However, in the formulas for thermal energy used there the term describing the rotational and vibrational internal degrees of freedom of the molecules was not taken into account. Adding in this term and requiring the reproduction of the relation connecting the density ρ , the pressure p , and the energy E in the working region, leads to a corrected zero isotherm which for $p > 0.1$ Mbar is well described by the interpolation formula

$$E_m^0 = 144.5\rho^2 - 3.68, \text{ kJ/g.} \quad (1)$$

At lower pressures the zero isotherm was given in tabular form on the basis of other experiments (cf. below).

In [3] the most probable zero isotherm of the atomic phase in the 2.8-10-Mbar range is shown graphically. It is satisfactorily described by the interpolation formula

$$P_a^0 = 1.27\rho^3, \text{ Mbar.} \quad (2)$$

A precise calculation of the zero isotherm of the atomic (metallic) phase of hydrogen is given in [5]. The calculated isotherm is appreciably "harder" than (2) and as a result doubts were raised in [5] as to the reliability of the experiment. In our opinion such a conclusion is premature. Let us recall that in the calculations the optimum structure of the solid metallic phase turned out to be anisotropic. Some rather persuasive arguments are presented in [6] in favor of the instability of such structures and in favor of the liquid state even at $T = 0$. If it is assumed that this possibility is realized at $T = 0$, or even for T slightly above zero, the objection to (2) is diminished. An anisotropic structure contains voids, and in the liquid state the atoms are more uniformly distributed over space. This can lead to an increase in the density of the liquid at the same pressure (analog - ice and water). Is not the experiment a reflection of just this fact in the present case?

Let us perform some more estimates. Let us recall the theoretical asymptotic behavior $\rho \rightarrow \infty$, which is obtained by assuming that the electrons are uniformly distributed over space (we retain this assumption in subsequent discussions):

$$E_a^0 = A/r^2 - B/r, \text{ Ry/atom,} \quad (3)$$

where r is the radius of a Wigner-Seitz cell in atomic units. The first term in (3) is the kinetic energy; $A = 2.210$. The second term contains contributions from the exchange interaction energy of the electrons ($B_{ex} = 0.916$) and the Madelung electrostatic energy ($B_{es} \approx 1.8$) which depends weakly on the lattice structure. Its value can be obtained in the following way. We imagine that hydrogen consists of independent spherical cells with a uniformly distributed negative charge (background) and a proton at the center. Then the electrostatic energy of a cell is exactly equal to $(B_{ep} + B_{ee})/r$, where $B_{ep} = 3$ is the contribution from the interaction of the proton with the background, and $B_{ee} = -6/5$ is the contribution from the interaction of the background with itself, so that $B_{es} \approx B_{ep} + B_{ee} = 1.8$, and in (3) $B = 2.716$. We note that both the calculated curve from [5] and all the other calculated curves cited in this paper are negligibly different from (3) in the $p > 3$ Mbar-range.

Now let us estimate the zero isotherm for low densities. We assume that each electron is strongly bound to its own nucleus, and that the atoms are spherically symmetric. Then in each atom the spread-out electron interacts only with its own proton. An equation of form (3) is obtained again, but now $B = B_{ep} = 3$. The new value of B differs from the old by only 10%, but this is sufficient to make the calculated zero isotherm somewhat "softer" than the experimental (2). These estimates show that (2) is not anomalous. For $p = 0$ and $B = 3$

we obtain $E_a^0 = -1.02$, which is also reasonable. For simplicity we set $B = 2\sqrt{A} = 2.973$, after which $E_a^0 = -1$ for $p = 0$, and the virial theorem is satisfied exactly: $3pV = 2(A/r^2) + (-2\sqrt{A}/r)$. Finally, for the atomic phase we take

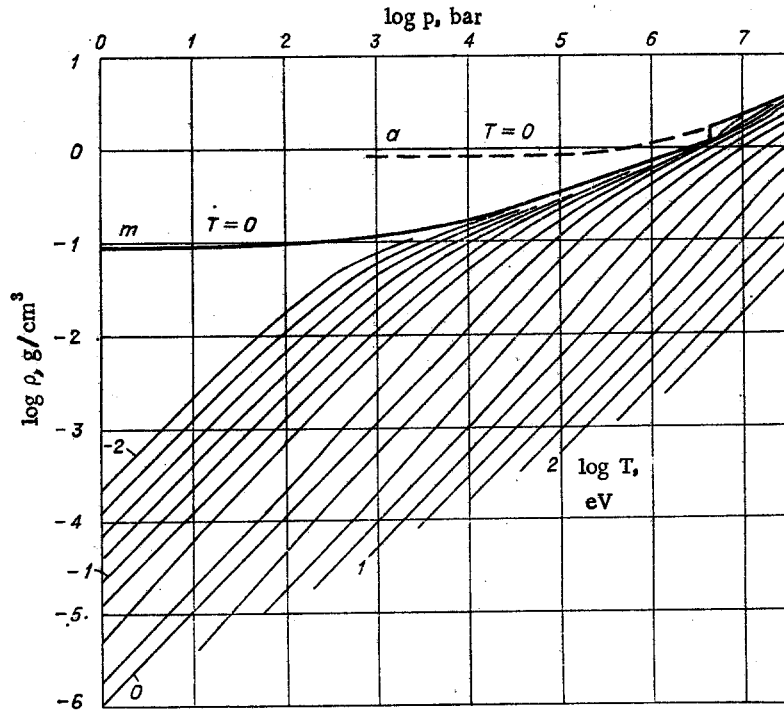


Fig. 1

$$E_a^0 = A/r^2 - 2\sqrt{A}/r + \Delta E, \quad (4)$$

where the constant $\Delta E = 1.1645$ (the sum of the ionization potential of the atom and half the dissociation energy of a molecule) is introduced for agreement of the zero energy levels in (4) and (1).

According to (4) and (1) the equilibrium of the molecular and atomic phases at $T = 0$ occurs for $1.15 \leq \rho \leq 1.61 \text{ g/cm}^3$ for $p = p_* = 4.40 \text{ Mbar}$. Generally speaking, p_* depends on temperature, and is very sensitive to nuances of the equations of state of the phases.

The CCM does not describe quantum phenomena at a temperature T below the Debye Θ . Let us estimate it. According to the Debye model quantum phenomena are unimportant for $T > \Theta$, while at $T = \Theta$ the entropy S in units of the Boltzmann constant k per molecule or atom is 4. We call the Debye temperature the temperature at which $S = 4$. In the CCM for the degrees of freedom of the centers of gravity of the particles

$$S(T, p) = \frac{5}{2} + \ln \frac{kT}{p\lambda^3}, \quad (5)$$

where λ is the de Broglie thermal wavelength. Setting $S = 4$ and $T = \Theta$ in (5), we obtain

$$\Theta = Cp^{2/5},$$

where p is in Mbar, Θ in $^\circ\text{K}$, and $C = 1300$ for the molecular phase and 2000 for the atomic phase.

Ordinarily, the dissociation of molecules in an ideal gas is called "temperature dissociation," and the transformation of the molecular phase into the atomic at the zero isotherm "pressure dissociation." The CCM combines both kinds of dissociation into one for all temperatures and pressures. The equations for equilibrium concentrations have the form of ordinary Saha equations, but in contrast with the case of an ideal gas, the equilibrium constants are multiplied by factors of the form $\exp(-\Delta\phi^0(p)/kT)$, where $\Delta\phi^0$ is the change in the covolume chemical potential in the given reaction. For example, in the formation of two atoms from one molecule $\Delta\phi^0 = 2\phi_a^0 - \phi_m^0$. This shift can be formally interpreted as the change in the dissociation energy of a molecule, which is a function of the pressure.

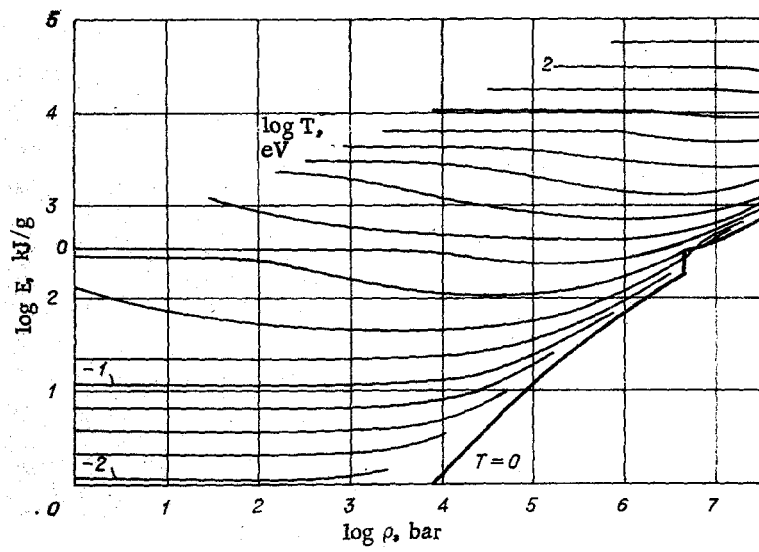


Fig. 2

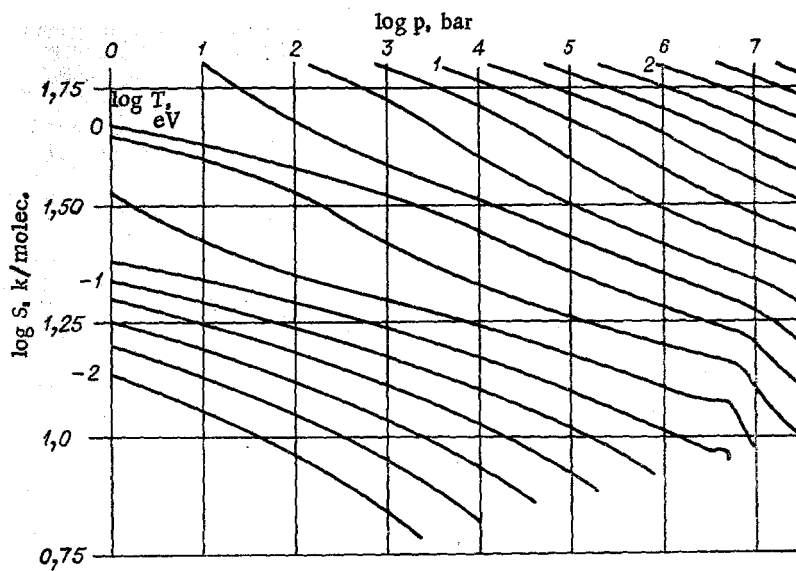


Fig. 3

TABLE 1

p, kbar	$v_m^0, \text{cm}^3/\text{mole}$	p, kbar	$v_m^0, \text{cm}^3/\text{mole}$	p, kbar	$v_m^0, \text{cm}^3/\text{mole}$
0,5	16,17	3,0	14,97	5,5	13,75
1,0	16,05	3,5	14,71	6,0	13,54
1,5	15,81	4,0	14,45	6,5	13,33
2,0	15,54	4,5	14,20	7,0	13,14
2,5	15,26	5,0	13,97		

TABLE 2

p , Mbar	V_e , cm ³ /mole	v , cm ³ /mole	T , °K	E , kJ/mole	s , /molec.	α_m
0,0395	10,5±0,3	10,8	1200	34	11,4	1,000
0,21	7,0±0,4	6,80	5000	178	15,8	0,975
0,86	3,4±0,8	3,67	7200	346	16,5	0,887

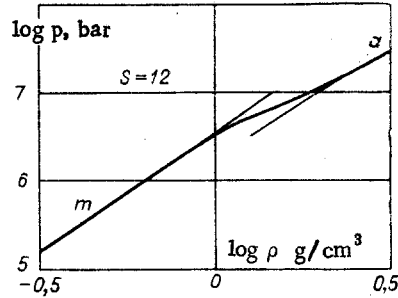


Fig. 4

It is clear that at sufficiently high temperatures a substance is homogeneous; i.e., it consists of components which are not separated into phases in space. On the other hand, at absolute zero, and near it, there is a region of coexistence of the molecular and atomic phases. Consequently, at some "intermediate" temperature a critical point must exist. For $T > 0$ the CCM does not describe two-phase states in principle; it is essentially "subcritical." Nevertheless, as the temperature is lowered the isotherms acquire a characteristic inflection close to the critical point under the influence of the contribution of zero isotherms. If the inflection is pronounced, its effect on the Poisson adiabat is hardly different from that of a phase transition of the first kind.

The calculated values of thermodynamic quantities are shown in Figs. 1-3 in the form of isotherms. Instead of the quantities themselves, their common logarithms are plotted. The difference in $\log T$ between two neighboring isotherms is 0.25; the maximum range of variation of T is from 0.01 eV ($\log T = -2$) to 316 eV ($\log T = 2.5$).

The second independent variable (the pressure p) is varied from 1 bar to 30 Mbar. We note that close-packed spheres having radii of 1 bohr correspond to a density of 2 g/cm³ and a pressure of 8 Mbar, so that for $p \leq 10$ Mbar atoms and molecules are still rather independent and only slightly compressed. For $p > 10$ Mbar the characteristic parameter for electron excitation will be the Fermi energy rather than the ionization potential. Therefore, a pressure of 10 Mbar is a rough estimate of the limit of applicability of the CCM for a plasma.

The zero isotherm of the molecular phase was taken from experiment up to 25 kbar [7] and extrapolated graphically to 100 kbar. With such a covolume the CCM reproduces the known experimental data on static compression up to 7 kbar for $T = 25-150^\circ\text{C}$ [8], and on shock compression up to ~ 40 kbar [9] with an error of no more than 5% for the density at the given pressure. We note that the static data [8] are reproduced with a very small error ($< 0.5\%$) if the covolume is taken from Table 1.

In addition, there are experiments [10] on single and double shock compression of liquid deuterium up to 210 ± 10 and 860 ± 50 kbar, respectively. Calculations using the CCM with the zero isotherms (1) and (4) agree with experiment within the limits of error of the measurements. Table 2 lists the calculated parameters for states at the front in three shock waves, and also, for comparison, the experimental values of the specific volume V_e .

According to our estimates, the working region in the experiments [3, 4] corresponds to an entropy S of ≈ 12 per molecule. This isoentropes is shown in Fig. 4. It is clear that the pronounced inflection on it is due to the dissociation of molecules into atoms. The thin lines denote isentropes in purely molecular and purely atomic phases. At a suffi-

ciently low temperature dissociations lead to a "softening" of the Poisson adiabat as a result of the formation of atoms, and adiabats with $S < 12$ partially pass under the zero isotherm $\rho_m^0(p)$ for $p < p_*$. The beginning of dissociation (anomaly) on the $S = 12$ adiabat is lowered to ~ 3 Mbar in agreement with the conclusions of the experimenters. We note that the construction of diagrams for equilibrium between purely molecular and purely atomic phases (each by the CCM) leads to an increase in p_* with increasing temperature, and the two-phase region on the $S = 12$ isentrope is almost the $p = 5.4$ -Mbar isobar and almost the $T = 0.41$ -eV isotherm.

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CALCULATIONS OF A HIGH-POWER UNDERWATER EXPLOSION TAKING VAPORIZATION INTO ACCOUNT USING THE GENERALIZED EQUATION OF STATE OF WATER

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The complexity of a theoretical investigation of high-power underwater explosions is mainly due to the fact that, according to estimates [1], at the initial instant gigantic pressures of up to 10^{10} bar and temperatures of tens of millions of degrees are reached. As a result, in the subsequent expansion, a large bubble is formed filled with water in the gaseous state and surrounded by concentric two-phase liquid-vapor layers. At the same time, in explosions using chemical explosives a cavity is formed containing mainly uncondensed products of the explosion, for which it is difficult to choose adequate equations of state suitable for calculating the action of the explosion [2-4]. In order to take into account in the calculations of a high-power underwater explosion the specific features connected with evaporation, dissociation of water, and ionization of its components, it is necessary to use the equation of state of water over a wide range of variation of the thermodynamic parameters. A fairly realistic model for calculating a high-power underwater explosion was set up in [5], where the equation of state of water describing the whole region enveloped by the shock wave was used, and the development of the explosion was considered, but the calculations were carried out for the initial stage of the formation of the two-phase region, and the effects of vaporization were not clarified in explicit form and were not analyzed.

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