ON THE THERMODYNAMICS OF PARTIALLY IONIZED HYDROGEN

1969

SovietRxiv

Abstract

Full Text

UDC 533.9

PHYSICS

E. V. SAMUILOV

ON THE THERMODYNAMICS OF PARTIALLY IONIZED HYDROGEN

(Presented by Academician V. N. Kondrat’ ev, 18 XI 1968)

A system is considered that consists of hydrogen atoms, protons, and electrons, deviating only weakly from an ideal one, i.e., under the condition

$$e^2/\bar{r}kT \ll 1, \tag{1}$$

where $\bar{r}$ is the mean distance between ions; the remaining notation is conventional. It is assumed that the interaction energy of two charged particles a and b, when the distance between them is r, has the form

$$U_{ab} = z_a z_b e^2 \exp(-\varkappa r)/r, \tag{2}$$

where z_a, z_b are integers equal to $+1$ or -1; $\varkappa$ is the Debye screening constant.

1. We start from the statistical sum of the grand canonical ensemble Ξ, represented in a form in which the physical groups are explicitly taken into account. Taking into account that two protons or two electrons do not form bound states, and restricting the calculations only to groups of one or two particles, the sum Ξ may be written in the form

$$\Xi = 1+\lambda_1^{(+)}Q_{10}^{00}+\lambda_1^{(-)}Q_{00}^{10}+\lambda_2^{(+-)}\overline{Q}_{0\,1/2}^{0\,1/2}+\lambda_1^{(+)2}Q_{20}^{00}+\lambda_1^{(-)2}Q_{00}^{20}+\lambda_1^{(+)}\lambda_1^{(-)}\overline{Q}_{10}^{10}, \tag{3}$$

where

$$\lambda_i^{(ab)} = \exp\left(\mu_i^{(ab)}/kT\right);$$

$\mu_i^{(ab)}$ is the chemical potential of a group consisting of i particles of species (ab) (protons are denoted by the plus index, electrons by the minus index). In the group statistical sum $Q_{l\,k/2\,m/3\ldots}^{i\,j/2\,s/3\ldots}$, the upper row of indices is used to denote the number of protons in the group, and the lower row for electrons. The first index in each row denotes the number of free particles of the given species, the second index the number of bound pairs of particles of the given species, etc.

The group statistical sums are related in the following way to the statistical sums of the canonical ensemble of n protons and r electrons:

$$Q_r^n = \sum_{\substack{i+j+\ldots\leq n\\ l+k+\ldots\leq r}} Q_{l\,k/2\,m/3\ldots}^{i\,j/2\,s/3\ldots}, \tag{4}$$

which depend on the volume V and the temperature T.

The sum $\overline{Q}_{0\,1/2}^{0\,1/2}$, describing the bound states of a proton and an electron, and the sum $\overline{Q}_{10}^{10}$, corresponding to the free states of a proton and an electron, are certain average quantities (as indicated by the bar above). The meaning of this averaging is clarified below. Because of the approximate method of calculation, the sums $\overline{Q}_{0\,1/2}^{0\,1/2}$, $\overline{Q}_{10}^{10}$, Q_{20}^{00}, Q_{00}^{20}, in addition to V and T, also depend on $\lambda_1^{(+)}$ and $\lambda_1^{(-)}$.

2. To compute the sums $\overline{Q}_{0\,1/2}^{0\,1/2}$, $\overline{Q}_{10}^{10}$ in the phase space of two particles, a proton and an electron, it is necessary to separate the regions of bound and free states. This can be done by determining the maximum value of the principal quantum number $n_{\max}$ at which the hydrogen atom is still stable, according to the Stark effect in a strong electric field. Assuming,

that the field around the hydrogen atom is produced by the nearest ion, located at a distance r^* from the hydrogen atom; the intensity ε of this field can be written in the form:

$$\varepsilon = -\frac{z_a e}{r^{*2}}(1 + \chi r^*)\exp(-\chi r^*), \tag{5}$$

which, according to (1), is related to $n_{\max}$ by the relation

$$\varepsilon = e/8n_m^4 a_0^2. \tag{6}$$

Choosing as the zero level of energy the energy of a proton and electron at rest and located at a large distance from one another, we find that for values of the total energy greater than

$$E_m = -e^2/2n_m^2 a_0, \tag{7}$$

the electron and proton will be in a free state. The mean field in which a free electron is found, being in the field of a proton and in the field of the ion nearest to this proton-electron system, as is not difficult to verify, may be approximated by the expression

$$\overline{U} = -e^2 e^{-\chi r}/r. \tag{8}$$

According to (2), the probability that the ion nearest to the atom lies in the region from r^* to $r^* + dr^*$ is

$$w(r^*)\, dr^* = 4\pi r^{*2} \bar{n} \exp\left(-4\pi \int_0^{r^*} \rho^2 \bar{n}(\rho)\, d\rho\right) dr^*, \tag{9}$$

where

$$\bar{n}(r^*) = \frac{n_+}{2} \exp\left(-\frac{U_s(r^*)}{kT}\right) + \frac{n_+}{2} \exp\left(-\frac{U_p(r^*)}{kT}\right); \qquad n_+ = \frac{\overline{N}_1^{(+)}}{V}; \qquad n_e = \frac{\overline{N}_1^{(-)}}{V};$$

U_s, U_p are the potentials of interaction of a proton with a hydrogen atom; $\overline{N}_1^{(+)}, \overline{N}_1^{(-)}$ are the mean numbers of protons and electrons, respectively, in the system.

3. Using the known expressions for $Q_n^{(3)}$ and relation (4), we find

$$Q_{00}^{10} = V\Lambda_+^{-3}; \qquad Q_{10}^{00} = Q_{eV}\Lambda_-^{-3}; \qquad Q_{00}^{20} = \frac{V^2}{2\Lambda_+^6}\,\bar{\varepsilon}; \qquad Q_{20}^{00} = Q_e^2 \frac{V^2}{2\Lambda_-^6}\,\bar{\varepsilon}, \tag{10}$$

where

$$\bar{\varepsilon} = 1 - \frac{4\pi}{V}\frac{e^2}{\chi^2 kT} + \frac{4\pi}{V}\frac{e^4}{4(kT)^2\chi}; \qquad \Lambda_i = h/(2\pi m_i kT)^{1/2}; \qquad Q_e = 2.$$

After transformations, the sum Q_1^1 can be written in the form

$$Q_1^1 = \frac{Q_e V}{h^3 \Lambda_+^3} \int \exp\left(-\frac{p^2}{2\mu kT} - \frac{U(r)}{kT}\right) dp\, dr, \tag{11}$$

where μ is the reduced mass; r is the distance between the proton and the electron; p is the momentum in the center-of-inertia system.

We represent the integral in (11) as the sum of two integrals: one over the region (p, r) corresponding to the free states of the proton and electron and defined by the relations

$$\left.\begin{array}{ll} p \geqslant 0; & p^2/2\mu + \overline{U}(r) \geqslant -|E_m(r^*)|; \\ -\overline{U}_{\min} \leqslant \overline{U}(r) \leqslant \infty & \end{array}\right\} \text{ region I,} \tag{12}$$

and the other over the region (p, r) corresponding to bound states of the proton and electron and defined by the relations

$$\left.\begin{array}{ll} p \geqslant 0; & p^2/2\mu + \overline{U}(r) \leqslant -|E_m(r^*)|; \\ -\overline{U}_{\min} \leqslant \overline{U}(r) \leqslant -|E_m(r^*)|, & \end{array}\right\} \text{ region II,} \tag{13}$$

where $-\overline{U}_{\min}$ is the minimum value of the interaction energy of the proton and electron. The sum (11) then splits into two terms. The first, in which the integral over region I enters as a factor, will be equal to Q^{10}_{10}, the second $Q^{0\,1/2}_{0\,1/2}$. The integral over the bound states of the proton and electron follows–

is to replace it by the quantum-mechanical sum over the discrete states of the hydrogen atom, as a result of which we obtain

$$Q^{0^{1/2}}_{0^{1/2}}(r^*) = 2V\Lambda_+^{-3} \sum_{n=1}^{n_m(r^*)} n^2 \exp\left(\frac{e^2}{2n^2 a_0 kT}\right). \tag{14}$$

The sum Q^{10}_{10} can be transformed to the form:

$$Q^{10}_{10}(r^*) = \frac{Q_e V^2}{\Lambda_+^3 \Lambda_-^3}\left[1 + \frac{4\pi}{V}\frac{e^2}{kT\chi^2} + \frac{4\pi}{V}\frac{e^4}{4(kT)^2\chi} - \frac{16\pi^{1/2}}{V}\int_0^{P_m(r^*)} f(P^2)\exp(-P^2)\,dP\right]. \tag{15}$$

where

$$f(P^2) = P^2 \int_{r_1(P)}^{r_2(P)} \exp\left[-\frac{\overline{U}(r)}{kT}\right] r^2\,dr;$$

$$P_m = \sqrt{(-|E_m| + \overline{U}_{\min})/kT};$$

for the potential (2) $r_1 = 0$, while r_2 is determined from the equation:

$$-\frac{e^2}{r_2}\exp(-\chi r_2) = -|E_m(r^*)| - P^2 kT. \tag{16}$$

The sums $\overline{Q}^{10}_{10}$ and $\overline{Q}^{0^{1/2}}_{0^{1/2}}$ are calculated by averaging the sums Q^{10}_{10} and $Q^{0^{1/2}}_{0^{1/2}}$ over all possible r^* $(0 \leq r^* \leq \infty)$ with the aid of (8).

4. Using the known relation between the mean number of particles of a given species in the system and the statistical sum Ξ (3), one can, in general form, determine $\overline{N}_1^{(+)}$, $\overline{N}_1^{(-)}$, $\overline{N}_2^{(+-)}$ ($\overline{N}_2^{(+-)}$ is the mean number of hydrogen atoms) through the quantities $\lambda_i^{(ab)}$, $Q_{i\,j/2\ldots}^{i\,k/2\ldots}$ and derivatives of the group sums with respect to $\lambda_i^{(ab)}$. The quantities $\lambda_i^{(ab)}$ may be regarded as a small parameter, with $\lambda_2^{(+-)} \sim \lambda_1^{(+)2}$. Using this circumstance, we find an expression for $\overline{N}_i^{(ab)}$ through $\lambda_i^{(ab)}$ in the first approximation and, substituting this expression in place of $\overline{N}_i^{(ab)}$ in Q_{20}^{00}, Q_{00}^{20}, $\overline{Q}_{10}^{10}$, $\overline{Q}_{0^{1/2}}^{0^{1/2}}$, calculate the derivatives of the group sums with respect to $\lambda_i^{(ab)}$. From the expressions now obtained in explicit form for $\overline{N}_i^{(ab)}$ through the group sums and $\lambda_i^{(ab)}$, by the method of successive approximations, we find $\lambda_i^{(ab)}$ and, using the condition of chemical equilibrium $\lambda_2^{(+-)} = \lambda_1^{(+)}\lambda_1^{(-)}$, obtain the law of mass action

$$\frac{\overline{N}_1^{(+)}\overline{N}_1^{(-)}}{\overline{N}_2^{(+-)}} = \frac{Q_{eV}}{Q_H\Lambda_-^3}\exp\left\{\frac{\overline{N}_1^{(+)}+\overline{N}_1^{(-)}}{V}\left[\frac{3}{2}\frac{\pi e^4}{(kT)^2\chi}\right.\right.$$

$$\left.-16\pi^{1/2}\int_0^\infty\int_0^{P_m}\left(f(P^2)\left(1+\frac{v(r^*)}{2}\right)+\varphi(P^2)\right)e^{-P^2}\,dP\,w(r^*)\,dr^*\right]+$$

$$\left.+\frac{2\overline{N}_2^{(+-)}}{\overline{N}_1^{(+)}+\overline{N}_1^{(-)}}\frac{1}{Q_H}\int_0^\infty\left(q(r^*)+Q_H(r^*)v(r^*)\right)w(r^*)\,dr^*\right\}, \qquad (17)$$

where

$$\varphi(P^2) = P^2\frac{\chi}{4}\left[\int_{r_1}^{r_2}\left(-\frac{\overline{U}_\chi}{kT}\exp\left(-\frac{\overline{U}}{kT}\right)r^2\,dr\right)+\right.$$

$$\left.+r_2^2\frac{\partial r_2}{\partial\varkappa}\exp\left[-\frac{\overline{U}(r_2)}{kT}\right]-r_1^2\frac{\partial r_1}{\partial\varkappa}\exp\left[-\frac{\overline{U}(r_1)}{kT}\right]\right\};$$

$$\nu(r^*) = \left[\left(1-4\pi\int_0^{r^*}\rho^2\overline{n}(\rho)\,d\rho\right)+\frac{\varkappa}{2}\left(\frac{1}{\overline{n}}\frac{\partial\overline{n}}{\partial\varkappa}-4\pi\int_0^{r^*}\frac{\partial\overline{n}}{\partial\varkappa}\rho^2\,d\rho\right)\right];$$

$$q(r^*) = \frac{1}{24}\,\frac{n_m(6n_m^2+6n_m+1)(\varkappa r^*)^2}{1+\varkappa r^*}; \qquad \overline{U}_\varkappa = \frac{\partial\overline{U}}{\partial\varkappa}; \qquad Q_H = Q_{0\,1/2}^{0\,1/2}\Lambda_1^3V^{-1}.$$

Using the known relation between the pressure p and the statistical sum Ξ (3), we obtain the equation of state

$$p = \frac{\overline{N}kT}{V} - \frac{(\overline{N}_1^{(+)} + \overline{N}_1^{(-)})^2}{V^2} \Bigg[\frac{\pi e^4}{4kT\varkappa} - 4\pi^{1/2}kT \int_0^\infty \int_0^{P_m} (f(P^2)(1+\gamma(r^*))$$
$$-2\varphi(P^2) - \psi(P^2)) \exp(-P^2)\,dP\,w(r^*)\,dr^*]$$
$$+ \frac{\overline{N}_2^{(+-)}kT}{VQ_H} \int_0^\infty \left(\frac{1}{3} q(r^*) \left(\frac{4(1+\varkappa r^*)}{(\varkappa r^*)^2} - 1 \right) - Q_H(r^*)\gamma(r^*) \right) w(r^*)\,dr^*, \tag{18}$$

where

$$\gamma(r^*) = 2\overline{n}_\varkappa(r^*) + \frac{r^*}{3}\frac{\partial \ln \overline{n}}{\partial r^*} + \frac{4}{3}\pi \overline{n}(r^*) r^{*3} - 4\pi \int_0^{r^*} \overline{n}(\rho)\rho^2\,d\rho; \qquad \overline{N} = \overline{N}_1^{(+)} +$$

$$+\overline{N}_1^{(-)} + \overline{N}_2^{(+-)}; \qquad \overline{n}_\varkappa = \frac{\varkappa}{4}\left(\frac{1}{\overline{n}}\frac{\partial \overline{n}}{\partial \varkappa} - 4\pi \int_0^{r^*} \frac{\partial \overline{n}}{\partial \varkappa}\rho^2\,d\rho \right); \qquad \psi(P^2) = -\frac{P^2}{3} r^* \left(r_2^2 \frac{\partial r_2}{\partial r^*} \times \right.$$

$$\left. \times \exp\left[-\frac{\overline{U}(r_2)}{kT} \right] - r_1^2 \frac{\partial r_1}{\partial r^*} \exp\left[-\frac{\overline{U}(r_1)}{kT} \right] \right).$$

All thermodynamic functions can be calculated in an analogous manner.

5. If one uses the expression for the free energy of ideal partially ionized hydrogen, in which the statistical sum of the internal degrees of freedom of the hydrogen atom is replaced by $\widetilde{Q}_H$, adds to this expression the correction for nonideality due to the interaction of protons and electrons (in approximation (1)) in the form in which it is given in (4) for a fully ionized gas, and obtains, with the aid of this free energy, the law of mass action and the equation of state, then the expressions obtained will differ from (17) and (18) in that they will not contain the integral term in the square brackets and the coefficients at $\pi e^4/kT\varkappa$ or $\pi e^4/(kT)^2\varkappa$ will contain an additional factor equal to $8/3$. The latter is explained by the model character of the potential (2). In calculations, the factor $8/3$ should additionally be taken into account before the square bracket in (17) and (18). The integral corrections in the square brackets make it possible, in taking account of the deviation of the system from ideality, to avoid simultaneous accounting for some part of the bound states both in the quantum-mechanical statistical sum of the atom and in the usual classical method of accounting for the interaction between charged particles.

State Scientific-Research
Energy Institute
named after G. M. Krzhizhanovsky

Received
25 X 1968

CITED LITERATURE

1. H. Bethe, E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Moscow, 1960.
2. S. Chandrasekhar, *Statistical Problems in Physics and Astronomy*, Moscow, 1947.
3. T. Hill, *Statistical Mechanics*, Foreign Literature Publishing House, 1960.
4. L. D. Landau, E. M. Lifshitz, *Statistical Physics*, Moscow, 1951.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.