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Abstract

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EQUILIBRIUM IONIZATION OF PARTICLES

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Two principal works are known in which the equilibrium ionization of particles is considered. For the first time, Saha (1), applying methods for calculating chemical equilibria to the ionization of metal atoms, obtained the well-known formulas for the concentration of electrons and the equilibrium constant in single ionization. In Eynbinder' s work (2), the ionization of solid particles was considered. Eynbinder, taking into account the possibility of the formation of various positive charges on the particles, set up a system of equations connecting the successive stepwise ionization of particles, and solved it for the case of a high degree of ionization*.

In the present work we shall give a general solution of the problem of equilibrium ionization of particles, covering all cases from multiple ionization of atoms to ionization of macroscopic particles.

Let us consider a system consisting of electrons and homogeneous particles P, which may have various positive or negative charges. The ionization equilibrium in such a system is completely determined by the law of mass action and by the laws of conservation of charge and mass, which may be written in the form

$$K_m = N_{m+1} N_e / N_m; \qquad N_e = \sum m N_m; \qquad N = \sum N_m; \qquad -\infty < m \leq M, \tag{1}$$

where K_m is the equilibrium constant for the process $P_m \rightleftarrows P_{m+1} + e$; N_m is the concentration of particles P with charge m; N_e is the concentration of electrons; N is the total concentration of particles; and m is the particle charge in units of the electron charge e_0. The limits of variation of m take into account all possible processes of ionization and electron capture in the system under consideration. The upper limit M corresponds to the maximum positive charge and is equal to the total number of electrons in the particle. The maximum negative charge may be regarded as infinite, since in principle all $M_\Sigma - M$ electrons of the system can "stick" to one particle.

From the expression for K_m, as was noted in (2), there follows the recurrence relation

$$N_m = \frac{K_{m-1}}{N_e} N_{m-1} = \frac{K_{m-1}}{N_e}\frac{K_{m-2}}{N_e} N_{m-2} = \cdots = N_0 \prod_{i=0}^{m-1} \frac{K_i}{N_e}, \tag{2}$$

which makes it possible to write the expression for the degree of ionization N_e/N:

$$\frac{N_e}{N} = \sum_{m=-\infty}^{M} m \prod_{i=0}^{m-1} \frac{K_i}{N_e} \Big/ \sum_{m=-\infty}^{M} \prod_{i=0}^{m-1} \frac{K_i}{N_e}. \tag{3}$$

Equation (3) is the general equation of ionization of homogeneous particles.

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* Eynbinder did not take into account that, along with positive charges, negative charges may also be formed on particles, which radically changes the solution for a low degree of ionization, when Eynbinder assumed only Saha' s equation to be valid.

The equilibrium constants K_m for an ideal gas have the form

$$K_m = 2(q_{m+1}/q_m)(2\pi m_e kT/h^2)^{3/2} \exp[-\varphi_m/kT], \qquad \varphi_m = \varphi_0 + me_0^2/r, \tag{4}$$

where m_e is the electron mass; k and h are the Boltzmann and Planck constants; T is the absolute temperature; q_m is the statistical weight of the particle P_m; φ_m is the work function for an electron from an m-fold charged particle, or its ionization energy. In the expression for φ_m, the term me_0^2/r takes into account the change in the work function due to the charge m of the particle; r is the characteristic size, coinciding with the radius for spherical particles*.

Expressions (4) make it possible to transform the products in (3)

$$\prod_{i=0}^{m-1} \frac{K_i}{N_e} = \left(\frac{K}{N_e}\right)^m \frac{q_m}{q_0} \exp\left[-\frac{m(m-1)}{2\sigma^2}\right], \tag{5}$$

where $K = 2(2\pi m_e kT/h^2)^{3/2} \exp[-\varphi_0/kT]$, $\sigma^2 = rkT/e_0^2$.

Substituting (5) into the general equation (3), after transformations we obtain

$$\frac{N_e}{N} = \sum_{m=-\infty}^{M} q_m m \exp\left[-\frac{(m-y)^2}{2\sigma^2}\right] \Big/ \sum_{m=-\infty}^{M} q_m \exp\left[-\frac{(m-y)^2}{2\sigma^2}\right]; \tag{6}$$

$$y = \sigma^2 \ln(K/N_e) + \frac{1}{2}. \tag{7}$$

The meaning of (6) can be understood if the same transformations are carried out in (2) and (5), which, without taking q_m into account, gives

$$N_m = N_0 \exp(y^2/2\sigma^2) \exp[-(m-y)^2/2\sigma^2]. \tag{8}$$

For continuous m and $M = \infty$, the normalization condition $N = \int_{-\infty}^{\infty} N_m \, dm = N_0 \sigma \sqrt{2\pi} \exp(y^2/2\sigma^2)$ makes it possible to obtain from (8) the law of distribution of charges over particles

$$N_m/N = (1/\sigma\sqrt{2\pi}) \exp[-(m-y)^2/2\sigma^2], \tag{9}$$

which coincides with the probability density of the normal Gaussian distribution. $N_m/N = f(m)$ has a maximum at $m = y$ (y is the center of the distribution) and inflection points at $m = y \pm \sigma$. In the terms of probability theory, the mean value, or mathematical expectation, of the particle charge is $M(m) = y$, and the measure of charge dispersion, or variance, is $D(m) = \sigma^2$. The quantity $\sigma = \sqrt{D(m)}$ has a simple meaning: σ is the number of charges between the mean $\overline{m} = y$ and the charge corresponding to the inflection point. As calculation shows, the number of particles with charges from $y - \sigma$ to $y + \sigma$ amounts to ~ 0.7 of the total number of particles.

By the change of variables $m - y = z$, we separate in (6) the center of summation y

$$\frac{N_e}{N} = y + \sum_{z=-\infty}^{M-y} q_m z \exp\left[-\frac{z^2}{2\sigma^2}\right] \Big/ \sum_{z=-\infty}^{M-y} q_m \exp\left[-\frac{z^2}{2\sigma^2}\right] = y + R, \tag{10}$$

whence it is seen that, owing to the discreteness of m, the finiteness of the upper limit, and the presence of statistical weights, N_e/N differs from y by the amount R.

The principal factor determining the deviation of N_e/N from y is the discreteness of m. The finiteness of the upper limit has a substantial effect only in the approximation to complete ionization, when $M - y \lesssim \sigma$, but in this case the limiting solution is trivial: $N_e/N = M$. The influence of statisti–

* For atoms, the relation between φ_m and φ_0 in the form (4) is valid approximately within the limits of each electron shell.

···weights manifests itself in a violation of the symmetry of the functions standing under the signs of the sums in (10). In the first approximation this can be eliminated by introducing the mean-weighted values $\bar{q}_m$ and reducing them. The absence of q_m for $M - y = \infty$ makes it possible to simplify the subsequent transformations.

Let us pass in R from sums to integrals by the Euler formula (3)

$$h\sum_{z=a}^{b} f(z) = \int_a^b f(z)\,dz + \frac{1}{2}h[f(a)+f(b)] + 2\sum_{n=1}^{\infty}\int_a^b f(z)\cos\frac{\theta}{h}(z-a)\,dz, \quad (11)$$

where h is the summation step and $\theta = 2\pi n$. In our case $h = \Delta m = 1$, $b = M - y = \infty$, $a = -(M_\Sigma - M) - y = -\infty$. Taking into account that the integrals in the numerator and denominator of R are respectively equal to

$$I_1 = \sigma\sqrt{2\pi}\exp(-\theta^2\sigma^2/2)\sin\theta y \quad \text{and} \quad I_2 = \sigma\sqrt{2\pi}+\sigma\sqrt{2\pi}\cdot 2\sum_{n=1}^{\infty}\exp(-\theta^2\sigma^2/2)\cdot\cos\theta y,$$

we obtain

$$R = 2\pi\sigma^2\sum_{n=1}^{\infty} n\exp[-2\pi^2n^2\sigma^2]\sin\theta y\Big/\left[1+2\sum_{n=1}^{\infty}\exp(-2\pi^2n^2\sigma^2)\cos\theta y\right]. \quad (12)$$

Further exact transformations do not lead to a simple expression for R; however, as will be shown below, $|R| \leqslant 1/2$. This makes it possible to write two expressions for the degree of ionization N_e/N: the exact one*

$$\frac{N_e}{N} = y - 4\pi\sigma^2\sum_{n=1}^{\infty} n\exp[-2\pi^2n^2\sigma^2]\sin\theta y\Big/\left[1+2\sum_{n=1}^{\infty}\exp(-2\pi^2n^2\sigma^2)\cos\theta y\right] \quad (13)$$

and the approximate one

$$N_e/N = [\sigma^2\ln(K/N_e) + 1/2] + R, \qquad |R| \leqslant 1/2. \quad (14)$$

The exact equation (13) is simplified in two limiting cases: for $\sigma^2 \gg 1/2\pi$ (large dispersion or a smooth distribution of charges over particles) and for $\sigma^2 \ll 1/2\pi$ (a sharply discrete distribution of charges).

Let us consider the first case. For all $\sigma^2 \gtrsim 1/2\pi$, only one term with $n = 1$ remains in the numerator in R. In this case, since $|\sin 2\pi y| \leqslant 1$, $|R| \leqslant 4\pi\sigma^2\exp[-2\pi^2\sigma^2]$, whence it follows that $|R| \leqslant 2e^{-\pi} \simeq 0.1$ for $\sigma^2 = 1/2\pi$, and it rapidly decreases as σ^2 increases. Neglecting R in comparison with 1/2, which enters into y (7), from equation (13) for $\sigma^2 \gtrsim 1/2\pi$ (practically for $\sigma^2 > 1/2\pi$) we obtain the ionization equation in the case of large dispersion

$$N_e/N = \sigma^2\ln(K/N_e) + 1/2 \qquad (\sigma^2 \gg 1/2\pi). \quad (15)$$

A number of interesting consequences follow from (15). Thus, representing it in another form:

$$N_e = K \exp[-(N_e/N - 1/2)/\sigma^2] \qquad (\sigma^2 \gg 1/2\pi), \tag{15'}$$

we obtain

$$N_e = K = 2(2\pi m_e kT/h^2)^{3/2} \exp[-\varphi_0/kT] \quad \text{for } |K/N - 1/2| \ll \sigma^2, \tag{16}$$

i.e. N_e does not depend on the number of particles and their sizes, forming, as it were, a saturated electron gas.

The essence of this phenomenon is that the increase $\Delta\varphi$ in the work function due to the charge of the particle is small in comparison with the mean kinetic energy of the electrons: $\Delta\varphi = (N_e/N - 1/2)e_0^2/r \ll kT$.

It is also seen from (15′) that at a low degree of ionization ($N_e/N \ll 1/2$) and $\sigma^2 \gg 1/2\pi$ the electron concentration is always constant: $N_e = K$. The constancy of N_e in this case is explained by the formation of negative ions in amounts approximately equal to the number of positive ions, which follows from the proximity of the center of the charge distribution to zero ($N_e/N = y \ll 1/2$)

* The denominator of the second term of equation (13) is the third Jacobi theta function $\vartheta_3(y, \tau)$,

and the numerator is its derivative with respect to y. Thus, (13) can be represented in the form

$$N_e/N = y + \sigma^2\, d \ln \vartheta_3/dy.$$

and a large dispersion of charges for $\sigma^2 \gg 1/2\pi$. Conversely, for a sufficiently high degree of ionization $N_e/N \gg 1/2$, when $\ln K \gg \ln N_e$, it follows from (15) that the electron concentration depends linearly on N and r: $N_e = N\sigma^2 \ln K$.

The second case ($\sigma^2 \ll 1/2\pi$), in contrast to the first, means an essentially discrete distribution of charges. In this case, in the sums of the remainder term R the values of neighboring terms are close to one another. Approximating the sums by integrals according to Euler' s formula (11), without the last term (the trapezoidal formula), we shall have

$$R = 2\pi\sigma^2 \int_0^\infty n \exp[-2\pi^2 n^2 \sigma^2] \sin\theta y\, dn \Big/ \int_0^\infty \exp[-2\pi^2 n^2 \sigma^2] \cos\theta y\, dn = y_0, \tag{17}$$

where $|y_0| \ll 1/2$. (17) is obtained after integration by parts in the numerator, taking into account that the quantity $y \geq 0$ can be represented in the form

$y = k + y_0$, where $k \geq -1$ is an integer, and, consequently, $\sin\theta y = \sin\theta y_0$, and one can always find such a k that $-1/2 \leq y_0 \leq +1/2$.

An analytical expression for R is given by the formula $R = \sigma^2 d \ln\vartheta_3/dy$, for which tables are available. However, in the case of small dispersion ($\sigma^2 \ll 1/2\pi$), when the ionization equilibrium is determined by a single ionization reaction $\mathrm{P}_{\bar{m}} \rightleftarrows \mathrm{P}_{\bar{m}+1} + e$, where $\bar{m} \leq y \leq \bar{m}+1$, writing the initial system (1) for $\widetilde{m} = \bar{m}$ in the form

$$K_{\bar{m}} = N_{\bar{m}+1} N_e / N_{\bar{m}}; \qquad N_e = \bar{m} N_{\bar{m}} + (\bar{m}+1) N_{\bar{m}+1}; \qquad N = N_{\bar{m}} + N_{\bar{m}+1}, \tag{18}$$

we immediately arrive at the ionization equation for small dispersion

$$K_{\bar{m}} = \frac{(N_e - \bar{m}N)N_e}{N(\bar{m}+1) - N_e} = 2\frac{q_{\bar{m}+1}}{q_{\bar{m}}} \left(\frac{2\pi m_e kT}{h^2}\right)^{3/2} \exp\left[-\frac{\varphi_{\bar{m}}}{kT}\right] \quad \left(\sigma^2 \ll \frac{1}{2\pi}\right). \tag{19}$$

In practice this formula is applicable already for $\sigma^2 \lesssim 1/2\pi$. Indeed, from (9) it is seen that the ratio of the concentrations of the particles determining the ionization to the concentrations of particles with other charges is $N_y/N_{y\pm1} \approx e^{1/2\sigma^2} = e^{\pi} \approx 23$ for $\sigma^2 = 1/2\pi$. It is important to note that (19) contains the ionization potential only for the determining reaction, and, consequently, the relation between $\varphi_{\bar{m}}$ and φ_0 is immaterial. Therefore the expression for σ^2, taking (4) into account, in this case is better written in the form $\sigma^2 = rkT/e_0^2 = \bar{m}kT/(\varphi_{\bar{m}} - \varphi_0)$, which is convenient for atoms to which equation (19) is mainly applicable.

The equations derived in this work make it possible to obtain previously known formulas. From (19), for $m = 0$ (single ionization), we obtain

$$K_0 = N_e^2/(N - N_e) = 2(q_1/q_0)(2\pi m_e kT/h^2)^{3/2} \exp[-\varphi_0/kT] \quad (\sigma^2 \lesssim 1/2\pi), \tag{20}$$

which is the Saha equation (^{1}).

From the approximate equation (14) it follows that, at a high degree of ionization, independently of the magnitude of σ^2,

$$N_e/N = \sigma^2 \ln(K/N_e) + 1/2 \qquad (N_e/N \gg 1/2). \tag{21}$$

This formula was obtained by Einbinder (^{2}) for $N_e/N \gg 1$. An analogous equation (without 1/2) in the form $N_e = K\exp[-(N_e/N)e_0^2/rkT]$ was written by Sagden and Thrush (^{4}) under the assumption that all particles have the same charge, and was also obtained by us (5) from the solution of the kinetic problem of thermionic emission of electrons under the same assumption.

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