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ON STATISTICAL THEORY OF RADIOLYSIS PROCESSES IN AQUEOUS SOLUTIONS OF RADIOACTIVE ELEMENTS. REACTION-DIFFUSION MODEL

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До статистичної теорії процесів радіолізу у водних розчинах радіоактивних елементів. Реакційно-дифузійна модель

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Анотація. Проаналізовано проблему опису процесів радіолізу у водних розчинах радіоактивних елементів на основі хімічних реакцій, що відбуваються між продуктами радіолізу води. Розглянуто реакційно-дифузійну кінетику розчинів та константи швидкостей хімічних реакцій.

On statistical theory of radiolysis processes in aqueous solutions of radioactive elements. Reaction-diffusion model

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Abstract. Problems of description of radiolysis processes in aqueous solutions of radioactive elements on the basis of chemical reactions, which occur between products of radiolysis are analysed. Reaction-diffusion kinetics of solutions and rate constants of chemical reactions are considered.

1. Introduction

Problems of prognostication of radiolysis processes in aqueous solutions of radioactive elements in nuclear reactors during their work and emergency situations as well as in aqueous solutions of the object "Shelter" of the Chornobyl atomic power station is quite actual. In nuclear reactors the radiolysis processes of water are caused by γ-irradiation, fast Compton electrons, recoil protons, α-particles and fragments of uranium, plutonium division nuclei. Properties of such aqueous solutions in these conditions extremely alter in broad interval of temperatures, playing the role of moderator or heat-carrier. In this connection the investigation dealt with prognostication of radiochemical processes in reactors being planned or built, is very important. A particular role in the ecological and nuclear safety on the object "Shelter" play aqueous solutions of the salts of uranium, plutonium, americium, curium, strontium, caesium as one of the main forms of existence of nuclear fuel inside the object. They had been created as a result of interaction of fuel-containing masses of nuclear magma with natural and technical water.

Four main types of interaction of water with nuclear fuel can be distinguished in the object. The first one is interaction of water and active core fragments in the Central Hall. (Some investigations on nuclear processes prognostication in this part of the object is being carried out in Scientific and Industrial Center "Kamerton" of Byelorussian Academy of Sciences [1,2]).

The second one is dealt with penetration of water through pores inside nuclear magma, which by its structure is strongly inhomogeneous porous glassy-like substance. Water, penetrating in pores, interacts actively with nuclear magma destroying it.

The third type of interaction is dealt with nuclear lavas inside the object "Shelter", which are partially filled up by the water with altering level during spring – summer seasons.

The fourth type is the interaction between water and nuclear dust. Aqueous solutions of radioactive elements inside object "Shelter" interact with various constructive materials too: with concrete and glassy-like lavas of nuclear fuel.

It is obvious that character of a such interaction to a certain degree depends on the state of aqueous solutions. Presence in aqueous solutions of uranium, plutonium, americium, curium and their interaction with fuel-containing lavas leads to intensive processes of water molecules radiolysis due to α- and β-decays, γ-irradiation. In process of radiolysis of aqueous solutions chemically active radicals are being created: hydrated electrons and hydrogen ions H^+, OH^- groups, molecular compounds H_2, HO_2, H_2O_2, that, to a great degree determine the character of interaction of aqueous solutions with various materials inside the "Shelter".

Experimental investigations of aqueous solutions of radioactive elements with mean concentration for uranium from 10 mg/l and higher, which were carried out inside the object, point out that pH is in the interval 6,5÷7 and 9÷10. The most interest present aqueous solutions in such places of interaction between nuclear magma and water, where a great yield of uranium in water and high level of α-, β- and γ-radiation is being observed.

High pH level $9 \div 10$ points out on certain (due to chemical reactions) breaking of balance between groups H^+, OH^- and fact that hydrogen ions H^+, which are being created in radiolysis processes, hydratation and different reactions, react quickly passing to molecular hydrogen and water molecules. Besides, atomic hydrogen can participate in restore reactions. Presented pH value corresponds to alkali solutions. From this point of view it is necessary to analyse chemical reactions of UO_2^{2+}, PuO_2^{2+}, AmO_2^{2+} in the system "fuel-containing masses – alkali solution" with consideration of radiolysis and lixiviation processes. In a parallel way one has analyse role and participation of ions Ca^{2+}, Mg^{2+}, Ce^{3+}, Fe^{3+}, CO_3^{2-}, Na^+, K^+ in chemical reactions. Due to exceed of OH^--groups one can suppose the ionic complexes $[UO_2[(OH)_2UO_2]]_n^{2+}$ with polymer structure on the basis of hydrogen bonds to exist in such solutions.

Particular attention attracts the interaction of aqueous solutions with glassy-like lavas of nuclear fuel. One question is of a great importance: in what degree the products of water radiolysis participate in destroying of these lavas; what is the character of their interaction and influence on diffusion processes of uranium and plutonium yields from nuclear magma into aqueous solutions?

An important factor of considerable change of nuclear magma state (due to nuclear physico-chemical transformations under contact with water) is the appearance of yellow spots on black ceramics [3,4]. For the first time such spots were observed in 1990 [5]. Samples of such creations had been observed by raster electron spectroscopy and roentgen-spectral analysis. As a result one was able to find out that yellow spots are needle-like crystals of uranium minerals with main phases [3]: epyantinite — $UO_3 2H_2O$, studytite — $UO_3 1.6CO_3 1.91H_2O$, and $Na_2UO_2(CO_3)_2 2H_2O$. All these minerals possess an important feature: they are highly solvable in water!

The question how radiolysis products act on chemical reactions with participation of uraninite UO_2^{2+}, plutoninite PuO_2^{2+} ions and other radioactive complexes is an important one as well.

So, at first one has to find out how radiolysis processes in aqueous solutions of the system "nuclear magma – water" occur and to set up the problem of their qualitative and quantitative analysis.

2. Kinetics of radiolysis processes in aqueous solutions of radioactive elements

We shall investigate aqueous solutions typical for the object "Shelter" with uranium, plutonium, americium, caesium, strontium content (averaged concentration — tens mg/l). Uranium and plutonium are in the form of aqueous solutions of uraninite UO_2^{2+} and plutoninite PuO_2^{2+} ions which can hydrolyse actively [6,7] creating hydrated ions, binary and multicomponent complexes, mononuclear and polynuclear products, colloid particles [7,8] and polymer structures [9]. From the point of view of statistical theory aqueous solutions of radioactive elements are the complex ionic-molecular systems with long-range Coulomb dipole interaction and short-range interaction leading to creation of the chemical bonds between ions and molecular products. In such solutions it is necessary to take into account phenomena of ions solvatation, hydratation, appearing and altering of the polymer structures. These aqueous solutions are under permanent influence of α-, β-, γ-radiation (both internal and external) from fuel-containing masses. That is why the state of these solutions is being determined by the character of radiolysis processes which change permanently the character of interaction between solutions particles because of ionized tracks emerging — domains of high concentration of e^-_{aq}, H_2O^+, H^+_{aq}, OH^-_{aq} ions.

In the general case the interaction process between ionizing particles (α-, β-, γ-radiation, uranium and plutonium decay products) and water molecules could be divided on three stages: physical, physico-chemical and chemical [10-15].

On the physical stage during time interval $\sim 10^{-16}$ sec after ionizing particle had pass through the excited H_2O^* and superexcited H_2O^{**} water molecules and ions H_2O^+ were created:

$$H_2O^* \to H_2O^+ + e^-_{aq}, \tag{1}$$

where the label $*$ denotes an excited molecule. The excited electrons during time interval about 10^{-15} sec have been hydrating and interact with water molecules

$$e^-_{aq} + H_2O \to H + OH^-. \tag{2}$$

H_2O^+ ions also interact with water molecules:

$$H_2O^+ + H_2O \to H_3O^+ + OH. \tag{3}$$

10^{-14} sec after the dissociation of the excited water molecules occur:

$$H_2O' \to H^+ + OH^-. \tag{4}$$

In case of large irradiation dose (the excitation energy of water molecules is about $10 \div 17$ eV) the hydrogen and oxygen radicals could be created on time 10^{-14} sec after the process had started:

$$H_2O^{**} \to 2H + O. \tag{5}$$

In the reactions (1), (4), (5) the excitation energy of water molecule is different hence we use various denotations.

Analysing the reactions (1)–(5), at the end of physico-chemical stage (up to time $10^{-13} \div 10^{-12}$ sec from the beginning) one can see that there are hydrated electrons e^-_{aq}, ions H^+, OH^-, $H_3O^+(H^+_{aq})$ and radical products O, H in aqueous solution. Initially they are concentrated in tracks and are characterized by strongly inhomogeneous space distribution. Hence those particles should diffuse in the bulk of solution quickly, reacting with each other and with dissolved compounds. High density of chemical radicals in tracks makes the reactions of captures them by dissolved compound noneffective in comparison with recombination. As a result the diffusive-recombination kinetics of chemical reactions appears. Its main point consists in competition between mutual diffusion of chemically active particles and reactions occurring inside tracks. The following reactions on chemical stage are possible in the tracks:

$$
\begin{aligned}
e^-_{aq} + H_2O^+ &\to H_2O, && (6)\\
e^-_{aq} + OH &\to OH^-, && (7)\\
H^+ + H_2O &\to H_3O^+, && (8)\\
OH^- + H_2O^+ &\to H_2O + OH, && (9)\\
OH^- + H^+ &\to H_2O, && (10)\\
OH^- + H_3O^+ &\to 2H_2O, && (11)\\
H + H &\to H_2, && (12)\\
H^- + H^+ &\to H_2, && (13)\\
e^-_{aq} + H_2O &\to OH^- + H, && (14)\\
e^-_{aq} + H_2O &\to OH + H^-, && (15)
\end{aligned}
$$

$$
\begin{array}{rcll}
e_{aq}^- + H & \rightarrow & H^-, & (16)\\
OH + OH & \rightarrow & H_2O_2, & (17)\\
H_3O^+ + e_{aq}^- & \rightarrow & H_2O + H, & (18)\\
H^- + H_3O^+ & \rightarrow & H_2O + H_2, & (19)\\
H^- + H_2O^+ & \rightarrow & H_2O + H, & (20)\\
H^- + H_2O & \rightarrow & OH^- + H_2, & (21)\\
e_{aq}^- + H^+ & \rightarrow & H. & (22)
\end{array}
$$

Treatment of hydrated electron in literature is ambiguous. It often makes understanding of some chemical transformations problematic. Sometimes e_{aq}^- denotes H_2O^- ion [19]:

$$e_{aq}^- + H \rightarrow H_2 + OH^-.$$

At the same time, e_{aq}^- is understood as an electron together with water molecules. They do not participate in chemical transformations and have a transport property:

$$e_{aq}^- + OH \rightarrow OH^-.$$

In our paper we have tried to avoid this duality because it leads to different values of diffusion coefficients and kinetic properties of particles H_2O^- and water molecules, which transfer electron $(H_2O)_n^-$, due to their different masses and dimensions. This should be applied to hydrated proton as well: H^+ or H_3O^+. Any dualities here can be avoided by introducing of a time limitation. It does mean we have the existence of pure proton H^+ immediately after ionized particle passing (10^{-14} sec). Proton is hydrated at once into hydroxonium ion H_3O^+, where it is connected with water molecule by persistent covalent donor - acceptor bound.

For hydrated electron everything looks more complicated, because connection mechanism of electron to water molecule is not definite. In such a way, from the chemical point of view there is problematically to interpret hydrated electron as the H_2O^- ion. In our kinetic calculations a hydrated electron does mean an electron surrounded by water molecules $(H_2O)_n^-$ and denoted by e_{aq}^- in chemical transformations. These water molecules transfer electron only and do not participate in any chemical transformations. In the case of interaction between hydrated electron and water molecules the last ones should be written separately to avoid expressions like

$$e_{aq}^- + e_{aq}^- \rightarrow H_2 + 2OH^-.$$

An important result of presented reactions is creation of molecular hydrogen H_2, hydrogen peroxide H_2O_2 and water H_2O.

Molecular products H_2, H_2O_2 can annihilate due to reactions

$$
\begin{array}{rcll}
e_{aq}^- + H_2O_2 & \rightarrow & OH + OH^-, & (23)\\
H + H_2O_2 & \rightarrow & OH + H_2O, & (24)\\
OH + H_2O_2 & \rightarrow & HO_2 + H_2O, & (25)\\
OH + H_2 & \rightarrow & H + H_2O, & (26)\\
2H_2O_2 & \rightarrow & 2H_2O + O_2, & (27)
\end{array}
$$

while radicals OH and H regenerate in water molecules.

$$H + OH \rightarrow H_2O. \tag{28}$$

Radicals HO_2 react fast to produce hydrogenium peroxide

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \tag{29}$$

Thus, as a result of ionizing irradiation action on aqueous solutions the particles with oxidation (OH radicals) and reduction (hydrated electrons and H atoms) properties are being generated simultaneously.

Hence, at the end of chemical stage (10^{-12}–10^{-8} sec) there are following products of water radiolysis in the tracks: ions e_{aq}^-, H_{aq}^+, OH_{aq}^-, which did not recombine and O, H, OH, HO_2, H_2, H_2O_2, O_2 which interact actively with each other and with substances dissolved in water, in particular, with uraninite ions UO_2^{2+}, plutoninite ions PuO_2^{2+}, ions Cs^+, Sr^{2+} and others charged particles – Fe^{3+}, Na^+, Cl^-, NO_3^-, SO_4^{2-}, CO_3^{2-}.

In particular, hydrogenium peroxide, created during radiolysis, participates in reactions with uraninite ions, forming uranium peroxide UO_4

$$UO_2^{2+} + H_2O_2 \rightarrow UO_4 + 2H^+, \tag{30}$$

Uranium peroxide (studtite) falls in sediment in form of $UO_4 \cdot 4H_2O$ when its solvability limit is exceeded. It can decay thermally according to reactions

$$
\begin{array}{rcll}
UO_4 + 2H^+ & \rightarrow & UO_2^{2+} + H_2O_2, & (31)\\
UO_4 & \rightarrow & UO_3 + \frac{1}{2}O_2, & (32)\\
UO_3 + 2H^+ & \rightarrow & UO_2^{2+} + H_2O. & (33)
\end{array}
$$

It is obvious, uranium mineral creations $UO_3 \cdot 2H_2O$ and $UO_4 \cdot 4H_2O$ appears (due to reactions presented above) on the surface of fuel containing masses when hydrargyrum peroxide in aqueous solutions are available.

In order to calculate yields of radiolysis products and to compare with experimental data the equations of chemical kinetics are used [10-15], which could be obtained on the basis of nonequilibrium statistical thermodynamics [17]. Ignoring the processes dealt with energy and momentum fluctuation and considering chemical processes in aqueous solutions to have reaction-diffusion character, one can write down the equation for reagents concentrations in the general form:

$$\frac{\partial}{\partial t}\rho_a(\vec{r};t) = G_a J + \sum_{m,n} K_{mn}\rho_m\rho_n - \sum_b K_{ab}\rho_a\rho_b + F_a. \tag{34}$$

$\rho_a, \rho_m, \rho_n, \rho_b$ denote concentrations of a, m, n, b- species particles ; K_{mn}, K_{ab} denotes, correspondingly, rate constants of creation and annihilation of a-specie particles in the reactions between m, n, b-species particles. $\sum\limits_{m,n}$ means summation over all reactions leading to creation of a-species particles, $\sum\limits_b$ is the sum of reactions when a-species particles disappear. F_a describes a-particles transfer due to molecular diffusion and water flow with velocity $\vec{v}(\vec{r};t)$:

$$F_a = -\mathrm{div}(\vec{v}(\vec{r};t)\rho_a) + \mathrm{div}(D_a \mathrm{grad}\rho_a). \tag{35}$$

D_a means diffusion coefficient of a-particles. G_a denotes yield of a-species particles during radiolysis. Units of measuring of G are particles/100eV, ρ – mol/10^{-3} m^3, radiation capacity RC is being measured in eV per (litre·sec).

$$J = RC/(100 N_\mathrm{A}). \tag{36}$$

Initial yield G_a during ionization (before reactions inside tracks) is being determined by formula [15]:

$$G_a = 100 N_A \frac{\mathrm{d}\rho_a}{\mathrm{d}D}\,|_{D=D^o} \tag{37}$$

or

$$G_a = 100 N_\mathrm{A}\frac{\rho_a}{D}. \tag{38}$$

where N_A is the Avogadro number, D — irradiation dose (don't muddle with diffusional coeffitions D_a).

Hence, change of concentration of the particles interacting according to (1)-(29) will be investigated on the basis of kinetic equations (34). In every equation for molecular products H_2O, H_2, H_2O_2 appear the concentrations of ions and other particles of solution. So the reaction-diffusion equations ought to be written for all particles entering radiolysis process. Besides, one has to take into consideration the reactions on the chemical stage.

System of equation (34) is nonlinear one and could be solved only numerically. However, sometimes it might be simplified. First of all, in case of weakly nonequilibrium radiolysis processes. Experimental data show that rate constants values for reactions between chemical radicals, and between radicals and other particles are much larger then others rate constants. That is why concentration of radicals is much smaller then concentration of stable products of radiolysis, thus one can suppose establishment of steady state for radicals after ionization, taking approximation of stationary concentrations:

$$\frac{\partial}{\partial t}\rho_R(\vec{r};t) = 0. \tag{39}$$

(R is a denotation for radical). Such a condition is not valid for stable products of radiolysis. So introducing denotations

$$\rho_R(\vec{r};t) = \{\rho_\mathrm{H}, \rho_\mathrm{OH}, \rho_{\mathrm{H}^+}, \rho_{\mathrm{OH}^-}, \rho_{\mathrm{H_2O}^+}, \rho_{\mathrm{e}^-_\mathrm{aq}}, \rho_{\mathrm{H_3O}^+}, \rho_{\mathrm{H}^-}\}$$

for chemical radicals and

$$\rho_M(\vec{r};t) = \{\rho_{\mathrm{H_2O}}, \rho_{\mathrm{H_2}}, \rho_{\mathrm{H_2O_2}}, \rho_{\mathrm{O_2}}\}$$

for stable molecular products of radiolysis, one can formally represent the system of equations (34) as a system for $\rho_M(\vec{r},t)$ and $\rho_R(\vec{r},t)$:

$$\frac{\partial}{\partial t}\rho_M(\vec{r};t) = G_M J + \sum_{m,n} K_{mn}\rho_m\rho_n - \sum_l K_{lM}\rho_l\rho_M + F_M, \tag{40}$$

$$0 = G_R J + \sum_{m,n} K_{mn}\rho_m\rho_n - \sum_l K_{lR}\rho_l\rho_R + F_R \tag{41}$$

with initial conditions $\rho_M(t=0) = \rho_M^0$ and $\rho_R(t=0) = 0$.

If the system of equations (41) could be solved with respect to radicals concentrations, then after substituting this solution into (40), we obtain closed chain of equations for concentrations of molecular products.

3. Rate constants of chemical reactions

For calculation of rate constants in aqueous solutions one can use formulae, which connect K_{ab} with diffusion coefficients of each component and with the structure of solution itself. In particular, for rapid reactions one can apply Smoluchovsky's expression for rate constants:

$$K_{ab} = 4\pi(D_a + D_b)R_{ab}, \tag{42}$$

where D_a, D_b are diffusion coefficients for reagents a and b. Value R_{ab} is called a collision radius. It approximately equals to the sum of radii of a- and b-molecules. On the basis of hydrodynamic level of description of chemical reactions in solutions [16,17] one can obtained the expression for rate constants of chemical reactions:

$$K_{ab}(t) = \int \mathrm{d}\boldsymbol{r}_{ab}\; k^0(\boldsymbol{r}_{ab}) g_{ab}(\boldsymbol{r}_{ab};t), \tag{43}$$

where $k^0(\boldsymbol{r}_{ab})$ denotes proper reactional ability, $g_{ab}(\boldsymbol{r}_{ab};t)$ — nonequilibrium radial distribution function of the particles in solution. In steady state $g_{ab}(\boldsymbol{r}_{ab})$ — equilibrium radial distribution function and the rate constant K_{ab} does not depend on time:

$$K_{ab} = 4\pi \int \mathrm{d}r_{ab} k^0(r_{ab}) g_{ab}(r_{ab}). \tag{44}$$

Proper reactional ability $k^0(r_{ab})$ of the molecules depends on mechanism of elementary reaction act and, in principle, can be calculated either by classical or quantum mechanics methods. The simplest form has Smoluchovsky proper reactional ability constant

$$k^0(r_{ab}) = k^0 \delta(r_{ab} - R_{ab})/4\pi r_{ab}^2. \tag{45}$$

Then

$$K_{ab} = k^0 g_{ab}(R_{ab}), \tag{46}$$

where $k^0 = 4\pi R_{ab}^2 (8/\beta\pi\mu)^{1/2}$, $\mu = m_a m_b/(m_a + m_b)$ – reduced mass of the particles a and b. So the problem of calculation of the rate constants of chemical reactions is reduced to evaluation of diffusion coefficients and structural distribution functions of reagents.

In view of statistical theory of interacting particles aqueous solutions of radioactive elements, in which radiolysis reactions take place, can be considered as a model electron-ion-atomic-molecular (plasma-molecular) system. The peculiarity of such a system is the long-range character of Coulomb and dipole forces between ions and electrons (H^+, OH^-, e^-_{aq}, H^-, H_3O^+) as well as between molecules (H_2, H_2O, H_2O_2). Except this, hydrogen atoms H and hydroxyl groups OH exist in a system. They participate actively in transport processes and chemical reactions in a solution.

Multiple dynamical processes, which are marked by both short-range and long-range correlations, arrive at phenomena of solvatation and complexformation in solutions. Investigation of structure, thermodynamical and kinetic properties of such a plasma-molecular solutions are actual. Besides, nonequilibrium distribution functions $g_{AB}(\boldsymbol{r};t)$, which are connected with chemical reactions constants (43), had not been studied yet appropriately. The considerable achievement in investigation of plasma-molecular systems has been reached in the paper [20]. On the other hand, constants of quasiequilibrium states of chemical reactions could be defined via (44) — pair distribution functions of electrons, ions, atoms and molecules. Methods of investigations of equilibrium distribution functions of particles of electrolytes (in the ion an in the ion-molecular approaches) are described well in [20,21].

For qualitatively estimations, rate constants can be calculated on the basis of ion-dipole model of aqueous solutions [18]. In the framework of this model the particles interact as hard spheres on short ranges with equilibrium distribution $g_{ab}(\sigma_{ab})$ ($\sigma_{ab} = \frac{1}{2}(\sigma_a + \sigma_b), \sigma_a, \sigma_b$ — hard spheres diameters) whereas on large distances — through ion, ion-dipole and dipole-dipole potentials, which are characterized by electrostatic screening. Equilibrium pair distribution function can be presented for ion-dipole system in approximation of the second virial coefficient as:

$$g_{ab}(r) = g_{ab}(\sigma_{ab}) \exp\{G_{ab}(r)\}, \tag{47}$$

where G_{ab} – screened potential of electrostatic interactions. For ion-dipole system it can be found [20,21] as:

$$G_{ab}(r) = -\beta \frac{Z_a Z_b e^2}{\varepsilon r} \exp\left\{-\frac{\kappa}{\sqrt{\varepsilon}} r\right\}$$

$$G_{as}(r) = \beta Z_a e d_s \frac{1}{\varepsilon r}\left(\frac{1}{r} + \frac{\kappa}{\sqrt{\varepsilon}}\right) \exp\left\{-\frac{\kappa}{\sqrt{\varepsilon}} r\right\} \cos\theta_s,$$

$$G_{rs}(r) = \beta d_s d_r \frac{1}{\varepsilon r}\left\{\left(\frac{2}{r^2} + \frac{2\kappa}{\sqrt{\varepsilon} r} + \frac{\kappa}{\sqrt{\varepsilon}}\right)\cos\theta_s \cos\theta_r - \right.$$
$$\left. -\frac{1}{r}\left(\frac{1}{r} + \frac{\kappa}{\sqrt{\varepsilon}}\right) \sin\theta_s \sin\theta_r \cos(\varphi_s - \varphi_r)\right\} \exp\left\{-\frac{\kappa}{\sqrt{\varepsilon}} r\right\},$$

$\kappa = (4\pi\beta \sum_a \frac{N_a}{V} Z_a^2 e^2)^{1/2}$ is the value, which is inversed to the Debaye screening radius, ε denotes dielectric penetreability, $\beta = 1/k_\mathrm{B}T$, k_B is the Boltzmann constant, T – is the temperature, $Z_a e$ denotes a-kind ion charge, d_s is the value of dipol moment for molecules, Q_s and φ_s are orientation angles. In particular, hydrated electron can be considered as an ion of charge $Z_{e^-_{aq}} = -1$, of charge distribution radius $\sigma_{e^-_{aq}} = 2.5 \div 3.0$ Å and of diffusion coefficient $4.9\pm0.25\cdot10^{-5}$ cm^2/sec.

Calculations of radiolysis rate constants on the basis of the presented formulae for a dipole model of aqueous solutin will be carried out in our further papers.

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