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PHYSICAL CHEMISTRY

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## Abstract

## Full Text

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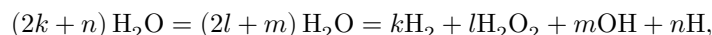
*PHYSICAL CHEMISTRY*

**B. V. Ershler and V. M. Byakov**

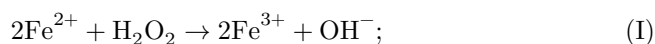
# ON THE APPLICABILITY OF THE EQUATIONS OF HOMOGENEOUS KINETICS TO RADIOLYSIS AT HIGH RADIATION INTENSITIES

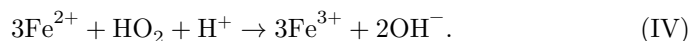
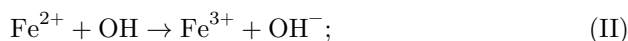
*(Presented by Academician A. N. Frumkin on 14 I 1962)*

Radiolysis under the action of soft and hard  $\gamma$ -quanta and fast electrons, at an intensity of absorbed energy of the order of  $10^{13}$ — $10^{16}$  eV/cm<sup>3</sup> · sec, is well described by the equations of homogeneous chemical kinetics. This is proved by the presence, at the indicated intensities, of  $I^{1/2}$ -regularities (see <sup>(1-3)</sup>) and by the good agreement of numerous data on the kinetics of radiolysis with theoretical calculations based on the simplified Allen model (<sup>(4)</sup> and others). In the latter, the process of radical diffusion is not taken into account; i.e., it is assumed that, under the action of radiation on water, particles H, OH, H<sub>2</sub>, and H<sub>2</sub>O<sub>2</sub> are formed with constant yields according to the equation



where  $k$ ,  $l$ ,  $m$ ,  $n$  are the numbers of the corresponding particles arising from water per 100 eV of absorbed energy. In describing the reactions of these particles with dissolved substances and with one another, their concentration is considered uniform throughout the solution. We shall attempt to show that such a simplified model correctly describes the kinetics of radiolysis up to very high radiation intensities, used in the interesting works of A. K. Pikaev and P. Ya. Glazunov (<sup>(5,6)</sup>). In the latter, an air-saturated solution of iron sulfate was irradiated with fast electrons, the intensity  $I$  of the absorbed energy reaching  $10^{23}$  eV/cm<sup>3</sup> · sec. As is known, at ordinary radiation intensities the oxidation yield of such a solution is  $G_{\text{max}} = 15.6$  iron ions/100 eV, where  $15.6 = 2l + m + 3n$ . This relation is obtained because all radicals oxidize iron by reactions which, in total, are written as follows:





In a solution of  $\text{FeSO}_4 + \text{O}_2$ , the acceptor of OH radicals is the  $\text{Fe}^{2+}$  ion with a concentration of  $1 \div 2 \cdot 10^{-3} N$  and higher, while the acceptor of the H atom is  $\text{O}_2$  molecules, with a concentration (in an air-saturated solution) an order of magnitude lower. As the radiation intensity increases, the concentration of all primary radiolysis products in the volume rises and, consequently, the reactions of radical recombination in the volume are also accelerated:



One should distinguish this bulk recombination of radicals, with which reactions (II) and (III) are able to compete, from recombination in the track, leading to the formation of “primary” molecules  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ ; with the latter reaction (II)

and (III) cannot compete, which explains the independence of the yields  $k, l, m, n$  on the concentrations of acceptors. The bulk recombination of radicals is accelerated with the square of their bulk concentration, whereas capture of radicals by an acceptor only with the first power of the bulk concentration. Therefore, as the radiation intensity is increased in  $\text{FeSO}_4 + \text{O}_2$  solutions, recombination in the bulk will begin to compete with capture, and the yield of iron oxidation will decrease. Obviously, in this way only reactions (V) and (VI) can reduce the yield, but not (VII); moreover, in the usual dosimetric solution reaction (V) will be more effective because the concentration of  $\text{Fe}^{2+}$  is greater than the concentration of  $\text{O}_2$ , and reaction (II) is faster than reaction (III). Taking reactions (I)–(V) into account, by the steady-state method we obtain the following equation for the dependence of the yield of iron oxidation  $G$  on the radiation intensity

**Fig. 1.** Values of the constants  $k_3/k_5^{1/2}$ , calculated from equation (1) using data <sup>(5,6)</sup> (a) and calculated in <sup>(4)</sup> from data <sup>(7,8)</sup> (b).

Figure 1: Values of the constants  $k_3/k_5^{1/2}$ , calculated from equation (1) using data (5, 6) (a) and calculated in (4) from data (7, 8) (b).

Figure 1: Figure 1: Values of the constants  $k_3/k_5^{1/2}$ , calculated from equation (1) using data (5, 6) (a) and calculated in (4) from data (7, 8) (b).

$$k_3/k_5^{1/2} = \left( \frac{I}{100N} \right)^{1/2} \frac{n - \frac{1}{3}(G_{\max} - G)}{\left[ \frac{1}{6}(G_{\max} - G) \right]^{1/2}} \cdot \frac{1}{(O_2)}, \quad (1)$$

where  $G_{\max} = 15.6$  is the maximum value of the yield of iron oxidation,  $k_3$  and  $k_5$  are the rate constants of reactions (III) and (V),  $N$  is Avogadro's number,  $(O_2) = 2.7 \cdot 10^{-4}$  mol/l is the concentration of  $O_2$  in an air-saturated solution. Figure 1 shows the value of the constant  $k_3/k_5^{1/2}$ , calculated from equation (1) using the data of works <sup>(5,6)</sup>, for high intensities; the value of this constant found for an intensity of  $10^{16}$  in work <sup>(4)</sup> is also given there. The good constancy of the constant  $k_3/k_5^{1/2}$  over an interval of 6-7 orders of magnitude of radiation intensity is evidence in favor of the applicability of the equations of homogeneous kinetics to radiolysis at high radiation intensities. It would be highly desirable to continue investigations at high radiation intensities for the accurate measurement of the kinetic constants of recombination reactions and for clarifying the limits of applicability of the equations of homogeneous kinetics to radiolysis. The possibility of a decrease in the oxidation yield due to overlap of tracks at high intensities, discussed in works <sup>(5,6)</sup>, will be considered by us elsewhere.

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12 I 1962

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

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