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Abstract

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RADIATION TRANSFORMATIONS OF A MIXTURE OF Fe^{2+} AND Fe^{3+} IONS IN ACID SOLUTIONS SATURATED WITH HYDROGEN UNDER PRESSURE

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In previous works ([1]-[3]), the oxidation of Fe^{2+} and the reduction of Fe^{3+} in solutions saturated with hydrogen under pressure were investigated, and certain kinetic characteristics of the oxidation and reduction processes were determined. Study of the radiolysis of solutions containing a mixture of Fe^{2+} and Fe^{3+} ions under H_2 pressure makes it possible, by varying the concentrations of the solution components, to obtain these data in several ways and, from their comparison, to draw more reliable conclusions about the mechanism of the process.

The system $Fe^{2+} + Fe^{3+}$ has already been studied ([4], [5]). However, in works ([4], [5]) the determination was limited to some single dependence, and on the basis of the data obtained one cannot draw definite conclusions about the mechanism of radiolysis and, consequently, about the rate constants of the reactions taking place.

It is evident that, in the presence of molecular hydrogen in the solution, part of the OH radicals is transformed into H atoms by the reaction

$$H_2 + OH \rightarrow H_2O + H, \tag{I}$$

which competes with the reaction

$$Fe^{2+} + OH \rightarrow Fe^{3+} + OH^-. \tag{II}$$

As a result of reaction (I), instead of the oxidizing OH radicals, H atoms appear, which can participate in both oxidation and reduction reactions. This broadens the limits of variation of the transformation yield and makes it possible to obtain more accurate dependences.

In the present work, the yields of oxidation of Fe^{2+} under the action of Co^{60} γ-rays were measured at various concentrations of Fe^{3+}, H_2, and Fe^{2+} in 0.8 N H_2SO_4 solution.

Method

The glass cell and the procedure for saturating the solution with hydrogen were described in detail earlier (^{1}, ^{2}). The solutions were prepared from chemically pure reagents in twice-distilled water. The dose rate was $\sim 2 \cdot 10^{15}$ eV/cm$^3 \cdot$ sec. The concentration of Fe^{2+} ions was determined spectrophotometrically with *o*-phenanthroline.

Results and Discussion

The dependence of the oxidation yield on the Fe^{3+} concentration was determined for a $\sim 10^{-3}$ M Fe^{2+} solution in 0.8 N H_2SO_4 saturated with H_2 at 100 atm. For each Fe^{3+} concentration, the initial portions of the oxidation curve were taken; the maximum change in the initial concentrations did not exceed 10%. The initial oxidation yields calculated from these data as a function of the Fe^{3+} concentration in the solution ($[Fe^{2+}] = 1.05 \cdot 10^{-3}$ M; $P_{H_2} = 100$ atm.) are given in Table 1.

Table 1

Conc. Fe^{3+}, mol/l	10^{-3}	$2 \cdot 10^{-3}$	$8.6 \cdot 10^{-3}$	$8.6 \cdot 10^{-2}$	$8.6 \cdot 10^{-1}$
$G(Fe^{3+})$, mol/100 eV	5.8	4.2	−1.05*	−4.2	−5.8

* The minus sign indicates that reduction is taking place.

As is seen from the table, with an increase in $[Fe^{3+}]$ the oxidation yield falls to zero, and with a further increase in $[Fe^{3+}]$ its reduction begins. Such a form of the dependence can probably be explained by competition for H atoms in the following two reactions:

$$H + Fe^{3+} \rightarrow H^{+} + Fe^{2+}; \tag{III}$$

$$H + H^{+} \rightarrow H_2^{+}. \tag{IV}$$

The H_2^+ ions formed are removed by the reaction

$$Fe^{2+} + H_2^{+} \rightarrow Fe^{3+} + H_2. \tag{V}$$

Assuming that the initial yield is determined by the occurrence of reactions (I)–(V), and also

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH, \tag{VI}$$

we obtain the following expression for the oxidation yield:

$$G(\mathrm{Fe}^{3+}) = G_\mathrm{H} + G_\mathrm{OH} + 2G_{\mathrm{H_2O_2}} - \left[G_\mathrm{H} + \frac{G_\mathrm{OH} + G_{\mathrm{H_2O_2}}}{1 + \dfrac{k_2[\mathrm{Fe}^{2+}]}{k_1[\mathrm{H}_2]}} \right] \frac{2}{1 + \dfrac{k_4[\mathrm{H}^+]}{k_3[\mathrm{Fe}^{3+}]}} \equiv A - \frac{2\alpha}{1 + \dfrac{k_4[\mathrm{H}^+]}{k_3[\mathrm{Fe}^{3+}]}}. \tag{1}$$

Let us transform it as follows:

$$1 + \frac{k_4[\mathrm{H}^+]}{k_3[\mathrm{Fe}^{3+}]} = \frac{2\alpha}{A - G(\mathrm{Fe}^{3+})}. \tag{2}$$

Since only $[\mathrm{Fe}^{3+}]$ changes in the solution, the expression on the right-hand side is a linear function of the ratio $[\mathrm{H}^+]/[\mathrm{Fe}^{3+}]$. In Fig. 1 such a dependence is presented, constructed from the data of Table 1. According to equation (2), the tangent of the angle of inclination is $k_4/k_3 = 9 \cdot 10^{-3}$, and the intercept $b_1 = 1$. From Fig. 1 we find $b_1 = 0.142\alpha = 1$, whence

$$\alpha = \left[G_\mathrm{H} + \frac{G_\mathrm{OH} + G_{\mathrm{H_2O_2}}}{1 + \dfrac{k_2[\mathrm{Fe}^{2+}]}{k_1[\mathrm{H}_2]}} \right] = $$

$$= 7.05.$$

Hence, using the known values of the yields $G_\mathrm{H}, G_\mathrm{OH}$ and $G_{\mathrm{H_2O_2}}$ and the concentration ratio $[\mathrm{Fe}^{2+}]/[\mathrm{H}_2] = 0.013$, we obtain $k_1/k_2 = 0.125 \pm 0.3$. This value can also be determined from the dependence of the oxidation yield on the hydrogen pressure. For this purpose we rewrite equation (1) in the form

$$\frac{k_1[\mathrm{H}_2]}{k_2[\mathrm{Fe}^{2+}]} = \left\{ \frac{G_\mathrm{OH} + G_{\mathrm{H_2O_2}}}{\frac{1}{2}[A - G(\mathrm{Fe}^{3+})] \left(1 + \dfrac{k_4[\mathrm{H}^+]}{k_3[\mathrm{Fe}^{3+}]} \right) - G_\mathrm{H}} - 1 \right\}^{-1} \equiv X. \tag{3}$$

Fig. 1. Graphical solution of equation (2) from the data of Table 1.

Fig. 2. Graphical solution of equation (3) from the data of Table 2.

Table 2

Hydrogen pressure H_2, atm	1	10	25	50	100
$G(Fe^{3+})$, mol/100 eV	2.9	0.85	−0.25	−0.75	−1.05

If only P_{H_2} changes, then X is a linear function of the ratio $[H_2]/[Fe^{2+}]$. Figure 2 presents the dependence of X, constructed from experimental data (Table 2), on $[H_2]/[Fe^{2+}]$ for a solution with $[Fe^{2+}] = 1.05 \cdot 10^{-3}\,M$, $[Fe^{3+}] = 8.6 \cdot 10^{-3}\,M$.

The tangent of the slope gives the value $k_1/k_2 = 0.138$. Previously this same quantity was determined by us in the radiolysis of Fe^{2+} solutions in 0.8 N H_2SO_4, saturated with H_2 and O_2, and was found to be 0.135. The values of k_1/k_2 obtained from radiolysis data by three methods agree well with the value obtained for radicals arising by reaction (VI) without radiation exposure(6). This confirms the identity of the radicals arising by reaction (VI) and during radiolysis.

Many authors believe that reaction (IV) and the following reaction (V) should be replaced by reaction (7)

$$Fe^{2+}(H_2O)_n + H \rightarrow FeOH^{2+}(H_2O)_{n-1} + H_2 \qquad \text{(IVa)}$$

or (8)

[Figure 3 graph]

Fig. 3. Graphical solution of equation (2) as a function of $[Fe^{2+}]/[Fe^{3+}]$ according to the data of Table 1 (dashed line) and Table 3 (solid line)

$$Fe^{2+} + H \rightarrow FeH^{2+} \xrightarrow{+H^+} Fe^{3+} + H_2. \qquad \text{(IVb)}$$

In this case, evidently, in equations (1) and (2), $[Fe^{2+}]$ will appear instead of the concentration of H^+. The dependence of the oxidation yield on $[Fe^{2+}]$ was determined

Table 3

Conc. Fe^{2+}, mol/l	$1.15 \cdot 10^{-4}$	$2.3 \cdot 10^{-4}$	$1.05 \cdot 10^{-3}$	$1.05 \cdot 10^{-2}$
$G(Fe^{3+})$, mol/100 eV	0	0.3	0.85	1.25

in a $\sim 10^{-2}\,M$ Fe^{3+} solution at a constant ratio $[Fe^{2+}]/[H_2]$. The results are given in Table 3 $\left([Fe^{3+}] = 8.6 \cdot 10^{-3}\,M;\ [Fe^{2+}]/[H_2] = \text{const}\right)$.

Since only $[Fe^{2+}]/[Fe^{3+}]$ changes, the right-hand side of equation (2) must be a linear function of this ratio. The desired dependence, constructed from the data of Table 1 (dashed line) and Table 3 (solid line), is presented in Fig. 3. The slopes of the curves and the ratios of constants calculated from them do not coincide, as would be expected in the case of reactions (IVa) and (IVb). Thus, the experimental results do not confirm the occurrence of reactions (IVa) and (IVb).

[Figure 4 graph]

Fig. 4. Graphical solution of equation (4) according to the data of Table 3

The experimentally observed dependence of the yield on $[Fe^{2+}]$ (see Table 3) is probably explained by the fact that, at low concentrations of Fe^{2+}, not all H_2^+ formed by reaction (IV) react with Fe^{2+}; some of them disappear by the reaction

$$H_2^+ \rightarrow H^+ + H. \tag{VII}$$

In this case, as is easily verified, in equations (1) and (2) the quantity k_4/k_3 must be replaced by

$$\frac{k_4}{k_3}\Big/\left(1 + \frac{k_7}{k_5[Fe^{2+}]}\right).$$

For determining k_7/k_5

and k_4/k_3, we rewrite equation (2) as follows:

$$1 + \frac{k_7}{k_5[Fe^{2+}]} = -\frac{k_4[H^+]/k_3[Fe^{3+}]}{\frac{2\alpha}{A - G(Fe^{3+})} - 1} \equiv \frac{\beta}{\frac{2\alpha}{A - G(Fe^{3+})} - 1}. \tag{4}$$

The expression on the right-hand side is a linear function of the quantity $\frac{1}{[\mathrm{Fe}^{2+}]}$. The desired dependence, constructed from the data of Table 3, is given in Fig. 4. The tangent of the angle of inclination is $k_7/k_5 = 1.5 \cdot 10^{-4}$ mole/l. The intercept is $b_2 = 1$, whence $k_4/k_3 = 1.03 \cdot 10^{-2}$.

In conclusion it should be noted that in sulfuric-acid solutions the effective concentration of Fe^{3+}, as was shown earlier (^{3}), may be considerably lower than the total concentration because of complex formation; this must be taken into account when determining the absolute value of the ratio k_4/k_3.

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