Oxidation of Ferrous Ions in Aqueous Solutions by Cobalt-60 Gamma Rays. II[1]*. Effect of Anions at High Dose*

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It is well-known that the Fricke dosimeter ($G(\mathrm{Fe}^{3+})=15.6$) is the best secondary standard dosimeter, but it has the upper limit of applicable doses due to the solubility of oxygen in the solution. The air-free system may also be applicable up to higher doses as a good dosimeter ($G(\mathrm{Fe}^{3+})=8.2$) for the same kind of radiations with the Fricke dosimeter, if the procedure of degassing oxygen is not minded. For this purpose, the property at high dose was examined.

The reaction scheme for the air-free system is usually assumed as follows:

$$\mathrm{Fe}^{2+}+\mathrm{OH}=\mathrm{Fe}^{3+}+\mathrm{OH}^- \qquad (1)$$

$$\mathrm{Fe}^{2+}+\mathrm{H_2O_2}=\mathrm{Fe}^{3+}+\mathrm{OH}^-+\mathrm{OH} \qquad (2)$$

$$\mathrm{Fe}^{2+}+\mathrm{H}+\mathrm{H}^+=\mathrm{Fe}^{3+}+\mathrm{H_2} \qquad (3)$$

As the dose increases, $G(\mathrm{Fe}^{3+})$ decreases gradually above a certain dose due to re-reduction of ferric ion produced, by the reaction

$$\mathrm{Fe}^{3+}+\mathrm{H}=\mathrm{Fe}^{2+}+\mathrm{H}^+ \qquad (4)$$

competing with reaction 3. However, this reaction may not be so simple, for ferric ion is usually associated with anions in the solution, as discussed later.

On the other hand, sodium chloride is usually added by 0.001 M as a stabilizer for the Fricke dosimeter to suppress the effect of organic impurities, for chloride ion scavenges OH radical, which reacts with the impurities, like

$$\mathrm{Cl}^-+\mathrm{OH}+\mathrm{H}^+=\mathrm{Cl}+\mathrm{H_2O} \qquad (5)$$

and this reaction does not affect the $G(\mathrm{Fe}^{3+})$ due to the following reaction[2]

$$\mathrm{Fe}^{2+}+\mathrm{Cl}=\mathrm{Fe}^{3+}+\mathrm{Cl}^- \qquad (6)$$

The effect of anions, especially halide ions, on the radiolysis of ferrous solutions at high dose was investigated in the present study to obtain the detailed information of reaction 4.

Experimental

The preparation of solutions and the irradiation method by 10 kc. cobalt-60 gamma rays were the usual ones as was mentioned in Part I[1]. The composition of the solutions used is listed in Table I. All the solutions containing halide salts were dissolved in the "standard solution", which contained 0.04 M ferrous ammonium sulfate in 0.8 N sulfuric acid.

The concentration of ferric ion was usually measured by a Shimadzu spectrophotometer. The molar extinction coefficient of ferric ion at 304 mμ, which was 2150 cm^{-1} at 24°C, was constant between 0.2 N and 1.2 N sulfuric acid, but increased by 0.8% for

TABLE I. COMPOSITION OF SOLUTIONS USED IN M AND THEIR k_4/k_3 IN Eq. iii

Run	$\mathrm{FeSO_4(NH_4)_2SO_4}$	$\mathrm{H_2SO_4}$	$\mathrm{Na_2SO_4}$	NaCl	KBr	KF	$\mathrm{O_2}$	k_4/k_3
a	0.5	0.4	—	—	—	—	Free	9.77
b	0.5	1.4	—	—	—	—	Free	0.85
c	0.5	2.4	—	—	—	—	Free	0.80
d	0.5	4.0	—	—	—	—	Free	0.63
e	0.5	0.4	1.0	—	—	—	Free	2.7
f	0.04	0.4	—	0.001	—	—	Free	0.77
g	0.04	0.4	—	0.01	—	—	Free	2.1
h	0.04	0.4	—	0.1	—	—	Free	14
i	0.04	0.4	—	0.5	—	—	Free	54
j	0.04	0.4	—	0.001	—	—	Satur.	—
k	0.04	0.4	—	0.01	—	—	Satur.	—
l	0.04	0.4	—	0.1	—	—	Satur.	—
m	0.04	0.4	—	—	0.1	—	Free	2.1
n	0.04	0.4	—	—	—	0.1	Free	0.14
p	0.04	0.4	—	—	—	—	Free	0.67

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[1] Part I: H. Hotta, A. Terakawa and S. Ohno, This Bulletin, 33, 442 (1960).

[2] H. A. Dewhurst, *Trans. Faraday Soc.*, **48**, 965 (1952).

the rise of one degree centigrade between 13 and and 38°C. However, this was measured by the titration method of potassium permanganate for solutions containing fluoride ion or a large amount of ferric ion.

Results

Dependence of the Concentration of Ferrous and Sulfate Ions.—The oxidation of ferrous ion in the nitrogen-saturated solution of 0.5 M ferrous ammonium sulfate in 0.8 N sulfuric acid is shown as "a" in Fig. 1. The $G(Fe^{3+})$ was initially 8.2, and gradually decreased above 7×10^6r (0.05 M in ferric ion). The result for the 0.1 M ferrous solution, measured up to 0.09 M in ferrous ion, was almost the same as solution a. The $G(Fe^{3+})$ for the 0.04 M ferrous solution began to come down at 4×10^6 r (0.03 M in ferric ion). The decrease of $G(Fe^{3+})$ at high dose is due to reaction 4 as mentioned in the "Introduction". On the other hand, the reaction

$$OH+H_2=H+H_2O \qquad (7)$$

may promote reaction 4 at high dose, at which hydrogen molecules are accumulated in the closed medium. The conversion ratio of ferric ion to initial ferrous ion at the bending point of the (Fe^{3+})-dose curve is different between the above solutions.

The effect of sulfate concentration on $G(Fe^{3+})$ at high dose in nitrogen-saturated 0.5 M ferrous ammonium sulfate solutions is shown in Fig. 1, that is, solutions b, c and d were dissolved in 2.8, 4.8 and 8 N sulfuric acid, respectively, and solution f contained 1 M sodium sulfate in 0.8 N sulfuric acid. The decrease of $G(Fe^{3+})$ is considerably suppressed by 2.8 N sulfuric acid, but this effect does not increase much by the more concentrated sulfuric acid. Sulfuric acid is more effective than sodium sulfate as compared between solutions b and e which contained the same amount of sulfate group (1.4 M).

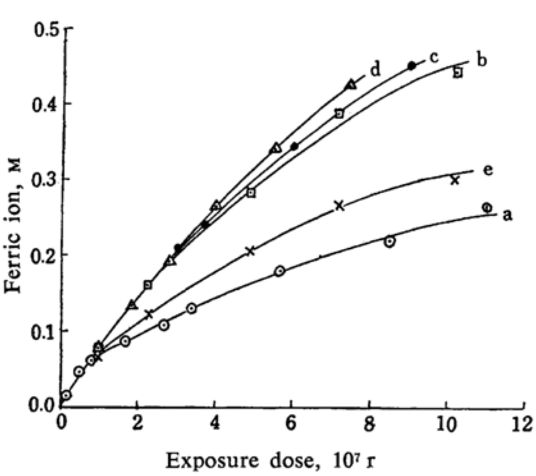


Fig. 1. Oxidation of ferrous ion in the nitrogen-saturated solutions a (⊙), b (▣), c (●), d (△) and e (×).

Effect of Halide Ions. — The oxidation of ferrous ion in the nitrogen-saturated standard solutions containing f 0.001 M, g 0.01 M, h 0.1 M and i 0.5 M sodium chloride, respectively, is shown in Fig. 2. As the concentration of of sodium chloride increases, the observed points depart at the lower dose from the straight line of solution f, and the $G(Fe^{3+})$ decreases with the increase of the dose.

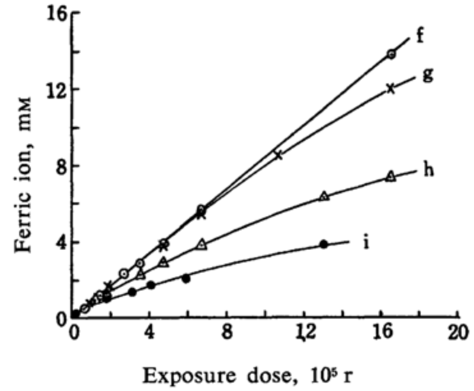


Fig. 2. Oxidation of ferrous ion in the nitrogen-saturated solutions f (⊙), g (×), h (△) and i (●).

On the other hand, the oxidation of ferrous ion in the oxygen-saturated standard solutions containing j 0.001 M, k 0.01 M, and l 0.1 M sodium chloride, respectively, is shown in Fig. 3. The thermal air oxidation of ferrous ion catalyzed by chloride ion, corrected in Fig. 3, were $(2.5\pm0.5)\times10^{-4}$ M in these solutions. The effect of chloride ion as seen in Fig. 2 does not appear even in solution l till oxygen is consumed.

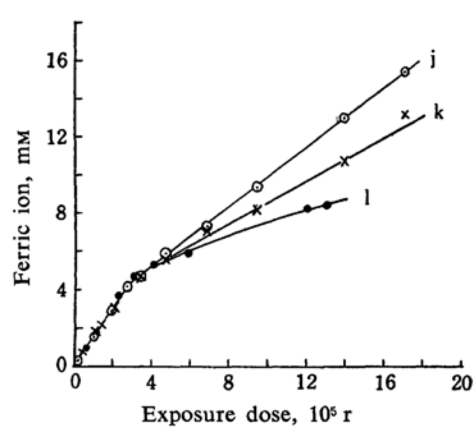


Fig. 3. Oxidation of ferrous ion in the oxygen-saturated solutions j (⊙), k (×) and l (●).

TABLE II. CONCENTRATION OF COMPLEXES IN M

Run	X	Fe^{III}	Fe^{3+}	$FeSO_4^+$	$Fe(SO_4)_2^-$	FeX^{2+}	FeX_2^+	FeX_3	X^-
h	Cl	0.01	9.1×10^{-5}	2.6×10^{-3}	7.3×10^{-3}	3.8×10^{-5}	4.9×10^{-6}	2.0×10^{-9}	0.1
i	Cl	0.01	9.0×10^{-5}	2.55×10^{-3}	7.2×10^{-3}	1.9×10^{-4}	1.2×10^{-4}	2.5×10^{-6}	0.5
m	Br	0.01	9.2×10^{-5}	2.6×10^{-3}	7.4×10^{-3}	4.6×10^{-6}	?	?	0.1
n	F*	0.01	5.3×10^{-5}	1.5×10^{-3}	4.2×10^{-3}	1.3×10^{-3}	2.6×10^{-3}	1.6×10^{-4}	1.55×10^{-4}
p	None	0.01	9.2×10^{-5}	2.6×10^{-3}	7.4×10^{-3}	—	—	—	—

Note: * On assumption that $\frac{(H^+)(F^-)}{(HF)}=1.17\times10^{-3}$ ($\mu=0.5$)[4].

TABLE III. ASSOCIATION CONSTANT OF FERRIC COMPLEXES AT 25°C

Ligand	K_1	K_2	K_3	Ionic strength	Reference
SO_4	95	9.4	—	1.0	5
F	1.62×10^5	8.9×10^3	500	0.5	4
Cl	4.2 ± 0.2	1.3 ± 0.4	0.04 ± 0.02	1.0	6
Br	0.5	—	—	1.0	6

Note: $K_n=\frac{(FeX_n^{n-3})}{(FeX_{n-1}^{n-4})(X^-)}$

Furthermore, the effect of 0.1 M various halide ions, namely, h sodium chloride, m potassium bromide n potasium fluoride, and p nothing, in the nitrogen-saturated standard solution, was studied as shown in Fig. 4. The effectiveness on the $G(Fe^{3+})$ is in the order of

$$Cl^- > Br^- > SO_4^{2-} > F^- \qquad \text{(i)}$$

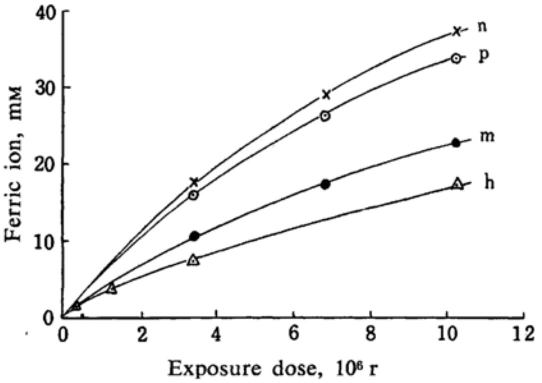


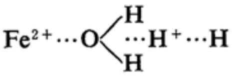
Fig. 4. Oxidation of ferrous ion in the oxygen-saturated solutions h (△), m (●), n (×) and p (⊙).

Discussion

If chloride ion is only a scavenger for OH radicals as mentioned in the "Introduction", the $G(Fe^{3+})$ should not be affected by the excess of chloride ion. However, the $G(Fe^{3+})$ in the air-free systems decreases at high dose with increase of chloride ion in Figs. 2 and 3. On the other hand, as mentioned already, ferric ions are more or less associated with anions; for example, as $FeCl^{2+}$, $FeCl_2^+$, $FeCl_3$ etc., and even if bare, hydrated with water molecules. Therefore, it is supposed that the reduction rate is different between those ferric complexes.

When the present hypothesis is correct, the observed series i for the effectiveness of various anions on the reduction of ferric ion might be understood by the properties and concentration of the complexes in the solutions. The concentrations of respective complexes in the irradiated standard solutions containing 0.1 M halide salt and 0.01 M ferric species are estimated in Table II without correction of activity on the asumption that ferrous and ammonium ions do not associate with any ion. The concentration of SO_4^{2-} is assumed to be 0.30 M in those solutions from Kerker's result[3]. Furthermore, the association constants of respective complexes in Table III[4-6] are used directly in the evaluation, for the association constant is usually not so changed between 0.5 and 1.0 of ionic strength expected from the above estimation for sulfuric acid.

Ferrous ion is considered to be also associated with hydrogen ion in the acidic solution through the oxygen atom of a water molecule like



$$Fe^{2+}\cdots O\begin{matrix} H \\ \cdots H^+\cdots H \\ H \end{matrix} \qquad \text{(ii)}$$

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[3] M. Kerker, *J. Am. Chem. Soc.*, **79**, 3664 (1957).
[4] J. Hudis and A. C. Wahl, ibid., **75**. 4153 (1953).
[5] R. A. Whiteker and N. Davidson, ibid., **75**, 3081 (1953).
[6] E. Rabinowitch and W. A. Stockmayer, ibid., **64**, 335 (1942).

and the approach of a hydrogen atom to the hydrogen ion is assumed to be the rate-determining step of reaction 3. Therefore, if the effect of reaction 7 is ignored, the reaction scheme in the "Introduction" leads to the equation for the rate of oxidation in the mixture of ferric and ferrous ions[7].

$$\frac{d\,(\mathrm{F^{III}})}{d\,(\mathrm{Dose})}=2G(\mathrm{H_2})+\frac{2G(\mathrm{H})}{1+\dfrac{k_4(\mathrm{Fe^{III}})}{k_3(\mathrm{Fe^{II}})}} \qquad \text{(iii)}$$

where k_3 and k_4 are the rate constants of reactions 3 and 4, respectively, and $(\mathrm{Fe^{III}})$ and $(\mathrm{Fe^{II}})$ are the concentration of ferric and ferrous species obtained by chemical analysis, respectively. Then, the appearent ratios, k_4/k_3, without considering complex formation, are obtained as listed in Table I as the measure of relative reduction rates. The larger value is more reliable.

Exactly speaking, since $(\mathrm{Fe^{III}})$ and $(\mathrm{Fe^{II}})$ do not always mean their free ion concentration $(\mathrm{Fe^{3+}})$ and $(\mathrm{Fe^{2+}})$, due to complex formation or imperfect dissociation, the apparent ratio should be rewritten as

$$\frac{k_4\,(\mathrm{Fe^{III}})}{k_3\,(\mathrm{Fe^{II}})}=\frac{1}{k_3\,(\mathrm{Fe^{2+}})}\sum(c_i)\,k_4^i \qquad \text{(iv)}$$

where c_1 and k_4^i are the concentration and rate constant of reduction reaction in reference to the i'th ferric complex, respectively, as

$$\mathrm{FeX^{2+}+H=Fe^{2+}+X^-+H^+} \qquad (8)$$

instead of reaction 4. If the difference between $(\mathrm{Fe^{II}})$ and $(\mathrm{Fe^{2+}})$ is ignored, the relative rate constant to reaction 3, the k_4^i/k_3, for respective ferric complexes are obtained in Table IV from the estimation in Table II. The contribution except for $\mathrm{Fe^{3+}}$, $\mathrm{FeSO_4{}^+}$, $\mathrm{FeX^{2+}}$ is also ignored in the evaluation, for the concentration or reaction rate of ignored complexes is small in comparison with those species. The value for $\mathrm{FeCl^{2+}}$ is obtained from k_4/k_3 of solutions g, h and i. The value of hydrated ferric ion corresponds to free ferric ion in Table II. The assumption for the concentration of $\mathrm{SO_4^{2-}}$ is effective for the values in Table IV, but not effective for the ratio between them. It is concluded from Table IV that the reduction rate of ferric chloride and bromide complexes by hydrogen atom is more than fifty times as great as hydrated ferric ions. Also that ferric sulfate complexes are much less reductive than hydrated ferric ion, and ferric fluoride complexes are scarcely reductive at all. It is also understood by the lower reductivity of ferric sulfate complexes why the dose-yield curve is straight ($G(\mathrm{Fe^{3+}})=8.2$) up to high dose in spite of the production of ferric ion.

TABLE IV. RELATIVE REDUCTION RATE AND STANDARD OXIDATION-REDUCTION POTENTIAL OF LIGAND

Ligand	k_4^i/k_3 in Eq. iv	Standard oxidation-reduction potential V.
Br	3000	1.065
Cl	3400±300	1.385
$\mathrm{H_2O}$	20～70	1.77
$\mathrm{SO_4}$	<2	1.98
F	≈0	2.85

The quantitative analysis is impossible for the result of the concentrated solutions as shown in Fig. 1 for the lack of fundamental constants. However, since the k_4/k_3 of sulfuric acid solution is approximately proportional to the ratio of concentration, $(\mathrm{Fe^{3+}})/(\mathrm{Fe^{III}})$ from Eq. iv, this ratio can give some information for those systems. That is, the ratio, $(\mathrm{Fe^{3+}})/(\mathrm{Fe^{III}})$, is a function of the concentration of sulfate ion, which suppresses the concentration of free ferric ion by the formation of ferric sulfate complexes as less-reductive species, including the dependence of association constant on ionic strength[5,8]. It is concluded from the ratios in Table I that the concentration of free ferric ion in the solutions decreases and that of free sulfate ion increases with increase of sulfuric acid up to 1 M, but neither concentration changes so much in the more concentrated sulfuric acid solution. The fact is confirmed by the study of the dissociation of sulfuric acid[3,9]. Sodium sulfate is not so effective as sulfuric acid for the suppresion of the reduction reaction in comparison between solutions b and e containing the same amount of sulfate group, for the dissociation of sulfuric acid is suppressed by sodium sulfate. The difference of k_4/k_3 between solutions a and p containing the same amount of sulfuric acid may be due to the effect of direct reaction with thermerized electron as suggested by Weiss[10] or other reactions in a hot track in the concentrated solution.

On the other hand, in Fig. 3, the $G(\mathrm{Fe^{3+}})$ in the presence of oxygen is not affected by chloride ion even in solution till oxygen is consumed. It is because all hydrogen atoms from the radiolysis of water associate rapidly with oxygen as $\mathrm{HO_2}$ which is an oxydizing reagent. According to Rothschild and Allen, the association rate is more than one hundred times as fast as the rate of reaction 3[7].

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[7] W. G. Rothschild and A. O. Allen, *Radiation Research*, **8**, 101 (1958).

[8] B. N. Mattoo, *Z. phys. Chem.*, **19**, 156 (1959).

[9] T. F. Young and L. A. Blatz, *Chem. Revs.*, **44**, 93 (1949).

[10] J. Weiss, *Nature*, **186**, 751 (1960).

Silverman and Dodson reported that the rate of electron exchange reaction between ferric chloride complex and ferrous ion is about ten times as fast as that between free ferric and ferrous ions(11). For such a case, the ligand atom gives a chance for multi-charged ions to anchor easily at the same site, and also serves as the bridge of electron transfer. Brown(12) suggested that the effectiveness may be a function of the electronegativity and polarizability(13). Since the reactivity of the hydrogen atom for the present reaction is not due to electrostatic force but due to unpaired electron, some difference is expected between the two cases. In fact, the electron exchange reaction between Tl^+ and Tl^{3+} is promoted in sulfuric acid(14), but ferric sulfate complex is less reductive for hydrogen atom than hydrated ferric ion as shown in Table IV. Anyhow, it is necessary for the reaction

$$Fe^{3+}-X^- + H \longrightarrow Fe^{2+} + XH \qquad (9)$$

even if XH is dissociated afterwards, that the ligand X loss one electron. The standard oxidation-reduction potential of the ligand to do so, ΔE, which may be a function of electronegativity and polarizability, corresponds to the reductivity of complexes in Table IV. The discrepancy for the order of bromide complex may be due to the uncertainty of its association constant. When the reduction rate of complexes might be expressed as

$$k = A \exp\left(-\frac{\Delta E}{RT}\right) \qquad (v)$$

the k_4^1/k_3 of fluoride complex is expected to be the order of 0.01.

Summary

The $G(Fe^{3+})$ of air-free acidic ferrous sulfate solutions decreases gradually with the increase of dose due to the re-reduction of ferric ion produced. The decrement depends on the property of anion as well as sulfuric acid in the solution in the order of

$$Cl^- > Br^- > SO_4^{2-} > F^-$$

The relative reduction rate of ferric complexes is obtained in Table IV as a result of the estimation of respective complexes in the solution; that is, ferric chloride and bromide complexes promote the reduction of ferric ion, and ferric sulfate and fluoride complexes suppress it.

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11) J. Silverman and R. W. Dodson, *J. Phys. Chem.*, **56**, 846 (1952).

12) Discussion in Ref. 11.

13) J. R. Tessman, A. H. Kahn and Wm. Shockley, *Phys. Rev.*, **92**, 890 (1953).

14) C. H. Brubaker, Jr., K. O. Groves, J. P. Mickel and C. P. Knop, *J. Am. Chem. Soc.*, **79**, 4641 (1957).

15) L. Pauling, "General Chemistry", Chap. 32, W. H. Freeman & Co., (1953).