Complex Ions in Acidic Iron Spring and its Catalase-Like Action

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Summary

Hot spring water usually possesses catalase-like action, which is stronger, the fresher the spring water, and the action gradually diminishes with passage of time. It has been reported by many workers that catalase-like action is closely connected with the state of iron(II) or (III) compounds containing in the water. Suzuki examined the catalase like action of acidic iron-alum solution, and proposed a empirical relation between the rate constant (K_V) for the decomposition of hydrogen peroxide and the concentration of iron(III), sulfate, and hydrogen ions as shown in the equation (2). On the other hand, Haber cleared that the rate constant (K_V) is given by the equation (5).

Limiting the species of trivalent iron in the acidic iron alum solution to Fe^{3+}, $FeSO_4^+$ and $FeOH^{2+}$, Haber's equation can be changed into the equation (7). In order to examine whether the equation (7) is experimentally established or not, the value of K on the acidic iron alum solutions was calculated from the results by using K_V (by Suzuki), $K_{FeSO_4^+}$ and k_2 (by the author), $K_{FeOH^{2+}}$ (by Rabinowitch et al.), from which approximately constant value of K is obtained as shown in Table II.

It is cleared from the above calculation that the catalase-like action of iron-alum aolution is not dependent on the total concentration of iron but the amount of free ferric ion (Fe^{3+}-aquo) in the solution. Namely inhibition of sulfate ion on the catalase-like action of acidic iron alum solution can be explained quantitatively by the complex formation between sulfate ion and iron(III) ion.

1.　Introduction

Acidic springs are a particular type of hot springs found only in Japan which are defined as the hot spring containing over 1 mg of hydrogen ion per kilogram of spring water. According to the components present in the spring, acidic springs are classified into acidic iron spring (acidic vitriol spring), acidic alum spring, and acidic sulfurated spring. Such acidic springs are known to have therapeutic effect in certain diseases such as chronic articular rheumatism, neuralgia, chronic skin deseases, and diabetes. Kusatsu, Noboribetsu, Nasu-Yumoto, Zao-Takayu, and Tamagawa are some of the famous spas among acidic springs in Japan.

Fresh hot springs, immediately after emergence, have better therapeutic effect and stronger biological action, and these effects diminish with passage of time. This phenomenon is called 'biological aging.' On the other hand, spring water of high-temperature under the high-pressure, when it emerges above the ground, undergoes changes, due to reduction in temperature and pressure, and contacting with air, in the state of dissolved components, with subsequent

liberation of gases and precipitation of undissolved matter. This phenomenon is called 'physicochemical aging.' One of such phenomenon is the catalytic or activation effect that often becomes an interestig problem. The hot spring usually possesses peroxidase or catalase-like action, which is stronger, the fresher the spring water, and the action gradually diminishes with passage of time. The theoretical discussions and experiments on this point using mineral water containing ferrous and bicarbonate ions held between Baudish and others,[1] and Fresenius[2] were well known.

Since then, catalytic capacity for decomposition of hydrogen peroxide has been used as measure to follow the aging phenomena of hot springs. There are numerous reports from this country regarding catalytic action of hot springs, notable among them being the work of Hattori,[3] Okabe,[4] and others.[5]

Suzuki[6] examined the relationship between various components in an acidic iron spring and its catalase-like action, and reported an interesting result in relation to complex ions of iron. On the other hand, Mashiko and the author studied the aging phenomenon of acidic iron springs and formation of complex ions through the measurement of oxidation reduction potentials[7] and analysis of absorption spectra.[8]

The present work is undertaken to examine the relationship between the complex ion and catalase-like action of artificially synthetized acidic iron springs from the analyses of the rate constant of hydrogen peroxide decomposition and stability constant of iron complex ions.

2. Catalase-Like Action of Iron (II) or (III) Sulfate Solution

When hydrogen peroxide is added to a sulfuric acid solution of iron (II) or (III) sulfate and the solution is allowed to stand for some time, hydrogen peroxide undergoes gradual decomposition. Concentration of hydrogen peroxide is titrated with potassium permanganate. If this decomposition reaction rate constant at $25°C$, K_v^{25} can be calculated from the following equation,

$$K_v^{25} = \frac{2.303}{t} \log \frac{A}{B}$$ (1)

where A is the value of first titration, B is that of the second titration, and t is the time elapsed between A and B titration.

According Suzuki's report, calculation of the values of K_v^{25} of sulfuric acid solution containing iron (II) or (III) gave the following results.

(1) Time variation in the values of K_v^{25} differed markedly between bivalent and trivalent iron ions, but the values become approximately constant in a stationary state (after a certain time after the addition of hydrogen peroxide) at the same concentration of sulfate ion, concentration of rion, and pH, irrespective of bivalent and trivalent iron solution.

(2) The value of K_v^{25} of an iron-alum solution at a stationary state was calculated, varying pH, the concentration of iron and sulfate ions, and it was found that the following equation was established experimentally.

$$K_v^{25} = \frac{5.37 \times 10^{-3} \times [C_{Fe^{3+}}]^{1.23}}{[H^+] [C_{SO_4^{2-}}]^{0.5}} \text{ mole} \cdot L^{-1} \cdot m^{-1}$$ (2)

where $C_{Fe^{3+}}$ is the total iron concentration and $C_{SO_4^{2-}}$ is the total sulfate concentration.

From this equation, it was found that the catalase-like action of a spring water is proportional to the total iron concentration and inversely proportional to the square root of the total sulfate concentration of sulfate ion.

(3) Effect of halogen, calcium, magnesium, aluminium, and phosphoric acid on the catalase-like

action was examined in the iron-alum solution system and it was found that halogens and especially phosphoric acid, markedly inhibited the catalase-like action, while other components rather accelerated this action.

3. Stability Constants of Iron Complexes determined from the Analyses of Absorption Spectra.

Absorptions of a spring water in the ultraviolet to visible range [8] are mainly due to the trivalent iron complex ions (Fe^{3+}–aquo, $FeSO_4^+$, $FeOH^{2+}$, etc.), sulfur compounds (H_2S, $S_2O_3^{2-}$ etc.), and humic substances in specific cases.

The absorption with a maximum at 300 nm, often observed in the spectra of acidic iron springs, is due to $FeSO_4^+$. $FeOH^{2+}$ and $FeCl^{2+}$ possess absorption maximum at 300 and 340 nm, respectively, but are not generally observed due to overlapping with the absorption of $FeSO_4^+$. Absorptions in the shorter wave-length range below 260 nm are chiefly due to Fe^{3+}–aquo but its absorption maximum (approximately around 240 nm) is not well observed.

By the absorption spectral analyses, stability constants of $FeSO_4^+$ and dissociation constant of sulfuric acid were calculated by the author[9]. The mixed solutions of iron (III) perchlorate, perchloric acid, and sulfuric acid or sodium perchlorate were used. For this measurement, the solutions were prepared with constant ionic strength, constant total iron concentration, constant hydrogen ion concentration, and varying concentration of sulfate ion. Dissociation constant of sulfuric acid k_2 (= $[H^+][SO_4^{2-}]/[HSO_4^-]$) is calculated by the same way. These constants are shown in Table I, and the relationship between ionic strength and stability constant of $FeSO_4^+$ or dissociation constant of sulfuric acid are shown in Figs. 1 and 2.

Table 1　Stability Constant ($K_{FeSO_4^+}$) and Dissociation Constant (k_2)

Ionic strength (I)		$K_{FeSO_4^+}$	$\log K_{FeSO_4^+}$	k_2
I	$\sqrt{I}$			
0.13	0.361	366	2.56	5.06×10^{-2}
0.30	0.548	164	2.22	7.86×10^{-2}
1.0	1.0	71.6	1.86	9.87×10^{-2}

$K_{FeSO_4^+} = [FeSO_4^+]/[Fe^{3+}][SO_4^{2-}]$
$k_2 \quad = [H^+][SO_4^{2-}]/[HSO_4^-]$

The curve in Fig. 1 fits the experimental formula reported by Kumai[10].

$$\log K_{FeSO_4^+} = 3.86 - \frac{6\sqrt{I}}{1 + 1.7\sqrt{I}} + 0.22 \cdot I \qquad (3)$$

4. Relationship between Catalase-Like Action and Complex Ions

According to Harber,[11] rate constant for the decomposition of hydrogen peroxide by iron (III) ion is represented by the following formula, where K is the proportionality constant.

$$-d\,H_2O_2/dt = K \cdot [Fe(III)] \cdot [H_2O_2]/H^+ \qquad (4)$$

The reaction rate constant of this formula is represented by the following formula,

$$K_v = K \cdot [Fe(III)]/H^+ \qquad (5)$$

It was pointed out by Suzuki that the inhibition of sulfate ion on the catalase like action of acidic iron-alum solution is closely dependent upon the formation of complex between ferric and sulfate ion. Accordingly, the above equation can be changed to the following formula, assuming
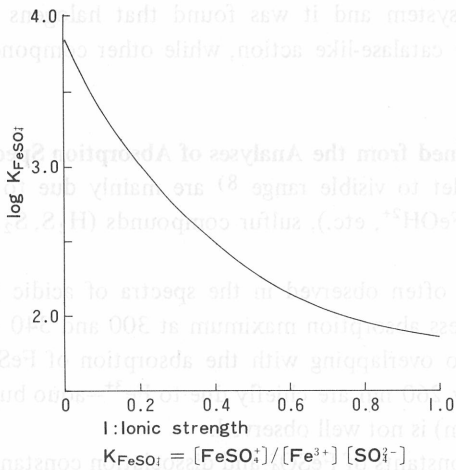
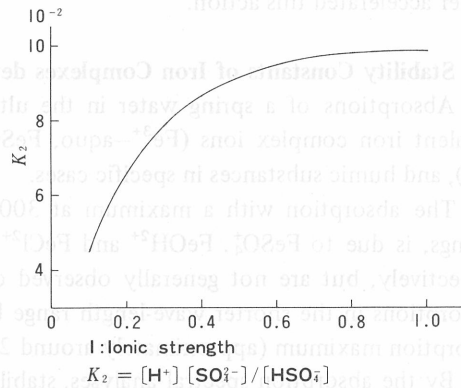**Fig. 1 Relationship between Ionic Strength and $K_{FeSO_4^+}$**

$K_{FeSO_4^+} = [FeSO_4^+]/[Fe^{3+}][SO_4^{2-}]$

Fig. 2 Relationship between Ionic Strength and k_2

$K_2 = [H^+][SO_4^{2-}]/[HSO_4^-]$

that the catalase-like action is not dependent on the total concentration of iron (III) ion but the amount of free ferric ion (Fe^{3+}).

$$K_v = K \cdot [Fe^{3+}]/H^+ \tag{6}$$

Relationship between the rate constant and stability constant of complex ions was examined with acidic iron-alum solutions, assuming the presence of limited species of trivalent iron such as Fe^{3+}, $FeSO_4^+$, and $FeOH^{2+}$, and the following equation was obtained.

$$K = \frac{K_v \{([H^+]+k_2)[H^+] + K_{FeSO_4^+} \cdot C_{SO_4^{2-}} \cdot k_2[H^+] + ([H^+]+k_2) \cdot K_{FeOH^{2+}}\}}{([H^+]+k_2) \cdot C_{Fe^{3+}}} \tag{7}$$

where K is proportionality constant,

$K_{FeSO_4^+} = [FeSO_4^+]/[Fe^{3+}][SO_4^{2-}]$

$K_{FeOH^{2+}} = [FeOH^{2+}] \cdot [H^+]/[Fe^{3+}]$

$k_2 = [H^+][SO_4^{2-}]/[HSO_4^-]$

$C_{Fe^{3+}} = Fe^{3+} + FeSO_4^+ + FeOH^{2+}$

$C_{SO_4^{2-}} = SO_4^{2-} + HSO_4^-$

In order to examine whether this equation is experimentally established or not, the values of K on the acidic iron-alum solutions were calculated from the results reported by Suzuki. The values of K_v^{25} of the solutions, varying pH, the concentration of iron and sulfate, were experimentally obtained by Suzuki[6]. The values of $K_{FeSO_4^+}$ and k_2 were measured by the author.[9] $K_{FeOH^{2+}}$ has been measured by other workers[12,13]. In this study, the relationship between $K_{FeOH^{2+}}$ and ionic strength shown in Fig. 3, which was reported by Rabinowitch et al, was used.

These values for K_v^{25}, H^+, $C_{SO_4^{2-}}$, $C_{Fe^{3+}}$, $K_{FeSO_4^+}$, k_2, and $K_{FeOH^{2+}}$ were put into the equation (7) to get the value of K. The values of K were nearly constant as shown in the last column of Table II.
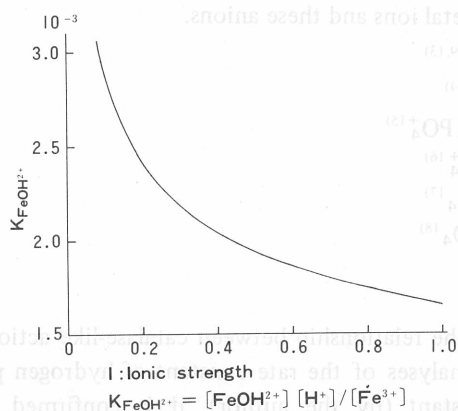
$$K_{FeOH^{2+}} = [FeOH^{2+}][H^+]/[Fe^{3+}]$$

Fig. 3 Relationship between Ionic strength and $K_{FeOH^{2+}}$

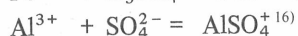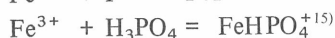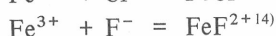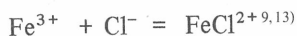**Table II Calculated Values of K (Proportionality Constant)**

I Ionic Strength	$C_{Fe^{3+}}$ Total Concentration of Iron (III) (mol/l)	$C_{SO_4^{2-}}$ Total Concentration of Sulfate Ion (mol/l)	pH	Rate Constant $K^{25} \cdot 10^{-3}$ $mol \cdot l^{-1} \cdot m^{-1}$	K Proportionality Const. $10^{-3} \cdot mol^{-1} \cdot m^{-1}$
0.11	10^{-3}	3.63×10^{-2}	2.67	2.59	99
0.13	"	4.26 "	1.70	0.26	63
0.24	"	7.76 "	1.49	0.13	52
0.29	"	9.54 "	2.83	2.61	71
0.16	1.5×10^{-3}	5.25 "	1.36	0.18	51
0.14	5×10^{-3}	3.89 "	1.93	3.38	96
0.19	"	5.89 "	1.69	1.50	74
0.15	10^{-2}	3.89 "	1.99	8.75	100
0.21	"	5.89 "	1.75	4.06	84
0.27	"	7.76 "	1.62	2.71	77
0.42	"	1.27×10^{-1}	1.88	3.92	79
0.45	"	1.37 "	2.24	8.11	78
0.68	"	2.14 "	2.32	8.17	76
0.74	4×10^{-2}	1.96 "	1.40	5.97	76

This fact has proved that the equation (7) is established experimentally and the inhibition of catalase-like action by sulfate ion is due to the formation of $FeSO_4^+$. In other words, the catalase-like action is not dependent on the total concentration of iron but the amount of free ferric ion in the solution, and the inhibition of the catalase-like action of sulfate ion is due to the decrease in the concentration of ferric ion by the formation of $FeSO_4^+$ between trivalent ferric ion and sulfate ion.

According Suzuki's experiment, this catalase-like action is markedly inhibited by halide ion and especially by phosphoric ion, and is slightly accelerated by calcium, magnesium, and

aluminium ions. These facts can also be understood qualitatively as the formation of the following complexes between these metal ions and these anions.
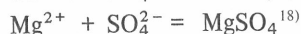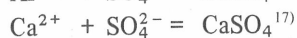
$$Fe^{3+} + Cl^- = FeCl^{2+\,9,13)} \qquad \text{inhibition}$$
$$Fe^{3+} + F^- = FeF^{2+\,14)} \qquad \text{marked inhibition}$$
$$Fe^{3+} + H_3PO_4 = FeHPO_4^{+\,15)} \qquad \text{marked inhibition}$$
$$Al^{3+} + SO_4^{2-} = AlSO_4^{+\,16)} \qquad \text{acceleration}$$
$$Ca^{2+} + SO_4^{2-} = CaSO_4^{17)} \qquad \text{acceleration}$$
$$Mg^{2+} + SO_4^{2-} = MgSO_4^{18)} \qquad \text{acceleration}$$

5   Conclusion

In the present work, the relationship between catalase-like action and iron complex ion are examined, and from the analyses of the rate constant of hydrogen peroxide decomposition (by Suzuki) and stability constant (by the author), it is confirmed that the inhibition of this catalase-like action by sulfate ion is due to the formation of $FeSO_4^+$ between ferric ion and sulfate ion. Futhermore, the effects of halogen, calcium, magnesium, aluminium and phosphoric acid on the catalase-like action of iron-alum solution can also be understood as the formation of complexes betweem metal ions and anions.

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