Autoxidation of Ferrous Ions in a Concentrated Aqueous Solution of Ferrous Chloride

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The kinetics of autoxidation reactions of ferrous chloride in hydrochloric acid solutions have been studied over the concentration ranges of Fe(II) 20–80 g dm⁻² and HCl 60–160 g dm⁻³ by changing oxygen partial pressure and temperature. The apparent second order dependence of reaction rate on ferrous ion concentration was caused by the change in the activity of hydrochloric acid due to the progress of oxidation reaction. The activation energy was found to be 51.5 kJ mol⁻¹ in 60 g dm⁻³ HCl solution, suggesting that the overall reaction rate was controlled by chemical reaction. By taking these into consideration, the actual rate was found to be of first order with respect to ferrous ion concentration and thus the conclusions reached in the previous paper¹ were general for the autoxidation of ferrous chloride in hydrochloric acid solution.

1 Introduction

The oxidation reactions of ferrous chloride in an aqueous hydrochloric acid solution with dissolved molecular oxygen would be important to the hydrometallurgical treatment of spent pickle liquors in iron and steel industry or the regeneration of ferric chloride leaching solution in copper hydrometallurgy. The present authors and their co-worker studied kinetically the autoxidation of Fe(II) in concentrated hydrochloric acid solutions¹. They obtained the expression

\[ \text{Rate} = k a_{Fe}^{+} a_{Cl}^{-} [\text{Fe(II)}] \rho_{O_2} \]  

(1)

as the rate equation. This equation suggests that \( a_{Fe}^{+} \) and \( a_{Cl}^{-} \) are the controlling factors of the concentration of actual reacting species of Fe(II).

As experienced in the autoxidation study of spent pickle liquors in which the concentration of ferrous chloride is higher than that in the previously studied concentrated hydrochloric acid solutions, the dependencies of reaction rate on the Fe(II) concentration and the hydrochloric acid activity differ from those shown by equation (1)².

It is important to elucidate whether the different mechanism controls the autoxidation reaction or the different dependencies from equation (1) were apparently observed by some reasons for the autoxidation of ferrous ions in concentrated ferrous chloride solutions.

This study was aimed to investigate the autoxidation reaction of ferrous ions in a concentrated ferrous chloride solution from the kinetic point of view to solve the problem mentioned above.

2 Experimental Procedures

The experimental procedures employed in this study for the measurements of the reaction rate are the same as described in the previous papers¹,².

3 Experimental Results and Discussion

Some typical examples of rate curves for the autoxidation reaction of ferrous chloride solutions are depicted in Fig. 1.

Figure 2 shows the relationship between the concentration of Fe(II) remaining in the solution and reaction time for the solutions containing 40 g dm⁻³ Fe(II) and 60–160 g dm⁻³ HCl. As an ordinate in this figure, \([\text{Fe(II)}]^{-1/2}\) was taken. The linear relation obtained for the solutions whose HCl concentration is below 140 g dm⁻³ shows that the reaction is of three halves order with respect to Fe(II) concentration under these conditions. The points for
Fig. 1 Typical examples of rate curve for the autoxidation of ferrous ions
(A) Fe(II) : 80 g dm⁻³, HCl : 120 g dm⁻³, Temp. : 55°C, P_O₂ : 1 atm
(B) Fe(II) : 40 g dm⁻³, HCl : 100 g dm⁻³, Temp. : 65°C, P_O₂ : 1 atm
(C) Fe(II) : 20 g dm⁻³, HCl : 140 g dm⁻³, Temp. : 65°C, P_O₂ : 1 atm

The higher concentration of hydrochloric acid, e. g. 160 g dm⁻³, do not lie well on a straight line, showing the transition towards first order dependence.

For the solutions containing 80 g dm⁻³ Fe(II) and 20-120 g dm⁻³ HCl, the three halves order dependency does not hold any more, showing that the oxidation rate is of second order with respect to the Fe(II) concentration as shown in Fig. 3. A further increase in hydrochloric acid concentration, e. g. 140 g dm⁻³ or 160 g dm⁻³ HCl causes the losing of linearity. The dependency of the reaction rate on the Fe(II) moves towards the direction of three halves order dependency.

From these observations, it is presumed that the rate of autoxidation reaction is related to the relative value of \([\text{Fe(II)}]/[\text{HCl}]\). It is obvious that the dependency of reaction rate on the Fe(II) concentration tends to move from first order towards second order by increasing the value of \([\text{Fe(II)}]/[\text{HCl}]\).

The effect of \(P_{O_2}\) on reaction rates of Fe(II) oxidation is shown in Fig. 4 as the plots of \(k\) vs \(P_{O_2}\). For the solution containing 80 g dm⁻³ Fe(II) and 60 g dm⁻³ HCl, it was found that the reaction rate is of first order with respect to \(P_{O_2}\). The plots of \(k\) against \(P_{O_2}\) will be explained later.

The present authors and their co-worker pointed out in the previous paper\(^1\) that the
activity of hydrochloric acid instead of its analytical concentration was more important in the kinetic study of Fe(II) autoxidation. According to their results, the reaction rate is of first order with respect to the activity of hydrochloric acid.

In Fig. 5, the rate constants $k_{3/2}$ and $k_1$, which were calculated from the slopes of the straight lines shown in Figs. 2 and 3, respectively, were plotted against $a_{HCl}$. The values of $a_{HCl}$ in this figure were determined by measuring the emf of Harned cell, whose test solutions contained the equivalent moles of calcium chloride to that of ferrous chloride. Calcium chloride was chosen as a resembling electrolyte to ferrous chloride. The purpose of the addition of calcium chloride to the test solutions is to take the effect of FeCl$_2$ on $a_{HCl}$ into consideration, and at the same time to compensate the effect of Fe(III), which is the product of the oxidation reaction, on the ionic strength of solution, and thus on $a_{HCl}$.

In the higher range of $a_{HCl}$, linear relations were roughly obtained between $k_{3/2}$ or $k_1$ and $a_{HCl}$. However, these straight lines do not pass the origin, and also $k_{3/2}$ and $k_1$ values deviate from the straight lines at the lower range of $a_{HCl}$.

The effect of temperature on the reaction rates of Fe(II) oxidation is shown in Fig. 6 as the plots of $k_1$ vs $T^{-1}$. Activation energy for the solution which contained 80 g dm$^{-3}$ Fe(II) and 60 g dm$^{-3}$ HCl was found to be 51.5 kJ mol$^{-1}$. The plots of $k$ against $T^{-1}$ will be explained later.

The results obtained in this study and the results reported in the previous paper were correlatively examined, because of the lack of mutual agreement.

The oxidation reaction of Fe(II) with dissolved molecular oxygen is an acid consuming
reaction and thus the progress of the reaction decreases the concentration of acid in the solution according to equation (2).

$$4 \text{Fe}(\text{II}) + \text{O}_2 + 4 \text{H}^+ = 4 \text{Fe}(\text{III}) + 2 \text{H}_2\text{O}$$

(2)

The solution system studied in the previous work\(^1\) contained a far larger amount of hydrochloric acid compared with that of ferrous chloride. Therefore, the change in acid concentration during the oxidation reaction of Fe(II) did not affect significantly the overall reaction rate. However, for a solution, whose hydrochloric acid concentration is comparable to or lower than that of Fe(II), the decrease in acid concentration cannot be neglected. In this case, the concentration of hydrochloric acid and, therefore, \(a_{\text{HCl}}\) change with the lapse of retention time, and thus reaction rate should be influenced. In order to obtain a knowledge on the change in \(a_{\text{HCl}}\) during the reaction, the emf of Harned cell was measured for the solution system HCl-CaCl\(_2\). The results are shown in Fig. 7, by plotting \(a_{\text{HCl}}\) against CaCl\(_2\) concentration. As the autoxidation reaction of Fe(II) progressed, hydrogen ions were consumed, but the concentration of chloride ions did not change throughout the reaction.

If we assume that the consumption of hydrogen ions is equivalent to the consumption of hydrochloric acid, the change of \(a_{\text{HCl}}\) can be estimated as a shift on a vertical line at a constant CaCl\(_2\) concentration as shown in Fig. 7. However, such an estimation should lead us to the underestimation of \(a_{\text{HCl}}\) value, because of the unchanged concentration of chloride ion.

In order to correct the effect of remained chloride ions on \(a_{\text{HCl}}\), \(a_{\text{HCl}}\) was conventionally determined for the solution containing the equivalent moles of calcium chloride to consumed hydrogen ions. The activity of hydrochloric acid thus determined should involve the effect of calcium ions added to the solution. However, it is thought that the presence of calcium ions, which is equivalent to the decreased amount of hydrogen ions, is useful to compensate the change of \(a_{\text{HCl}}\) value due to the change of the oxidation state of iron. The inclined lines in Fig. 7 can be used for the determination of conventional \(a_{\text{HCl}}\). Two examples of the variation of \(a_{\text{HCl}}\) with time determined by this method are shown in Fig. 8. If the ratio of [Fe(II)]/[HCl] is large, the change of \(a_{\text{HCl}}\) is sufficiently

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**Fig. 7** Relationship between \(\log a_{\text{HCl}}\) and \(C(\text{CaCl}_2)\)/mol dm\(^{-3}\)

(1) HCl : 140 g dm\(^{-3}\), (2) HCl : 130 g dm\(^{-3}\)
(3) HCl : 120 g dm\(^{-3}\), (4) HCl : 110 g dm\(^{-3}\)
(5) HCl : 100 g dm\(^{-3}\), (6) HCl : 90 g dm\(^{-3}\)
(7) HCl : 80 g dm\(^{-3}\), (8) HCl : 70 g dm\(^{-3}\)
(9) HCl : 60 g dm\(^{-3}\), (10) HCl : 50 g dm\(^{-3}\)

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**Fig. 8** Variation of \(a_{\text{HCl}}\) with time due to the progress of the oxidation reaction

(A) Fe(II) : 40 g dm\(^{-3}\), HCl : 140 g dm\(^{-3}\), Temp. : 65°C, \(P_{\text{O}_2}\) : 1 atm
(B) Fe(II) : 80 g dm\(^{-3}\), HCl : 100 g dm\(^{-3}\), Temp. : 55°C, \(P_{\text{O}_2}\) : 1 atm
large, and this can be seen in Fig. 8.

The authors and their co-worker elucidated that the oxidation rate of Fe(II) in a concentrated hydrochloric acid solution in which the change of HCl concentration can be neglected, was expressed by

\[-d \frac{[Fe(II)]}{dt} = k [Fe(II)] a_{HCl}\] (3)

Nevertheless, second order dependence of Fe(II) concentration on reaction rate was observed for the system whose [Fe(II)]/[HCl] was large, as shown in Fig. 3. Also we observed three halves power dependence for the solution having intermediate [Fe(II)]/[HCl] ratio as shown in Fig. 2. However, it was already mentioned that the changes of \(a_{HCl}\) for these cases could not be neglected.

Now let us assume that the reaction rate of Fe(II) oxidation is of first order with respect to [Fe(II)] in all cases. Also we assume that the apparent three halves or 2nd order dependency observed is due to the variation of \(a_{HCl}\) with time. Then equation (3) can be rewritten as equation (4).

\[-d \frac{[Fe(II)]}{dt} = k [Fe(II)] a_{HCl}(t)\] (4)

By integrating equation (4), we obtain equation (5).

\[-\ln [Fe(II)] = k \int_0^t a_{HCl}(t) \, dt + C\] (5)

where \(C\) is an integral constant.

If we consider equation (4) as a general rate equation for the autoxidation of Fe(II) aqueous solution, a linear relationship must be hold between \(-\ln [Fe(II)]\) and \(\int_0^t a_{HCl}(t) \, dt\), in spite of the change of [Fe(II)]/[HCl], as can be expected from equation (5).

In Fig. 9, the relationship between \(-\ln [Fe(II)]\) and \(\int_0^t a_{HCl}(t) \, dt\) for two solutions containing 80 g dm\(^{-3}\) Fe(II) and 60 g dm\(^{-3}\) HCl, and 40 g dm\(^{-3}\) Fe(II) and 140 g dm\(^{-3}\) HCl, respectively, are shown. The values of \(\int_0^t a_{HCl}(t) \, dt\) used in this figure were obtained from the \(a_{HCl}\)-time plot in Fig. 8 by means of the graphical integration method. As can be clearly seen in Fig. 9, the linearity of respective lines is satisfactory, and thus the assumption mentioned above are deemed to be appropriate. Thus, the three halves or second order dependence on Fe(II) concentration of the autoxidation rate for a concentrated ferrous chloride solution can be attributed to the effect of the change of \(a_{HCl}\) with time due to the progress of the oxidation reaction. By taking \(a_{HCl}(t)\) instead of \(a_{HCl}\) into consideration, we can obtain the same rate equation described in the previous paper\(^{13}\).

The oxidation rate of Fe(II) can be regarded as of first order with respect to both Fe(II) concentration and \(a_{HCl}\). From the slope of the straight line A (or B) in Fig. 9, a rate constant \(k\) can be calculated.

The dotted line in Fig. 4 shows the relationship between \(k\) and \(pO_2\). The reaction rate is obviously of first order with respect to \(pO_2\). This result agrees with that obtained by plotting apparent rate constant \(k\) against \(pO_2\).

The dotted line in Fig. 6 shows the dependency of \(k\) on temperature. The activation energy calculated from the straight line was 51.5 kJ mol\(^{-1}\), which agreed with the actigation energy value calculated from \(k_1\) vs. 1/\(T\) plots. The value of this activation energy is obviously smaller than 78.2 kJ mol\(^{-1}\) for the autoxidation Fe(II) in concentrated hydrochloric acid solution\(^{13}\). However, we also observed that the presence of sodium chloride lowered the activation energy value\(^{13}\). The solution studied in this work contained a large amount of ferrous chloride, and this would cause the lower
activation energy.

From these findings, we can conclude that the following rate equation is general for the autoxidation reaction of Fe(II) in hydrochloric acid solutions.

\[ -\frac{d[\text{Fe(II)}]}{dt} = k \cdot a_{\text{HCl}} \cdot t \cdot [\text{Fe(II)}] \cdot \rho_{\text{O}_2} \]  

(6)

Yano et al. studied the autoxidation reaction of ferrous chloride in a dilute hydrochloric acid solution. They reported that the reaction rate was of second order with respect to Fe(II) concentration. Their experiments were done for the solutions having large ratios of [Fe(II)]/[HCl]. The apparent second order dependence on [Fe(II)] observed by them is consistent with the result of the present work.

4 Conclusion

Apparently the rates of autoxidation reactions of concentrated ferrous chloride solutions were of 2nd order or of three halves order with respect to ferrous ion concentration. By considering the consumption of hydrogen ions due to Fe(II) autoxidation reaction, and thus the variation of hydrochloric acid activity with time, it was found that the reaction rate was essentially of first order with respect to ferrous ion concentration. Accordingly, the rate equation reported in the previous paper is deemed to be general for the autoxidation of Fe(II) in hydrochloric acid solutions.

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References:
2) M. Iwai and H. Majima, submitted for publication to Denki Kagaku.

(p. 716 よりつづく)

エビとカニとカイ 食事は台湾旅行の楽しみの中でも最大級のものの一つであろう。中国系の料理はもちろ んのこと各国の料理が揃っているが何と言っても嬉しかっ たのは海鮮料理である。これはほとんど養殖によるもの だそうだが各々 10 種にも及ぶエビ、カニ、カイ（若千 のチカカも含まれる）を材料とした国際有名料理だそう だが紹興酒がピッタリくるところをみるややは中国系 の料理の新種とみた。せっとレストランに通うかたわ ら一両分の会食者（10 人位）がないときは市場で材料を 仕入れてきて珍料理を考案したのは言うまでもない。

食事に関して閉口したことが一つだけあった。多くの 場合、中央の回転卓上の大皿や大鉢には共用のハシやス ブーンはなく各自のハシとスプーンで料理を口（あるい は取り皿）に運ぶことになる。出発前、台湾のある日 本人から台湾の衛生・医療事情は良好で熱帯の風土病や 論文のページ

伝染病の心配はまったくないが肝炎には暮々気をつけ るようにとのことまごとした注意を受けた。当初はこの 注意を守って他人のハシが触れた部分や一定温度以下に さがったスープは一切口にしないよう細心の注意を払っ たがこれではご鰐走の味は半減するし、人々の発熱とし ており大学でも町でも肝臓を病んでいそうな人は見当ら ズ、しいに馬鹿馬鹿しくなってきた。そして 1 ヶ月を 過ぎた頃には何の関係もなく大皿の残りものを掘き集め るようになった。筆者も家族も一週間ほど日本から遊び にきた友人達も誰一人として肝炎に罹ったものがいない ことは言うまでもない。ただ、“同じ釜の飯を食う”と いうことは比喻としては連帯感や親近感を表わすものと して異論のあろうはずもないが、近代社会の食習慣と しては心理的にも公衆衛生上も工夫あるべきと感じられ

(p. 747 つづく)