An Experimental Study on the Kinetics of the Reaction of Fe$^{II}$(EDTA) with Oxygen in Aqueous Solutions

Abstract

The kinetics of the reaction of oxygen with aqueous Fe$^{II}$(EDTA) solutions has been determined in a range of process conditions ($C_{Fe^{II}(EDTA)} = 15 - 60$ mol/m$^3$, $P_{O_2} = 5 - 20$ kPa, pH = 5 - 8, $T = 298 - 328$ K, $C_{NaCl} = 0 - 15$ kg/m$^3$) using a gas-liquid stirred cell reactor. The oxygen absorption rates were modelled using an expression derived by De Coursey based on the penetration theory of mass transfer. Within the range of process conditions applied, the reaction was shown to be first order in oxygen and second order in iron chelate. The temperature dependence of the kinetic constant may be expressed as ($pH = 7$, no salt addition): $k_{12} = 5.3 \cdot 10^3 \cdot e^{-\frac{4098}{T}}$ (m$^3$/mol$^2$ s).

The kinetic constant is essentially independent of the pH in the range 5 < pH < 8. When applying a NaCl concentration of 15 kg/m$^3$, the kinetic constant increases with 35% ($T = 328$ K). The oxidation of Fe$^{III}$(EDTA) to Fe$^{II}$(EDTA) is not the sole oxygen consuming reaction. The extent of side reactions, possibly related to EDTA ligand degradation, is a function of the pH and the oxygen concentration.
4.1. Introduction
In the BiodeNOx process, various other components are present in flue gas which can interfere with the BiodeNOx process and give rise to undesired side reactions with the iron chelate. One of the major components is molecular oxygen, which is typically present in amounts between 2 and 10 vol % [53]. Oxygen reacts with the iron chelate to form Fe$^{III}$(EDTA) according to the overall reaction:

$$O_2 + 4Fe^{II}(EDTA) + 2H_2O \rightarrow 4Fe^{III}(EDTA) + 4OH^-$$ (1)

This complex is not able to bind NO, and, for this reason, the efficiency of the BiodeNOx absorption unit may decrease. The presence of oxygen in the flue gas cannot be avoided and the rate of oxidation compared to the rate of NO absorption has to be reduced as much as possible by optimising the absorption process. For this purpose, reliable kinetic data on the oxidation reaction in the BiodeNOx operating window are required.

The reaction has been the object of several studies. A summary of the literature available is represented in Table 1 and the kinetic data are shown in Table 2. A considerable spread in the orders of the reactants has been observed. In some cases, the reaction was observed to be first order in iron chelate, in other cases second order. This change in the order in iron chelate appears to be a function of the concentration of ferrous chelate [45, 57]. At low concentrations, the reaction seems to be first order in iron chelate whereas the order changes to 2 at increasing Fe$^{II}$(EDTA) concentrations.

Table 1. Overview of literature studies performed on the oxidation of Fe$^{II}$(EDTA) in water.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>T (K)</th>
<th>pH</th>
<th>$C_{Fe^{II}(EDTA)}$ (mol/m$^3$)</th>
<th>$C_{O_2}$ (mol/m$^3$)</th>
<th>Ratio EDTA/Fe</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stopped flow</td>
<td>295</td>
<td>2 - 6</td>
<td>0.1 - 0.2</td>
<td>0.25</td>
<td>1 - 40</td>
<td>Travin and Skurlatov [95]</td>
</tr>
<tr>
<td>Bubble column</td>
<td>293 - 333</td>
<td>6 - 8</td>
<td>&lt;20</td>
<td>0.018 - 0.064</td>
<td>1 - 2</td>
<td>Sada and Kumazawa [96]</td>
</tr>
<tr>
<td>Bubble Column</td>
<td>298</td>
<td>3 - 7</td>
<td>2.5</td>
<td>0.125 - 1.5</td>
<td>5</td>
<td>Brown and Mazzarella [97]</td>
</tr>
<tr>
<td>Stopped flow</td>
<td>286 - 323</td>
<td>2 - 7</td>
<td>2.5 - 20</td>
<td>0.125</td>
<td>1 - 20</td>
<td>Zang and van Eldik [45]</td>
</tr>
<tr>
<td>Stirred cell</td>
<td>293 - 331</td>
<td>7.5</td>
<td>0 - 100</td>
<td>0 - 1.25</td>
<td>1.2</td>
<td>Wubs [57]</td>
</tr>
<tr>
<td>Stopped flow</td>
<td>298</td>
<td>1 - 6</td>
<td>2.5</td>
<td>0.125</td>
<td>1</td>
<td>Seibig and van Eldik [98]</td>
</tr>
</tbody>
</table>

Mechanistic proposals have been put forward to explain this effect. Recent studies suggest that the order in iron is 2 when using iron concentrations relevant for the BiodeNOx process (10 < Fe < 100 mol/m$^3$) [57]. In addition, all studies imply that the reaction is first order with respect to oxygen [45, 57, 95 - 98]. This work describes a kinetic study on the reaction of $C_{Fe^{II}(EDTA)}$ with oxygen under conditions relevant to the BiodeNOx process ($C_{Fe^{II}(EDTA)} = 15 - 60$ mol/m$^3$, $P = 10^5$ Pa, $P_{O_2} = 5 - 20 \cdot 10^4$ Pa, pH = 5 - 8, $T = 298 - 328$ K, $C_{NaCl} = 0 - 15$ kg/m$^3$). Although various studies have been performed in the past, the results are not always reliable due
to improper attention to mass transfer issues. In addition, a lack of kinetic information was found for the typical BiodeNOx process conditions ($T > 300$ K, $pH \neq 7.5$ and for an iron chelate concentration $> 10$ mol/m$^3$).

Table 2. Orders in reactants for the reaction between Fe$^{II}$(EDTA) and oxygen.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>pH</th>
<th>Order in Fe$^{II}$(EDTA)</th>
<th>Order in O$_2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>6</td>
<td>1</td>
<td>1</td>
<td>Travin and Skurlatov [95]</td>
</tr>
<tr>
<td>293 – 330</td>
<td>6 - 8</td>
<td>0.5</td>
<td>1</td>
<td>Sada and Kumazawa [96]</td>
</tr>
<tr>
<td>298</td>
<td>4.5 - 7</td>
<td>1 - 2</td>
<td>1</td>
<td>Brown and Mazzarella [97]</td>
</tr>
<tr>
<td>286.5 - 322</td>
<td>5</td>
<td>1 - 2</td>
<td>1</td>
<td>Zang and van Eldik [45]</td>
</tr>
<tr>
<td>293 - 361</td>
<td>7.5</td>
<td>2</td>
<td>1</td>
<td>Wubs [57]</td>
</tr>
<tr>
<td>298</td>
<td>2.5 - 6</td>
<td>1</td>
<td>1</td>
<td>Seibig and van Eldik [98]</td>
</tr>
</tbody>
</table>

Special attention is given to pH effects and to a high salt loading in the aqueous phase on the oxygen absorption rates. The flue gas often contains acidic components such as SO$_x$ or HF and HCl and these may reduce the pH of the solution. This could possibly lead to negative effects on the absorption rates and micro-bacterial growth. To avoid these effects, a constant pH is desired and buffering and/or the addition of bases is required. This will evidently lead to high salt concentrations in the Fe-chelate solution and this might have an effect on the oxygen absorption rates.

4.2 Experimental Section

4.2.1 Chemicals

FeCl$_2$.4H$_2$O (p.a.), titriplex (EDTA-Na$_2$) (p.a.), and Na$_2$CO$_3$ were obtained from Merck; NaOH (33% in water) from Boom, Ce(SO$_4$)$_2$.4H$_2$O (> 99%) from Acros. N$_2$O (> 99%), O$_2$ (> 99.99%), and N$_2$ (> 99.99) were obtained from Hoekloos. Reverse osmosis water was applied to prepare the various solutions.

4.2.2 Preparation of the Fe$^{II}$(EDTA) solution

Aqueous solutions of Fe$^{II}$(EDTA) are extremely air-sensitive and were handled under a protective nitrogen atmosphere. The Fe$^{II}$(EDTA) solution was prepared by dissolving a predetermined amount of titriplex in degassed water ($1.5 \times 10^{-4}$ m$^3$). The turbid solution turned transparent when the pH was increased from 4 to 9 by carefully adding some drops of a 4 M NaOH solution. The appropriate amount of FeCl$_2$.4H$_2$O (Fe : EDTA = 1 : 1.2 mol/mol) was added to the EDTA solution, giving a slightly green, clear solution with a pH of about 3. Next, the solution was diluted with degassed water to $9 \times 10^{-4}$ m$^3$. At this stage, the pH was adjusted to the desired value by the addition of a NaOH solution. Finally, degassed water was added to adjust the total volume to $10^{-3}$ m$^3$. 

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4.2.3 Experimental set up and instrumentation
The kinetic experiments were carried out using two different stirred cell reactors, both made of glass. The two reactors differed in dimensions and in the lay out of the mechanical stirring devices. Both reactors were equipped with four glass baffles and could be operated in batch as well as in continuous mode with respect to the gas phase, and in batch mode with respect to the liquid phase. A schematic representation of reactor 1 is given in Fig. 1.

Figure 1. The stirred cell reactor (1) used in this study. 1, 2: magnetic valve for the gas in- and outlet, 3: metal cover, 4: double walled glass reactor, 5: stirring device, 6, 7: gas and liquid phase stirrer, 8: temperature sensor, 9: pressure indicator.

Table 3. Characteristics of the stirred cell contactors.

<table>
<thead>
<tr>
<th></th>
<th>Reactor 1</th>
<th>Reactor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total reactor volume (m³)</td>
<td>1.98 · 10⁻³</td>
<td>1.245 · 10⁻³</td>
</tr>
<tr>
<td>Liquid volume (m³)</td>
<td>10⁻³</td>
<td>0.3 · 10⁻³</td>
</tr>
<tr>
<td>Interfacial area (m²)</td>
<td>8.34 · 10⁻³</td>
<td>7.79 · 10⁻³</td>
</tr>
<tr>
<td>Gas impeller (m)</td>
<td>Six blade turbine</td>
<td>Six bladed turbine</td>
</tr>
<tr>
<td></td>
<td>d = 6 · 10⁻²</td>
<td>d = 6 · 10⁻²</td>
</tr>
<tr>
<td>Liquid impeller (m)</td>
<td>Six blade turbine</td>
<td>Magnetic stirrer</td>
</tr>
<tr>
<td></td>
<td>d = 4 · 10⁻²</td>
<td>d = 2 · 10⁻²</td>
</tr>
<tr>
<td>Ns liquid stirrer (rpm)</td>
<td>120</td>
<td>100</td>
</tr>
<tr>
<td>Ns gas impeller (rpm)</td>
<td>120</td>
<td>2000</td>
</tr>
</tbody>
</table>

The stirrer of reactor 1 had six blades for the gas phase and six smaller ones for the liquid phase. For reactor 2, a stainless steel turbine impeller was used for the gas phase, while a magnetic stirrer in combination with an external magnetic drive was used for the liquid phase. The rotation speed of the magnetic drive was determined using a stroboscope (Philips PR 9107). The double wall of the reactors allowed the use of water to regulate the temperature in the reactor (Julabo, MV basis). Typical dimensions of the stirred cell contactors are given in Table 3. A temperature indicator (PT-100) and a pressure transducer (Trafag, ECO 2.5 A) were used to monitor the temperature and pressure during an experiment.
4.2.4 Constant pressure experiments
The constant pressure experiments were performed in reactor 1. An experimental procedure described in detail by Wubs [57] was applied. Before starting an experiment, the head space of the reactor was evacuated to remove the air, until the vapour pressure of water was established. At this point, oxygen gas was supplied to the reactor until the desired pressure was reached. Subsequently, the inlet valve was closed, the stirrer activated and the absorption started. The experiment was allowed to proceed until the pressure reached a pre-set minimum value, after which extra gas was supplied until the original pre-set maximum pressure was reached again. By repeating this procedure several times, the pressure profile appeared as a saw tooth like curve.

4.2.5 Decreasing pressure experiment
A number of physical absorption experiments using inert N₂O were performed in order to determine the solubility of the gas in the various solutions and the hydrodynamics of both reactor set ups. These experiments were carried out at decreasing pressure. The gas was supplied to the reactor until the pressure reached a pre-set value. At this point, the inlet valve was closed, the stirrer activated and the absorption started. The absorption was allowed to proceed until the pressure inside the reactor reached a constant value. A typical pressure profile is shown in Fig. 2. A similar procedure was applied when performing oxygen absorption experiments at decreasing pressure.

![Image](image-url)

Figure 2. Absorption profile of N₂O in an aqueous Fe(II)(EDTA) solution. \( T = 328 \) K, \( C_{Fe(II)(EDTA)} = 60 \) mol/m³, \( P_{N₂O}^{i} = 90580 \) Pa, \( P_{N₂O} = 69500 \) Pa.

4.2.6 Determination of the concentration of Fe(II) in solution
The concentration of Fe(II) in the solution was determined before and after every oxidation experiment by titration using a 0.1 M Ce(SO₄)₂ solution. A 0.025 M ferroine solution was used as redox indicator. To obtain reproducible results, the iron-chelate sample was diluted with an approximate 10-fold volume of sulphuric acid (2 M) and degassed by adding approximately 1 g of NaHCO₃. After adding some drops of the ferroine indicator, the colour of the solution turned red/orange. At this point,
the titration was started by the drop wise addition of the cerium solution until the colour of the solution changed from red-orange to clear blue-green [72].

4.3 Theory
4.3.1 Calculation of the kinetics of the oxidation reaction at various process conditions
The enhancement factor $E_A$ for reactive absorption processes is generally defined as:

$$E_A = \frac{J_{\text{reaction}}}{J_{\text{physical}}}$$

$E_A$ may be determined experimentally for each absorption experiment using the following relation:

$$E_A = \frac{J_{\text{reaction}}}{J_{\text{physical}}} = \frac{J_{O_2}}{k_L C_{O_2}^{1/2}} = \frac{1}{k_L} \frac{He_{O_2}}{P_{O_2}} \frac{V_G}{RT_L} \left( - \frac{dP_{O_2}}{dt} \right)$$

The various theories for mass transfer accompanied by chemical reaction in parallel have provided relations between $E_A$ and the Hatta ($Ha$) number [73]. Here, the $Ha$ number for reaction (1) is defined as:

$$Ha = \frac{1}{k_L} \left( \frac{2 D_{O_2} k_{pq} C_{Fe^{II}(EDTA)}^{p} C_{O_2}^{q-1}}{q+1} \right)$$

where $p$ and $q$ represent the orders of the reaction respect to $O_2$ and $Fe^{II}(EDTA)$ and $k_{pq}$ is the kinetic rate constant.

In case $Ha$ is smaller than 0.2, the oxygen absorption rate is not enhanced by chemical reaction and the enhancement factor ($E_A$) is equal to 1. In case $2 < Ha < E_{A,\infty}$, the reaction takes place in the fast regime and $E_A$ is equal to $Ha$. Here $E_{A,\infty}$ is defined as [73]:

$$E_{A,\infty} = \frac{1}{\sqrt{r_B}} + \frac{r_B C_{Fe^{II}(EDTA)}}{v_B C_{O_2}^{1/2}}$$

In case $Ha >> E_{A,\infty}$, the absorption process occurs in the instantaneous reaction regime and $E_A = E_{A,\infty}$.

As shown later, the intermediate regime between fast and instantaneous regime appears to be of particular interest for this study. Several relations between $E_A$ and $Ha$ have been derived for this regime. A useful relation is an explicit expression derived by De Coursey using the penetration theory of Dankwerts [99]:

$$E_A = -\frac{Ha^2}{2(E_{A,\infty} - 1)} + \sqrt{\frac{Ha^4}{4(E_{A,\infty} - 1)^2} + \frac{E_{A,\infty} \cdot Ha^2}{(E_{A,\infty} - 1)^2} + 1}$$

The relation was derived for reacting components having equal diffusivities and extended to compounds with different diffusivities. The maximum inaccuracy of this
expression is around 13% for a ratio of diffusion coefficients in the order of 0.02 and it decreases to 6% for equal diffusivities. Later, the authors derived a refined, implicit relation, which is more accurate for species with unequal diffusivities [75]. In case of an irreversible reaction, this relation can be written as:

\[
\frac{1}{Ha^2} + \frac{1}{q(E_A \sqrt{r_B} + 1)} = \frac{1}{E_A^2 - 1}
\]

(7)

where:

\[
q = \frac{C_{Fe^{II}(EDTA)}}{V_B C_{O_2}}
\]

(8)

and:

\[
r_B = \frac{D_{Fe^{II}(EDTA)}}{D_{O_2}}
\]

(9)

The equation is valid for any value of \(Ha\) and it can be extended to an irreversible reaction of any order, taking into consideration the correct definition of \(Ha\). This implicit relation is in good agreement with the results based on numerical solutions using a rigorous mass balance approach and a mean deviation of 11% was observed [76].

### 4.3.2 Solubility and mass transfer coefficients

Knowledge of the solubility of oxygen and the hydrodynamics in the stirred cell contactor as a function of the process conditions are required to determine the kinetics of the oxidation reaction. The solubility of oxygen in the liquid phase may be described by the Henry coefficient, which is defined as the ratio of the partial pressure of a gas and its concentration in the bulk liquid at equilibrium:

\[
He = \left( \frac{P_{O_2}}{C_{O_2}} \right)_{eq}
\]

(10)

For physical absorption of a gas in a batch set-up, a mass balance gives the following relation for the Henry coefficient:

\[
He = \frac{P^w - P^o \cdot RTV_l}{P^w - P^o \cdot V_G}
\]

(11)

In case of oxygen, the solubility cannot be measured directly due to the fact that oxygen reacts with Fe^{II}(EDTA). To determine the \(He\) value for \(O_2\), physical absorption experiments using an inert gas (nitrous oxide) are performed. The measured solubility of the inert gas may be used to calculate the oxygen solubility using the following relation:
\[
\left(\frac{He}{He_w}\right)_{O_2} = A_G \left(\frac{He}{He_w}\right)_{N_2O}
\]

The term \(A_G\) represents a correction term, which is a function of the total ion concentration and temperature. The solubility of \(N_2O\) in water is given by Versteeg and van Swaaij [77]. The solubility of oxygen in water is given by Benson and Krause [100]. The effect of salts on the solubility of gases may be estimated using the following relation:

\[
\log\left(\frac{He_{salt}}{He_w}\right) = \sum (h_i + h_G) \cdot C_i^{\text{ion}}
\]

where \(h_i\) is a ion specific parameter, \(h_G\) a gas specific parameter and \(C_i^{\text{ion}}\) is the concentration of ions [101]. This equation can be used in the temperature range 273 - 363 K with the correction of the gas specific parameter in the following way:

\[
h_G = h_{G,0} + h_T (T - 298.15)
\]

where \(h_{G,0}\) is the reference parameter and \(h_T\) is the gas specific parameter for the temperature effect. Combining eqs (12-14) for \(O_2\) and \(N_2O\) allows the elimination of the unknown values of \(h_i\) [44]:

\[
\log \left(\frac{He_{O_2}}{He_{N_2O}}\right) = \sum \left[h_{G,0,N_2O} - h_{G,0,O_2} + \left(h_{T,N_2O} - h_{T,O_2}\right)(T - 298.15K)\right] \sum_{i=1}^{N} C_i^{\text{ion}} = \log A_G
\]

The \(h_{G,0}\) and \(h_T\) were taken from the literature [44]. For an ion concentration up to 1500 mol/m³, \(A_G\) is 1.03 at 293 K and 1.05 at 333 K [101].

The mass transfer coefficient of oxygen in the liquid phase \((k_L)\) is a function of the temperature, the composition of the liquid phase and the stirrer-speed and geometry. \(k_L\) may be obtained experimentally by performing physical absorption experiments using an inert gas like \(N_2O\) in the batch set-up. A mass balance leads to the following relation:

\[
k_{L,at} = \left(\frac{\alpha}{\alpha + 1}\right) \ln \left(\frac{P_{O_2}^0}{(\alpha + 1)P_{O_2} - \alpha P_{O_2}^0}\right)
\]

with:

\[
\alpha = \frac{V_G \cdot He}{V_L \cdot RT}
\]
The $k_{La}$ for oxygen can be calculated from the experimentally determined value for N$_2$O using the following relation [73]:

$$\left(k_{La}\right)_{O_2} = \left(k_{La}\right)_{N_2O} \cdot \sqrt{\frac{D_{O_2,w}}{D_{N_2O,w}}} \quad (18)$$

$D_{N_2O,w}$ is given by Versteeg and van Swaaij [77]. $D_{O_2,w}$ may be calculated using the relation given by St-Denis and Fell [102]. The diffusion coefficient of oxygen in Fe$^{II}$(EDTA) solutions ($D_{O_2}$) may be calculated from $D_{O_2,w}$ using a relation given by Ho et al. [80].

### 4.3.3 Determination of the stoichiometric coefficient

To obtain information of possible other oxygen consuming reactions besides the main reaction, the stoichiometric coefficient of iron for the reaction has to be determined experimentally. For the reaction:

$$O_2 + \nu_B Fe^{II}(EDTA) \rightarrow \text{products} \quad (19)$$

the stoichiometric coefficient $\nu_B$ may be calculated considering that:

$$C_{Fe^{II}(EDTA)} = C_{Fe^{II}(EDTA)}^0 - \frac{\nu_B N_{O_2}}{V_L} \quad (20)$$

The concentrations of the iron chelates before and after reaction ($C_{Fe^{II}(EDTA)}^0$ and $C_{Fe^{II}(EDTA)}$) were determined experimentally by titration, while the total number of moles of oxygen absorbed, $N_{O_2}$, was calculated from the absorption profiles of decreasing pressure experiments.

### 4.4 Results and discussion

Absorption experiments were performed using pure oxygen at pressures ranging from 5 to 20 kPa and initial Fe$^{II}$(EDTA) concentrations in the range of 15 and 60 mol/m$^3$. In all cases, an EDTA chelate molar ratio of 1.2 : 1 was applied. A first group of experiments was carried out at different temperatures (298 - 328 K) and an initial fixed pH = 7 to determine the temperature dependence of the kinetic constant of the reaction. Subsequently, experiments with a variable pH (5 - 8) were applied at 328 K to probe possible pH effects on the kinetics. Finally, experiments in the presence of NaCl (5 - 15 kg/m$^3$) were performed (328 K) to determine any effect of the presence of salt on the gas absorption rates and the intrinsic kinetics.

### 4.4.1 Determination of reaction orders and absorption regime

To determine the absorption regime and subsequently the kinetic data, the order in reactants needs to be known. The order in oxygen may be obtained from decreasing pressure experiments. For such experiments, a mass balance for oxygen for the gas phase leads to:

$$-\frac{dP_{O_2}}{dt} = c \cdot P_{O_2} \quad (21)$$
A plot of $\ln(P_{O2}'/P_{O2})$ versus time is expected to give a straight line, provided that $c$ is independent of the initial oxygen partial pressure. This is the case when the reaction is first order in oxygen and when the reaction takes place in the fast regime ($E_A \ll E_{A∞}$).

![Figure 3. First order dependency of the reaction in oxygen. $T = 328$ K, $C_{Fe(II)(EDTA)}^0 = 50$ mol/m$^3$, pH = 7, $C_{O2}' = 0.036$ mol/m$^3$.](image)

For a typical experiment in the fast regime, a linear relation between $\ln(P_{O2}'/P_{O2})$ and the time was observed (Fig. 3) and this confirms that the reaction is first order in oxygen.

In our studies, $C_{Fe(II)(EDTA)}$ always exceeded 10 mol/m$^3$ and as a consequence an order in Fe of two was assumed. The validity of this assumption will be discussed later on. When the reaction is first order in oxygen and second order in iron, the Ha number for the system is defined as:

$$Ha = \frac{C_{Fe(II)(EDTA)}}{k_L} \sqrt{D_{O2}k_{12}}$$  \hspace{1cm} (22)

Knowledge on the regime of absorption may be obtained from the theory of mass transfer and reaction in parallel. In case the absorption occurs in the fast regime, $E_A$ equals $Ha$ and eq. (22) may be rewritten as:

$$C_{O2} \frac{dE_A}{dC_{Fe(II)(EDTA)}} = C_{O2} \frac{dE_A}{C_{Fe(II)(EDTA)}} \sqrt{D_{O2}k_{12}}$$  \hspace{1cm} (23)

In this regime, $C_{O2}$ is expected to vary linearly with $C_{O2}'$.

In case the absorption process takes place in the instantaneous regime, eq. (5) holds and this may be rewritten as:
Absorption experiments were performed in reactor 2 to determine $E_A$ as a function of $C_{O_2}^i$. The results are given in Fig. 4. A linear dependency was observed at low $C_{O_2}^i$, whereas a leveling off occurs at higher $C_{O_2}^i$ values. Although not conclusive, this suggests that the reaction takes place in the fast regime at low $C_{O_2}^i$ and that the regime changes from fast to instantaneous at higher oxygen concentrations.

![Graph showing the relationship between $C_{O_2}^i$ and $dE_A/dC_{Fe(EDTA)}$](image)

**Figure 4.** Determination of the reaction regime for the reaction between Fe$^{II}$(EDTA) and oxygen. $C_{Fe(EDTA)}^{O} = 50$ mol/m$^3$, $T = 328$ K, pH = 7. ■: measured; solid line: for illustrative purposes only.

Additional evidence that the reaction takes place in a regime between fast and instantaneous is obtained when considering the $E_A$ as a function of $C_{O_2}^i$ (Fig. 5). In case the reaction is a fast first order reaction in oxygen, the $E_A$ is expected to be independent of the $C_{O_2}^i$ (eq. (22)). In case the reaction is instantaneous, a plot of $\ln(E_A)$ vs $\ln(C_{O_2}^i)$ is expected to give a straight line with a slope of -1 (eq. (5)). The observed slope is -0.15, which is again a strong indication that the reaction takes place in the intermediate regime between fast and instantaneous. On the basis of these findings, it seems appropriate to apply the implicit De Coursey relation (eq. (7)) to describe the absorption process in the stirred cell contactor.
Figure 5. Enhancement factor as a function of the interfacial oxygen concentration. $C_{Fe^{II}(EDTA)}^0 = 50 \text{ mol/m}^3$, $T = 323 \text{ K}$, pH = 7.

4.4.2 Determination of the kinetic constant of the oxidation reaction at various temperatures

A set of experiments at different temperatures was performed in reactor 2 to determine the temperature dependence of the kinetic constant. The experiments were carried out at an initial pH = 7, an initial Fe$^{II}$(EDTA) concentration of 50 mol/m$^3$ and $C_{O_2}^i$ between 0.04 and 0.4 mol/m$^3$. The rate constant at different temperatures may be calculated by combining eq. (7) and eq. (22). This results in:

$$k_{12} = \frac{k_L^2}{C_{Fe^{II}(EDTA)}^2 D_{O2}} \cdot \frac{(E_A^2 - 1) \cdot q(E_A \sqrt{r_y} + 1)}{q(E_A \sqrt{r_y} + 1) - E_A^2 + 1}$$  \hspace{1cm} (25)

The experimentally determined $k_{12}$ values at various temperatures are graphically provided in the form of an Arrhenius plot (Fig. 6). In this figure, also earlier data provided by Wubs [57] and Zang and Van Eldik [45] are given. The activation energy ($E_a$) and the pre-exponential factor of the oxidation reaction were calculated to be 34.1 (+/- 0.4) kJ/mole and 5326 (+/- 2) m$^6$/mole$^2$·s, respectively. Our results are within the broad range of values reported in the literature, see Fig. 6 for details. Zang and van Eldik reported an $E_o$ of 36.6 kJ/mole which is close to the value found by us, however, the kinetic constants are significantly higher than our values. Van Eldik used a different experimental technique (single phase system, stopped flow) compared to the multi-phase stirred cell contactor used in this study. Their kinetic data were analysed assuming pseudo first order reactions which is only correct when one of the reactants is in large excess. These conditions are not always fulfilled in their study. In addition, when determining the order in oxygen, first order behaviour in Fe$^{II}$(EDTA) was assumed, whereas in a subsequent stage, it is concluded that an order in Fe of two is more appropriate.
The low temperature kinetic constants are in close agreement with earlier studies by Wubs [57]. However, the high temperature results deviate considerably and the $E_a$ reported by Wubs (27.2 kJ/mole) is significantly lower than found by us. These differences are likely related to the differences in calculation procedures. Wubs applied the explicit relation by De Coursey (eq.(6)) to calculate the kinetic data, which is less accurate in case of unequal diffusivities. Moreover, a value of $v_B$ of 2, instead of 4 was applied in the calculation, which is not appropriate.

### 4.4.3 pH effects on the absorption rates and the intrinsic kinetics

A number of constant pressure experiments in reactor 1 at 328 K was performed to determine the influence of pH variation (5 – 8) on the kinetics of the oxidation of Fe$^{II}$(EDTA). A $C^0_{Fe^{II}(EDTA)}$ between 15 and 60 mol/m$^3$ and a $P_{O_2}$ of 18 kPa were used. The results were compared with the experiments obtained at pH = 7. $E_A$ was calculated as a function of $C_{Fe^{II}(EDTA)}$ using eq. (3). An overview of the experimental results is provided in Fig. 7 (pH = 5) and 8 (pH = 8). The maximum $E_A$ was about 17 for both experimental series.

The kinetic constants of the reaction at various pH’s were calculated using eq. (22). To do so, $He_{O2}$ and $k_L$ as a function of the pH need to be known. The measured $He_{O2}$ in Fe$^{II}$(EDTA) solutions at different pH’s is provided in Fig. 9. As expected, the $He_{O2}$ increases with $C_{Fe^{II}(EDTA)}$. However, a clear effect of the pH on $He_{O2}$ is absent. The effects of the pH on the $k_L$ in Fe$^{II}$(EDTA) at 328 K were determined experimentally. A significant effect of the pH was absent.

The kinetic constant values at 328 K were subsequently calculated from the experimental enhancement factors, using eq. (22). The results are provided in Table 4.
Figure 7. $E_A$ as a function of $C_{FeII(EDTA)}$ at pH = 5. ■ experimental data, $T = 328$ K, $C_{O_2} = 0.158$ mol/m$^3$. Solid line: calculated according to eq. (7). $T = 328$ K, $k_{12} = 0.030$ m$^6$/mol$^2$ s, $k_L = 2.40 \cdot 10^{-5}$ m/s, $P_{O_2} = 18$ kPa, $D_{O_2} = 2.05 \cdot 10^{-9}$ m$^2$/s, $r_B = 0.213$ [103], $v_b = 4$. Dotted line: calculated according eq. (7) for a 1,1 order reaction with $k_{11} = 0.95$ m$^3$/mol·s.

Figure 8. $E_A$ as a function of $C_{FeII(EDTA)}$ at pH = 8. ■ experimental points, $T = 328$ K, $C_{O_2} = 0.158$ mol/m$^3$. Solid line: calculated according to eq. (7). $T = 328$ K, $P_{O_2} = 18$ kPa, $k_{12} = 0.024$ m$^6$/mol$^2$ s, $k_L = 2.40 \cdot 10^{-5}$ m/s, $D_{O_2} = 2.05 \cdot 10^{-9}$ m$^2$/s, $r_B = 0.213$ [103], $v_b = 4$. Dotted line: calculated according eq. (7) for a 1,1 order reaction with $k_{11} = 0.81$ m$^3$/mol·s.
Figure 9. $He_{O2}$ in Fe$^{II}$(EDTA) solutions. $T = 328$ K, $P_{H2O} = 40$ kPa. •: pH = 8; ▼: pH = 5.

Table 4. $k_{12}$ at $T = 328$ K as a function of the pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>$C_{Fe(EDTA)}$ (mol/m$^3$)</th>
<th>$k_{12}$ (m$^6$/mol$^2$ s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8(a)</td>
<td>60</td>
<td>0.024 ± 0.005</td>
</tr>
<tr>
<td>7(b)</td>
<td>50</td>
<td>0.020 ± 0.001</td>
</tr>
<tr>
<td>5(a)</td>
<td>60</td>
<td>0.030 ± 0.005</td>
</tr>
</tbody>
</table>

(a): constant pressure experiments, $C_{Fe(EDTA)} = 15 - 60$ mol/m$^3$, $C_{O2} = 0.158$ mol/m$^3$ (reactor 1).
(b): decreasing pressure experiments, $C_{Fe(EDTA)} = 50$ mol/m$^3$, $C_{O2} = 0.036 - 0.16$ mol/m$^3$ (reactor 2).

It appears that the pH effects on $k_{12}$ are relatively small and within the error of the determination. Brown and Mazzarella [97] observed that the kinetic constant for the oxidation reaction is pH independent for a pH $> 5$ ($T = 298$ K). Zang and van Eldik [45] studied the effect of the pH in the range of 1 – 7. The kinetic constant was not pH dependent at pH values exceeding 5. However, at further lowering the pH, the kinetic constant increases until a pH of 3. Upon further lowering the pH, the $k_{12}$ decreases again.

With the experimentally determined dependency of the $E_A$ versus the $C_{Fe(II)(EDTA)}$ (Fig. 7 and 8), the assumption that the reaction is indeed second order in iron and not first order in the experimental range of conditions can be verified. In case the reaction is first order in oxygen, the dependency of the $E_A$ versus the $C_{Fe(II)(EDTA)}$ may be predicted using eq. (7), taking into account the correct definition of $Ha$. The results for both pH series are given in Fig. 7 and 8. Quantitatively, the experimental profiles are more in line with a second order reaction in iron than with a first order dependency. Statistical analyses using the sum of squares method also indicates that the model assuming a second order dependency in iron describes the experimental points more satisfactorily.
4.4.4 The effect of salt addition on the absorption rate and the kinetics of the reaction

A number of constant pressure absorption experiments was performed in the presence of various amounts of NaCl (5, 10, 15 kg/m³) to probe the effects of salinity on the gas absorption rates and the intrinsic reaction kinetics ($T = 328$ K, pH = 7, $C_{FeII(EDTA)}^0 = 50$ mol/m³ and $P_{O2} = 18000$ Pa). The observed $E_A$ values as a function of $C_{FeII(EDTA)}$ are given in Fig. 10.

![Figure 10. $E_A$ values at different NaCl concentrations, $T = 328$ K, pH = 7. □: $C_{NaCl} = 5$ kg/m³, ●: $C_{NaCl} = 10$ kg/m³, ▲: $C_{NaCl} = 15$ kg/m³. Lines: calculated according to eq. (7), $C_{O2}^p = 0.156$ mol/m³, $D_{O2} = 2.05*10^{-9}$ m²/s, $r_B = 0.213$ [103], $v_B = 4$. Solid line: $k_{12} = 0.019$ mol/m³·sec, $k_L = 2.40*10^{-5}$ m/s. Dotted line: $k_{12} = 0.022$ mol/m³·sec, $k_L = 2.31*10^{-5}$ m/s. Dashed line: $k_{12} = 0.027$ mol/m³·sec, $k_L = 2.11*10^{-5}$ m/s.](image)

Figure 10. $E_A$ values at different $C_{NaCl}$ values, $T = 328$ K, pH = 7. □: $C_{NaCl} = 5$ kg/m³, ●: $C_{NaCl} = 10$ kg/m³, ▲: $C_{NaCl} = 15$ kg/m³. Lines: calculated according to eq. (7), $C_{O2}^p = 0.156$ mol/m³, $D_{O2} = 2.05*10^{-9}$ m²/s, $r_B = 0.213$ [103], $v_B = 4$. Solid line: $k_{12} = 0.019$ mol/m³·sec, $k_L = 2.40*10^{-5}$ m/s. Dotted line: $k_{12} = 0.022$ mol/m³·sec, $k_L = 2.31*10^{-5}$ m/s. Dashed line: $k_{12} = 0.027$ mol/m³·sec, $k_L = 2.11*10^{-5}$ m/s.

It is clear that $E_A$ increases with increasing salt concentration. This effect may be the result of changes in either the physical and hydrodynamics properties of the liquid (e.g. $k_L$) and/or effects on the intrinsic kinetics. To gain more insights in these effects, the $k_L$ and gas solubility of oxygen at various salt loadings were determined ($T = 328$ K, $C_{FeII(EDTA)} = 50$ mol/m³ and pH = 7). The $He_{O2}$ was rather insensitive to the salt concentration in the concentration range applied. We therefore applied an average $He_{O2}$ value of $2.3*10^5$ Pa·m³·mol⁻¹ in the calculations. The $k_L$ values were calculated and the results are given in Fig. 11. $k_L$ decreased when increasing the salt loading in line with an observed reduction of the $D_{O2}$ at higher salt concentrations [104]. Here, the $D_{O2, w}$ decreased up to 5 % when increasing the salt concentration from 5 to 16 kg/m³.

With the $k_L$ and the solubility of oxygen in the presence of salts known, the kinetic constants at various salt concentrations may be calculated using eq. (25). The results are given in Fig. 12. Despite the relatively large error, $k_{12}$ appears to increase with $C_{NaCl}$. 

![Figure 12. Calculated kinetic constants at various salt concentrations.](image)
Figure 11. $k_L$ of oxygen as a function of the concentration of $C_{NaCl}$ at $T = 328$ K, $C_{Fe^{II}(EDTA)} = 50$ mol/m$^3$ and pH = 7.

Figure 12. $k_{12}$ versus $C_{NaCl}$ at $T = 328$ K, pH = 7, $C_{Fe^{II}(EDTA)} = 50$ mol/m$^3$ and $C_{O_2} = 0.156$ mol/m$^3$. 
4.4.5 Side reactions

There is considerable evidence in the literature that the reaction of an Fe-chelate with oxygen does not only lead to iron oxidation but also to the formation of degradation products [56, 58]. However, the type and number of oxygen consuming side reactions is still not clear to date, although it appears that chelate degradation may be involved as well. Information on the extent of the occurrence of oxygen consuming side reactions may be obtained by determination of the stoichiometric coefficient of iron. If only iron oxidation takes place, the stoichiometric coefficient, $v_B$, is equal to 4, see reaction (1). If other oxygen consuming reactions occur simultaneously, the experimentally determined $v_B$ is reduced.

$v_B$ was determined using eq. (20) for a number of absorption experiments performed in reactor 2 using different oxygen pressures (between 5 and 45 kPa) and pH values between 5 and 8, at a constant $C_{Fe^{II}(EDTA)}^0 = 50 \text{ mol/m}^3$ and $T = 328 \text{ K}$, see Fig. 13. The $v_B$ values ranged from 3 to 4 and are dependent on $C_{O_2}^i$. At low $C_{O_2}^i$, $v_B$ is close to 4, indicating that other oxygen consuming reactions only take place to a minor extent. Upon increasing $C_{O_2}^i$, $v_B$ drops rapidly and subsequently levels off to a value close to three. This remarkable sudden step change in the $v_B$ as a function of the $C_{O_2}^i$ has not been reported to date. So far, we do not have a sound explanation for this observation. Variations of $v_B$ of reaction (1) as a function of experimental conditions have been observed in literature [44, 105]. However, the wider range of $C_{O_2}^i$ applied in those studies and the scatter in the data did not allow the observation of the clear step change in $v_B$ as a function of $C_{O_2}^i$.

The shape of the curves is also a function of the pH. At low pH, the sudden drop of $v_B$ occurs at a lower $C_{O_2}^i$ value. Hence, the extent of side reactions may be reduced by working at relatively high pH while keeping the oxygen concentrations low.

Figure 13. $v_B$ as a function of $C_{O_2}^i$ for different initial pH values. $C_{Fe^{II}(EDTA)}^0 = 50 \text{ mol/m}^3$, $T = 328 \text{ K}$. ■: pH = 7, ●: pH = 8, ▲: pH = 5.
4.5. Conclusions

The kinetics of the reaction of oxygen with Fe\textsuperscript{II}(EDTA) at conditions that are typical for the BiodeNOx process (C\textsubscript{Fe\textsuperscript{II}(EDTA)} = 15 - 60 mol/m\textsuperscript{3}, pH = 5 - 8, T = 328 K, P\textsubscript{O\textsubscript{2}} = 5 – 20 kPa) have been determined. In this experimental range, the reaction is first order in oxygen and second order in iron chelate. At pH = 7, the temperature dependence of the kinetic constant (298< T < 328 K) may be expressed as:

\[ k_{12} = 5.3 \times 10^3 \cdot e^{-\frac{4098}{T}} \text{ (m}^6\text{/mol}^2\text{ s}) \]

The value of the kinetic constant appears to be independent of the pH in the range 5 - 8. The kinetic constant is a function of the salt loading and a 35% increase was observed when performing the reaction in a 15 kg/m\textsuperscript{3} NaCl solution.

The overall stoichiometric coefficient of the reaction deviates from the theoretical value of 4, suggesting that other oxygen consuming reactions take place as well. A remarkable, unprecedented step change in the \( v_B \) as a function of the C\textsubscript{O\textsubscript{2}} was observed. Higher oxygen concentrations and, to a lesser extent, low pH values promote the side reactions and cause the stoichiometric coefficient to drop to about 3.

The side reactions may involve reactions of oxygen with the EDTA chelate, leading to the undesired degradation of the EDTA ligand. This study suggests that the EDTA degradation rates may be reduced by working at a relatively high pH value and low oxygen concentrations.

The experimental data obtained in this study will be applied for the design of a reactive NO absorption unit using Fe\textsuperscript{II}(EDTA) as the reactant. Here, the oxidation reaction is an undesirable side reaction which needs to be suppressed to enhance NO absorption rates.