

Revisiting the Anodic Dissolution of Pure Iron in Strong Acids

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ABSTRACT

The goal of the research reported herein was to accomplish a quantitative mechanistic analysis of iron dissolution in strong acid in a potential range in the proximity of its open circuit potential (OCP), leading to articulation of a revised narrative of BDD[†] mechanism for iron dissolution; additional mechanistic pathways were postulated in addition to the hypothesized mechanisms of BDD and Heusler. Thirty-eight different pathways were investigated here and theoretical Butler-Volmer equations were written for each. The kinetic consequences of each pathway and the corresponding theoretical values of the main kinetic parameters were determined, and the theoretical outcomes were compared to the experimental observations. It was found that in strong acids ($\text{pH} \leq 4$) in the potential range of ± 50 mV vs. OCP, the mechanism of iron dissolution agrees well with three pathways, and all three were explainable within the same framework of BDD mechanism, where the reaction of OH^- with iron produces the adsorbed intermediate FeOH_{ads} . One single dissolution pathway which corresponds to the conversion of FeOH_{ads} to $\text{Fe(II)}_{\text{sol}}$ is dominant in the potential range adjacent to the OCP. Near OCP the effect of hydrogen reduction was taken into account using the linearity of the cathodic potentiodynamic branch to approximately extract the pure anodic data points from both anodic and cathodic sweeps.

Key words: Anodic dissolution, Iron, Strong Acid

INTRODUCTION

Reviewing literature related to corrosion research brings to light the importance of understanding the mechanisms involved, and how this is essential to aid in development of mathematical models for corrosion prediction. The current research documents possible mechanisms for the dissolution of pure iron in strong acid in a potential range in the potential range of ± 50 mV vs. OCP, providing explanations for corrosion engineers and researchers working with mild steel. Prediction of corrosion rate relies on the precise understanding of the anodic and cathodic processes at the metal surface in the potential range close to the OCP. In the case of iron dissolution, not far from OCP, there are two common mechanisms in strong acids ($\text{pH} \leq 4$) reported in the literature; namely, the “catalytic mechanism” proposed by Heusler

[†]BDD stands for co-authors’ names Bockris, Drazic and Despic who proposed the mechanism of iron dissolution: Bockris, J.O., Drazic, D. & Despic, *Electrochimica Acta* 4, 325–361 (1961).

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et al.¹, and the “consecutive mechanism” postulated by Bockris, et al.² which is also known as “BDD mechanism”. Heusler’s model is based on the second order dependence on OH⁻ ions and the anodic Tafel slope of 30 mV/decade, while BDD mechanism predicts a first order of dependency on OH⁻ and an anodic Tafel slope of 40 mV/decade. Over a wider range of overpotentials far from the OCP, Keddum, et al., reported that iron dissolution occurs through three different but interrelated dissolution paths in which four adsorbed intermediates are involved in seven elementary steps.³ Bockris’ approach^{2,4} for elucidation of the mechanism near the OCP was methodical in terms of utilizing the Butler-Volmer equation as a means to reasonably deduce the mechanism since it immediately provides the metrics to prove, or disprove, a particular hypothesis.

In the present study, Bockris’ style analysis of the Butler-Volmer equation for understanding the mechanism of iron dissolution is revisited. Additional mechanistic pathways for the occurrence of iron dissolution in addition to those postulated models of BDD and Heusler are presented. For all proposed pathways, the theoretical Butler-Volmer was derived, and the corresponding theoretical consequences of each pathway were computed and compared with the experimental metrics. Finally, the most likely mechanism for iron dissolution in strong acids (pH ≤ 4) was established for the potential ranges in close proximity to the OCP. Measurements of OCP, linear polarization resistance (LPR), and potentiodynamic sweeps were utilized to collect the experimental metrics. The present study is limited to the potential ranges not far from OCP in order to validate the existing mechanistic interpretation and to find if the proposed pathway involving formation and dissolution of FeOH_{ads} is actually the predominant path or not. Mechanisms at higher overpotentials far from OCP are not discussed in this study.

EXPERIMENTAL PROCEDURE

Equipment

Figure 1 depicts the 2-liter glass cell (with a rotating cylinder electrode (RCE) as working electrode, four platinum-coated titanium mesh counter electrodes, and Ag/AgCl reference electrode) which was used to investigate corrosion in this work. RCE specimen was 99% pure iron. The four counter electrodes were used to provide a more symmetric current distribution around the rotating working electrode. All RCE specimens were polished to 0.25-micron, rinsed with deionized (DI) water and isopropanol, sonicated for 5 minutes, and air dried. Prior to each measurement the OCP was monitored for at least 20 minutes to ensure it was stable. The anodic and cathodic polarization curves were collected separately, always starting at OCP, and were corrected for the effect of IR drop due to the 0.15 M Na₂SO₄ electrolyte. The solution resistance was determined using LPR and electrochemical impedance spectroscopy (EIS) measurements, its mean value being used. EIS measurements were performed at OCP in a frequency range from 100 kHz to 1 Hz at 10 points/decade. All potentiodynamic sweeps were collected at a 0.125 mV/s scan rate with sampling rate of 1 s⁻¹. LPR measurements were performed at the same scan rate over a potential range of ±5 mV vs. OCP. A Solartron 1470E[‡] potentiostat was used for LPR, OCP and potentiodynamic measurements. The OCP was monitored for 5 min prior to each measurement. The EIS measurement was done using a VersaSTAT3[§] potentiostat instrument.

[‡] Trade Name

[§] Trade Name

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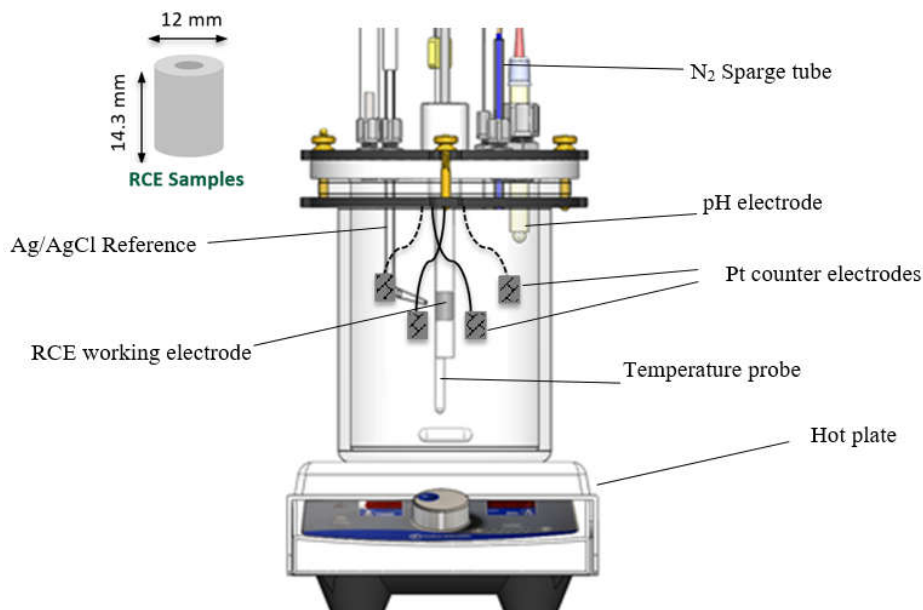


Figure 1. Schematic representation of the experimental cell setup.

Experimental Conditions

Table 1 summarizes the experimental conditions used in this study.

Table 1. Experimental conditions

Parameters	Values
pH	2.0, 2.5, 3.0, 3.5, and 4.0
Temperature	30°C
RCE Rotational Speed	2000 rpm
Electrolyte	0.15 M Na ₂ SO ₄
Setup	2L Glass cell
RCE working electrode	99% pure Fe
pN ₂	0.97 bar

The 0.15 M Na₂SO₄ supporting electrolyte was purged for about 2 hr with N₂ gas prior and during each experiment throughout this study. The temperature was controlled (to $\pm 0.5^\circ\text{C}$) using a HH11B OMEGA** thermometer. The pH was adjusted using 0.1 M H₂SO₄ or 0.1 M NaOH solution as necessary.

RESULTS AND DISCUSSION

Speculation of the Possible Pathways of Iron Dissolution

The overall anodic half-reaction for iron dissolution, i.e., $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$, is a multistep reaction. Speculation of the possible pathways for a particular overall reaction is not a random affair, and several diagnostic criteria must be utilized to elucidate the mechanistic pathway. Table 2 summarizes the hypothesized pathways for iron dissolution in strong acids. Mechanisms (a) through (e) are taken from Bockris & Reddy (1970)⁴, and mechanism (f) represents the mechanism proposed by Heusler.¹ The rest of the schemes, i.e., pathways (g) through (s) and (a') through (s') are additional mechanistic speculations made in the present study. The goal was to test the feasibility of iron dissolution via other possible pathways. Other so-called branching pathways were also explored.⁵ Mechanisms (a') through (s') indicate the branching process for the corresponding elementary steps (a) through (s), respectively.

** Trade Name

According to the literature⁶⁻⁸, all possible entities in both the solution side and the electrode side can be postulated; 'rds' indicates the rate-determining step.

Table 2. Possible proposed pathways for iron dissolution in strong acid

a	$\text{Fe} + \text{OH}^- + \text{FeOH}_{\text{ads}} \leftrightarrow (\text{FeOH})_2 + e^-$ rds $(\text{FeOH})_2 \rightarrow 2\text{FeOH}_{\text{ads}}$ $\text{FeOH}_{\text{ads}} \leftrightarrow \text{FeOH}^+ + e^-$ $\text{FeOH}^+ \leftrightarrow \text{Fe}^{2+} + \text{OH}^-$	b	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ $\text{FeOH}_{\text{ads}} \leftrightarrow \text{FeOH}^+ + e^-$ rds $\text{FeOH}^+ + \text{Fe} \rightarrow \text{Fe}_2\text{OH}^+$ $\text{Fe}_2\text{OH}^+ \leftrightarrow \text{Fe}^{2+} + \text{FeOH}_{\text{ads}} + e^-$ $\text{FeOH}_{\text{ads}} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + e^-$	c	$\text{Fe} + \text{OH}^- \xrightarrow{\text{rds}} \text{FeOH}^+ + 2e^-$ $\text{FeOH}^+ \leftrightarrow \text{Fe}^{2+} + \text{OH}^-$	d	$\text{Fe} + \text{OH}^- \leftrightarrow \text{FeOH}_{\text{ads}} + e^-$ $\text{FeOH}_{\text{ads}} + \text{OH}^- \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + \text{H}_2\text{O} + e^-$ $\text{FeO}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{HFeO}_2^-$ $\text{HFeO}_2^- + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + \text{OH}^-$ $\text{Fe}(\text{OH})_{2,\text{ads}} \leftrightarrow \text{Fe}^{2+} + 2\text{OH}^-$
e	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ rds $\text{FeOH}_{\text{ads}} \rightarrow \text{FeOH}^+ + e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	f	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ $\text{Fe} + \text{FeOH}_{\text{ads}} \leftrightarrow \text{Fe}(\text{FeOH})_{\text{ads}}$ $\text{Fe}(\text{FeOH})_{\text{ads}} + \text{OH}^- \xrightarrow{\text{rds}} \text{FeOH}^+ + \text{FeOH}_{\text{ads}} + 2e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	g	$\text{Fe} + \text{FeOH}_{\text{ads}} + \text{OH}^- \leftrightarrow (\text{FeOH})_{2,\text{ads}} + e^-$ $(\text{FeOH})_{2,\text{ads}} \leftrightarrow (\text{FeOH})_2^+ + e^-$ rds $(\text{FeOH})_2^+ \rightarrow \text{FeOH}^+ + \text{FeOH}_{\text{ads}}$ $\text{FeOH}^+ \leftrightarrow \text{Fe}^{2+} + \text{OH}^-$	h	$\text{Fe} + \text{FeOH}_{\text{ads}} + \text{OH}^- \xrightarrow{\text{rds}} (\text{FeOH})_{2,\text{ads}} + e^-$ $(\text{FeOH})_{2,\text{ads}} \leftrightarrow (\text{FeOH})_2^+ + e^-$ rds $(\text{FeOH})_2^+ \rightarrow \text{HFeO}_2^- + \text{H}^+ + e^-$ $\text{HFeO}_2^- + \text{H}^+ \leftrightarrow 2\text{FeOH}^+$ $2\text{FeOH}^+ + 2\text{H}^+ \leftrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$
i	$\text{Fe} + \text{H}_2\text{O} \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + 2\text{H}^+ + 2e^-$ $\text{FeO}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{HFeO}_2^-$ $\text{HFeO}_2^- + \text{H}^+ \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}}$ $\text{Fe}(\text{OH})_{2,\text{ads}} \leftrightarrow \text{Fe}^{2+} + 2\text{OH}^-$	j	$\text{Fe} + \text{H}_2\text{O} \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + 2\text{H}^+ + 2e^-$ $\text{FeO}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{HFeO}_2^-$ $\text{HFeO}_2^- + \text{H}^+ \leftrightarrow \text{FeOH}^+ + \text{OH}^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	k	$\text{Fe} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + 2e^-$ $\text{Fe}(\text{OH})_{2,\text{ads}} \xrightarrow{\text{rds}} \text{Fe}(\text{OH})_2^+ + e^-$ $\text{Fe}(\text{OH})_2^+ \leftrightarrow \text{FeO}(\text{OH})_{\text{ads}} + \text{H}^+$ $\text{FeO}(\text{OH})_{\text{ads}} \leftrightarrow \text{FeOH}_{\text{ads}} + \frac{1}{2}\text{O}_2$ $\text{FeOH}_{\text{ads}} \leftrightarrow \text{FeOH}^+ + e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	l	$2\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{Fe}_2\text{H}_2\text{O}^+ + e^-$ $\text{Fe}_2\text{H}_2\text{O}^+ \leftrightarrow \text{Fe}_2(\text{OH})^+ + \text{H}^+ + e^-$ rds $\text{Fe}_2(\text{OH})^+ \rightarrow \text{Fe}^{2+} + \text{FeOH}_{\text{ads}} + e^-$ $\text{FeOH}_{\text{ads}} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + e^-$
m	$2\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{Fe}_2\text{H}_2\text{O}^+ + e^-$ $\text{Fe}_2\text{H}_2\text{O}^+ + \text{OH}^- \xrightarrow{\text{rds}} 2\text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ $2\text{FeOH}_{\text{ads}} \leftrightarrow 2\text{FeOH}^+ + 2e^-$ $2\text{FeOH}^+ + 2\text{H}^+ \leftrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$	n	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeO}(\text{OH})_{\text{ads}}$ $\text{FeO}(\text{OH})_{\text{ads}} \leftrightarrow \text{FeOH}_{\text{ads}} + \frac{1}{2}\text{O}_2$ rds $\text{FeOH}_{\text{ads}} \rightarrow \text{FeOH}^+ + e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	o	$\text{Fe} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + \text{H}_2 + e^-$ $\text{Fe}(\text{OH})_2^+ \xrightarrow{\text{rds}} \text{FeO}(\text{OH})_{\text{ads}} + \text{H}^+$ $2\text{FeO}(\text{OH})_{\text{ads}} + 2\text{H}^+ \leftrightarrow (\text{FeOH})_2^+ + \text{H}_2\text{O} + \text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + e^-$	p	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{FeO}^{2+} + 2e^-$ $\text{H}_2\text{FeO}^{2+} \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + 2\text{H}^+$ $\text{FeO}_{\text{ads}} + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + e^-$ $\text{Fe}(\text{OH})_2^+ \rightarrow \text{FeOH}^+ + \text{H}^+ + \frac{1}{2}\text{O}_2 + e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$
q	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{FeO}^{2+} + 2e^-$ rds $\text{H}_2\text{FeO}^{2+} \rightarrow \text{FeOH}^+ + \text{H}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	r	$\text{Fe} + \text{OH}^- \rightarrow \text{FeOH}^+ + 2e^-$ rds $\text{Fe} + \text{FeOH}^+ + \text{H}_2\text{O} \rightarrow \text{HFeO}_2^- + 2\text{H}^+ + 2e^-$ $\text{HFeO}_2^- \leftrightarrow \text{FeO}_{\text{ads}} + \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	s	$\text{Fe} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + 2e^-$ $2\text{Fe}(\text{OH})_{2,\text{ads}} \xrightarrow{\text{rds}} \text{Fe}(\text{OH})_{2,\text{ads}} + \text{Fe}(\text{OH})_2^+ + e^-$ $\text{Fe}(\text{OH})_2^+ \leftrightarrow \text{FeOH}^+ + \text{H}^+ + \frac{1}{2}\text{O}_2 + e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	a'	$\text{Fe} + \text{OH}^- + \text{FeOH}_{\text{ads}} \leftrightarrow (\text{FeOH})_{2,\text{ads}} + e^-$ rds $(\text{FeOH})_{2,\text{ads}} \rightarrow \text{FeOH}_{\text{ads}} + \text{FeOH}^+ + e^-$ des $\text{FeOH}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}_{\text{ads}} \leftrightarrow \text{FeOH}^+ + e^-$ $\text{FeOH}^+ \leftrightarrow \text{Fe}^{2+} + \text{OH}^-$
b'	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ $\text{FeOH}_{\text{ads}} \leftrightarrow \text{FeOH}^+ + e^-$ rds $\text{FeOH}^+ + \text{Fe} \rightarrow \text{Fe}_2\text{OH}^+$ des $\text{Fe}_2\text{OH}^+ \rightarrow \text{Fe}_2\text{OH}^+$ $\text{Fe}_2\text{OH}^+ \leftrightarrow \text{Fe}^{2+} + \text{FeOH}_{\text{ads}} + e^-$ $\text{FeOH}_{\text{ads}} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + e^-$	c'	$\text{Fe} + \text{OH}^- \xrightarrow{\text{rds}} \text{FeOH}^+_{\text{ads}} + 2e^-$ des $\text{FeOH}^+_{\text{ads}} \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ \leftrightarrow \text{Fe}^{2+} + \text{OH}^-$	d'	$\text{Fe} + \text{OH}^- \leftrightarrow \text{FeOH}_{\text{ads}} + e^-$ $\text{FeOH}_{\text{ads}} + \text{OH}^- \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + \text{H}_2\text{O} + e^-$ $\text{FeO}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{HFeO}_2^-$ des $\text{HFeO}_2^- \rightarrow \text{HFeO}_2^-$ $\text{HFeO}_2^- + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + \text{OH}^-$ $\text{Fe}(\text{OH})_{2,\text{ads}} \leftrightarrow \text{Fe}^{2+} + 2\text{OH}^-$	e'	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ rds $\text{FeOH}_{\text{ads}} \rightarrow \text{FeOH}_{\text{ads}}^+ + e^-$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$
f'	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ $\text{Fe} + \text{FeOH}_{\text{ads}} \leftrightarrow \text{Fe}(\text{FeOH})_{\text{ads}}$ rds $\text{Fe}(\text{FeOH})_{\text{ads}} + \text{OH}^- \rightarrow \text{FeOH}_{\text{ads}}^+ + \text{FeOH}_{\text{ads}} + 2e^-$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	g'	$\text{Fe} + \text{FeOH}_{\text{ads}} + \text{OH}^- \leftrightarrow (\text{FeOH})_{2,\text{ads}} + e^-$ $(\text{FeOH})_{2,\text{ads}} \leftrightarrow (\text{FeOH})_{2,\text{ads}}^+ + e^-$ rds $(\text{FeOH})_{2,\text{ads}}^+ \rightarrow \text{FeOH}_{\text{ads}}^+ + \text{FeOH}_{\text{ads}}$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{OH}^-$	h'	$\text{Fe} + \text{FeOH}_{\text{ads}} + \text{OH}^- \xrightarrow{\text{rds}} (\text{FeOH})_{2,\text{ads}} + e^-$ $(\text{FeOH})_{2,\text{ads}} \leftrightarrow (\text{FeOH})_{2,\text{ads}}^+ + e^-$ des $(\text{FeOH})_{2,\text{ads}}^+ \rightarrow (\text{FeOH})_2^+$ $(\text{FeOH})_2^+ \rightarrow \text{HFeO}_2^- + \text{H}^+ + e^-$ $\text{HFeO}_2^- + \text{H}^+ \leftrightarrow 2\text{FeOH}^+$ $2\text{FeOH}^+ + 2\text{H}^+ \leftrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$	i'	$\text{Fe} + \text{H}_2\text{O} \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + 2\text{H}^+ + 2e^-$ $\text{FeO}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{HFeO}_2^-$ des $\text{HFeO}_2^- \rightarrow \text{HFeO}_2^-$ $\text{HFeO}_2^- + \text{H}^+ \leftrightarrow \text{FeOH}^+ + \text{OH}^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$
j'	$\text{Fe} + \text{H}_2\text{O} \xrightarrow{\text{rds}} \text{FeO}_{\text{ads}} + 2\text{H}^+ + 2e^-$ $\text{FeO}_{\text{ads}} + \text{OH}^- \leftrightarrow \text{HFeO}_2^-$ des $\text{HFeO}_2^- \rightarrow \text{HFeO}_2^-$ $\text{HFeO}_2^- + \text{H}^+ \leftrightarrow \text{FeOH}^+ + \text{OH}^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	k'	$\text{Fe} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + 2e^-$ rds $\text{Fe}(\text{OH})_{2,\text{ads}} \rightarrow \text{Fe}(\text{OH})_2^+ + e^-$ $\text{Fe}(\text{OH})_2^+ \leftrightarrow \text{FeO}(\text{OH})_{\text{ads}} + \text{H}^+$ $\text{FeO}(\text{OH})_{\text{ads}} \leftrightarrow \text{FeOH}_{\text{ads}} + \frac{1}{2}\text{O}_2$ $\text{FeOH}_{\text{ads}} \leftrightarrow \text{FeOH}_{\text{ads}}^+ + e^-$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	l'	$2\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{Fe}_2\text{H}_2\text{O}^+ + e^-$ des $\text{Fe}_2\text{H}_2\text{O}^+ \rightarrow \text{Fe}_2\text{H}_2\text{O}^+$ $\text{Fe}_2\text{H}_2\text{O}^+ \leftrightarrow \text{Fe}_2(\text{OH})^+ + \text{H}^+ + e^-$ rds $\text{Fe}_2(\text{OH})^+ \rightarrow \text{Fe}^{2+} + \text{FeOH}_{\text{ads}} + e^-$ $\text{FeOH}_{\text{ads}} + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O} + e^-$	m'	$2\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{Fe}_2\text{H}_2\text{O}^+ + e^-$ rds $\text{Fe}_2\text{H}_2\text{O}^+ + \text{OH}^- \rightarrow 2\text{FeOH}_{\text{ads}} + \text{H}^+ + e^-$ $2\text{FeOH}_{\text{ads}} \leftrightarrow 2\text{FeOH}_{\text{ads}}^+ + 2e^-$ des $2\text{FeOH}_{\text{ads}}^+ \rightarrow 2\text{FeOH}^+$ $2\text{FeOH}^+ + 2\text{H}^+ \leftrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$
n'	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{FeO}(\text{OH})_{\text{ads}}$ $\text{FeO}(\text{OH})_{\text{ads}} \leftrightarrow \text{FeOH}_{\text{ads}} + \frac{1}{2}\text{O}_2$ rds $\text{FeOH}_{\text{ads}} \rightarrow \text{FeOH}_{\text{ads}}^+ + e^-$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	o'	$\text{Fe} + 2\text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + \text{H}_2 + e^-$ des $\text{Fe}(\text{OH})_2^+ \rightarrow \text{Fe}(\text{OH})_2^+$ rds $\text{Fe}(\text{OH})_2^+ \rightarrow \text{FeO}(\text{OH})_{\text{ads}} + \text{H}^+$ $2\text{FeO}(\text{OH})_{\text{ads}} + 2\text{H}^+ \leftrightarrow (\text{FeOH})_2^+ + \text{H}_2\text{O} + \text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + e^-$	p'	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{FeO}^{2+} + 2e^-$ rds $\text{H}_2\text{FeO}^{2+} \rightarrow \text{FeO}_{\text{ads}} + 2\text{H}^+$ $\text{FeO}_{\text{ads}} + \text{H}_2\text{O} \leftrightarrow \text{Fe}(\text{OH})_2^+ + e^-$ des $\text{Fe}(\text{OH})_2^+ \rightarrow \text{Fe}(\text{OH})_2^+$ $\text{Fe}(\text{OH})_2^+ \leftrightarrow \text{FeOH}^+ + \text{H}^+ + \frac{1}{2}\text{O}_2 + e^-$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	q'	$\text{Fe} + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{FeO}^{2+} + 2e^-$ rds $\text{H}_2\text{FeO}^{2+} \rightarrow \text{FeOH}_{\text{ads}}^+ + \text{H}^+$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$
r'	$\text{Fe} + \text{OH}^- \leftrightarrow \text{FeOH}^+ + 2e^-$ $\text{Fe} + \text{FeOH}^+ + \text{H}_2\text{O} \xrightarrow{\text{rds}} \text{HFeO}_2^- + 2\text{H}^+ + 2e^-$ $\text{HFeO}_2^- \leftrightarrow \text{FeO}_{\text{ads}} + \text{FeOH}_{\text{ads}}^+$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$	s'	$\text{Fe} + 2\text{OH}^- \leftrightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + 2e^-$ rds $2\text{Fe}(\text{OH})_{2,\text{ads}} \rightarrow \text{Fe}(\text{OH})_{2,\text{ads}} + \text{Fe}(\text{OH})_2^+ + e^-$ $\text{Fe}(\text{OH})_2^+ \leftrightarrow \text{FeOH}_{\text{ads}}^+ + \text{H}^+ + \frac{1}{2}\text{O}_2 + e^-$ des $\text{FeOH}_{\text{ads}}^+ \rightarrow \text{FeOH}^+$ $\text{FeOH}^+ + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{H}_2\text{O}$				

For each mechanistic scheme, the theoretical Butler-Volmer equation was computed. β_a^i and β_c^i are the anodic and the cathodic Tafel slopes for a specific mechanism, respectively. p_{OH^-} or the theoretical