Mechanism of Anodic Dissolution of Iron and Steel in CO2 Environments

A dissertation presented to

the faculty of

the Russ College of Engineering and Technology of Ohio University

In partial fulfillment

of the requirements for the degree

Doctor of Philosophy

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August 2023

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This dissertation titled

Mechanism of Anodic Dissolution of Iron and Steel in CO2 Environments

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Abstract

BAGHERI HARIRI, MOHIEDIN, Ph.D., August 2023, Chemical Engineering <u>Mechanism of Anodic Dissolution of Iron and Steel in CO2 Environments</u>, Director of Dissertation: Srdjan Nesic

The goal of this dissertation research was to investigate the mechanism of a multistep reaction during sweet corrosion, *i.e.*, the anodic dissolution of iron in strong and weak acidic environments containing dissolved CO₂. The fundamental theories in studying the oxidative dissolution reaction were revisited to ultimately represent a simpler narrative for the purpose of relating it to corrosion studies. With a good understanding of underpinning theory, the iron dissolution reaction was broken down into individual elementary steps. This enabled the elaboration of how different factors have the potential to mechanistically affect the overall reaction rate.

Most of the related fundamental research has focused on investigating the mechanism of iron dissolution in strong acids using complicated mechanistic schemes, whereas the impact effect of CO₂ on the kinetics of individual elementary steps is missed and little is known about how environmental factors (pH, CO₂, temperature, *etc.*) can mechanistically affect the reaction. A quantitative analysis of the reaction in a potential range near the corrosion potential revealed that the dominant adsorbed intermediate that triggers the dissolution is most likely $FeOH_{ads}$, with the conversion of $FeOH_{ads}$ to $Fe(II)_{sol.}$ the predominant dissolution path in this potential range. This finding was consistent with the acclaimed *BDD* mechanism (Bockris-Drazic-Despic), also known as Bockris' theory.

A qualitative interpretation of the role of CO_2 was accomplished. It was found that the effect of CO_2 in the active dissolution range was negligible, while its effect in the transition and pre-passivation ranges of the anodic sweeps was marked. A systematic methodology based on electrochemical transient measurements was introduced to further investigate the effect of CO₂ on the rate parameters of individual elementary steps. As a result, sets of kinetic rate constants were extracted that elucidated the impact of CO₂ and other environmental factors. It was found that each experimental factor affects the rate constants of one/two specific elementary reaction(s) more notably than others. For example, pH, CO₂, or steel composition impacts the chemisorption steps, whereas temperature influences the dissolution steps more significantly. A theory must be welltested for a set of observations, therefore, to authenticate the validity of the obtained kinetic dataset, they were ultimately put into the model to re-create the experimental observations. The model provided a fine match to the experimental data. Finally, a few mathematical correlations were introduced to extrapolate the trend of observations to untested conditions. These simplified models can serve as a basis for future model development purposes.

All experiments were conducted in a 2-liter glass cell with a three-electrode system integrating iron/steel as a working electrode, Ag/AgCl saturated reference electrode, and a platinum-coated titanium mesh counter electrode. Different types of electrochemical techniques (steady-state & transient) were utilized to accomplish a systematic study of the effect of environmental parameters on the kinetics of iron dissolution. This study offers some important insights into how environmental factors (*e.g.*, pH, dissolved CO₂, temperature, steel type, *etc.*) can mechanistically impact the rate of the elementary steps as well as the overall reaction of iron dissolution.

Dedication

To my parents, Marzieh and Jalal for giving me everything, for all your sacrifices and endless support throughout my life, I owe you my entire life, these papers are nothing to give. And to my brother, Mehdi for his permanent support and help.

Acknowledgments

I would like to express my deepest gratitude and appreciation to my advisor, Dr. Srdjan Nesic, for all his guidance and support from the very beginning. He always provided me with valuable guidance about the theoretical frame of this dissertation and helped me to move in the right direction. I do appreciate all his support. I remember in July 2019, when I had no academic supervisor and was looking for someone to pursue my Ph.D. under his/her supervision, in those days I found Dr. Srdjan Nesic and Dr. David Young so supportive. Thank you very much for that.

I would like to also express my gratitude and appreciation to the faculty and staff at Institute for Corrosion and Multiphase Technology (ICMT), especially to Dr. Bruce Brown and Dr. David Young for all the helpful discussions, their support, and guidance about my experimental research. I want to acknowledge them for their very valuable feedback on my dissertation and everything here at ICMT. Although they were normally so busy, they never hesitated to help, guide, or train us. Thank you very much. I would like to thank my committee members, Dr. Yoon-Seok Choi, Dr. Marc Singer, Dr. Katherine Cimatu, and Dr. Howard Dewald for their helpful feedback and their time. Additionally, I would like to thank our safety coordinator and technician, Mr. Alexis Barxias, who also never hesitated to help or train us even when he was busy in the main lab area fixing something, he used to pause his work for a minute and help us to solve our issues. I appreciate our laboratory engineer Mr. Cody Shafer as well. I do thank our amazing administrative coordinator Mrs. Becky Matthews who was very nice to us and so helpful with many administrative issues. I would like to thank Mr. Thomas Riggs, our amazing department staff who left Ohio University in 2019.

I am extremely grateful to my mother, father, and my brother, you always supported me unconditionally. I deeply appreciate you and love you. Last but not least, I would like to express sincere appreciation to the following industrial sponsors for their financial support: Baker Hughes, Chevron Energy Technology, Clariant Corporation, ConocoPhillips, ExxonMobil, BP, M-I SWACO (Schlumberger), Multi-Chem (Halliburton), Occidental Oil Company, Pertamina, Saudi Aramco, Shell Global Solutions and TotalEnergies.

Finally, I would like to thank all my friends in Athens and back in Tehran. Thank you all and I wish you good health, happiness, and success in your life!

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Glossary

Absorption — The process by which a substance or object takes in a liquid, gas, or chemical and makes it a part of itself (compare it with adsorption).

Adsorption — Adhesion of an intermediate, complex, or species such as ions, molecules, or atoms, from a gas, liquid, or dissolved solid to the surface (compare it with absorption).

Anodic — It means relating to an anode where oxidation occurs (electrons are detached from the anode's surface).

Aqueous— Of or containing water, typically as a solvent or medium.

Buffer- A salt or solution that tends to maintain a constant hydrogen ion concentration.

Buffering effect— The ability of a solution to resist changes in pH.

Butler–Volmer equation— also known as Erdey-Grúz–Volmer equation, is one of the most fundamental relationships in electrochemical kinetics that described how electrical current of an electrode can depends on the voltage difference between the electrode and the bulk electrolyte.

Cathodic — It means relating to a cathode where reduction occurs (electrons move into the cathode's surface).

Catalyst — A chemical compound that speeds up the rate of reaction without being produced or consumed.

Catalytic — Related to or involved in the action of a catalyst.

Charge transfer coefficient — A dimensionless quantity that is commonly used in kinetic studies of the electrode processes. For a single-step and a multistep reaction, it can take values between 0 to 1 and greater than 0, respectively.

Chemical potential — Refers to the energy that can be absorbed or released due to a change in the particle amount of the given species (units Joule/mole).

Chemisorbed — Adsorption that involves a chemical reaction between the surface and the adsorbate.

Cold work — To work and form (metal) without using heat.

Corrosion — A natural process that converts a metal or other materials to more chemically stable forms such as oxide, hydroxide, *etc*.

Deprotonation — The removal or transfer of a hydrogen cation (H^+) from a molecule to form a conjugate base.

Dislocation— Line defects that exist in metals.

Dissociation— A general process in which a compound or a molecule split into simpler entities that are capable of recombining under certain conditions.

Dissolution — In terms of corrosion, when metal atoms oxidatively detach from the surface of a [anodic] workpiece into the aqueous electrolyte.

Dissolution path — Refers to an elementary step where an adsorbed intermediate at the surface transforms into an aqueous complex/ion in the solution.

Double layer capacitance— Refers to the lineup of charges at the interface of an electrode in contact with an electrolyte, causing the electricity to be stored.

Electrical potential— The amount of work needed to move a unit of electric charge from a reference point to a specific point in an electric field (units Joules/coulomb or Volt).

Electrochemical potential— Refers to the superposition or summation of chemical and electrical potential (units Joules/mole).

Electrochemistry — A branch of chemistry that deals with the relation of electricity to chemical changes and with the interconversion of chemical and electrical energy.

Electrode — A conductor that is used to establish electrical contact with a nonmetallic part of a circuit such as an electrolyte, vacuum, air, semiconductor, *etc*.

Electrolyte — A medium containing ions, hydrated complexes, or other species that is electrically conductive due to the movement of those ions, but not conducting electrons.

Electron tunneling— The passage of electrons through a potential barrier that they would not be able to cross according to classical mechanics.

Elementary step — A basic building block of an overall reaction that cannot be broken down any further.

Equilibrium — A situation where both reactants and products are present in concentrations that do not change with time, and there is no significant alteration in the system.

Equilibrium potential — Reversible potential (or Nernst potential) defined for any given ionic species as the potential at which the ionic species is in equilibrium, *i.e.*, no movement of ions due to the concentration/activity gradient.

Exchange current density — The current density in the absence of net electrolysis at zero overpotential.

Galvanostatic — Variation of potential *vs*. time due to an imposed current perturbation to a system initially at equilibrium.

Helmholtz double layer (HDL)— Refers to the structural distribution of charged ions at the boundary of an electrode in contact with an aqueous electrolyte.

Hydration— A chemical reaction in which a substance combines with water.

Hydrolysis— The chemical breakdown of a metal or compound due to its reaction with water.

Hydroxide— A chemical compound containing one or more hydroxide anions (OH⁻).

Impedance — A measure of the opposition to the electrical flow or alternating current.

Inductive — The impedance of an electrochemical system sometimes behaves as an inductive. It refers to the situation when an adsorbed semi-passive/passive layer or fouling is forming at the electrode surface. Potentiostat non-idealities might also lead to some measurement errors in the form of inductive loops in impedance measurements.

Intermediate — Any reacting species which is no longer starting reactant, has not yet become a product and is not in a transition state.

iR-drop — Refers to the potential drop due to the solution resistance.

Irreversible — Refers to a reaction in which the reactants convert to products and the products cannot convert back to the reactants (opposite to reversible).

Kinetics — A branch of chemistry that deals with investigating the rates of chemical, electrochemical, or biochemical reactions.

Monolayer — A single continuous layer of molecules or atoms in thickness.

Open Circuit Potential (OCP) — The potential at steady-state that is established between the working electrode and the environment with respect to the reference electrode that is placed in the electrolyte close to the working electrode.

Overall reaction — The sum of the elementary steps in the mechanism gives a balanced overall reaction.

Oxide - A compound of oxygen and another element or radical. For example, water (H₂O) is an oxide.

Oxidation — A reaction that occurs when a substance comes into contact with an oxidizing agent *e.g.*, O_2 .

Oxidation state— Or oxidation number, or valency is the hypothetical charge or total number of electrons that an atom either gains or losses in order to form a chemical bond with another atom.

Passive — Unreactive except under special or extreme conditions (opposite to active).

Polarization — The act of deriving a system away from its equilibrium state (polarized state).

Polarization resistance — Ratio of the applied potential to the resulting current response. It can be measured by LPR or EIS.

Potentiodynamic sweep — In this study, it refers to the polarization technique when the potential of the electrode is varied stepwise over a potential window at a selected rate (*i.e.*, scan rate), and the current is continuously monitored with respect to the corresponding potential.

Potentiostatic — Variation of current *vs*. time due to an imposed potential perturbation to a system initially at equilibrium.

Physisorbed — Adsorption that does not involve a chemical reaction between the surface and the adsorbate.

Rate-determining step (rds) — Or rate-limiting step, is the slowest step of an (electro)chemical reaction that determines the speed at which the overall reaction proceeds.

Reaction mechanism — The set of elementary steps whose overall impact is given by the net reaction is called the reaction mechanism.

Reduction — Acquisition of electrons by a substance or species decreasing its oxidation state.

Reversible — Refers to a reaction that simultaneously proceeds in both directions (forward and backward) and can be stimulated to do so.

Solution resistance — Opposition to the current flow through the bulk solution, measurable by EIS.

Sour corrosion — The corrosion of metal due to contact with a highly acidic environment containing hydrogen sulfide (H_2S).

Steady-state — Dynamic equilibrium condition when the system exhibits a negligible change over an arbitrarily long period of time.

Strong acid — Acids that are completely or nearly 100% ionized in their solutions. In this study, strong acid refers to experiments where the test solution was continuously sparged with N_2 (pH was adjusted by adding strong acids such as HCl or H₂SO₄).

Superpolarization — Immediately after applying a potential/current stimulation to the electrode/electrolyte interface, a sharp spike is usually obtained in the collected current/potential response. This sharp peak during the early stages of transient response is called superpolarization.

Sweep — In this study refers to potentiodynamic curves (see potentiodynamic).

Sweet corrosion — The corrosion of metal due to contact with carbon dioxide (CO₂) or similar corrosive agents but excluding hydrogen sulfide (H₂S — when the ratio of p_{CO2}/p_{H2S} is above 500).

Symmetry factor — Related to the charge transfer coefficient and used in describing the kinetics of the electrochemical reactions; can take values between 0 and 1.

Tafel equation — an equation in electrochemical kinetics relating the rate of an electrochemical reaction to the overpotential.

Tafel slope — Shows how fast an electrode can produce current in response to an applied external potential and is usually estimated from the linear portion of the polarization curves.

Thermodynamics — A branch of physical science that studies energy, transformations, and the relation between energy and matter. It deals with the relations between heat, work, chemical, electrical, mechanical, and other forms of energy.

Time constant — In general refers to a parameter that characterizes the response to a step input of a 1st order, linear time-invariant system. In EIS data each semicircle might be an indication of an individual time constant.

Transient — The response of a system to an external perturbation which is usually monitored with respect to time. In this work, it refers to potentiostatic or galvanostatic measurements.

Weak acid —Acids that partially dissociate into their ions in an aqueous solution. In this study, weak acid refers to experiments where the solution (tested at $pH \ge 4$) was continuously sparged with CO₂ (there was no need to adjust the pH by adding strong acids such as HCl or H₂SO₄).

Nomenclature

α_a	Anodic charge transfer coefficient
A a,overall	Anodic charge transfer coefficient for overall reaction
<i>a</i> _c	Cathodic charge transfer coefficient
\boldsymbol{b}_a	Anodic Tafel slope, V/dec.
b a,ov	Anodic Tafel slope for the overall reaction, V/dec.
b_c	Cathodic Tafel slope, V/dec.
В	Stern–Geary constant, V/dec.
ß	Symmetry factor
b_i	Tafel value for elementary step 'i', V/dec.
С	Capacitance, F
С	Concentration, mol/l
D	Diffusion coefficient, m ² /s
D_{H^+}	Diffusion coefficient, m ² /s
<i>d_{RCE}</i>	Outer diameter of RCE, cm
∆H	Enthalpy of activation, J/mol
Δμ	Change of the chemical potential, J/mol
Erev	Reversible potential, V
Ecorr.	Corrosion potential, V
η	Overpotential, V
F	Faraday's constant, C/mol
[H ⁺] _B	Bulk concentration of H^+ , mol/l
i ₀	Exchange current density, A/m ²
iα	Charge transfer current density, A/m ²
<i>i</i> _a	Pure anodic current density, A/m ²
i_c	Pure cathodic current density, A/m ²
icorr.	Corrosion current density, A/m ²
i net	Net current density, A/m ²
Ι	Ionic strength, mol/l

i _{lim}	Limiting current density, A/m ²
<i>k</i> _m	Mass transfer coefficient, m/s
k _{hyd} f	Forward hydration reaction rate
<i>k</i> i	Rate constant, mol/m ² .s
<i>k</i> _{0,i}	Rate constant for elementary step ' <i>i</i> ' at $E = 0$, mol/m ² .s
<i>k</i> _{0,a}	Rate constant for the overall reaction at $E = 0$, mol/m ² .s
K	Equilibrium constants
μ	Viscosity, kg/m.s
$\overline{\mu_{\iota}}$	Electrochemical potential, J/mol
μ_i	Chemical potential, J/mol
n	Number of electrons transferred
n b	number of electrons transferred after rds
n f	number of electrons transferred before <i>rds</i> , the,
<i>n</i> _r	number of electrons transferred only during rds
р	Pressure, bar
ρ	Density, kg/m ³
R	Gas constant, J/kg.mol
R_E	Resistance, Ω
Re	Reynolds number
R_p	Polarization resistance, $\Omega.cm^2$
R_s	Solution resistance, Ω
Sc	Schmidt number
Sh	Sherwood number
Τ	Temperature, K
θ	Fractional surface coverage
φ	Electrical potential, V
и	Rotation speed, rad/s
V	Number of rate-limiting steps
Zi	Charge of the ion or number of electrons transferred

Scope of Work

A multistep electrochemical process, *i.e.*, the anodic dissolution of iron in aqueous solutions (pH < 7) is investigated in this dissertation research. Fundamental studies investigating the anodic dissolution of iron are usually based on speculative theories that describe the abovementioned multistep reaction. This dissertation also follows a similar theoretical style in which a reliable theory is developed to ultimately model the pattern of experimental observations and subsequently describe the involved reaction kinetics. The main criterion for selecting a plausible theory is based on the number of experimental parameters that it can rationalize. Presumably, a strong theory should explain a more diverse range of experimental observations. The existing theoretical perspective in iron dissolution usually follows an extremely complicated style in computation and data analysis. The major theories in iron anodic dissolution will be revisited in this study to finally establish a simplified but more practical theory applicable to the underlying research focus, *i.e.*, studying the aqueous corrosion of iron/steel at steady-state.

Chapter 1: Introduction

Corrosion is a pernicious phenomenon, being estimated to costing the U.S. economy approximately \$1.1 trillion per year¹, representing 6.2 percent of the nation's gross domestic product (GDP). It is estimated that the indirect cost to the end-user can double the impact of corrosion on the U.S. economy, making the cost of corrosion, including indirect costs, \$551.4 billion or more¹. These issues are very important to address because, in addition to the negative economic impact of corrosion, it can lead to safety hazards and environmental catastrophes. Chemical leakage, "pinhole" leakage, or a crack, split, or rupture of the pipeline, oil pipeline breakdown, and even fire can cause most corrosion problems: when exposed to electrical components and materials corroded. CO₂ corrosion (*i.e.*, sweet corrosion) by far is one of the most common types of attack experienced in oil and gas production systems. Gaseous CO₂ is not corrosive for steels, however, upon its dissolution and hydration in water giving carbonic acid, it creates an acidic corrosive environment. Carbonic acid in the water-based electrolyte does not have any effect unless after its dissociation. Since a water-based system is presented in this work, whenever it is said the effect of CO₂, it means the influence of dissolved CO₂, *i.e.*, the presence of carbonic acid and its subsequent impact on the reaction mechanism.

There are always two reaction sets acting during sweet corrosion, namely the cathodic and anodic processes. Although extensive research has been carried out on modeling the cathodic reactions during CO₂ corrosion, previous studies have not been able to lay out a well-defined approach to mechanistically describe the exact impact of

^{1.} https://www.g2mtlabs.com/cost-of-corrosion/

 CO_2 and other experimental factors on the steady-state anodic dissolution of iron. The cathodic reaction is mainly controlled by the water chemistry of the electrolyte. However, the anodic one is attributed to the oxidation of the electrode itself where factors such as material, alloying elements, metallurgical characteristics, and chemical composition of the electrode become more influential. When a metal is in contact with a corrosive environment, corrosion is defined via an electrochemical interaction between the cathodic and anodic sides (*i.e.*, between species in the electrolyte and the electrodes). Manipulating the environment or cathodic side to tackle the corrosion is simpler than changing the properties of the steel itself, but the cathodic reactions are intrinsically linked with anodic ones. Studies that review ground-breaking literature of past corrosion studies bring to light the importance of understanding the anodic dissolution mechanism, to aid in developing mathematical models for corrosion prediction of mild steel in the sweet or sour oilfield environment. The most dominant anodic reaction for the dissolution of iron/steel in corrosion systems is $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-}$, which is inherently a complicated multistep reaction. Little is known about the exact influence of CO₂ on the mechanism of iron dissolution, and it is unclear how environmental factors can mechanistically impact the kinetics of this multistep reaction. The goal of the current study is to enhance understanding of the mechanism of iron dissolution during the aqueous CO₂ corrosion of mild steel. In addition to corrosion, the anodic dissolution of iron is also an important topic to be investigated in other fields, such as designing batteries (e.g., iron-air batteries, iron-anode-based rechargeable batteries), material finishing, metal digestion, electropolishing, and anisotropic etching.

Chapter 2: Background & Literature Review

2.1. Importance of the Steady-State Potentiodynamic Polarization Curves

It is worth mentioning that potentiodynamic data only carries information about the overall reaction at steady-state [1]. During a multi-step process such as corrosion at steady-state, all steps will proceed as fast as the rate of the slowest step, *i.e.*, the ratedetermining step (rds) [1]. In other words, the kinetics of the overall reaction at the steady-state is governed by the rate of the *rds* step. Corrosion is a steady-state situation between a metal in contact with a corrosive environment. The steady-state situation of such electrochemically-based processes is usually described using potentiodynamic sweeps or polarization curves. As shown in Figure 1, the polarization curves represent the steady-state where the anodic (anodic branch) and cathodic (cathodic branch) sides of a corrosion system are observed. Indeed, the corrosion rate is generally calculated using the extrapolation Tafel method from the potentiodynamic polarization curves [2, 3]. The linear polarization resistance (LPR) measurement is a technique based on steady-state polarization curves, but the range of required polarization is much smaller for the LPR. LPR is a method of estimating corrosion rate using polarization curves in a small potential window around OCP (±5 mV) (Figure 1). This technique was first described by Wagner and Traud [4] and Stern, et al., [5] according to an expression known as the Stern-Geary equation [6]:

$$i_{corr.} = {}^{B}/R_{p} = {}^{b_{a}b_{c}}/{}_{2.3R_{p}(b_{a}+b_{c})}$$
 (1)

Tafel slope is a criterion that shows how fast an electrode can produce current in response to an applied external potential [7]:

$$b_c = (\frac{dE}{dlog|i|})_c = \frac{2.3RT}{\alpha_c F}$$
⁽²⁾

$$b_a = \left(\frac{dE}{d\log|i|}\right)_a = \frac{2.3RT}{\alpha_a F} \tag{3}$$



Figure 1. *The Butler-Volmer equation in semi-logarithmic Tafel plots (potentiodynamic sweeps) is used to determine the corrosion rate based on the Stern-Geary equation [8]*

Tafel plots that are obtained from the linear portion of the potentiodynamic data are semi-logarithmic graphs that correlate the log of the measured current to the overpotential. The Tafel equation serves as a linearized representation of the well-known Butler-Volmer expression that is widely used to extract essential kinetic parameters [9, 10]. The Butler-Volmer equation for a single-step or multi-step reaction is expressed as [11]:

$$i = i_0 \left\{ exp \left[(1 - \beta) \frac{F\eta}{RT} \right] - exp \left[-\beta \frac{F\eta}{RT} \right] \right\}$$
(Eq. 4 for single-step reaction)
$$i = i_0 \left\{ exp \left[\alpha_a \frac{F\eta}{RT} \right] - exp \left[-\alpha_c \frac{F\eta}{RT} \right] \right\}$$
(Eq. 5 for multi-step reaction)

The potentiodynamic measurement is of fundamental importance in studies related to corrosion and electrochemical kinetics as it directly provides information that is used to determine critical kinetic parameters such as corrosion rate, charge transfer coefficient, Tafel slope, exchange current density, *etc.* [12]. In this regard, formulating a quantitative correlation to model the steady-state potentiodynamic curves is a vital task to be performed by researchers in the field of corrosion and electrochemical science. This work will focus on the anodic branch of the polarization curves. Figure 2 shows an example of the anodic branch for a pure iron RDE sample in 0.5 M Na₂SO₄ electrolyte at pH 5 (25 °C) [13].



Figure 2. Anodic sweep for pure iron RDE sample in 0.5M Na₂SO₄ at pH 5 (25°C), scan rate: 6.6 mV/s, rotation rate: 4140 rpm [13]

In Figure 2, at low anodic overpotentials, active dissolution (A) takes place, while there is a slight decrease in current density at more positive overpotentials (transition domain that is shown by 'T'). This behavior is sometimes defined as the "*s*-shape"
segment of the anodic sweep in the transition region. The active range of potential is a state of an electrode when it is polarized to the active dissolution domain (A). At more positive overpotentials beyond the transition region, there is an increase in current which is defined as the pre-passivation range (PP), followed by the passive state and a marked drop in the current density (P) [13].

2.2. Basics of Metal Dissolution

Metals are crystalline and even synthesized single-crystal surfaces have several energetic sites such as steps, kinks, terraces, ad-atoms at the surface, *etc.* (Figure 3) [14].



Figure 3. The model of the metal surface with several energetic sites such as kink, terrace, and step sites [14]

Ad-atoms are less stable meaning that they need a smaller activation energy than terraces or kinks to be removed from the metal surface. Depending on the electrode potential and the required driving force for initiating the reaction, the removal of metal atoms might take place via terrace spots or directly from the step or kink sites [15]. During corrosion, the electrochemical dissolution of metals in aqueous electrolytes often is driven by a cathodic reaction (*e.g.*, hydrogen evolution in acids) that occurs concurrently. Metal ad-atoms are removed due to a suitable corrosion reaction, which inherently creates an electrochemical cell provoking oxidative dissolution at the metal surface [16].

Metal dissolution in an aqueous environment is a complex process that usually involves the adsorption of anions, the formation of adsorbed intermediates, and the hydration of evolved cations [14]. Anodic dissolution is when the metal is positively polarized acting as an anode workpiece and dissolves into the electrolyte to finally form cations [17]. The anodic dissolution in aqueous environments is a complex multistep reaction that is usually triggered by the adsorption of anions such as halides (e.g., Cl⁻) or hydroxide (OH⁻), in the latter case forming a hydroxide monolayer [18]. It is then followed by a sequence of elementary steps in parallel to ultimately produce metal ions in the electrolyte [19]. Modern surface analytical tools are inevitably utilized to get a better understanding of the mechanistic details of metal dissolution on an atomic level. However, even using state-of-the-art techniques, it is impractical to detect the unstable intermediates and eventually hypothesize a mechanistic pathway for dissolution, which is intrinsically a complex multistep process [14]. As was mentioned previously, a considerable amount of underlying literature on the anodic dissolution of iron is built based on speculation. In the following Section 2.3, fundamental theories on the anodic dissolution of iron are discussed.

2.3. Theories on Anodic Dissolution of Iron

Iron dissolution has been the subject of a large number of studies over the last 50 years. In the case of iron dissolution, the overall reaction in an aqueous environment is known as:

$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-}$$
 (6)

In reality, this reaction does not simply take place as Eq. 6 since it is a multistep process that entails several elementary steps. An elementary step is the key building block of an overall reaction that cannot be broken down any further. Understanding the reaction in greater detail is important since it helps to obtain valuable information about kinetics. The reaction mechanism acts as a tool for this by allowing the breakdown of the overall reaction into a series of elementary steps. The set of elementary steps whose overall impact is given by the net reaction is called the reaction mechanism. There are two fundamental mechanisms speculated in the literature; namely, the "consecutive or non-catalytic mechanism" proposed by Bockris, *et al.* [20], and the "catalytic mechanism" hypothesized by Heusler, *et al.* [21]. These two mechanisms will be discussed in the following sections.

2.3.1. Non-Catalytic Mechanism

In 1961 Bockris, Drazic, and Despic introduced the most famous mechanism for iron dissolution, which is known as the *BDD* mechanism (known as Bockris' theory). They performed short-time galvanostatic measurements and proposed seven different pathways for the abovementioned overall reaction (Eq. 6). For each pathway, they evaluated the kinetic consequences. They concluded that the following reaction sequence (Eqs. (7-9)) could appropriately satisfy kinetic requirements as well as experimental observations [20–24]. They then solved the Butler-Volmer equation in parallel with the law of mass action and obtained a good consistency between theory and experiments when assuming the second step as the *rds* step [20]. This mechanism, shown in Figure 4, is known as the non-catalytic, or consecutive, theory of iron's oxidative dissolution.

Bockris' non-catalytic mechanism:	
$Fe + OH^{-} \stackrel{k_{1,B}}{\longleftrightarrow} FeOH_{ads.} + e^{-}$	(7)
$FeOH_{ads.} \xrightarrow{rds,B} FeOH^+ + e^-$	(8)
$FeOH^+ \stackrel{k_{3,B}}{\longleftrightarrow} Fe^{2+} + OH^-$	(9)

Figure 4. The non-catalytic mechanism proposed by Bockris et al. [20]

The non-catalytic theory predicts the first order of dependency with respect to OH^- ions with an anodic Tafel slope of 40 mV/dec. The non-catalytic route as proposed by Bockris, *et al.*, [20, 25] is mainly ascribed to the active range of iron dissolution (Figure 2). As will be seen in the next Section 2.3.2, for both non-catalytic and catalytic mechanisms the first step (Eqs. (7 & 11)) is the same. In fact, the first step in both theories is a hydrolysis step that could also be expressed as:

$$Fe + H_2 O \leftrightarrow FeOH_{ads.} + H^+ + e^- \tag{10}$$

The generation of OH^- could occur by the deprotonation, or dissociation, of water molecules [26]. The hydrolysis reaction is triggered due to the huge tendency of

transition metals to form a variety of different complexes when they are positively polarized in aqueous environments [27]. When the metal is anodically polarized, the water dipole tends to adsorb on the surface with its negative side to the positive metal [27]. As a result, the required energy for deprotonation is provided by the resulting electrical energy as well as the adsorption energy of the bond formed between the metal cation (*e.g.*, Fe^{2+}) and OH^- [27]. FTE², XPS³, and voltametric measurements showed evidence for bound water and the presence of iron species with oxidation states of 1+, 2+, 3+, 4+, and 5+ during anodic dissolution at different environmental conditions [28, 29]. In some literature [24], 80% of water content is reported during the hydration of adsorbed semi-passive monolayer following the $Fe^{2+}-Fe^{3+}$ conversion. Therefore, regardless of the anion presence in the environment, water molecules (or OH^-) are the first entity to be adsorbed on the iron surface in aqueous systems.

2.3.2. Catalytic Mechanism

The catalytic theory as proposed by Heusler, *et al.* [21] is different from the consecutive mechanism in a way that $FeOH_{ads.}$ in the *rds* step is hypothesized to be a catalytic metal-ligand interaction that directly induces the dissolution of iron. This mechanism, which is described according to Eqs. (11–13) (Figure 5), is basically similar to the non-catalytic scheme, except that only the *rds* is different.

²⁻ Fourier Transform Ellipsometry

³⁻ X-ray Photoelectron Spectroscopy

Heusler's catalytic mechanism:	
$Fe + OH^{-} \stackrel{k1,H}{\longleftrightarrow} FeOH_{ads.} + e^{-}$	(11)
$Fe + FeOH_{ads.} + OH^{-} \xrightarrow{rds,H} FeOH_{ads.} + FeOH^{+} + 2e^{-}$	(12)
$FeOH^+ \stackrel{k_{3,H}}{\longleftrightarrow} Fe^{2+} + OH^-$	(13)



The catalytic theory [21] is based on the second-order dependence on OH^- ions with an anodic Tafel slope of 30 mV/dec. The reason that is called catalytic is basically because of the formation of an intermediate that can react more readily with another reactant to induce the dissolution reaction to occur more rapidly. This catalytic intermediate is neither consumed nor produced. In other words, in this theory, it is postulated that there is an elementary step that is autoactivated by one of its products, *i.e.*, $FeOH_{ads}$ herein. This can be seen by adding the second and third elementary steps (Eqs. (12 & 13)) in Heusler's scheme to get Eq. 14, where $FeOH_{ads}$ is present on both sides of the known overall reaction, Eq. 6, acting as a catalytic ligand.

$$Fe + FeOH_{ads.} \rightarrow Fe^{2+} + FeOH_{ads.} + 2e^{-}$$
 (14)

In Heusler's mechanism, the *rds* step (Eq. 12) is sometimes written as a sequence of two sub-elementary steps (Eqs. (15 & 16)):

$$Fe + FeOH_{ads.} \rightarrow [Fe(FeOH)]$$
 (15)

$$[Fe(FeOH)] + OH^{-} \rightarrow FeOH^{+} + FeOH_{ads.} + 2e^{-}$$
(16)

In this case, the catalytic species is hypothesized to be [Fe(FeOH)] but it does not change the main principle of this theory as the action of a catalytic intermediate is always predicted. Adding these two Eqs. (15 & 16) one can again obtain the *rds* step written according to Eq. 12.

The occurrence of the non-catalytic or catalytic mechanism is dependent on the surface activity and the surface density of the crystal imperfections [30]. It is claimed that the non-catalytic mechanism takes place when the surface activity is low, while the catalytic route is more plausible at the high surface density of active sites [31, 32]. The electrode surfaces with more imperfections facilitate the catalytic path, while the noncatalytic mechanism is predominant for nearly perfect surfaces with no defects [33]. This view was also supported by Worch, et al. [34] who studied the behavior of dissolution for single crystal and polycrystalline pure iron in sulfate-containing media. They concluded that Bockris' mechanism is dominant for finely roughened surfaces, whereas Heusler's model is more likely when the electrode surface consists of densely packed stepped faces or dislocations [34]. The state of the iron surface plays a critical role, and factors such as impurities, phase distribution, the density of dislocations, crystallinity, cold work, etc., might switch the mechanism from one to the other [27,35, 36]. To experimentally investigate these two theories, being able to manipulate the surface characteristics and examine the response is a more challenging task and is beyond the scope of this dissertation. Therefore, the ideal theoretical approach is to incorporate these two principles into a single scheme.

2.3.3. Mixed Multipath Mechanism

The transformations in the anodic sweep as shown in Figure 2 cannot be explained only by relying on a single dissolution path (or a single adsorbed intermediate)

as hypothesized by Bockris [20] and Heusler [21]. The bend in the sweeps might indicate a switch in the mechanism of dissolution or reaction path [33–36]. In other words, the non-catalytic and catalytic ideas should be merged into a unique comprehensive version. In 1981 and 1986, Keddam, et al., [37–40] reported that more than a single dissolution path should exist since several time constants during their electrochemical impedance spectroscopy (EIS) measurements and few transformations in the anodic sweeps had been observed under certain experimental conditions. They accomplished a systematic analytic screening of 40 different mechanistic schemes in which three Fe-containing intermediates were involved and using numerical simulation they concluded that the mechanism presented in Figure 6 is the most plausible one [37–40]. Evaluation of the data over the whole range of the anodic sweeps affording a basis for developing a mechanistic scheme accounting for a mixed behavior (non-catalytic and catalytic). It has been claimed that more than one single intermediate and actually three dissolution paths might exist under certain experimental conditions [38–40]. Therefore, Keddam, et al., combined both consecutive (BDD mechanism) and catalytic (Heusler) ideas into a single inclusive scheme (Figure 6) to define a plausible explanation for such observations [37]. Keddam, et al., used a specific type of notation, where instead of stating the exact chemical composition for an adsorbed intermediate the oxidation state of iron for that particular entity is mentioned using roman numerals [37]. For example, in their scheme, $FeOH_{ads}$ and $FeOH^+$ were translated to $Fe(I)_{ads}$ and $Fe(II)_{sol}$, respectively, and the catalytic ligands were noted by '*' superscript next to that specific intermediate. They also excluded those elementary steps that corresponded to the dissociation of the iron complex in the solution, e.g., the dissociation reaction of $FeOH^+$ to Fe^{2+} (e.g., step 3 in Bockris' and Heusler's model) was not included and only the steps that are taking place at the electrode surface were taken into account. This way they could further diminish the unnecessary complexities in depicting the complete mechanistic pathway. Keddam's model seems to be more comprehensive as it can explain the observations for a wider range of pH and overpotentials. Presumably, under certain experimental conditions, a particular pathway (non-catalytic or catalytic) could be dominant over the other one. Figure 6 illustrates Keddam's overall mechanism for iron dissolution. Seven preliminary steps are involved in Keddam's scheme for describing anodic dissolution. It is worth mentioning that the first and the second elementary steps are similar to the mechanism proposed by Bockris [20]. The first two elementary steps can be written according to Eqs. (17 & 18), which represents the non-catalytic scheme proposed by Bockris [20]. The only difference is that the first step in Keddam's model is assumed to be irreversible as the contribution of the backward reaction is negligibly small and this forward reaction is very fast [27, 41].

$$Fe + OH^{- \stackrel{K_1}{\rightarrow}} Fe(I)_{ads.} + e^{-}$$
(17)

$$Fe(I)_{ads.} \xrightarrow{k_2} Fe(II)_{sol.} + e^-$$
 (18)



Figure 6. (*a*) The adapted scheme proposed by Keddam et al., [37] to encapsulate both consecutive and catalytic pathways into a single mechanism for iron dissolution, and (b) the modified scheme hypothesized by Moradighadi in the presence of chloride [42]

According to this scheme, initially, a monovalent iron complex is adsorbed at the electrode surface and the reaction proceeds through the dissolution of this adsorbed monovalent entity to a bivalent complex in the electrolyte. In this scheme (Figure 6), the first and the second elementary steps or the active dissolution path relate to the same theory described by Bockris, *et al.* (non-catalytic) [20]. The other two paths (*Transition Path* and *Pre-passivation Path*) are written according to Heusler's model [21], or the catalytic route (compare the elementary steps 4 and 6 in Figure 6 with Eq. 14). According

to the EIS studies done by Moradighadi *et al.* [42], this multipath scheme (Figure 6 (b)) becomes even more complex in concentrated chloride solutions. Moradighadi *et al.* [42] reported that a fourth chloride-based adsorbed intermediate forms at the electrode surface in the concentrated chloride-based solutions. They claimed that a fourth dissolution path could be coupled with this three-pathway mechanism proceeding the dissolution of iron [42]. Another important point to mention is that in both Heusler's (Figure 5) and Keddam's (Figure 6) scheme, one of the elementary steps contains two electrons being transferred. According to quantum theory, transfer of two electrons in one step is less likely and this indicates that these elementary steps are not taking place as they are written. Although they could potentially be broken down to other sub-elementary steps, for the sake of keeping the scheme less complicated, they decided to consider that step with two electrons being transferred as a single building block. Alternatively, a different scenario such as branching mechanism as proposed by Drazic, *et al.* [35], needs to be put forward to replace it.

2.4. Speculations on the Effect of CO₂ on the Mechanism of Anodic Dissolution

For iron dissolution in a CO₂-saturated environment, there is no approved mechanism for the anodic dissolution of iron in acidic media. Several researchers attempted to adopt Bockris' model of dissolution [20] to propose the possible role of CO₂ in anodic reactions, which mainly involves the active engagement of carbonate intermediates with some adsorption-derived semi-passive films [43, 44]. As of now, there is no accepted mechanism on how dissolved CO₂ may influence the mechanism, but there are speculations. An interaction between dissolved carbonate species and Fe^{2+} ions creating mixtures such as $FeHCO_{3ads}$ and $FeHCO_{3ads}^+$ is reported to take place during iron dissolution in weak acids [43, 44]. The formation of a soluble complex such as $FeHCO_{3ads}^+$, especially at high pH (~ 8–9) in weak acids, was also reported by other researchers that could exacerbate the iron dissolution reaction [45]. It was also stated that direct adsorption of CO₂ could form chemical ligand species that act to replace $Fe(OH)_2$ and increase the exchange current density of the anodic dissolution reaction, which is proportional to pCO₂ (up to 1 bar pCO₂ and beyond 1 bar, this effect becomes negligible) [46]. Based on Bockris' mechanism, Nesic, *et al.*, speculated that the decrease in the current in the transition region in CO₂ media (with pH ~ 3) could be attributed to surface coverage by carbonate-type adsorption-related intermediates [43]:

$$FeCO_{2ads} + H_2O \leftrightarrow FeHCO_{3ads} + H^+ + e^-$$
(19)

$$FeHCO_{3_{ads}} \leftrightarrow FeHCO_{3,ads}^+ + e^-$$
 (20)

$$FeHCO_{3ads} + H_2O \rightarrow FeOH_2CO_{3ads} + H^+$$
(21)

This speculation is similar to what was proposed by Guo, *et al.*, for the anodic dissolution of 2% Cr steel in acidic media in sweet environments [47]. However, Almeida, *et al.*, have more recently claimed that even in CO₂ environments, the H^+ and OH^- are still the dominant adsorbed species triggering oxidative dissolution [48, 49]. Even in the presence of CO₂, Bockris' theory has been frequently used by many researchers as the predominant mechanism to mimic the behavior of the anodic dissolution of iron [50–52].

Castro's group [53–57] investigated the electrodissolution and passivation mechanism of iron at a pH range from 8.9 to 10.5 in the presence of

carbonate/bicarbonate buffers using EIS, XPS, and voltametric measurements. They reported the formation of adsorbed $Fe(I)_{ads.}$ and $Fe(II)_{ads.}$ intermediates which actively transformed to $Fe(II)_{sol.}$ due to their reaction with bicarbonate [54]. The formation of soluble complexes such as $FeHCO_3^+$ and $Fe(HCO_3)_2$ were hypothesized mainly due to the interaction between $Fe(I)_{ads.}$ with bicarbonate [53]. They postulated that the formation of a pre-passive $Fe(OH)_2$ is the first oxidation step, followed by its partial removal due to its reaction with bicarbonate-producing carbonate [53, 55]. Then, the second step of dissolution relates to the growth of the anodic layer with the synchronous dissolution of iron *via* the dissolution of the outer part of the porous oxide layer [53, 55]. Finally, the dissolved ferrous ions can be precipitated as $FeCO_3$ or $Fe(HCO_3)_2$ [53, 56]. The formation of a bi-layer structure in alkaline carbonate/bicarbonate media (pH 8.9) was also reported by Valentini, *et al.*, who described the formation of an outer *FeCO₃* layer on top of an inner hydrous $Fe(OH)_2$ layer [58].

Figure 7 exhibits the influence of dissolved CO_2 and pH change on anodic polarizations of 0.5% Cr steel in NaCl solutions. A slight increase in acidity notably influences the anodic branch and higher pH leads to a higher anodic peak current.



Figure 7. Anodic polarization of 0.5% Cr steel in 0.5M NaCl+0.05M KHPhth under the condition of (\circ) pH 4-Ar sparged, (\bullet) pH 3.4- Ar sparged, ($\mathbf{\nabla}$) pH 3.7-Ar sparged, and (∇) pH4-CO₂ sparged all at 19°C [44]

Obviously, the dissolved CO₂ is significantly changing the transition and prepassivation range, whereas it has no detectable effect on the active dissolution regime [44]. Hence, the effect that dissolved CO₂ has on the acceleration of anodic dissolution is mainly due to its contribution in destabilizing the semi-passive adsorbed layers forming during the transition and pre-passivation domains without speeding up the active anodic dissolution rate [44, 49]. In other words, during the anodic polarization of steel, CO₂ has more affinity to react with absorbed ligands or with semi-passive films formed during the transition and pre-passivation steps other than actively participating in the kinetics of the ferrous ion formation half reaction [44, 49]. Similarly, Hurler, *et al.*, also found that CO₂ did not affect the active or passive ranges of dissolution, but it influences the transition or pre-passivation state more remarkably [59].

Nesic, *et al.*, [43] used galvanostatic analysis and speculated different pathways for the dissolution of iron in the presence of CO₂ at different pH values. For different pH

ranges, a different Tafel slope, a particular mechanism, and a different reaction order with respect to pH were obtained. For the weak solutions with pH < 4, 4 < pH < 5, and pH > 5, they theoretically speculated the Tafel slopes of 20-35 mV/dec., 30-60 mV/dec., and 80–120 mV/dec., respectively. Nesic, et al., [43] claimed that the Langmuir type adsorption is predominant in more acidic media where the surface coverage with adsorbed intermediate is minimal. By increasing the pH, the surface coverage due to the adsorbed species increases; thus, Frumkin-type adsorption becomes the dominant mechanism. As pH goes beyond 5, the iron experiences a saturated level of adsorbed intermediates, *i.e.*, the maximum coverage [43]. Their proposed mechanism for the anodic dissolution of iron in the presence of dissolved CO_2 was speculative, and no definite proof was provided in that work [43]. As was mentioned before, literature has offered contradictory results for the effect of CO₂ and the existing accounts fail to figure out the exact contribution of CO₂ in the dilemmatic nature of arguments between noncatalytic vs. catalytic theories. Additionally, no previous study has investigated the effect of environmental factors (pH, temperature, CO₂, etc.) on the kinetics of the elementary steps shown in Figure 6. Therefore, further investigation is needed in this area.

2.5. Electrochemistry of CO₂ Corrosion

 CO_2 gas itself is not corrosive, but upon its dissolution and hydration forms a weakly acidic environment due to H_2CO_3 formation. H_2CO_3 then follows through several dissociation steps as below [60]:

CO₂ dissolution:
$$CO_{2(g)} \rightleftharpoons CO_{2(aq)}$$
, $(K_{sol} = \frac{C_{CO_{2}(aq)}}{P_{CO_{2}(g)}})$ (22)

CO₂ hydration:
$$CO_{2(aq)} + H_2O_{(l)} \rightleftharpoons H_2CO_{3(aq)}$$
, $(K_{hyd} = \frac{C_{H_2CO_{3(aq)}}}{C_{CO_{2(aq)}}})$ (23)

$$H_{2}CO_{3} \text{ dissociation: } H_{2}CO_{3(aq)} \rightleftharpoons H_{(aq)}^{+} + HCO_{3(aq)}^{-}, (K_{ca} = \frac{c_{HCO_{3(aq)}}c_{H_{(aq)}}}{c_{H_{2}CO_{3(aq)}}})$$
(24)

$$HCO_{3}^{-} \text{ dissociation: } HCO_{3}^{-}_{(aq)} \rightleftharpoons H^{+}_{(aq)} + CO_{3}^{2-}_{(aq)} , (K_{bi} = \frac{c_{co_{3}^{2-}_{(aq)}}c_{H^{+}_{(aq)}}}{c_{HCO_{3}^{-}_{(aq)}}})$$
(25)

Water dissociation:
$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$
, $(K_{wa} = C_{H^+_{(aq)}}C_{OH^-_{(aq)}})$ (26)

where the CO₂ hydration step is claimed to be the slowest step in this sequence [60]. A considerable amount of literature has claimed that at the same acidity level (*i.e.*, same pH), the corrosion rate of iron when exposed to dissolved CO₂ is higher than that when CO₂ is absent [44, 59–63]. Some reports have shown that CO₂ boosts the corrosion rate mainly by promoting the cathodic reaction (*i.e.*, hydrogen evolution) [60]. The overall reaction of iron corrosion in a sweet environment can be expressed as:

$$Fe_{(s)} + CO_{2(aq)} + H_2O_{(l)} \to FeCO_{3(s)} + H_{2(g)}$$
 (27)

One of the first discussions on the mechanism of CO₂ corrosion was proposed by de Waard, *et al.*, in 1975 [64] where they considered the reduction of carbonic acid as the main species involved during CO₂ corrosion. This mechanism, which is known as direct reduction, fails to explain the exact nature of CO₂ corrosion in several ways [60, 65]. For example, it ignores H₂CO₃ dissociation and its buffering effect through which H₂CO₃ serves as a hydrogen ion reservoir. The direct reduction mechanism disregards the reduction of those H^+ ions coming from H₂CO₃ dissociation. At the same time, the influence of mass transfer of oxidant species (H₂CO₃, *HCO*₃⁻, and *H*⁺) on the limiting current was also disregarded in the direct H₂CO₃ reduction mechanism [65]. According to the classic mechanistic viewpoint presented in the literature [60, 64–66], H^+ reduction and direct reduction of the other weak acids are the dominant cathodic reactions expressed as below:

$$2H_{(aq)}^+ + 2e^- \to H_{2(g)} \tag{28}$$

$$2H_2CO_{3(aq)} + 2e^- \rightleftharpoons H_{2(g)} + 2HCO_{3(aq)}^-$$
(29)

$$2HCO_{3(aq)}^{-} + 2e^{-} \rightleftharpoons H_{2(g)} + 2CO_{3(aq)}^{2-}$$
(30)

$$2H_2O_{(l)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH_{(aq)}^- \tag{31}$$

However, this view has evolved over time, especially after the studies done by Kahyarian *et al.* [67–69], who reported that the "buffering effect" of the weak acid is the governing mechanism that can significantly influence the kinetics and thermodynamics of the cathodic reactions. The main contribution of carbonic acid as a weak buffer is claimed to be through its homogeneous chemical dissociation, *i.e.*, the buffering feature, rather than its direct reduction [67–69]. Instead of using a direct reduction mechanism, they applied mass conservation inside the boundary layer, diffusion equations and the Pitzer's model to conduct the speciation calculations for non-ideal aqueous situations [67–69]. This led to achieving more realistic predictions for the rate cathodic reactions.

In a pH range lower than 4 when the concentration of H^+ in media is significant, the predominant cathodic reaction is hydrogen ion reduction (Eq. 28). At pH greater than 4 and below 5 de Waard, *et al.*, reported that Eq. 29 becomes more important, and at pH values above 5 Eq. 30 plays the most important role [66, 70]. However, Tran, *et al.*, postulated that cathodic reactions *via* Eqs. (29 & 30) are negligible; at pH levels below 6 under a moderate experimental condition (T< 80°C and pCO₂ < 10 bar), the hydrogen reduction reaction is again the predominant cathodic reaction during CO_2 corrosion of steel [71]. In 1 wt.% NaCl solution at 30°C (total pressure 1 bar), and in an open system with an excess concentration of CO_2 gas, Eqs. (22–26) were used to calculate the concentration of various species in CO_2/H_2O equilibrium under the abovementioned conditions. Figure 8 shows the concentration of different species at different pH values associated with the equilibria involved between CO_2 and H_2O .



Figure 8. *pH* dependency of concentration for various species in CO_2/H_2O equilibrium in an open system ($T=30^{\circ}C$, total pressure= 1 bar, solution: 1 wt.% NaCl)

In a large body of literature [47, 72–74], the Bockris' mechanism is believed to be dominant for iron and steel dissolution in sweet media, however, as of now, it is unclear how dissolved CO_2 exactly impacts the chemistry, kinetics, and sequence of the elementary steps. In addition, as mentioned before, there are many contradictory aspects in the current published literature about the exact influence of CO_2 on the mechanism of iron dissolution.

Chapter 3: Research Gaps & Objectives

It should be understood that any electrochemical reaction is the summation of two or more reaction steps in a multistep sequence. For the iron dissolution reaction, some studies have yielded an understanding of what these multistep reactions could be, but there are still several gaps in the current understanding that have not been clearly answered by any of the existing studies or research within the field. In this investigation, the following research gaps can be listed:

- Most of the earlier studies on anodic dissolution are built based on very complicated theories/models which are speculative and sometimes hard to comprehend. A complex theory is not appropriate if there is no direct proof for it, and for sure is not practical for building models. According to Occam's razor principle, a theory/model should not be multiplied beyond necessity and a simpler theory is preferred as long as it seems realistic and covers the empirical observations. There is a need to revisit the fundamental studies in the anodic dissolution of iron to put forward a simpler but more practical narrative.
- A considerable amount of literature has focused on using steady-state techniques to investigate the mechanism of iron dissolution. The steady-state method alone cannot provide detailed information about the elementary steps and help us understand the rate determining step - *rds*. Using transient techniques to understand the effect of CO₂ and other environmental parameters was rarely done in early kinetic studies of metal dissolution. Therefore, more systematic investigations using the transient approach are needed.

- Most of the basic studies on iron dissolution ended up with speculative conclusions. In the existing literature [13,37,38, 75], the anodic potentiodynamic sweeps were usually modeled by determining the kinetic parameters by simple fitting of experimental data, without a critical interpretation of the physical meaning of the results. No previous study has established a well-defined procedure based on transient analysis to estimate and extract the characteristic kinetic rate constants of the elementary steps. Comparing these characteristic numbers across different conditions is important since it helps to decode the role of experimental parameters on the reaction kinetics.
- There are many contradictory aspects in the current published literature about the effect of CO₂, pH and temperature on the kinetics of iron dissolution. Actually, very little is known about the exact impact of dissolved CO₂ on the mechanism of iron dissolution, and it is not clear how different experimental conditions can mechanistically impact the kinetics of the elementary steps.

The goal of the research reported in this dissertation is to investigate the effect of environmental factors (CO₂, pH, and temperature) on the mechanism of anodic dissolution. To achieve this, it is essential to state the following objectives:

- Effectively and reproducibly utilize transient techniques in parallel with the steadystate potentiodynamic method under different experimental conditions.
- Use the steady-state technique to accomplish a quantitative analysis and to reestablish the narrative of Bockris' model for iron dissolution in strong acids.

- Apply transient techniques to accomplish a qualitative and quantitative investigation of the possible effect of CO₂ on anodic dissolution or iron.
- Seek for a less complex theoretical explanation than the existing ones as related to the mechanism of the iron dissolution reaction.
- Introduce a procedure based on transient measurements, that enables us to calculate the important kinetic rate constants. These constants are characteristic numbers that quantify how different factors can impact the rate of the elementary steps and the overall reaction.
- Establish a simple and effective method to model the steady-state anodic potentiodynamic sweep over a wide range of environmental conditions by applying a set of characteristic constants calculated based on transient analysis.
- Enhance modeling capabilities to explain how different environmental parameters can affect the mechanism of iron dissolution as the dominant anodic reaction during the corrosion of mild steel in conditions similar to that seen in oilfield environments.

Chapter 4: Experimental & Methodology

To fulfill the research objectives, in this chapter the experimental setup, apparatus, electrochemical techniques, materials, and the basic procedure that was used for sample preparation are described.

4.1. Experimental Setup

All electrochemical measurements in this study were performed in a 2-liter glass cell setup. Figure 9 schematically illustrates the 2-liter glass cell used in this project.



Figure 9. Schematic representation of the experimental cell setup (courtesy of Cody Shafer, research engineer, ICMT, Ohio University)

This glass cell setup provides a three-electrode cell configuration where the rotating cylinder electrode (RCE) specimens work as the working electrode and a Cole-Parmer[®] Ag/AgCl saturated KCl which uses a carbon tip on the end of the Luggin capillary to bring the reference potential close to the working electrode measurement

point. The platinum-coated titanium mesh counter electrode (CE) was used for completing the circuit to allow the charge to flow. Depending on the experiment a ringshape or four rectangular-shaped counter electrodes were used to provide a more symmetric current distribution around the RCE electrode.

4.2. Apparatus, Techniques, and Materials

The electrochemical measurements were performed using Gamry[®] (Reference 600), Solartron[®] 1470E, or VersaSTAT3[®] potentiostat/galvanostat instruments. Table 1 summarizes the chemical composition of the RCE specimens used in this project.

Material (wt.%)	Cr	С	Mn	Ni	Si	Мо	Р	V	Al	S	Fe
Pure Fe	-	-	-	-	-	-	-	-	-	-	99.99
X65	0.25	0.13	1.16	0.29	0.26	0.16	0.009	0.047	-	0.009	Balance
2% Cr steel	1.9	0.042	1.4	0.308	0.254	-	0.008	-	0.022	< 0.003	Balance

Table 1. Chemical composition of the RCE specimens used in this study

The electrolytes were prepared using NaCl (Crystalline/Certified ACS) from Fisher Chemical dissolved in deionized water. In some cases, Na₂SO₄ was used to prepare the supporting electrolyte. All the chemicals used in the present work were analytical grades purchased from Fisher Scientific. The pH of the electrolytes was monitored using a Cole-Parmer[®] pH probe connected to an OAKTON[®] pH 6+ handheld meter. The temperature was controlled using an HH11B OMEGA[®] thermometer. The errors in monitoring pH and temperature were within the ranges of ± 0.02 pH units and $\pm 0.5^{\circ}$ C, respectively. Diluted NaOH, HCl, or H₂SO₄ were used to adjust the pH. A Corning[®] 6795-420D PC-420D stirring hot plate was utilized to stir and heat the test solutions. Fe^{2+} concentration was measured using a Thermo Scientific GENESYS 10S UV-Vis spectrophotometer, employing FerroZine[®] and FerroVer[®] reagents; absorbances were measured at wavelengths of 562 nm and 510 nm, respectively, according to the technique described in reference [76]. Highly pure N₂ or CO₂ gas was sparged continuously for about 2 hours prior to and during each experiment through the test solution to deoxygenate the electrolyte during all measurements and, in the case of CO₂, facilitate test electrolyte saturation with carbonic species.

4.3. Electrochemical Techniques

4.3.1. Open Circuit Potential (OCP) Monitoring

After RCE specimens were exposed to the test solution and before each measurement, the OCP was monitored *vs.* an Ag/AgCl reference electrode to establish a stable value within ± 2 mV. The sample period and the stability of the monitored OCP were set at 0.5 sec. and 0 mV/s, respectively.

4.3.2. Electrochemical Impedance Spectroscopy (EIS)

It is important to ensure that the solution resistance for all measurements was the same. Before each measurement, and after OCP stabilization, the EIS was recorded, and the solution resistance was always within the range of $3.5 - 4.0 \Omega$.cm². Before each experiment, running an EIS could diagnose any possible systematic error that might exist in the electrochemical setup as well. The initial and final frequencies for collecting impedance data were set at 10 kHz and 0.01 Hz, respectively. The impedance data points

were obtained for every 5 points/dec. at an AC voltage of 10 mV root-mean-square (RMS). The oscillation of the potential was performed around OCP (0 V vs. OCP).

4.3.3. Linear Polarization Resistance (LPR)

The corrosion rates of RCE specimens were calculated using LPR measurements over the potential window of ± 5 mV vs. OCP with a rate of 0.125 mV/s. The corrosion current (*i*_{corr.}) was determined using the Stern-Geary equation. The corrosion rate in mm per year can be estimated according to the following equation:

Corrosion rate (mm/year) =
$$\frac{3.27 \times 10^{-5} \times i_{\text{corr.}} (A/m^2) \times EW}{\text{Density}(g/cm^3)}$$
(32)

where EW is the equivalent weight (for iron = of 27.92 gr).

4.3.4. Potentiodynamic Measurements

The potentiodynamic measurements were used to monitor the steady-state response of the specimens in the test solution. The sample period used to obtain the data was one data point per second. The cathodic branch was collected first to keep the electrode surface intact. Afterward, the specimens were polished with 1200-grit abrasive paper and immersed in the solution test till OCP reached its initial stable value (normally it took 5–10 minutes for OCP to achieve stability). The anodic branch was collected by positively polarizing the surface. The polarization curves were collected at the scan rate of 0.5 mV/s. All potentiodynamic sweeps presented in this study were corrected for the effect of solution resistance (*iR-drop*). The solution resistance, R_s , was first measured using EIS. To correct the cathodic sweep at a measured potential (*E_{measured}*), the multiplication of *I_{measured}×R_s* was added to the measured potential. In contrast, for correcting the anodic sweep, the multiplication of $I_{measured} \times R_s$ was subtracted from the measured potential.

4.3.5. Potentiostatic Measurements

Potentiostatic techniques with a high sampling rate (~3.33 microseconds per data point) were utilized to measure the transients and to quantitatively determine the kinetics of the elementary step at fixed applied potentials ranging from +60 to +300 mV vs. OCP. It was important to enhance the speed setting of the potentiostat/galvanostat GAMRY Reference 600 instrument to be able to capture the data points with a very high sampling rate (in the order of a few microseconds). The minimum sample period of the GAMRY (2×10^{-6} seconds) was used for collecting the potentiostatic transients. As is shown in Appendix A, among the cell test systems available at ICMT, only GAMRY could acquire the transient data point at such a high rate. In the potentiostatic technique, the perturbation signal is a constant potential, and the response is the current vs. time. After applying the potential stimulation, the potentiostatic responses were collected for at least 0.1 seconds.

4.3.6. Galvanostatic Measurements

The galvanostatic transient was utilized to qualitatively examine the influence of dissolved CO₂ on the anodic dissolution of iron. The rate of data acquisition needed for collecting galvanostatic information was 100 data points per second. In the galvanostatic technique, the perturbation signal is a constant current, and the response is the potential *vs.* time. After applying the current stimulation, the galvanostatic responses were collected for about 5 minutes.

4.4. Electrode Fabrication and Sample/Test Preparation

The small-size specimens with a length of about 14.3 mm were cut from a long rod (~ 12 mm outer diameter) to make RCE sample workpieces. By drilling a hole with a diameter of about 5 mm in the shaft into which a polytetrafluoroethylene (PTFE) insulator is inserted, the RCE specimens were manufactured. PTFE is chemically inert and as an electrically non-conductive material can efficiently prevent the flow of electrons. The PTFE tip capable of holding RCE was mounted at the lower end of the shaft. All RCE specimens were polished up to 1200-grit abrasive paper (or up to 0.25-micron diamond polishing for a few experiments), rinsed with deionized (DI) water, and sonicated in isopropanol alcohol, and dried with cold nitrogen gas before every experiment. Figure 10 (a) shows the disassembled accessories of an RCE shaft. After assembling the RCE shaft, it was mounted into a Modulated Speed Rotor (MRS) model AFMSRCE purchased from Pine Research instruments (Figure 10 (b)).



Figure 10. (a) Disassembled RCE specimens and accessories, and (b) MRS rotor

Chapter 5: Validation of Bockris' Mechanism in Strong Acids Based on Steady-State Measurements

5.1. Introduction

Identifying the mechanism of an electrochemical reaction entails speculating the sequence of possible elementary steps, which is not a routine process. There might be a number of possibilities for the sequences of the steps. Identifying the mechanism includes speculating about the most probable pathways first, and then evaluating the kinetic consequences of each selection. In the next step, the most important criterion of how plausible a mechanism is, depends on the experimental evidence that it can rationalize. Reviewing literature related to corrosion research brings to light the importance of understanding the mechanisms involved, and how this is essential to aid in the development of mathematical models for corrosion prediction. This chapter documents possible mechanisms for the dissolution of pure iron in strong acid 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. As mentioned in Section 2.3, in the case of iron dissolution, there are two common mechanisms in strong acids reported in the literature: namely, the "catalytic mechanism" proposed by Heusler, et al., [21], and the "non-catalytic mechanism" postulated by Bockris, et al., [20] which is also known as the "BDD mechanism". Numerous studies have reported similar experimental observations aligned with the noncatalytic mechanism supporting Bockris' hypothesis in different solution chemistries

(e.g., acetic acid-perchloric acid, acetate, chloride, sulfate, and bromide-containing electrolytes, CO₂-sparged media, etc.) [31,77, 78–82]. Bockris' approach [1, 20] 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 chapter, Bockris' style of analysis of the Butler-Volmer equation for understanding the mechanism of iron dissolution is revisited. Additional mechanistic pathways for the occurrence of oxidative iron dissolution in addition to those postulated models of *BDD* and Heusler are tested. For all proposed pathways, the theoretical Butler-Volmer relationship is derived, and the corresponding theoretical consequences of each pathway are computed and compared with the experimental metrics. Finally, the most likely mechanism for iron dissolution in strong acids is established for the potential ranges near the OCP. This study is based on the assumption that there is no solid corrosion product layer forming at the electrode surface. In addition, for all mechanistic pathways, it is assumed that the mass-transfer resistance is insignificant. In this chapter, all reaction pathways are written within the range near the corrosion potential, *i.e.*, the potential range not far from OCP.

5.2. Objectives

The objective of the present chapter is to accomplish a quantitative analysis of oxidative iron dissolution in strong acid in a potential range in the proximity of its OCP, leading to the articulation of a revisited narrative of the *BDD* mechanism [20] for iron dissolution. Thirty-eight different pathways are investigated herein and the theoretical

Butler-Volmer equations are written for each. The kinetic consequences of each pathway and the corresponding theoretical values of the main kinetic parameters are determined, and the theoretical outcomes are compared to the experimental observations to finally find the most likely explanation for iron dissolution in strong acids.

5.3. Methodology

Table 2 summarizes the experimental conditions used in this chapter.

Parameters	Values
pH (±0.02)	2.0, 2.5, 3.0, 3.5, and 4.0
Temperature (±0.5 °C)	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

 Table 2. Experimental conditions

Measurements of OCP, LPR, and potentiodynamic sweeps are utilized to collect the experimental metrics. The cathodic branch was collected first to keep the electrode surface intact. Then, the anodic branch was collected by positively polarizing the surface after the potential returned to its stable OCP value. The cathodic and anodic sweeps were performed from OCP to -700 mV and +300 mV *vs*. OCP, respectively. The potential scan rate of 0.125 mV/s was used. All potentiodynamic sweeps presented in this work were corrected for the effect of solution resistance (*iR-drop*). All experimental measurements are done using the cell setup, equipment, and procedures explained in Chapter 4. All RCE specimens were polished to 1200 grit silicon carbide paper and 0.25micron, rinsed with deionized (DI) water and isopropanol, sonicated for 5 minutes, and air dried. Before each measurement, the OCP was monitored for at least 20 minutes to ensure it was stable. EIS measurements were performed at OCP in a frequency range from 100 kHz to 1 Hz at 10 points/dec. to monitor the solution resistance. LPR measurements were performed at the same scan rate over a potential range of \pm 5 mV *vs*. OCP. A Solartron 1470E potentiostat was used for LPR, OCP, and potentiodynamic measurements. The OCP was monitored for 5 min before each measurement. The EIS measurement was done using a VersaSTAT3 potentiostat instrument. The 0.15 M Na₂SO₄ supporting electrolyte was sparged for about 2 hours with N₂ gas prior to and during each experiment throughout this study. The pH was adjusted using 0.1 M H₂SO₄ or 0.1 M NaOH solution as necessary. The investigation presented in this chapter is limited to the potential ranges not far from OCP to validate the existing mechanistic interpretation and to find if the proposed pathway involving the formation and dissolution of *FeOH_{ads}* is actually the predominant path or not.

5.4. General Procedure to Elucidate the Mechanism of a Multistep Reaction

The general steps for elucidation of the mechanism for a multistep electrochemical reaction are illustrated in the flowchart shown in Figure 11.



Figure 11. *The general flowchart for the elucidation of the mechanism of a multistep electrochemical reaction*

The first step is knowing the overall reaction. This is usually easy, and it comprises a Coulombic analysis of the reaction, *i.e.*, computing the number of the Coulombic charges necessary to accomplish the reaction [1]. After identifying the overall reaction, one must speculate the possible entities in the solution to begin thinking about the pathways that consist of an initial diffusion of species from the bulk to the electrode, undergo charge transfer, and produce products on the electrode surface or move back into the solution. When there are species in the bulk solution, there are always adsorbed entities on the electrode surface which might influence the reaction rate. The surface coverage θ is the fraction of the electrode which is covered with a particular adsorbed

species. To write the pathways, one also needs to speculate all plausible adsorbed entities on the electrode surface. Knowing all the species on both the solution and the electrode side of the interface, one embarks upon writing the possible reaction steps, to propose possible pathways. In the next step, by computing the theoretical Butler-Volmer equation, one might try to theoretically compute the kinetic consequences of each of the *n* pathways. Then using the experimental measurements, the kinetic evidence needs to be carefully collected to be able to test the reaction model and then the comparison between the numerical predictions of various models and the experimentally obtained parameters. For a plausible reaction mechanism, the pattern of the theoretical predictions must match the pattern of the experimental response. Additionally, for each possible pathway, a particular step might be considered as *rds*, and again by computing the consequences of that guess, and collecting the experimental metrics, the probable *rds* can be determined (depending on how comparable are theory and experiment).

5.5. Obtaining Theoretical Butler-Volmer for Speculated Pathways

In determining the mechanism for a particular multistep reaction, such as the anodic dissolution reaction of iron, one must meticulously follow the logical steps below: <u>Stage 1</u>: The first step is knowing the overall reaction. In the case of iron dissolution, it is widely known that the solution accumulates ferrous ions, and therefore the dissolution must involve the transfer of two electrons *via* the overall reaction:

$$Fe_{(s)} \to Fe_{(aq)}^{2+} + 2e^{-}$$
 (33)

The probability of simultaneously two-electron transfer tunneling at once is low, and the species must go through consecutive steps. Assume that this reaction occurs *via* two successive one-electron transfer steps:

$$Fe_{(s)} \to Fe_{(aq)}^+ + e^- \tag{34}$$

$$Fe^+_{(aq)} \to Fe^{2+}_{(aq)} + e^-$$
 (35)

However, this sequence is not feasible because it ends up in the order of dependency of reaction with respect to the OH^- equal to zero, which is not consistent with the real experimental observations. Experimental results clearly showed the dependency of iron dissolution on the pH of the solution. Hence, OH^- must somehow participate in the mechanism of the iron anodic dissolution and there should exist a few sub-elementary steps where OH^- ion is involved during dissolution.

<u>Stage 2</u>: Identifying all possible entities in the solution. In the case of iron andic dissolution in strong acid, according to the literature [83–85], the possible species in a sulfate-based electrolyte are:

- Fe^{2+}
- OH^- in equilibrium with H^+
- $FeOH^+$
- $Fe_2(OH)^+$
- *Fe* $(OH)_{2}^{+}$
- *HFeO*₂⁻
- $(FeOH)_2^+$
- $HFe_2O_2^+$
- H_2FeO^{2+}
- Na^+
- SO4²⁻

In sulfate-based electrolytes (such as in this case Na₂SO₄ solution), it was experimentally observed that the reaction rate does not depend on the concentration of the supporting electrolyte, *i.e.*:

$$p(Na^+) = \left(\frac{dlogi}{dlogc_{Na+}}\right) \approx 0 \tag{36}$$

$$p(SO_4^{2-}) = \left(\frac{dlogi}{dlogc_{SO42-}}\right) \approx 0 \tag{37}$$

Hence, the Na^+ and SO_4^{2-} are not participating in the primary mechanistic steps of the dissolution reaction because they are inactive species that only provide the electrical conductivity required for the controlled-potential conditions during a particular electrochemical measurement. p(j) represents the order of the reaction with respect to the entity *j*.

<u>Stage 3</u>: During iron anodic dissolution inside the Helmholtz double layer, there must be entities adsorbed at the electrode surface that react with the species in the electrolyte to move the overall reaction forward through a consecutive series of electrochemical/chemical steps. One can postulate all possible adsorbed entities at the surface of the electrode by considering the basic chemistry of the possible compounds as:

- FeOH_{ads}
- Fe(OH)_{2,ads}
- FeO_{ads}
- FeO(OH)_{ads}
- (FeOH)_{2,ads}
- $FeOH^+$, ads
- $Fe_2(OH)^+$, ads
- $Fe(OH)_2^+$, ads
- $HFeO_2^{-}$, ads
- $(FeOH)_2^+$, ads
- $HFe_2O_2^+$, ads

• H_2FeO^{2+} , ads

Stage 4: Knowing all possible entities, one must speculate probable reaction pathways that might occur among the entities, leading to the overall reaction (Eq. 33). The speculative invention of the possible pathway is not a routine affair, and several diagnostic criteria must be utilized in the next stages to unravel the most probable mechanistic pathway. Mechanisms (a) through (e) are taken from Ref. [1], and mechanism (f) represents the mechanism proposed by Heusler [21]. The rest of the mechanisms, *i.e.*, pathways (g) through (s) are speculated in this study, for the first time to test the feasibility of iron dissolution through other consecutive steps. The possible mechanistic pathways for the anodic dissolution of iron are listed below. Butler-Volmer equation actually can provide a quick shortcut to the deduction of the mechanism since it immediately provides the values for b_a and b_c for that particular postulated pathway. One must obtain the theoretical Butler-Volmer equation for each of these proposed pathways, considering that the *rds* is the only step for which the forward and the backward reaction rates are not equal and assuming all other steps, other than rds are in near-equilibrium (*i.e.*, their forward and backward reaction are almost equal).

It is necessary first to theoretically determine the Butler-Volmer equation for a multistep reaction. Assume that there is a multistep reaction as:

$$A + ne \rightarrow Z$$
 (38)

Assume that this overall reaction occurs via a sequence of elementary steps as below:

 $A + e \rightarrow B$ (Step 1)

 $B + e \rightarrow C$ (Step 2)

 $C + e \rightarrow D$ (Step 3)
$P + e \rightarrow R \qquad (\text{Step } n_f)$ $\nu(R + e \rightarrow S) \qquad (rds \text{ Step})$ $\nu S + e \rightarrow T \qquad (\text{Step } n_b = n - n_f - \nu n_r)$.

 $Y + e \rightarrow Z$

.

In this case when the elementary reactions are written as cathodic reaction and the cathodic and anodic charge transfer coefficients can theoretically be calculated according to the following equations [1, 11]:

$$\alpha_c = \frac{n_f}{\nu} + n_r \beta \tag{39}$$

$$\alpha_a = \frac{n_b + \nu n_r}{\nu} - n_r \beta \tag{40}$$

where β is always assumed to be equal to 0.5 [1, 11]. Therefore, the cathodic and anodic Tafel slopes can theoretically be calculated as:

$$b_c = \frac{2.3RT}{\left(\frac{n_f}{\nu} + n_r\beta\right)F}$$
(41)

$$b_a = \frac{2.3RT}{\left(\frac{n_b + \nu n_r}{\nu} - n_r\beta\right)F}$$
(42)

Remember that in this case the summation of $n_b+n_f+vn_r$ is going to be equal to n, the total number of electrons transferred during the overall reaction. Since the rate of net reaction is always equal to $r_{net} = i_{net} = r_a - r_c = i_0(i_a - i_c)$, then the theoretical Butler-Volmer equation for the abovementioned overall reaction can be calculated as [1, 11]:

$$i = i_0 \left\{ exp\left[\left(\frac{n_b + vn_r}{v} - n_r \beta \right) \frac{F\eta}{RT} \right] - exp\left[- \left(\frac{n_f}{v} + n_r \beta \right) \frac{F\eta}{RT} \right] \right\}$$
(43)

Analogously, in the following section, this procedure is implemented for the case of iron anodic dissolution, which is a multistep reaction. Different theoretical pathways are speculated and for each pathway, the expected theoretic anodic and cathodic Tafel slopes (b_d^j, b_d^j) and the corresponding theoretical Butler-Volmer equation (i^j) are obtained. The superscript *j* index shows the item number for the proposed mechanism. β^{j} is the symmetric factor which is assumed to be equal to 0.5 [11]. Remember that the abovementioned equations are for the case when the reactions are written as cathodic reactions. In the following calculations, the steps are written as anodic reactions, therefore we should count n_f as the number of electrons being transferred after the rds step and vice versa. In the following section, different reaction sequences (mechanisms a through s') are speculated for the iron dissolution reaction first. Then the magnitude of n_{f} , n_b , v, n_r , α_a , α_c , b_a , and b_c are obtained for each case. For the first few mechanisms, the derivation of the Butler-Volmer equation is shown, and for the rest of the pathways, the same steps are followed to find the Butler-Volmer equation. Ultimately, the $p_{OH^{-i}}$ (dependency of the anodic exchange current density on the concentration of OH⁻ ion) and $E_{OH^{-1}}$ (the dependency of corrosion potential on OH^{-1} ion) as the additional kinetic metrics are computed for each scheme according to the following correlations [20,22, 23]:

$$p_{OH^-}^i = \frac{\partial \log(i_{0,a})}{\partial \log(C_{OH^-})} \tag{44}$$

$$E_{OH^-}^i = \frac{\partial E_{corr}}{\partial \log (C_{OH^-})} \tag{45}$$

Consider the first hypothesized mechanism, *i.e.*, the mechanism (a).

Mechanism (a):

$$Fe + OH^- + FeOH_{ads.} \leftrightarrow (FeOH)_2 + e^-$$
 Step 1

$$(FeOH)_2 \xrightarrow{rds} 2FeOH_{ads.}$$
 Step 2

$$FeOH_{ads.} \leftrightarrow FeOH^+ + e^-$$
 Step 3

$$FeOH^+ \leftrightarrow Fe^{2+} + OH^-$$
 Step 4

For this mechanism, $n_f^a = 1$, $n_b^a = 1$, $v^a = 1$, $n_r^a = 0$, and therefore b_c^a and b_a^a can be obtained as:

$$\begin{aligned} \alpha_c^j &= \frac{n_f^j}{\nu^j} + n_r^j \beta^j & \to |b_c^j| = \left| \left(\frac{dE_c^j}{dlogi_c^j} \right)_c \right| = \frac{2.3RT}{\alpha_c^j F} = \frac{2.3RT}{\left(\frac{n_f^j}{\nu^j} + n_r^j \beta^j \right)_F} \\ \alpha_a^j &= \frac{n_b^j + \nu^j n_r^j}{\nu^j} - n_r^j \beta^j & \to |b_a^j| = \left| \left(\frac{dE_a^j}{dlogi_a^j} \right)_a \right| = \frac{2.3RT}{\alpha_a^j F} = \frac{2.3RT}{\left(\frac{n_b^j + \nu^j n_r^j}{\nu^j} - n_r^j \beta^j \right)_F} \\ |b_c^a| &= \left| \left(\frac{dE_c^a}{dlogi_c^a} \right)_c \right| = \frac{2.3RT}{\left(\frac{n_f^a}{\nu^a} + n_r^a \beta^a \right)_F} = \frac{2.3RT}{F} \\ |b_a^a| &= \left| \left(\frac{dE_a^a}{dlogi_a^a} \right)_a \right| = \frac{2.3RT}{\left(\frac{n_b^a + \nu^a n_r^a}{\nu^a} - n_r^a \beta^a \right)_F} = \frac{2.3RT}{F} \end{aligned}$$

To obtain the theoretical Butler-Volmer equation for this pathway, we need to take into account the correction factor due to the adsorption of the $FeOH_{ads.}$, during *rds*. Steps one, three, and four are at equilibrium, which means their forward and backward reaction rates are equal. The only step which has contributed to the rate of the overall reaction is *rds*, *i.e.*, step 2. Writing the law of mass action for this *rds* step, we have:

$$\dot{\nu} - \vec{\nu} = k_{-2}^{a} \theta_{(FeOH)_{2}} - k_{2}^{a} \theta_{FeOH}^{2}$$
(46)

After rearranging all steps in the cathodic direction and writing the law of mass action at equilibrium for step 1 we have:

$$v_1^e = v_{-1}^e \longrightarrow k_{-1}^a \theta_{FeOH} C_{OH^-} e^{(1-\beta)F\eta/RT} = k_1^a \theta_{(FeOH)_2} e^{-\beta F\eta/RT} \longrightarrow$$

$$\frac{\theta_{FeOH}}{\theta_{(FeOH)_2}} = \frac{K_1}{C_{OH^-}} e^{-F\eta/RT}$$
(47)

where
$$K_i = \frac{k_i}{k_{-i}}$$
 always.

To obtain the concentration term for θ_{FeOH} and $\theta_{(FeOH)2}$ it is necessary to write the law of mass action for all equilibrium steps.

$$k_{-3}^{a}\theta_{FeOH}e^{(1-\beta)F\eta/RT} = k_{3}^{a}(1-\theta_{FeOH})C_{FeOH} + e^{-\beta F\eta/RT} \rightarrow$$

$$\theta_{FeOH} = K_{3}^{a}C_{FeOH} + e^{-F\eta/RT}$$
(48)

$$k_{-4}^{a}C_{FeOH^{+}} = k_{4}^{a}C_{Fe^{2+}}C_{OH^{-}} \to C_{FeOH^{+}} = K_{4}^{a}C_{Fe^{2+}}C_{OH^{-}}$$
(49)

Inserting (49) in (48) we have:

$$\theta_{FeOH} = K_3^a K_4^a C_{Fe^{2+}} C_{OH^-} e^{-F\eta/RT}$$
(50)

Inserting (50) in (47):

$$\theta_{(FeOH)_2} = \frac{C_{OH^-}}{K_1} \theta_{FeOH} e^{\frac{F\eta}{RT}} = \frac{C_{OH^-}}{K_1} K_3^a K_4^a C_{Fe^{2+}} C_{OH^-}$$
(51)

Inserting expressions for θ_{FeOH} and $\theta_{(FeOH)2}$ in Eq. 45, the predicted theoretical Butler-Volmer equation will be obtained as:

$$r^{a} = k_{-2}^{a} \frac{C_{OH^{-}}}{K_{1}} K_{3}^{a} K_{4}^{a} C_{Fe^{2}} C_{OH^{-}} - k_{2}^{a} (K_{3}^{a} K_{4}^{a} C_{Fe^{2}} C_{OH^{-}})^{2} e^{-2F\eta/RT}$$
(52)

Placing $\vec{k}_a = k_{-2}^a \frac{K_3^a K_4^a}{K_1}$ and $\vec{k}_a = k_2^a (K_3^a K_4^a)^2$, we obtain the following rate equation for

mechanism (a):

$$r^{a} = \bar{k}_{a} (C_{OH^{-}})^{2} C_{Fe^{2+}} - \bar{k}_{a} (C_{Fe^{2+}} C_{OH^{-}})^{2} e^{-2F\eta/RT}$$
(53)

During the anodic dissolution of iron, in the backward direction, the dependency of current on the overpotential can be expressed as:

$$\dot{r}_a = \dot{k}_a (C_{OH^-})^2 C_{Fe^{2+}}$$
(54)

Therefore, $p_{OH^{-}a}$, the order of dependency of anodic exchange current density on the concentration of hydroxide ion ($C_{OH^{-}}$) is going to be equal to:

$$p_{OH^-}^a = \left(\frac{\partial \ln\left(\tilde{r}_a\right)}{\partial \ln C_{OH^-}}\right)_{C_{Fe2+}} = 2$$

During steady-state corrosion, the $E_{OH^{-i}}$, the dependency of corrosion potential on $C_{OH^{-i}}$ for mechanism (a) can theoretically be estimated according to the following correlation [20,22, 23]:

$$E_{OH^{-}}^{a} = \left(\frac{\partial(E_{corr.})}{\partial\log(C_{OH^{-}})}\right)_{C_{Fe2+}}^{a} = -2.3 \left(\frac{p_{OH^{-}+1}^{a}}{\alpha_{a}^{a} + \alpha_{c}^{a}}\right)_{F}^{RT} = -2.3 \left(\frac{2+1}{1+1}\right)_{F}^{RT} = -0.09 \text{ V/dec.}$$

For the rest of the mechanisms (b through s), similar calculations based on the Butler-Volmer equation were followed to determine the theoretical kinetic consequences. The corresponding detail and the mechanistic steps are presented in Appendix B.

Another possibility that might happen for a particular mechanism is that, depending on the Gibbs free energy, a particular elementary step, more often, the ratedetermining step might be subdivided into more sub-elementary steps. This subelementary step is usually a desorption step that changes the position of the ratedetermining step and adds one additional step to a particular pathway. This phenomenon is called branching [35]. A few studies also provided evidence that supports the existence of a branching process [14]. Figure 12 schematically shows the branching of a particular dissolution step to sub-elementary steps (1) and (2).



Figure 12. Schematic illustration of the branching process

Once branching takes place, the desorption steps are going to control the overall rate of the reaction, *i.e.*, the desorption step will be the rate-determining step. Considering the branching process, nineteen additional pathways corresponding to each mechanism mentioned above must be also taken into account. Mechanisms a' through s' and the corresponding calculation of the Butler-Volmer equation for each mechanism are provided in Appendix B.

Table 3 summarizes the computed theoretical outcomes corresponding to each mechanism. The values of cathodic Tafel slopes were measured to be greater than or equal to 120 mV/dec. under our experimental conditions. The values of cathodic Tafel slopes which are shown as infinity (∞) indicate a very high cathodic Tafel slope, a number usually much greater than 120 mV/dec.

Mechanism	b_a^i	b ⁱ _c	р ^і _{0н} -	$E_{OH^-}^i$	Mechanism	b ⁱ _a	b ⁱ _c	р ^і _{0н} -	$E^i_{OH^-}$
a	60	-60	2	-90	a'	30	-60	0.5	-30
b	30	-30	1	-30	b'	30	-30	1	-30
c	60	-60	1	-60	c'	30	x	1	-60
d	40	-120	2	-90	d'	30	x	3	-120
e	40	-120	1	-60	e'	30	x	1	-60
f	30	-60	2	-60	f'	20	x	1	-40
g	24	-120	0	-20	g'	30	x	1	-60
h	120	-24	1	-40	h'	30	-60	1	-40
i	60	-60	0	-30	i'	30	x	3	-120
j	60	-60	0	-30	j'	30	x	3	-120
k	24	-40	2	-45	k'	15	x	3	-60
l	24	-40	1	-30	l'	60	-20	0	-15
m	40	-24	1	-30	m'	30	x	2	-90
n	120	-120	0	-60	n'	60	x	0	-60
0	60	-60	0	-30	0'	60	-60	0	-30
р	30	-30	0	-15	p'	20	-60	2	-45
q	30	∞	0	-30	q'	30	x	0	-30
r	20	-60	1	-30	r'	15	x	3	-30
S	24	-40	4	-75	s'	15	x	3	-60
L					1	1	1		

mechanistic pathways at 303 K (b_a^i , b_c^i , and $E_{OH^{-i}}$ are in mV/dec.)

In the next step, a few experimental metrics will be collected. The goal is to collect accurate experimental parameters and compare them with theoretical predictions to find the most likely mechanism for iron dissolution.

5.6. Collecting Experimental Metrics

Four different experimental metrics were gathered; namely, the anodic Tafel slope (b_a) , cathodic Tafel slope (b_c) , order of reaction with respect to $OH^-(p_{OH^{-}i})$, and dependency of corrosion potential on the concentration of OH^- in the bulk solution $(E_{OH^{-}i})$.

<u>Variation of $E_{corr.}$ as a Function of $[OH^-]$ ($E_{OH^-}^i$): The variation of corrosion potential as a function of time for iron in 0.15 M Na₂SO₄ solution at four different pH values is shown in Figure 13. pH was adjusted using diluted H₂SO₄ or NaOH solutions.</u>



Figure 13. (a) OCP variation over time, and (b) dependency of corrosion potential on pH for pure iron in 0.15 M Na₂SO₄ solution, at 30 °C ($pN_2 = 0.97$ bar)

The dependency of corrosion potential on pH, $\frac{\partial (E_{corr.})}{\partial log (C_{OH-})}$, was measured to be about $E_{OH-}^{i} = -51 \pm 2 \text{ mV/dec.}$

Measured values of anodic and cathodic Tafel slopes (b_a and b_c): Near OCP, the anodic Tafel slope can interfere with the hydrogen reduction reaction and vice versa. Hence, it is important to take into consideration the impact of cathodic on the anodic sweep and vice versa. Oftentimes, especially when the pH is lower than 4, the linear portion of the cathodic Tafel can be obtained relatively easily from potentiodynamic sweeps, however, there is no reasonable linearity for the anodic branch. It is mainly due to the rapid kinetics of anodic dissolution, or dominance of adsorption phenomena, which might cause undesirable disturbance of the linear Tafel range [3]. According to Keddam's analysis, the anodic Tafel slope determined at low current densities near OCP is under the influence of the adsorption-desorption reaction of hydrogen [37, 38]. Hence, it is important to take into consideration the impact of the cathodic current on anodic sweeps and vice versa. A linear portion of the cathodic sweep was chosen (dotted box in Figure 14) and cathodic Tafel was calculated to be -185 mV/dec. This cathodic Tafel line will be used to extract the pure cathodic current values $(i_{cathodic})$ given that the measured values on the cathodic polarization are in fact the net values of the current. The black line in Figure 14 is the cathodic current densities used for the extraction of anodic current. As the potential goes to more negative values close to the linear range (the region where the black line overlays the cathodic sweep), the magnitude of the anodic current becomes insignificant compared to the cathodic current densities. On the anodic side, the magnitude of the anodic current is always greater than the cathodic current values. To extract the linear range of the anodic branch, the linearity of the cathodic branch can be used to determine the pure anodic data points, given that the measured values for the

potentiodynamic sweeps are in fact the net values of the current. In other words, the pure anodic current could be determined by subtracting the net current from the pure cathodic current (extrapolated black line in Figure 14) [86, 87]:

$$i_{an.} = i_{net} - i_{cathodic} \tag{55}$$

Considering that the cathodic and anodic sweeps were collected separately, by subtracting the net current from the cathodic current, we will have two sets of anodic data points. One set of anodic data points is obtained from the net cathodic sweep (Eq. 56), and the other ones are attained from the net anodic curve (Eq. 57) [86]:

$$i_{an.}^{1} = i_{cathodic_net} - i_{cathodic}$$
⁽⁵⁶⁾

$$i_{an.}^2 = i_{anodic_net} - i_{cathodic} \tag{57}$$

This way, two different anodic Tafel slopes are extracted adjacent to OCP. One anodic Tafel slope is calculated from the cathodic branch and the other one is determined using the anodic branch. Therefore, using the steady-state potentiodynamic measurements from each experimental condition, the b_a is reported as the average between these two anodic Tafel slopes. Figure 14 represents this approach for anodic Tafel slope determination of pure iron in 0.15 M Na₂SO₄ electrolyte (pH 2) at 30°C. The intersection of the cathodic line with the point where the two anodic Tafel lines meet each other lies on the OCP. The regions that are shown in gray, red, and blue indicate the data points that are used for determining the cathodic Tafel slope, anodic Tafel slope on the cathodic branch, and anodic Tafel slope on the anodic branch, respectively.



Figure 14. Determination of the anodic Tafel slope using the linearity of the cathodic sweep for pure iron in strong acid 0.15 M Na₂SO₄ solution, at 30 °C ($pN_2 = 0.97$ bar) at pH 2

The anodic Tafel slope for iron dissolution in strong acid at pH 2 was measured to be in the range of 20.6 - 35.7 mV/dec. (average $b_a = 28.2 \text{ mV/dec.}$). The R_p value under our experimental condition at pH 2 was measured to be about 11 Ω . Knowing the b_a , the corrosion current density (*i*_{corr}.) is determined to be about $1.8 \pm 0.6 \text{ A/m}^2$. The intersection of the cathodic line with the point where two anodic Tafel lines met each other, lies on the OCP line. This intersection point (shown in yellow) adequately lies in the range of 1.8 $\pm 0.6 \text{ A/m}^2$, which is the range for corrosion current density. A similar approach was followed to determine a range for the anodic Tafel slope at pH 2.5, 3.0, 3.5, and 4.0 (Figure 15).



Figure 15. Determination of the anodic Tafel slope using the linearity of the cathodic sweep for pure iron in strong acid 0.15 M Na₂SO₄ solution, at 30 °C ($pN_2 = 0.97$ bar) at (a) pH 2.5, (b) pH 3.0, (c) pH 3.5, and (d) pH 4.0

Table 4 summarizes the anodic Tafel slopes, R_p , and $i_{corr.}$ values obtained according to the abovementioned potentiodynamic approach.

pН	b_a (mV/dec.)	$R_p \left(\Omega. \mathrm{m}^2 \right)$	i_{corr} (A/m ²)
2.0	28.1 ± 7.5	5.5×10 ⁻³	1.8 ± 0.6
2.5	47.5 ±11.7	5.6×10 ⁻³	3.0 ± 0.6
3.0	36.4 ±12.3	5.2×10 ⁻³	2.5 ± 0.7
3.5	40.6±15.8	5.4×10 ⁻³	2.7 ± 0.9
4.0	38.8 ±6.7	6.4×10 ⁻³	2.2 ± 0.3

 $M Na_2 SO_4$ solution, at 30 °C

Figure 16 shows the average values of the anodic Tafel slopes with their corresponding error bars.



Figure 16. Calculated anodic Tafel slopes at different pH for pure iron in strong acid at 30 °C, in 0.15 M Na₂SO₄ ($pN_2 = 0.97$ bar)

The anodic Tafel slope is expected to be in a range of $38.2 \pm 10 \text{ mV/dec}$. The error bars were determined by taking the standard deviation among different sets of experiments at a fixed solution pH. The relatively large error bar of $\pm 10 \text{ mV/dec}$. means

that this experimental metric needs to be used carefully when it comes to comparison with theory. As the error for experimental anodic Tafel slope is relatively high, when comparing experimental values with the corresponding theoretical predictions, first the parameters other than b_a will be used.

<u>Variation of $i_{0,an}$ as a Function of $[OH^-]$ ($p^i_{OH^-}$):</u> To calculate the anodic exchange current density, the line passing through the ($E_{corr.}, i_{corr.}$) point was extrapolated to the standard reversible potential of iron dissolution ($E^0_{rev,an}$). $E^0_{rev,an}$ for iron dissolution was taken as -687 mV vs. Ag/AgCl [20, 87]. This potential depends on ferrous ion concentration and a fixed potential was picked here only to estimate the order of the reaction, which is extracted from the slope not the intercept. The intersection of the extrapolated line with the reversible potential is approximately the exchange current density of iron dissolution ($i^0_{an,Fe}$). Figure 17 shows this method of determining $i^0_{an,Fe}$ for pure iron in 0.15 M Na₂SO₄ solution (pH 2) at 30 °C. Table 5 lists the values of $i^0_{an,Fe}$ for different pH values calculated using this methodology.



Figure 17. Calculated $i^0_{an,Fe}$ for pure iron in strong acid at pH 2 at 30 °C, in 0.15 M

 $Na_2SO_4 (pN_2 = 0.97 bar)$

Table 5. Calculated values $i^{0}_{an,Fe}$ at pH values in strong acid 0.15 M Na₂SO₄ solution, at 30 °C

рН	i _{0,an} (A/m ²)
2.0	7.01×10^{-5}
2.5	4.99×10 ⁻³
3.0	5.44×10 ⁻³
3.5	3.13×10^{-2}
4.0	1.03×10^{-1}

The procedure shown in Figure 17 to define the $i_{0,anodic}$ associated with the averaged anodic Tafel line for pH 2 was repeated for similar experiments at pH 2.5, 3, 3.5, and 4. The exact value of the reversible potential as the reference potential for determining the exchange current density does not matter but the same potential used at pH 2 was required to be used for all analyses. To find the dependency of $i_{0,anodic}$ on pH,

the log of the exchange current density vs. the log of the concentration of hydroxide (OH^{-}) was plotted to determine the $p_{OH^{-}i}$. According to this analysis, in strong acid for pure iron at pH \leq 4, the order of reaction dependency with respect to OH^{-} was found to be about 1.42 ±0.3. The same slope will be obtained even if a slightly different reversible potential value is used for calculating the anodic exchange current density. By plotting exchange current density as a function of the concentration of hydroxide (OH^{-}) , both axes in the logarithmic scale, the slope of the line was estimated to be about 1.42 ±0.3 (Figure 18). Therefore, in strong acid for pure iron at pH \leq 4, the order of dependency reaction with respect to OH^{-} was found to be about 1.42.

$$p_{OH^-}^i = \left(\frac{\partial \ln(i_{0,a})}{\partial \ln C_{OH^-}}\right)_{C_{Fe2+}} \approx 1.42 \pm 0.3$$
(58)



Figure 18. Variation of $i_{an,Fe}^0$ as a function of the concentration of OH^- for pure iron in strong acid at 30 °C, in 0.15 M Na₂SO₄ (pN₂ = 0.97 bar)

Now that all experimental metrics have been collected (listed in Table 6), we need to compare these experimental findings with the theoretical predictions as previously summarized in Table 3, to find the most plausible mechanisms out of those 38 speculations.

Experimental parameter	Measured value
$b_a{}^{Exp.}$	$38.2 \pm 10 \text{ mV/dec.}$
$b_c^{Exp.}$	254 ±44 mV/dec.
E _{OH} - ^{Exp.}	-51 ± 2 mV/dec.
рон-Ехр.	1.42 ±0.3

Table 6. *Experimental findings for iron dissolution in strong acid* $(pH \le 4)$

5.7. Comparing Theory vs. Experiment: Most Possible Pathways

By comparing the findings listed in Table 6 with those in Table 3, it was determined that there is consistency between the experiment and the theory when assuming mechanisms (e), (e'), (c'), and (g'). Table 7 represents the comparison between experimental findings with theoretical predictions of pathways (e), (e'), (c'), and (g').

Table 7. Comparison between experiment vs. theory for the most likely mechanisms for iron dissolution in strong acid ($pH \le 4$)

Mechanism	b_a (mV/dec.)	р он- ^{Ехр.}	$E_{OH-}^{Exp.}$ (mV/dec.)
Experimental observations	38.2 ± 10	$1.42 \pm \! 0.3$	- 51 ±2
Theoretical mechanism (e)	40	1	- 60
Theoretical mechanism (e')	30	1	- 60
Theoretical mechanism (c')	30	1	- 60
Theoretical mechanism (g')	30	1	- 60

Based on a decent consistency between theory and the observations for mechanisms (e), (e'), (c'), and (g'), it seems that these four are the most possible ones for the iron anodic dissolution in strong acid near OCP ($\pm 50 \text{ mV vs. OCP}$), when pH ≤ 4 . Table 8 represents these four schemes with the highest level of consistency when comparing them with experimental results.

e	$Fe + H_20 \leftrightarrow FeOH_{ads.} + H^+ + e^-$ $FeOH_{ads.} \xrightarrow{rds} FeOH^+ + e^-$ $FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$	е'	$Fe + H_2 0 \leftrightarrow FeOH_{ads.} + H^+ + e^-$ $FeOH_{ads.} \xrightarrow{rds} FeOH_{ads.}^+ + e^-$ $FeOH_{ads.}^+ \xrightarrow{des} FeOH^+$ $FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$
c'	$Fe + OH^{-} \xrightarrow{rds} FeOH^{+}_{ads.} + 2e^{-}$ $FeOH^{+}_{ads.} \xrightarrow{des} FeOH^{+}$ $FeOH^{+} \leftrightarrow Fe^{2+} + OH^{-}$	g'	$Fe + FeOH_{ads.} + OH^{-}$ $\leftrightarrow (FeOH)_{2,ads.} + e^{-}$ $(FeOH)_{2,ads.} \leftrightarrow (FeOH)_{2,ads}^{+} + e^{-}$ $(FeOH)_{2,ads}^{+} \xrightarrow{rds} FeOH_{ads.}^{+} + FeOH_{ads.}$ $FeOH_{ads.}^{+} \xrightarrow{des} FeOH^{+}$ $FeOH^{+} \leftrightarrow Fe^{2+} + OH^{-}$

Table 8. Most likely pathways for iron dissolution in strong acid ($pH \le 4$)

<u>Comparison between mechanism (e) and mechanism (e')</u>: Mechanisms (e) and (e') are assumed to be virtually the same as mechanism (e') is basically written based on (e). Mechanism (e') takes place when the rate-determining step in mechanism (e) is divided into two sub-elementary steps, *i.e.*, one surface reaction which concert adsorbed *FeOH*_{ads} to its adsorbed cation followed by a desorption step that dissolves this adsorbed cation into the solution. The branching process was first explained by Drazic [35], who proposed that a change in the position of the rate-determining step from the second electron exchange to a slow desorption step of an intermediate might occur sometimes. They claimed that depending on the pH of the solution and the surface activity, a particular portion of the reaction may proceed through a direct $FeOH_{ads}^+$ path or via $Fe(OH)_{2,ads}$ path (branching), providing the reaction order with respect to OH^- equal to 1.6 to 1.8 (but never 2) [35]. Schweickert, *et al.*, [88] and Keddam, *et al.*, [37] also speculated similar branching processes during iron anodic dissolution. As was mentioned previously, both mechanisms (e) and (e') are based on the same pathway for iron anodic dissolution, except that the latter one assumes branching of the *rds* step in mechanism (e).

<u>Feasibility of mechanism (c')</u>: The probability of two electrons tunneling simultaneously across the metal-solution interface is so low that is has become wellaccepted that the electrode excludes the paths which would involve multiple electron transfers in one single step. The simultaneous transfer of two electrons requires an activation energy much higher than that of a single electron transfer [89]. Therefore, the possibility of mechanism (c') is expected to be much less than those of the other three left pathways (e), (e'), and (g').

<u>Comparison between mechanism (e') and (g')</u>: Figure 19 schematically compares the pathways (e') and (g'). It can be shown that both mechanisms (e') and (g') are basically manifesting a similar story for the dissolution of iron. Mechanism (e') is based on the adsorption of one single $FeOH_{ads.}$ and its subsequent conversion to $FeOH_{ads.}^+$ followed by its desorption into the solution. Similarly, the mechanism (g') is also showing the same idea except that it describes dissolution through the adsorption of two $FeOH_{ads.}$ and its conversion to two $FeOH_{ads.}^+$ species. Mechanism (g') assumes that the dissolution starts by consuming adsorbed $FeOH_{ads.}$ acting as a catalyst, so it presumes that there exist $FeOH_{ads.}$ at the electrode surface since the beginning. Pathways (e') and (g'), independently of sequences, produce the same species, through the same desorption *rds* step. Therefore, both mechanisms (e') and (g') are fundamentally a similar scheme, while (g') seems to describe a more complicated version of (e'). It is worth mentioning that the mechanism (g') is different from the mechanism proposed by Heusler [21]. Mechanism (g') is speculated for the first time in this study and after the computational analysis, it was found that it results in reasonable kinetic predictions for the electrode reaction. Interestingly, it was found that the mechanism (g') is also based on the same pathway as described earlier by Bockris, *et al.* [20]. Mechanism (e) is Bockris' model for iron dissolution and (e') is the branched version of mechanism (e).



Figure 19. *Comparison of pathways (e') and (g'). They both describe the same principle for iron anodic dissolution*

Following the Occam's razor principle, between mechanisms (e') and (g'), the simplest explanation should be considered as the most likely one. Hence, compared to the scheme (g'), the mechanism (e') is the more appropriate mechanistic pathway for explaining the iron anodic dissolution in strong acid ($pH \le 4$).

Both (e') and (e') mechanisms are valid: Figure 20 schematically illustrates the two most probable pathways among the 38 proposed pathways. Both mechanisms (e) and (e') could accurately and reasonably predict the experimental observation during iron anodic dissolution in strong acid (pH \leq 4), depending on the number of active sites available for intermediate adsorption [35].



Figure 20. The most probable mechanisms (e) and (e') for iron anodic dissolution in strong acid ($pH \le 4$). Assuming no scale formation and in an overpotential range not far from OCP

Mechanism (e) predicts an anodic Tafel slope of 40 mV/dec., while the branched version of mechanism (e), *i.e.* (e'), anticipates the anodic Tafel slope of 30 mV/dec. The occurrence of either pathway (e) or (e') depends on the adsorption energy and the

properties of the active surface of the electrode. The density of the active sites and the properties of the electrode surface can be changed due to heat treatment, cold work, strain, hydrogen adsorption, properties of the metallic interface, etc. [8, 35]. When the adsorption energy of the intermediates of $FeOH_{ads}^+$ or $Fe(OH)_{2,ads}^+$ has increased the rate of the rate-determining step in mechanism (e) will be increased, while the rate of desorption step in mechanism (e') is decreased. Hence, the conversion of FeOHads to FeOH_{ads}⁺ will no longer be the rate-controlling step, instead FeOH_{ads} tends to first be converted to *FeOHads*⁺ before dissolving into the solution. Therefore, when the adsorption energy of the intermediate of $FeOH_{ads}^+$ or $Fe(OH)_{2,ads}^+$ is increased, the mechanism (e) tends to branch [35]. This is the case when the iron dissolution dominantly takes place through mechanism (e'). It has been claimed that for small coverage by adsorbed intermediate and assuming Langmuir-type adsorption, the anodic Tafel slope of 30 mV/dec. is explainable. Therefore, the change of the anodic Tafel slope from 40 to 30 mV/dec. can be attained within the framework of the same mechanism (e), only by changing the position of the rate-determining step that is due to the change of the number of the active sites on the electrode surface. A decrease in the anodic Tafel slope from 40 mV/dec. to 30 mV/dec. is not an indication of the change in the mechanism of anodic dissolution (pH \leq 4). A shortened version of the analysis presented in this chapter has been published by our team in Ref. [87].

5.8. Summary

To summarize, thirty-six different pathways in addition to Bockris' and Heusler's models for the anodic dissolution of iron in strong acid were proposed near OCP (± 50

mV vs. OCP, pH \leq 4). Among those, the experimental observations were consistent only with three mechanisms (e), (e'), and (g'). These three mechanisms explain the same principle, where the reaction of OH^- with iron produces the adsorbed intermediate $FeOH_{ads}$. $FeOH_{ads}$. then is dissolved into the solution to release Fe^{2^+} . Hence, $FeOH_{ads}$. presumably is always the first produced intermediate at the electrode surface during iron dissolution. This agrees well with the fundamental mechanistic theory as described by Bockris [20]. According to this theory, in the vicinity of OCP, the dominant adsorbed intermediate that controls the dissolution of iron is most likely $FeOH_{ads}$. and the dissolution of $FeOH_{ads}$ to the $Fe(II)_{sol}$ is the predominant pathway in the potential range close to the OCP. Hence, the predominant dissolution path in such a condition is through the generation of adsorbed $FeOH_{ads}$ and its subsequent dissolution into the solution. In some experimental cases, the switch from 40 mV/dec. (classic Bockris' mechanism) to 30 mV/dec. was obtained. These changes are still explainable within the same framework of mechanism (e), *i.e.*, the Bockris' or *BDD* mechanism [20].

Chapter 6: Qualitative Study on the Effect of CO₂ on Anodic Dissolution of Iron Based on Transient Measurements: Revisiting Keddam's Mechanism

6.1. Introduction

Several studies [47, 53–57, 90] attempted to introduce a modified mechanism for anodic dissolution in sweet environments by relying on Bockris' mechanism [20] to explain the possible role of CO₂ (see Section 2.4). There is a consensus among the earlier studies hypothesizing that the main influence of CO₂ or bicarbonate species is to destabilize the adsorbed $FeOH_{ads.}$ intermediate through the following reaction [48,49, 91]:

$$HCO_3^- + FeOH_{ads} \rightarrow FeHCO_3^+ + OH^- + e^-$$
(59)

Although extensive research has been performed on studying the effect of CO_2 on the overall corrosion behavior of iron/steel using steady-state measurements, the impact on the kinetics of the elementary steps is not well understood yet. No previous study has examined the effect of CO_2 on anodic dissolution within the framework of Keddam's mechanism [37]. It is important to bear in mind that *BDD* mechanism holds only for active dissolution in the vicinity of the OCP, while Keddam's mechanism covers a much wider potential range. This chapter seeks to use transient electrochemical techniques to accomplish a qualitative/semi-quantitative study and shine new light on the effect of CO_2 on the transient dissolution properties of iron. Some observations and speculations on the effect of CO_2 on the kinetics of the reaction will be presented in this chapter.

6.1.1. Necessity of Using Transient Measurements

To understand the influence of CO_2 or other environmental factors on the kinetics of anodic dissolution, knowing the overall reaction of iron anodic dissolution, Eq. 6, is not enough since this net reaction remains the same as the dominant anodic reaction regardless of the absence or presence of CO₂ under different environmental conditions. Therefore, the elementary steps need to be investigated in further detail to understand such an influence. The overall reaction does not provide us with enough information about the kinetics, therefore understanding the net reaction in greater detail is critical. Knowing the reaction mechanism as well as the elementary steps act as a tool that allows us to break the overall reaction into a few smaller building blocks. For a multi-step reaction, all non-rds steps are virtually in equilibrium, *i.e.*, their forward and backward reaction rates are assumed equal. As it was mentioned in Section 2.1, the use of the potentiodynamic data for calculating corrosion rate is usually accomplished based on the Butler-Volmer analysis [1]. The Butler-Volmer equation is written for a single *rds* step under steady-state conditions. In steady-state measurements, the response of the system under the control of *rds* at steady-state is monitored. A considerable amount of literature [92-96], has utilized steady-state potentiodynamic techniques, analysis of Tafel, and a few characteristic ratios (e.g., $\frac{dlogi_{0,a}}{dpH}$, $\frac{dE_{corr}}{dpH}$, $\frac{di_{corr}}{dpH}$, $\frac{di_{max}}{dpH}$) extracted from polarization curves to investigate the mechanism of iron dissolution. Relying on these factors and the steady-state analysis alone to elucidate the mechanism of a multistep reaction is an extremely challenging task as they provide too little information about the overall reaction which depends on the rate of the rds step. In other words, steady-state techniques such as conventional potentiodynamic methods carry information about only the *rds* [38–40]. Thus, to recognize the impact of CO₂ or other environmental factors on the kinetics of the elementary steps, utilizing transient measurements which are potentiostatic, galvanostatic, and EIS is inevitable [99–104]. Transient measurements are conducted over very short periods of time (milliseconds) and have the capability of distinguishing the transitions between different elementary steps, which makes this technique highly applicable to capture various phenomena happening during iron dissolution.

6.1.2. How are Bockris and Keddam's Mechanisms Different?

The non-catalytic mechanism of Bockris allows the accurate description of iron dissolution only at low current densities (close to the OCP) and particularly at lower bulk solution pH [105]. As discussed in Chapter 5, Bockris' interpretations were mainly based on the Butler-Volmer analysis, which is inherently written for a *rds* step. Bockris' mechanism cannot explain many of the observations at higher pH values, such as the non-linearity of the anodic sweep near the pre-passivation range (*s-shape*), multiple transformations in the potentiodynamic sweeps, and multiple time constants in EIS data as reported by Keddam, *et al.* [37]. Neither the non-catalytic nor catalytic mechanisms alone are capable of explaining this observation over a wide range of experimental conditions. Both theories presented by Bockris and Heusler stem from a common initial hydrolysis step that assumed the formation of $FeOH_{ads.}$ via a reversible step, however, Keddam, *et al.* considered this step in a non-equilibrium state [37]. Non-catalytic and catalytic mechanisms predict the anodic Tafel slope of 40 mV/dec. and 30 mV/dec.,

respectively. However, it has been reported that the anodic Tafel slope could have a much wider range, from less than 30 mV/dec. to even higher than 100 mV/dec., depending on the metallurgical factors [14]. From the initial EIS studies done by Epelboin and Keddam [41], it was proven that iron dissolution is far more complex than what was hypothesized by Bockris [20]. Evaluation of the EIS data over done by Keddam, *et al.*, [37] provided a basis for developing a scheme that accounted for a mixed behavior (non-catalytic and catalytic). Bockris' mechanism [20], anticipated the presence of one single pathway over a narrow range of experimental conditions, while the presence of three pathways was confirmed by Kedam, *et al.* [37], based on EIS analysis.

6.1.3. What is Special About Environments With pH > 4?

Almost all the mechanistic theories on iron anodic dissolution present evidence that the dissolution rate continuously increases with increasing hydroxyl concentration at the pH level well below the onset of passivity (~ pH 4) [31,79, 82]. Oftentimes under this condition (pH < 4), no transition peak or "*s-shape*" behavior is experimentally observed for iron during potentiodynamic measurements. Moreover, the dependency of the dissolution rate on *OH*⁻ concentration according to a first or second-order reaction is claimed to be more legitimate in the pH range less than or equal to 4 [106]. Usually, more than a single time constant has been reported during potentiodynamic measurements in aqueous environments with pH greater than 4 [107, 108]. These transformations are claimed to be due to the formation of more than a single adsorbed intermediate [13, 32]. There is a need to put more effort into understanding the behavior at higher pH (> 4) since it seems that the behavior becomes more complex due to the formation of a few semi-passive/passive adsorbed intermediates [92].

6.2. Research Gaps

Several research gaps have not been answered yet by any of the existing studies. Numerous studies focused on utilizing only steady-state techniques to postulate the effect of CO_2 on mainly the corrosion behavior and not on the anodic dissolution of iron/steel. As it was mentioned before, the steady-state method on its own cannot provide enough information about the elementary steps. Using transient techniques to understand the effect of CO_2 is essential. Little is known about the exact impact of dissolved CO_2 on the rate of the elementary steps.

6.3. Objectives

In this chapter, the aim is to:

- Use the galvanostatic transient technique to perform a qualitative interpretation of the role of CO₂ in the dissolution mechanism in the potential ranges close to OCP.
- Utilize the potentiostatic transient technique to conduct a semi-quantitative analysis in terms of the impact of CO₂ on the kinetics of the elementary steps in the active dissolution range and the potential ranges close to OCP.
- Revisit the complex reaction scheme proposed by Keddam, *et al.* [37] to determine the kinetic rate constants in CO₂ aqueous environments in the active dissolution range.

6.4. Hypotheses

Many studies have demonstrated that CO_2 enhances the corrosion rate; more significantly by influencing the kinetics of the cathodic reactions [109–111]. However, there has been little quantitative analysis of the effect of CO_2 on the kinetics of the elementary steps.

The hypotheses that will be tested in this chapter are:

- CO₂ alters the kinetics of the elementary steps in a way that enhances the rate of the overall anodic dissolution of iron.
- CO₂ destabilizes the adsorbed intermediates, thereby delaying the adsorption of intermediates during iron anodic dissolution.
- CO₂ impacts the kinetics of the adsorption processes and the elementary steps;
 therefore, it changes the charge accumulation in the Helmholtz Double-Layer (HDL).

6.5. Methodology

All experiments were conducted according to the protocols described in Chapter 4. Two different transient electrochemical techniques, namely galvanostatic and potentiostatic methods were used. The galvanostatic and potentiostatic measurements were performed for pure iron under the test condition summarizes in Table 9. The potentiostatic measurements were collected in a sulfate-based solution, exactly under the same experimental condition as performed by Keddam, *et al.* [37], to reproduce them and enable a direct comparison of results.

Parameter	Condition for galvanostatic test	Condition for potentiostatic test
pH (± 0.02)	3.00	5.00
pN ₂ or pCO ₂ (bar)	0.97	0.97
Electrolyte	1 wt% NaCl	$0.5 \text{ M Na}_2 \text{SO}_4$
Temperature (± 0.5 °C)	30 °C	25 °C
Test set-up	2L glass cell	2L glass cell
Motor rotation speed (rpm)	2000	2000
Sample	RCE- Pure iron	RCE- Pure iron
$R_s(\Omega.cm^2)$	~ 3.8	~ 3.8

 Table 9. Experimental conditions for transient measurements

As mentioned previously in Sections 2.3 and 6.1.2, Bockris' path [20] in the active range of dissolution is a vital portion of the larger mechanistic scheme hypothesized by Keddam, *et al.* [37]. In this chapter, potentiodynamic and transient measurements are utilized to estimate the kinetic rate constants for the two electron-transfer steps in the active dissolution range. The computed parameters will be compared to those reported by Keddam, *et al.* [37], to assess the differences. Ultimately, the influence of CO_2 on the kinetics of these two elementary steps and the possible explanations for such an effect is discussed.

6.5.1. Electrochemical Techniques

The sample preparation and electrochemical tests were done using the equipment and procedures explained in Chapter 4. Table 10 lists the electrochemical techniques that have been used in this chapter.

Technique	Measurement condition	Goal
Galvanostatic measurement	100 data points per second (At a constant current density of +10 A/m^2)	To qualitatively analyze the dissolution kinetics
Potentiostatic measurement with a high sampling rate	3.33 µs per data point (At constant potentials of +60 to +110 mV vs. OCP)	To estimate the kinetic rate constants
Potentiodynamic sweeps	0 to +0.6 V vs. OCP @ 0.5 mV/s	To measure the steady- state response (all scans were corrected for the effect of solution resistance).
EIS	10k – 0.1 Hz	To measure the solution resistance ($R_s \sim 3.8 \ \Omega.cm^2$)

 Table 10. Electrochemical techniques used in this chapter

6.5.2. Potentiostatic Approach to Estimate Kinetic Constants in Active Dissolution Range

In this section, an approach is introduced to calculate the kinetic rate constants in the active range of dissolution using potentiostatic measurements. As discussed earlier, regarding the elementary steps in the active dissolution range, there is a consensus between the non-catalytic mechanism (Bockris) and the multipath scheme (Keddam). Both mechanisms agree that the active dissolution range proceeds through the following initial steps:

$$Fe + OH^{-} \stackrel{k_1}{\to} Fe(I)_{ads} + e^{-}$$
(60)

$$Fe(I)_{ads} \xrightarrow{k_2} Fe(II)_{sol} + e^-$$
 (61)

A method based on theory needs to be found to calculate the kinetic rate constants related to these two elementary steps (Eqs. (60 & 61)). Before doing that, a few assumptions must be made. First, it has been assumed that no solid corrosion product layer is produced as the exposure time to the solution for a freshly polished specimen in all these experiments was short enough only to stabilize OCP before every measurement. In some of the experiments, the data points at 3–6 microseconds are used for computational purposes obtained on freshly polished specimens. Hence the assumption of having no corrosion product layer is sensible. Additionally, it is assumed that any change associated with the mass-transfer effect is minimized as the rotation rate in every experiment was high (2000 rpm). At high rotation rates, the current response does not increase by further increasing the rotation speed of the electrode, which is consistent with what was reported in the literature [30,37, 38]. The third assumption that has been made was that the reaction rate for the elementary step (*i*) follows an exponential function of potential as described by Eq. 62 (consistent with the Butler-Volmer equation):

$$k_i = k_{i,0} \exp(B_i E) \tag{62}$$

where $k_{0,i}$ is k_i at the reference potential of zero vs. reference electrode (RE). B_i is proportional to the charge transfer rate for a particular elementary step and is inversely proportional to the "Tafel" slope or the magnitude of the polarization (b_i) that is needed to force that specific elementary step in the forward direction:

$$b_i = \frac{2.3}{B_i}$$
 (63)

 b_i is different from the commonly known Tafel slope, as the latter one is defined for the overall cathodic or anodic reaction for a single *rds* step. b_i (in V/dec.) and $k_{0,i}$ (in mol/m².s) are the kinetic rate constants for each elementary step (*i*). In this study, when 'kinetic rate constants' are mentioned, it is referring to b_i and $k_{0,i}$. Furthermore, it was assumed that the adsorption is the Langmuir type.

Constant anodic overpotential in a range of +60 to +110 mV vs. OCP was applied and the corresponding chronoamperometric response was monitored every 3.3 microseconds. Figure 21 shows an example of potential perturbation and the current response at the anodic overpotential of 70 mV vs. OCP in 0.5 M Na₂SO₄ at pH 5 at 25 °C.



Figure 21. (*a*) Anodic potential perturbation of +70 mV vs. OCP and (b) the corresponding current response of the Fe RCE electrode in 0.5 M Na₂SO₄ at pH 5, 25 °C, 2000 rpm

At OCP, the iron surface is almost entirely covered with hydrogen and during the positive perturbation, the hydrogen desorption is achievable only at high enough overpotentials (> 60 mV vs. OCP) [37]. By applying a positive perturbation, the sudden

lack of electrons near the surface of the electrode leads to a quick "pile-up" of $Fe(I)_{ads}$ according to the first step (Eq. 60). Initially, the second step (Eq. 61) cannot move as fast as the first step. At the moment that the potential perturbation is applied, the second step cannot provide any electrons, so all electrons are taken from the first reaction step. As a result, $Fe(I)_{ads}$ starts accumulating at the electrode surface. With the buildup of Fe(I)_{ads} according to step 1, the second step can now participate in providing more electrons to meet the need caused by the externally applied potential. The dissolution of $Fe(I)_{ads}$ according to step 2 is not as fast as the pile-up of $Fe(I)_{ads}$ (step 1), hence the initial change in potential overshoots the equilibrium potential, which is called a "superpolarization peak", and is due to the collective effect of double layer capacitance and adsorption of $Fe(I)_{ads}$ [35].

To model this event, assume that θ_1 is the fraction of the surface that is covered with $Fe(I)_{ads}$. θ_1 is a function of time and potential, but at a fixed potential, it's only a function of time ($\theta_1(t)$). k_i is only a function of potential, so at a fixed potential, it's a constant value. Writing the charge balance equation, " $1-\theta_1$ " fraction of the surface is available for step 1 and " θ_1 " fraction of the surface is available for step 2, hence the total current is given by:

$$\frac{\iota(t)}{F} = k_1(1 - \theta_1(t)) + k_2\theta_1(t)$$
(64)

At OCP the surface is completely covered by hydrogen and the surface coverage due to $Fe(I)_{ads}$ is almost negligible [37], therefore the initial coverage $\theta_1(t=0) \approx 0$. Therefore, according to Eq. 64, the current response right after the potential perturbation at time $t = 0^+$ is equal to k_1 , *i.e.*, the current response at a few microseconds right after the potential stimulation correlates to only the accumulation of $Fe(I)_{ads}$. at the electrode surface through step 1:

$$\frac{i(0^+)}{F} \approx k_1 \tag{65}$$

It was important to use the high-speed setting of the potentiostat/galvanostat instrument to be able to capture the data points with a very high sampling rate (in order of a few microseconds). Given that the dependence of k_1 on potential was defined as an exponential function, one can obtain the kinetic rate constants for the first elementary step by having a set of potentiostatic measurements at different overpotentials. By plotting the natural logarithm of k_1 vs. potential, the kinetic rate constants for the first elementary step are obtained as shown in Figure 22.



Figure 22. Approach to computing the kinetic rate constants for the first elementary step $(B_1 \text{ and } k_{0,1})$. (a) perturbations at different potentials, (b) current response for each potential, and (c) plot of $ln(k_1)$ as a function of potential to obtain B_1 and $k_{0,1}$

Kinetic rate constants for the second elementary step can be derived by writing the mass balance expression (Eq. 66) to describe the variation of θ_1 as a function of time. θ_1 is produced in the first step and is consumed in the second step, thus:

$$\beta \frac{d\theta_1}{dt} = k_1 (1 - \theta_1) - k_2 \theta_1 \tag{66}$$

where β is a constant, linking the fraction of the surface coverage, θ_1 , and the surface concentration of the adsorbed species. By solving the first order differential Eq. 66, $\theta_1(t)$ can be expressed according to Eq. 67:

$$\theta_1(t) = \left(\frac{k_1}{k_1 + k_2}\right) \times \left\{1 - e^{-\left(\frac{k_1 + k_2}{\beta}\right)t}\right\}$$
(67)

From Eqs. (64 & 67) one obtains:

$$\frac{d(i(t))}{dt} = \frac{Fd\theta_1}{dt}(k_2 - k_1) \tag{68}$$

$$\frac{d\theta_1(t)}{dt} = \left(\frac{k_1}{\beta}\right) \times e^{-\left(\frac{k_1+k_2}{\beta}\right)t}$$
(69)

Substituting Eq. 69 into Eq. 68, and taking the natural logarithm of both sides, one obtains:

$$ln\left(\frac{di(t)}{dt}\right) = ln\left(\frac{Fk_1(k_2-k_1)}{\beta}\right) - \left(\frac{k_1+k_2}{\beta}\right)t$$
(70)

Therefore, by plotting $ln\left(\frac{di(t)}{dt}\right)$ as a function of time at a fixed potential and given

that k_1 was already determined, k_2 can be calculated at a constant potential (Figure 23 (a)). The dependence of k_2 on potential was defined as an exponential function, thus by following the same methodology for a set of potentiostatic measurements, the kinetic rate constants for the second elementary step (B_2 and $k_{0,2}$) can be attained by plotting the natural logarithm of k_2 vs. potential as shown in Figure 23 (b).


Figure 23. Approach to computing the kinetic rate constants for the second elementary step (B_2 and $k_{0,2}$). (a) natural logarithm of the first derivative of the current density as a function of time at a fixed potential, and (b) plot of $ln(k_2)$ as a function of potential to obtain B_2 and $k_{0,2}$

6.6. Results and Discussion

Different types of electrochemical stimuli could create a time-dependent behavior at the metal surface – solution interface. These stimuli can be a shift in the constant DC potential or a sinusoidal waveform perturbation. The transient response to these stimuli can provide important insights into the electrode behavior that can provide an understanding of the reaction kinetics at the electrode surface. The galvanostatic measurement has the capability of distinguishing the transitions between different steps during a multi-step reaction such as iron dissolution. Analysis of the galvanostatic or constant current transient techniques has been utilized by many researchers to investigate the kinetics of iron dissolution [99–102, 112]. During the galvanostatic dissolution of transition metals (*e.g.*, Fe, Co, Zn, V), the appearance of a superpolarization peak has been reported by many researchers [100, 113–115]. Although the superpolarization effect contains valuable information, only a few researchers have attempted to discover this effect and ultimately elucidate reaction mechanisms [116–119]. Too little attention has been paid to using this technique as a tool to decode the effect of CO_2 on mild steel corrosion mechanisms. In Section 6.6.1, a basic qualitative analysis of the effect of CO_2 on the galvanostatic dissolution of iron and the superpolarization effect is presented.

6.6.1. Galvanostatic Dissolution of Iron

Bockris, *et al.* [20] used the galvanostatic measurements in the active dissolution range (+10 A/m² *vs.* corrosion current density) to elucidate the reaction mechanism in strong acids. Similarly, before running any galvanostatic measurements in these experiments, a potentiodynamic sweep was first collected. Then the appropriate anodic current density under which the iron is in the active state was specified accordingly. Figure 24 shows a potentiodynamic sweep for iron in strong acid (environmental conditions: $pN_2 = 0.97$ bar, pH 3, 30°C, and 1 wt% NaCl solution). After monitoring OCP for 30 min, the LPR corrosion rate was determined to be about 1.95 mm/y. A current density equal to +10 A/m² (*vs. icorr.*) was selected in the active anodic regime, and in the following galvanostatic measurements, the iron was anodically stimulated by applying a current density of +10 A/m² *vs. icorr.* As shown in Figure 24, an increase of about 50 mV (*vs.* OCP) from the steady-state potential was observed when +10 A/m² perturbation was applied.



Figure 24. Polarization curve of iron in strong acid, 1 wt.% NaCl solution, 0.97 bar pN₂, pH 3, 30°C, 0.125 mV/s scan rate

At OCP, the net current is zero (Figure 25 (a)). After OCP became stable, the iron was anodically polarized to $\pm 10 \text{ A/m}^2$ (or 1 mA/cm²). After excitation, the steady-state potential was increased by about 50 mV (consistent with the polarization expected from the potentiodynamic sweep in Figure 24). Immediately after stimulating the current, and in a very short time (below 100 msec), a sudden jump in the potential was observed (Figure 25 (b)). This sharp spike is the superpolarization peak [100, 112]. It is believed that the superpolarization is due to the partial blockage of the surface with adsorbed hydroxyl and the peak intensity and its decay depend on the level of coverage and the surface stability [100, 112]. Using a larger applied current, more acidic media or longer wait time (*i.e.*, longer time of exposure to solution before perturbation) have been reported to magnify the superpolarization peak intensity [100, 112]. This

superpolarization behavior in the transient response contains valuable information about the mechanism of iron dissolution.



Figure 25. (*a*) Anodic excitation signals of $\pm 10 \text{ A/m}^2$ and (*b*) the corresponding response of iron in strong acid (environmental conditions: 0.97 bar pN₂, pH 3, 30°C)

6.6.1.1. Interpretation of Transient Response During Dissolution. According to Bockris' mechanism [20], there are two possible adsorbed components during anodic dissolution, H^+ and OH^- , which are the two main species actively involved in the dissolution mechanism. These species can further absorb on the surface of iron and produce the adsorbed intermediates, in this case, $FeOH_{ads}$ [20]. For simplification, the molecular structure of each species is replaced with a single circle represented in Figure 26.



Figure 26. Schematic representation of the species involved in the iron anodic dissolution (strong acid)

Before Superpolarization peak: t < t_{superpolarization peak}

Before polarizing the iron (at OCP), the net current is zero. The electrode is then anodically polarized by applying a constant steady current; thus, the excess electrons move out of the iron, which makes the electrode polarity positive. During a galvanostatic measurement, the current density is constant, which means that the overall reaction must occur at a constant rate, *i.e.*, the iron is oxidized to Fe^{2+} at a constant rate through the following three reaction steps (Bockris' mechanism):

$$Fe + H_2 0 \stackrel{(1)}{\leftrightarrow} Fe0H_{ads.} + H^+ + e^-$$
(71)

$$FeOH_{ads.} \xrightarrow{ras} FeOH^+ + e^-$$
 (72)

$$FeOH^+ + H^+ \stackrel{(3)}{\leftrightarrow} Fe^{2+} + H_2O \tag{73}$$

When the surface is stimulated at $t \le t_{superpolarization peak}$, the ion arrangement in the Helmholtz Double-Layer (HDL) changes, *i.e.*, the applied perturbation signal disturbs the ion configuration adjacent to the electrode in the HDL. In a very short time (less than 100

milliseconds), a particular contribution of that applied current is to produce a capacitive effect of the HDL (Figure 27) [1].



Figure 27. HDL plane formed adjacent to the anodically polarized iron

According to the following equation for charging a capacitor, there is a positively increasing voltage across the capacitor in a very short time, immediately after stimulation [1]:

$$V_{DL,Charging} \propto (1 - e^{-\frac{t}{R_E C}})$$
(74)

By disturbing the ion arrangement, the local concentration of ions changes, thus altering the chemical potential of species. Hence, according to Eq. 75, the electrical potential must change such that it conserves the overall electrochemical potential, which is the work done on the system [1]:

$$\overline{\mu}_i = \mu_i + z_i F \varphi \tag{75}$$

In a multi-step reaction, all steps will proceed as fast as the rate of the slowest step, which is the *rds*. When an external current is applied to the electrode/electrolyte interface, each

step has an individual contribution to that current [1]. The situation is similar to a case where we have a series of electrical resistances, each resistor represents an individual contribution (R_{I}, R_{II}, R_{III}), and the overall resistance of the system is equal to the sum of the resistances $(R_T = R_I + R_{II} + R_{III})$. Imagine that the resistivity for a single step (for example R_{II} is much larger than any other steps ($R_{II} >> R_I, R_{III}$), then all resistance terms become insignificant compared to R_{II} . Therefore, the overall resistance of the system will be approximately equal to R_{II} ($R_T \approx R_{II}$), which is the rds [1]. Immediately after applying a small current stimulation (slightly higher than $i_{corr.}$), the first step (Eq. 71) begins, which triggers the active dissolution of iron. The first step (Eq. 71) is fast compared to the next step (Eq. 72), which is the *rds*. The electrode polarity is more positive; thus, water molecules or OH⁻ tend to be more attracted and move toward the surface to participate in the first step (Figure 28 (a)). The interaction between OH⁻ and the Fe electrode through the first step, Eq. 71, produces the adsorbed $FeOH_{ads}$ intermediate. During this time, H^+ concentration also increases in the HDL because the first step (Eq. 71) is not the rds, the faster kinetics of this reaction allows it to consume OH⁻ to form excess FeOH_{ads} intermediate. This depletion of OH^- or accumulation of H^+ , *i.e.*, a considerable pile-up of positive charge (Figure 28 (b)), is expected in the HDL when $t < t_{superpolarization peak}$. The corresponding galvanostatic response of the iron electrode under a constant applied anodic current density of $\pm 10 \text{ A/m}^2$ is illustrated in Figure 28 (c).



Figure 28. Schematic representation of the ion arrangement during step (1), (a) OH^- is moving toward iron electrode through step (1), (b) H^+ pile-up in HDL, (c) galvanostatic response of anodically polarized iron at +10 A/m^2 (environmental conditions: 0.97 bar pN_2 , pH 3, 30°C, and 1wt% NaCl solution)

The first calculation on the data collected before the superpolarization peak is focused on the contribution of the HDL capacitance which is at its maximum due to the significant H^+ "pile-up" [112]. According to Eq. 76, before the *t*_{superpolarization peak, $d\eta/dt$ is positive and the applied current is positive, which makes the capacitance positive [1].}

$$i_{app} = C \left(\frac{d\eta}{dt} \right) \tag{76}$$

As the reaction proceeds, the adsorbed $FeOH_{ads}$ further oxidizes to $FeOH^+$ (Eq. (72)), thereby increasing the $FeOH^+$ concentration in the HDL. At the same time, electroneutrality needs to be maintained in the HDL. As the concentration of $FeOH^+$ is increasing, the H^+ has the driving force to diffuse away from the HDL to satisfy the solution electroneutrality [1, 112]. In addition to the electroneutrality in the HDL, two other driving forces for H^+ diffusion are:

a) electrostatic repulsion (polarity and *FeOH*⁺)

b) concentration gradient (due to the temporary H^+ accumulation)

Hence, H^+ concentration tends to reduce in HDL by its diffusion from the electrode surface to the solution (Figure 29 (a)). Consequently, the concentration of *FeOH*⁺ increases in the HDL, and the electrode surface is partially blocked with *FeOH*_{ads} intermediate (this is the second step, Eq. 72, which is the *rds*), as depicted in Figure 29 (b).



Figure 29. Schematic of the ion arrangement representing the rds step during iron anodic dissolution, (a) diffusion of H^+ from surface to the solution, (b) partial blockage of the surface with FeOH_{ads.}

Right After the Superpolarization Peak: $t = t_{superpolarization peak} + \varepsilon$

As the formation of adsorbed FeOH occurs in the first step (Eq. 71), the iron surface is partially blocked with $FeOH_{ads}$ intermediates. This reaction can be observed before the superpolarization peak as an inductive resistance to a change in current which causes a fast positive change in potential. However, at a time equal to $t_{superpolarization peak + \varepsilon}$ (right after the peak), the slope is negative, showing the relaxation of the inductive behavior to come to equilibrium at the new positive shift in the total current (Figure 30). For an inductor (Figure 30 (b)), the potential across the inductor varies in the opposite direction to resist the imposed current stimulation. This inductive behavior corresponds to the adsorption processes at the electrode surface, and it proves that the initiation of adsorption phenomena in the first step (Eq. 71) is due to the partial coverage of the surface with *FeOH_{ads}*. Therefore, the superpolarization spike happens between the first step (Eq. 71) and the *rds* (Eq. 72). The superpolarization is mainly attributed to the combined effect of H^+ pile-up and the surface blockage due to the adsorption of *FeOH_{ads}* intermediate [1, 112].



Figure 30. Galvanostatic response of anodically polarized iron at $+10 \text{ A/m}^2$. The insets show the variation of potential vs. time for (a) capacitance behavior and (b) inductive behavior

Transition time: $t > t_{superpolarization peak}$

As time goes on, when $t > t_{superpolarization peak}$, H^+ diffuses away from the HDL into the solution. OH^- gradually depletes in HDL. $FeOH^+$ tends to diffuse away from the HDL and oxidizes to Fe^{2+} , producing OH^- in the bulk solution according to the third step, Eq. 73, in the overall reaction sequence [20]. Therefore, the concentration gradient of OH^- provides the driving force for its diffusion from the bulk solution to the electrode surface to support the first reversible step (Figure 31).



Figure 31. Schematic representation of the ion movements adjacent to the iron surface during galvanostatic anodic dissolution ($t > t_{superpolarization peak}$)

During galvanostatic measurements, the electrons are continuously removed from the iron at a constant rate. H^+ diffuses away from HDL, and after a time, the concentration of H^+ becomes insufficient in HDL to further oxidize $FeOH^+$ to Fe^{2+} according to the third step, Eq. 73, or in other words, the reaction begins to come under the control of H^+ diffusion [1]. The HDL was disturbed due to the abrupt change in current and the system experienced a superpolarization peak, and, subsequently it is trying to return to a steady-state condition. Therefore, the charge configuration in the HDL changed to conserve the electrochemical energy of the system according to [1, 112]: $\Delta\mu^{FeOH} + \Delta\mu^{H+}_{HDL} + \Delta\mu^{e^-} = 0$ (77)

The potential relaxation, *i.e.*, the anodic decay which is shown in the galvanostatic response in Figure 32, implies that the system is trying to obtain its stable condition. During this anodic decay, the accumulation of OH^- in the HDL is maximum, and the build-up of OH^- in the HDL is dominant (Figure 32 (inset)). The diffusion is not happening as rapidly as the electron tunneling [1]; thus, the system needs a particular time to respond to that initial excitation. The speed at which the system responds to the perturbation is called the transition time, *i.e.*, the transition time from superpolarization to the diffusion-controlled plateau [1].



Figure 32. *Galvanostatic response of anodically polarized iron at* $+10 \text{ A/m}^2$. *The inset shows the schematic representation of ion arrangement during anodic decay*

Steady state: $t \rightarrow t_{\infty}$

Eventually, as time goes to infinity, the system reaches steady-state, when, on the solution side, the electroneutrality of the ions is satisfied, *i.e.*, Fe^{2+} and $FeOH^+$ ions have migrated to the bulk solution. The bulk solution will have a different pH than the pH at the metal surface. Furthermore, on the electrode side, the surface characteristics, *e.g.*, R_p , roughness, *etc.*, change in a way to accommodate the forced flow of electrons and charged species. (Figure 33).



Figure 33. *Galvanostatic response of anodically polarized iron at* $+10 \text{ A/m}^2$. *The insets show the schematic representation of ion arrangement at steady-state*

6.6.1.2. H^+ Concentration Profile and Superpolarization Effect. As discussed in the previous section, after the superpolarization, H^+ diffuses away from the HDL to the bulk solution. By solving Fick's 2nd law in parallel with a function that was given in the literature for the surface coverage with adsorbed $FeOH_{ads}$ [1, 112], and by having the

initial and the boundary conditions, the H^+ concentration profile during iron anodic dissolution was simulated using Python with Numpy library and Matplotlib (Figure 34).

$$d[H^{+}]/_{dt} = D_{H^{+}} \begin{pmatrix} d^{2}[H^{+}]/_{dx^{2}} \end{pmatrix}$$

$$[H^{+}] = [H^{+}]_{B} \qquad 0 < x, t = 0$$

$$[H^{+}] = [H^{+}]_{B} \qquad x = \infty, t > 0$$
(78)



Figure 34. The H^+ concentration profile during iron anodic dissolution in strong acid represents the superpolarization effect (H^+ accumulation).

As illustrated in Figure 34, both time and distance from the metal surface are represented by a change in color during iron anodic dissolution in strong acid. It can be observed that adjacent to the electrode surface, the temporary high concentration of H^+ , which represents the accumulation of H^+ due to the superpolarization effect that happened in the HDL during iron dissolution over a very short time (< 100 msec). The gradient changes in color with an increase in time (vertically up in the y-axis) showing the diffusion of H^+ ions away from the surface, but also indicating the surface pH is different from the bulk pH and seems to be reaching a steady-state after only 7 seconds.

There are a few unique characteristics of the anodic galvanostatic dissolution of iron. The superpolarization appearance is mainly due to the partial blockage of the surface with the adsorbed intermediates and the temporary build-up of H^+ for a very short time. Even small polarizations above OCP can activate dissolution and the corresponding adsorption and diffusion phenomena in anodic dissolution. To confirm these unique characteristics of anodic dissolution, for one experiment, instead of positive current stimulation, a negative current density (-10 A/m^2) was applied (Figure 35 (a)). The negative applied current means that the electrons are fed to the electrode, which is the same as cathodic polarization. Figure 35 (b) illustrates the corresponding anodic and cathodic galvanostatic responses. The superpolarization peak is only seen in the anodic transient. By contrast, for the cathodic transient, no superpolarization was obtained, which means that the adsorption and the diffusion of species are not the limiting factors in Tafel regions for cathodic reactions. Although a slight positive polarization above OCP can activate the adsorption and those transitions, there is no limitation for the reduction of ions in the cathodic transient. Thus, the ions can be reduced through a simple charge transfer step without any limitation. Therefore, no superpolarization is expected in the case of cathodic transients in strong acids.



Figure 35. (a) Anodic and cathodic perturbation signals of $\pm 10 \text{ A/m}^2$ and the corresponding (b) anodic and cathodic responses of iron in strong acid. The inset shows the anodic and cathodic polarization curves of iron in strong acids (environmental conditions: $pN_2 = 0.97$ bar, pH 3, 30°C)

6.6.1.3. Effect of CO₂ on Galvanostatic Dissolution. Figure 36 shows the polarization curve of iron in weak acid 1 wt.% NaCl solution sparged with CO₂ at 30°C $(pCO_2 = 0.97 \text{ bar})$.



Figure 36. Polarization curve of iron in weak acid, 1 wt. % NaCl solution, $pCO_2 = 0.97$ bar, pH 3, 30°C, scan rate = 0.125 mV/s

Similar to the strong acid, the current density of $\pm 10 \text{ A/m}^2$ in the active dissolution range is selected as the excitation signal. Compared to the strong acid (OCP = $-396 \text{ mV}_{N2} vs.$ standard hydrogen electrode (SHE)), in weak acid, the OCP is slightly more negative (OCP = $-398 \text{ mV}_{CO2} vs.$ SHE). Additionally, the corrosion rate in weak acid was 1.99 mm/y, slightly more than observed in strong acid (1.95 mm/y) at the same bulk solution pH. Figure 37 illustrates the anodic excitation current signal and the corresponding potential-time response of the iron in weak acid (pCO₂ = 0.97 bar, pH 3, 30° C). The superpolarization behavior is again observed in the presence of CO₂ similar to the observations in a strong acid solution at the same pH.



Figure 37. (*a*) Anodic excitation signals of $\pm 10 \text{ A/m}^2$ and (*b*) the corresponding response of iron in weak acid (environmental conditions: $pCO_2 = 0.97$ bar, pH 3, $30^{\circ}C$)

Figure 38 compares the galvanostatic curves of iron in strong and weak acid 1 wt.% NaCl solution (pH 3, 30°C).



Figure 38. Comparison between the galvanostatic response of iron in strong acid and weak acid (pH 3, 30°C)

The superpolarization peak height with respect to the OCP was about $\eta_{max,CO2} =$ 53 mV in weak acid, which was smaller than in strong acid ($\eta_{max,N2} = 63$ mV). As

discussed previously, according to Bockris and Drazic's interpretation [100, 112], the superpolarization behavior is attributed to the partial blockage of the surface due to the adsorbed species. Hence, the surface coverage with adsorbed intermediates in the presence of CO₂ could be less than that in strong acid, *i.e.*, during anodic dissolution, CO₂ could decrease the fraction of the surface covered with adsorbed intermediates [100, 112]. A closer look at the data points collected in the first milliseconds shows that the time to reach the superpolarization peak value in strong acid was about $t_{max} = 60$ msec. However, in weak acids, the time to reach the superpolarization peak value superpolarization peak value was slightly longer, about $t_{max} = 80$ msec (Figure 39).



Figure 39. Comparison between galvanostatic curves and t_{max} values during iron dissolution reaction in strong and weak acid

As discussed previously, at t < 100 ms after the galvanostatic change, the ion species must shift to maintain equilibrium conditions adjacent to the surface in the HDL due to the double-layer charging and the activation of the adsorption processes. This phenomenon creates a temporary capacitive behavior at the surface. Eq. 76 was used to determine the overall capacitance associated with this charging effect in strong and weak acid environments. Table 11 lists the main parameters obtained from galvanostatic analysis in strong and weak acids.

Table 11. The extracted parameters obtained from galvanostatic data during iron

 dissolution in strong and weak acids (pH 3, 30°C)

Environment	Strong acid-0.97 bar N ₂	Weak acid-0.97 bar CO ₂
$\eta_{max} (\mathrm{mV})$	63	53
t_{max} (msec)	60	80
$E_{st.st}$ mV vs. SHE	-352	-358
$C (\mu F/cm^2)$	952	1509
<i>Charge,</i> Q (C/cm ²)	6×10 ⁻⁵	8×10 ⁻⁵

The magnitude of the capacitance in the presence of a weak acid is larger than that in the presence of a strong acid. An estimation of the charge accumulation showed that in the absence and presence of CO₂, the charge accumulation is about 6×10^{-5} C/cm² and 8×10^{-5} C/cm², respectively. Hence, the DL charging effect in the presence of aqueous CO₂ is more intense than with a strong acid, *i.e.*, the charge accumulation during iron dissolution at a very short time is more significant when having CO₂ in the electrolyte. The magnitude of the capacitance obtained here (952 µF/cm²) is comparable with what Bockris, *et al.* [112] reported for the maximum capacitance during the iron dissolution reaction in strong acid. They reported the maximum capacitance magnitude should be in the order of $10^3 \,\mu\text{F/cm}^2$ in strong acid [112]. Thus, it could be that CO₂ increases the charge accumulation during the early step of iron dissolution (as shown in Table 11). Looking at the data points after the superpolarization, where the main phenomenon is the adsorption of intermediates, the decay after the spike is more rapid in strong acids (Figure 40). A possible explanation for this is that CO₂ suppresses the adsorption of intermediates during iron dissolution. Thus, the decay slope in the presence of CO₂ is smaller than that in strong acid.



Figure 40. *Comparison between galvanostatic curves and the decay slope after the superpolarization during iron dissolution reaction in strong and weak acid*

This finding is in agreement with what was reported in the literature, where they claimed that CO₂ decreases the Tafel slope in the active anodic dissolution regime during polarization measurements [90]. This is also consistent with Linter and Burstein's findings, which reported that CO₂ might undermine the adsorbed intermediate during iron anodic dissolution [44]. This finding supports the hypotheses that were presented in Section 6.4, where it was speculated that CO₂ destabilizes the adsorbed complexes. In summary, based on what has been discussed above, the main influences of CO₂ presence on iron dissolution are:

1) It increases the temporary charge accumulation in a very short time, immediately after applying the excitation signal (< 100 ms).

2) It reduces the adsorption of intermediates and reduces the partial blockage due to the adsorption. This validates one of the hypotheses suggested earlier in Section 6.4 about the role of CO_2 on changing the kinetics of the elementary steps.

6.6.2. Potentiostatic Dissolution of Iron

The potentiostatic technique as the second transient method has been used to conduct a semi-quantitative analysis in terms of the impact of CO_2 on the kinetics of the elementary steps in the active dissolution range. Keddam's multipath mechanism [37], and his style of interpretation and experiments have been followed to accomplish a semiquantitative study of the kinetics in the active dissolution domain.

6.6.2.1. Kinetics of Reaction in Active Domain. The kinetics of anodic dissolution in strong acid (0.5 M Na₂SO₄ solution at pH 5) in the active range is quantitatively described according to the same mechanistic framework that was detailed

by Keddam, *et al.* [37]. The test conditions were equivalent to those used by Keddam, *et al.* [37]. The kinetic outcomes will be then compared with those reported in Keddam's work [37].

The kinetic rate constants of the elementary steps in the active dissolution range are estimated in this section according to the methodology described in Section 6.5.2. Figure 41 (a) shows the anodic potentiodynamic sweeps of the RCE iron electrode in 0.5 M Na₂SO₄ solution at pH 5 at 25 °C (2000 rpm). The red box indicates the range of potentials that have been used for transient measurements. The potentiostatic response of iron under the same experimental conditions at different overpotentials from +60 to +110 mV vs. OCP is displayed in Figure 41 (b). The potentiodynamic sweep is the average of four different sets of experiments with an average OCP value of -723 ± 6 mV vs. Ag/AgCl. The potentiostatic data presented here are the averaged responses of three repeatable measurements.



Figure 41. (*a*) Anodic sweep and (*b*) potentiostatic measurements at different overpotentials for RCE iron electrode in 0.5 M Na₂SO₄ solution at pH 5, 25 °C, 2000 rpm

Zooming in on Figure 41 (b) for the time shorter than 0.02 millisecond (before the superpolarization peak), one can see the initial increase of the current density over a very short period (Figure 42 (a)). The data points acquired at $t = 6.7 \mu s$ were used to determine k_1 at a fixed potential. For a set of different potentials, given that k_1 was defined to be an exponential function of potential, one can obtain B_1 and $k_{0,1}$ by plotting $k_1 vs$. potential in a semi-log graph as depicted in Figure 42 (b).



Figure 42. (a) Anodic potentiostatic measurements at different overpotentials in strong acid and (b) plot of $ln(k_1)$ vs. applied potentials for RCE iron electrode in 0.5 M Na₂SO₄ solution sparged with 0.97 bar N₂ at pH 5, 25 °C, 2000 rpm

Hence, under these experimental conditions, the average values of B_1 and $k_{0,1}$ associated with the first elementary step are estimated to be about $35.8 \pm 2 \text{ V}^{-1}$ and $10^{1.48\pm0.04} \text{ mol/cm}^2$.s, respectively. $k_{0,1}$ is obtained to be about $10^{1.48\pm0.04} \text{ mol/cm}^2$.s when E_{ref} is set at 0 V *vs*. Ag/AgCl reference electrode. To compare this value with the corresponding parameter in the work done by Keddam, *et al.* [37], one needs to bring this

value with respect to the SSE reference electrode (Hg, Hg₂SO₄ saturated K₂SO₄). Keddam, *et al.* [37] used SSE as the reference electrode. $k_{0,1} = 10^{1.48\pm0.04}$ mol/cm².s is k_1 at $E_{ref} = 0$ V vs. Ag/AgCl and is equal to $10^{8.6\pm0.72}$ when $E_{ref} = 0$ V vs. SSE reference electrode. Table 12 compares the computed B_1 and $k_{0,1}$ with the corresponding values reported by Keddam, *et al.* [37], who calculated k_0 values at $E_{ref} = 0$ V vs. SSE. The environmental test conditions in this work are similar to those in Keddam's study [37], except that they added 4 mM CH₃COONa buffer to minimize the pH fluctuation during EIS measurement. It is suggested that this buffering agent might cause a slight difference between these results and those reported by Keddam, *et al.* [37].

Table 12. *Kinetic rate constants,* $k_{0,1}$ *and* B_1 *, obtained in* 0.5 *M* Na₂SO₄ *solution sparged with* 0.97 *bar* N₂ *at pH* 5*,* 25 °C

Parameter-strong acid	This study	Keddam, <i>et al.</i> [37]
$B_1(V^{-1})$	35.8 ±2	38.4
b ₁ (mV)	64.2 ±4	59.9
$k_{0,1}$ (mol/cm ² .s)- $E_{ref.}$ at 0 V vs.	$10^{1.48\pm0.04}$	-
Ag/AgCl		
$k_{0,1}$ (mol/cm ² .s)- $E_{ref.}$ at 0 V vs. SSE	$10^{8.6\pm0.72}$	10 ^{10.6}

The magnitude of B_1 and $k_{0,1}$ parameters are close to the ones found in the previously published study [37] as shown in Table 12.

To calculate the kinetic rate constants for the second elementary step, the first derivative of the current response with respect to time was determined at different overpotentials. Figure 43 (a) represents the variation of the natural log of di/dt vs. time

for the anodic current responses recorded at different overpotentials from +60 to +110 mV vs. OCP in 0.5 M Na₂SO₄ solution at pH 5, 25 °C. The equation of the regression line at a fixed potential was used to determine k_2 . Similarly, k_2 has an exponential dependence on potential, thus B_2 and $k_{0,2}$ can be estimated from the equation for the regression line of $ln(k_2)$ vs. *E* plot (Figure 43 (b)).



Figure 43. (a) The first derivative of anodic current vs. time at different overpotentials in strong acid and (b) $ln(k_2)$ vs. applied potentials for RCE iron electrode in 0.5 M Na₂SO₄ solution sparged with 0.97 bar N₂ at pH 5, 25 °C, 2000 rpm

 B_2 and $k_{0,2}$ are estimated to be about 9.5±2 V⁻¹ and 10^{0.79±0.5} mol/cm².s at $E_{ref.} = 0$ vs. Ag/AgCl under these experimental conditions. Table 13 compares the kinetic rate constants of the second elementary step with the corresponding values reported in previous studies [37].

Table 13. *Kinetic rate constants,* $k_{0,2}$ *and* B_2 *, obtained in* 0.5 *M Na*₂*SO*₄ *solution sparged*

Parameter-strong acid	This study	Keddam, <i>et al</i> . [37]
$B_2 (\mathrm{V}^{-1})$	9.5 ±2	7
$b_2 (\mathrm{mV})$	242 ±25	328.5
$k_{0,2}$ (mol/cm ² .s)- E _{ref.} at 0 V vs.	$10^{0.79\pm0.5}$	-
Ag/AgCl		
$k_{0,2}$ (mol/cm ² .s)- E _{ref.} at 0 V vs. SSE	$10^{2.8\pm0.8}$	10 ^{-3.09}

with 0.97 bar N_2 at pH 5, 25 °C

Although the B_2 value is close to what was estimated by Keddam, *et al.*, [37] the $k_{0,2}$ values are different from what was reported. It is important to bear in mind that the kinetic rate constants obtained previously [37] were modified manually after each calculation up to a point where a good agreement with their experimental results was attained. In that sense, they asserted that different sets of kinetic rate constants are also possible for a unique environmental test condition [37].

6.6.2.2. Source of Error in Estimation of the Kinetic Rate Constants. All

electrochemical measurements including steady-state potentiodynamic and potentiostatic measurements were repeated at least three times to confirm reproducibility. Standard deviations, as shown by error bars, are used to indicate the estimated error or uncertainty and to provide a sense of the precision of each measurement. To compare the determined kinetic rate constants with the corresponding values reported in the literature, the reference potential of 0 V *vs.* Ag/AgCl was selected. Additionally, to compare the calculated kinetic values with those reported by Keddam, *et al.*, [37] the same reference potential of E = 0 V *vs.* SSE (Hg, Hg₂SO₄ saturated K₂SO₄) reference electrode (RE) is

also provided. The kinetic rate constants, $k_{0,i}$, were determined at the reference potential of 0 V vs. Ag/AgCl or SSE.

Depending on the RE with respect to which the kinetic rate constants are computed, a different set of $k_{0,i}$ values might be obtained. To convert the electrode scale from Ag/AgCl to SSE, one needs to subtract 0.441 V from the potential vs. Ag/AgCl since $E_{SSE} = E_{Ag/AgCl} - 0.441$ V. As shown in Figure 44, choosing a different RE for reporting kinetic rate constants will alter the $k_{0,i}$ but does not affect the computed values of B_i (Eq. 79). This is due to the change of only the intercept of the regression line when using a different RE (the slope stays the same) as in Figure 44.

$$k_{i} = (k_{i,0,Ag/AgCl}) e^{(B_{i}E_{Ag/AgCl})} = (k_{i,0,Ag/AgCl}) e^{(B_{i}(E_{SSE} + 0.441))} = (k_{i,0,SSE}) e^{(B_{i}E_{SSE})}$$
(79)
where

$$k_{i,0,SSE} = (k_{i,0,Ag/AgCl}) e^{(0.441B_i)}$$
(80)

Hence, depending on the reference electrode, a different value for the kinetic rate constants, $k_{0,i}$, might be reported.



Figure 44. Calculation of B_i and $k_{0,i}$ when using a different reference electrode will alter the reported value for $k_{0,i}$. Potentials reported vs. (a) Ag/AgCl and (b) SSE reference electrode

The reference potential of 0 V *vs.* RE that is set for computing $k_{0,i}$ can lead to a certain level of uncertainty in reported values. As shown in Figure 45, a slight alteration in the regression line (or the slope B_i) may cause an error in $k_{0,i}$ in both potentiodynamic and transient measurements. This uncertainty in $k_{0,i}$ values needs to be reported accordingly.



Figure 45. Source of error in determining $k_{0,i}$ for the data obtained from (a) potentiodynamic and (b) transient measurements

6.6.2.3. Effect of CO₂. Thus far, there is no approved explanation of how dissolved CO₂ may influence the mechanism of anodic dissolution of iron, however, there are several theories [44,46, 120]. Literature has emerged that offers contradictory findings about the influence of CO₂ on the mechanism of the anodic dissolution of iron. Almost all studies about unraveling the effect of CO₂ on the mechanism of iron dissolution are based on speculations of possible reaction pathways and theoretical predictions. The most important key in the feasibility of a pathway depends on the number of experimental observations that can be fully explained.

When trying to determine the CO₂ effect, the first reasonable assumption to make is that formation of a monovalent ligand ($Fe(I)_{ads,CO2}$) is occurring (Eq. 81). Next, this monovalent adsorbed ligand is converted to a divalent iron complex ($Fe(II)_{sol,CO2}$) through a dissolution path (Eq. 82). Eqs. (81 & 82) basically refer to an analogous pathway described earlier by Eqs. (71 & 72), respectively, for a strong acid environment.

$$Fe + OH^{-} \stackrel{k_1}{\to} Fe(I)_{ads,CO2} + e^{-}$$
(81)

$$Fe(I)_{ads,CO2} \xrightarrow{k_2} Fe(II)_{sol,CO2} + e^-$$
(82)

In the present study, it is assumed that CO₂ does not affect the intermediates/pathways and only influences the kinetic rate constants. The EIS studies done by Moradighadi *et al.* [42], have supported such an assumption, where introducing CO₂ did not affect the number of time constant or EIS characteristic loops [42]. By following the same approach outlined in Section 6.5.2, the kinetic rate constants for the first two elementary steps (Eqs. (81 & 82)) were estimated in 0.5 M Na₂SO₄ solution sparged with 0.97 bar CO₂ at pH 5 and 25 °C. The average OCP value in weak acid was -718 ± 3 mV *vs.* Ag/AgCl. Figure 46 and Figure 47 illustrate the methodology to approximate the kinetic rate constants for the first and the second elementary steps, respectively, in the presence of CO₂.



Figure 46. (a) Anodic potentiostatic measurements at different overpotentials in weak acid and (b) plot of $ln(k_1)$ vs. applied potentials for RCE iron electrode in 0.5 M Na₂SO₄ solution sparged with 0.97 bar CO₂ at pH 5, 25 °C, 2000 rpm



Figure 47. (a) The first derivative of anodic current vs. time at different overpotentials in weak acid and (b) $ln(k_2)$ vs. applied potentials for RCE iron electrode in 0.5 M Na₂SO₄ solution sparged with 0.97 bar CO₂ at pH 5, 25 °C, 2000 rpm

Table 14 represents a comparison between the kinetic rate constants for iron dissolution in strong and weak acids at pH 5 (25 °C). k_0 values are reported at $E_{ref} = 0$ V vs. Ag/AgCl. B_i is proportional to the charge transfer coefficient, *i.e.*, a greater B_i means faster charge transfer kinetics for the elementary step (*i*). On the other hand, b_i is related to the polarization required to initiate the elementary step (*i*), *i.e.*, a greater polarization is needed for the stimulation of a step that has a larger b_i value. $k_{0,i}$ is the reaction rate for the elementary step (*i*) at the reference potential of 0 V vs. Ag/AgCl.

Parameter	Strong acid	Weak acid
$B_{I}(\mathrm{V}^{-1})$	35.8 ±2	22.6 ±3
b_l (mV)	64.2 ±4	101 ±8
k0,1	$10^{1.48\pm0.04}$	$10^{-1.77\pm0.18}$
$B_2(\mathrm{V}^{-1})$	9.5 ±2	13.7 ±2
$b_2(\mathrm{mV})$	242 ±25	167 ±25
$k_{0,2}$	$10^{0.79\pm0.5}$	$10^{1.1 \pm 0.6}$

 Table 14. Comparison of kinetic rate constants obtained in strong and weak acid for iron

dissolution reaction in 0.5 M Na₂SO₄ solution at pH 5, 25 °C, $E_{ref} = 0$ V vs. Ag/AgCl

Comparing the kinetic rate constants of the first and the second steps in both strong and weak acid media, one finds that $B_2 < B_1$. The $k_{0,2}$ value in the presence of a weak acid is greater than the $k_{0,1}$, which is the opposite of that in the strong acid. Table 15 represents the maximum, minimum, average, and % error for only $k_{0,i}$ values in both strong and weak acids. Although there is an obvious decrease in $k_{0,1}$ from a strong acid to a weak acid, there is too much error in $k_{0,2}$ values to conclude only by comparing $k_{0,i}$ values. It is important to also take into account the other kinetic rate constants (b_i and B_i) as well to discover the influence of CO₂.

Table 15. Summary of $k_{0,i}$ values in strong and weak acids, for iron dissolution reaction

in 0.5 M Na₂SO₄ solution at pH 5, 25 °C

	Strong acid		Weak acid					
	min	avg	max	error%	min	avg	max	error%
k 0,1	27.5	30.2	33.1	9.6%	0.011	0.017	0.026	51%
k0,2	1.95	6.17	19.5	216%	3.16	12.6	50.12	298%

As seen in Table 14, b_2 for weak acids is smaller than for strong acids.

Furthermore, B_2 for a weak acid is greater than in strong acid implying that the charge transfer kinetics for the second elementary step become faster as CO₂ is sparged into the solution. Comparing B_i and $k_{0,i}$ together from a weak to strong acid, it can be seen that CO₂ limited the kinetics of the 1st elementary step while it accelerated the rate of the 2nd step. Step 1 is already fast and since the 2nd step is the *rds* step, CO₂ more likely accelerates the overall kinetics of the anodic reaction by boosting the rate of the *rds*. Figure 48 illustrates the comparison between the anodic sweeps in strong and weak acid media.



Figure 48. Comparison of the anodic sweeps in strong and weak acid media: 0.5 M Na_2SO_4 solution sparged with 0.97 bar gas (0.97 bar N_2 or 0.97 bar CO_2) at pH 5, 25 °C, 2000 rpm, scan rate 0.5 mV.s⁻¹

As shown in Figure 48, the current density in the active dissolution range is not noticeably affected by CO₂, whereas the enhancement of the anodic current density in the

potential range of transition and pre-passivation is significant. The observation of the active domain not being affected by CO₂ was also reported elsewhere by Linter, et al. [44] who suggested that dissolved CO₂ destabilizes the adsorbed intermediate (they called it the oxidation film) without affecting the active dissolution region. They reported that CO₂ considerably shifts the anodic sweep to higher current densities in the potential range of transition and above without affecting the active dissolution regime [44]. As seen in Figure 48, no passivation was obtained in CO₂-sparged electrolyte which implies that CO₂ more likely promotes the breakdown of an inhibiting type of intermediate that was responsible for the appearance of the passivation behavior in strong acid. Although the range of potential scans in both cases was similar (0 to +600 mV vs. OCP), the potential range appears to be different after the *iR-drop* correction as the magnitude of the current at a fixed potential was not the same in strong and weak acids. The initial and final concentration of dissolved Fe^{2+} was measured at the end of the anodic sweeps using spectrophotometric analysis. The results, as shown in Table 16, indicate that the concentration of dissolved Fe^{2+} in the weak acid is almost three times greater than in the strong acid. This confirms that CO₂ is enhancing the rate of the overall anodic reaction.

Table 16. Concentration of dissolved Fe^{2+} after anodic sweeps in strong and in weak acid media: 0.5 M Na₂SO₄ solution at pH 5, 25 °C, 2000 rpm

Environment	0.97 bar N_2	0.97 bar CO ₂		
ppm Fe ²⁺	3.71	10.69		

As discussed above, CO₂ decelerates the 1st elementary step related to pile up of $Fe(I)_{ads}$ at the surface, while it speeds up the rate-determining step which is the dissolution of $Fe(I)_{ads}$ to $Fe(II)_{sol}$. This meant the overall net reaction increased in the presence of CO₂ as confirmed by a higher concentration of dissolved Fe^{2+} . This observation validates one of the hypotheses made in Section 6.4 about the enhancement of the reaction kinetics in the presence of CO₂. The 1st elementary step is already fast, therefore as CO₂ accelerates the 2nd *rds* step, the kinetics of the overall reaction increase. Since the 1st elementary step forms excess $Fe(I)_{ads,CO2}$ a decrease in the rate of this step has much less influence on the overall reaction rate than an acceleration of the *rds* step. The large loss of Fe^{2+} in presence of carbonate-bicarbonate buffers was also reported by Castro, *et al.* [56]. They claimed that the acceleration of dissolution in such weak acid media was due to the formation of a soluble Fe(II)-HCO₃⁻ mixture [56].

The present chapter was deliberately designed on the assumption of having only the first two elementary steps (*i.e.*, active dissolution path) according to non-catalytic theory as the most fundamental dissolution route reported in the literature. The adsorbed intermediate was assumed to be a single non-catalytic ligand ($Fe(I)_{ad}$.) in accordance with the non-catalytic mechanism. However, based on the more inclusive multi-path mechanism proposed by Keddam, *et al.* [37], the catalytic intermediate also plays a critical role during the anodic dissolution of iron. By incorporating this catalytic ligand in addition to $Fe(I)_{ads.}$ in the current theory and having a more thorough viewpoint, one can develop a more precise explanation of the dissolution behavior when it comes to the effect of CO₂ or other environmental factors. This mission, *i.e.*, developing a more
advanced theory by assuming two adsorbed intermediates instead of one (*i.e.*, catalytic $Fe(I)_{ads.}^*$ in addition to non-catalytic $Fe(I)_{ads.}$), will be the objective of Chapter 7 and Chapter 8.

6.7. Summary

The influence of CO_2 on the constant current (galvanostatic data) and constant potential (potentiostatic data) dissolution of iron was presented in this chapter. The qualitative and semi-quantitative data were used to validate/invalidate the hypotheses about the effect of CO_2 presence on iron dissolution. The following conclusions are drawn:

> The qualitative analysis based on galvanostatic data indicated that:

- Superpolarization in anodic dissolution is mainly due to the temporary accumulation of H⁺ and partial surface blockage with an adsorbed ligand (most likely *FeOH_{ads}*.).
- In the potential relaxation regime, the anodic dissolution is under the combined control of H^+ diffusion and surface coverage with adsorbed $FeOH_{ads.}$
- CO₂ can accelerate charge accumulation during the early stage of dissolution.
- CO₂ hinders the adsorption of intermediates by destabilizing adsorbed ligands.
- > The semi-quantitative analysis based on potentiostatic data indicated that:
 - A simple approach was introduced for computing the kinetic rate constants for the first two elementary steps in the active dissolution range.

- Although CO₂ decelerated the first elementary step, it promoted the overall kinetics of the anodic dissolution by promoting the rate of the 2nd elementary step (*i.e.*, *rds* step).
- Dissolved CO₂ did not notably affect the current density in the active dissolution range, while its effect in the transition and pre-passivation ranges of the sweeps was marked.
- The incorporation of both catalytic and non-catalytic intermediates in basic theory is essential to deliver a more credible explanation for observations such as multiple transformations in anodic sweeps. This will be accomplished in Chapters Chapter 7 and Chapter 8.

Chapter 7: Quantitative Determination of the Reaction Kinetics in CO₂ Environments: An Approach for Modeling the Anodic Potentiodynamic Sweeps 7.1. Introduction

Although extensive research has been carried out on modeling the cathodic potentiodynamic sweep during corrosion of iron/steel, previous studies have not been able to lay out a well-defined approach to mechanistically describe the kinetics and model steady-state anodic dissolution at different experimental conditions. In Chapter 5, thirty-eight different pathways were investigated for the mechanism of iron dissolution in strong acid, and it was found that the experimental observations in the active range of dissolution were well explainable by relying on Bockris' non-catalytic theory and assuming only a single adsorbed intermediate [20, 87]. In Chapter 6, it was found that not all experimental observations are interpretable based on a theory assuming only a single adsorbed entity (*i.e.*, $Fe(I)_{ads.}$). It is hypothesized in this chapter that one should incorporate a second catalytic adsorbed intermediate to replicate the observations over a wide range of conditions. This will be consistent with Keddam's conceptualization [37], which combined both non-catalytic and catalytic ideas into a single scheme (Figure 6) to model both potentiodynamic sweeps and impedance data over the entire range of potentials, even up to the passivation range.

In Chapter 6, a method based on potentiostatic measurements was introduced to determine the kinetic rate constants of the elementary steps involved in the active dissolution path (k_1 and k_2). In this chapter, steady-state and transient measurements will be concurrently used to determine the kinetic rate constants of the elementary steps

involved in not only the active dissolution path, but also in the transition one. Then the effect of CO_2 and pH on each elementary step will be explored. The main challenge is exploring a systematic approach using transient analysis based on a simplified theory to calculate the kinetic rate constants. This is the first work reporting such a methodical framework for describing and acquiring the kinetics based on an updated mechanistic scheme for iron anodic dissolution.

7.2. Research Gaps

There are a few questions that have not been answered by any of the existing works:

- Although it seems comprehensive, Keddam's multipath scheme (Figure 6) [37] is very complex. Seven elementary steps with 20 kinetic rate constants simply make the theory too complicated to be applied in models. Twenty parameters in Keddam's multipath mechanism make it almost impossible to determine independent values for each of them according to a methodical approach. The scheme developed by Keddam, *et al.* [37] needs to be abridged to have less freedom enabling the introduction of a systematic method for estimating the constants and subsequently modeling the anodic sweeps.
- Keddam, *et al.* [37] used numerical fitting to get values for a large number of constants for *k_i* to model the entire range of potentiodynamic data as well as EIS data, without much interpretation. It is more helpful to extract a smaller number of physically meaningful characteristic constants guiding us to understanding the effects being modeled. Such an investigation is missed in the literature.

• No previous study has introduced a systematic method to estimate the kinetic rate constants of elementary steps using a simplified theory.

7.3. Objectives

In this chapter, the multipath mechanism proposed by Keddam, *et al.* [37] is revisited. A simplified version of this scheme based on the same premises and the underlying physics is introduced. Then using the simplified mechanistic scheme presented herein, a procedure based on transient analysis is established, that enables the estimation of a series of kinetic rate constants that can be used for subsequent modeling of the anodic sweeps. The findings of the present research enhance the ability to explain how different environmental factors such as CO₂ presence and pH mechanistically affect the kinetics of the elementary steps during iron anodic dissolution.

7.4. Experimental Method

A 2-liter glass cell with an RCE as a working electrode was used. A ring-shaped platinum-coated titanium mesh counter electrode was used for completing the circuit to allow the charge to flow, and an Ag/AgCl reference electrode was used with respect to which all potentials were measured. The ring-shaped Pt counter electrode was used to provide a more symmetric current distribution around the RCE. An overview of the experimental setup and test matrix is shown in Figure 49.

Condenser	Parameter	Condition
Ag/AgCl RE		4
Rotor pH meter	pH (± 0.02)	5
		6
	Environment	Strong acid ⁴ : 0.97 bar N ₂
		Weak acid ⁵ : 0.97 bar CO ₂
		2.9 wt.% (~0.55 M) NaCl
	Electrolyte	$(R_s \sim 0.78 {\pm} 0.08 \ \Omega \ for \ all$
RCE WE Pt coated CE		measurements)
	Temperature (±0.0.5) °C	25 °C
	Test set-up	2L glass cell
	Motor rotation speed	2000
	Sample	RCE- Pure iron

Figure 49. Overview of the RCE experimental setup and test matrix

All experiments and the test procedure were accomplished according to the explanations in Chapter 4. Potentiodynamic and potentiostatic measurements with a high sampling rate (~3 microseconds per data point) were conducted using a Gamry potentiostat Reference 600. All potentiodynamic sweeps presented in this work were corrected for the effect of solution resistance (*iR-drop*). It was important to enhance the speed setting of the potentiostat/galvanostat instrument to be able to capture the data points with a very high sampling rate (~ a few microseconds). Each test was repeated at least four times to reduce the statistical uncertainty. Uncertainty for all measurements is reported in this study. All RCE specimens were polished up to 1200-grit, rinsed with DI water and isopropanol alcohol, and dried with nitrogen gas before every experiment. High-purity N₂ or CO₂ gas was sparged continuously through the test solution to de-oxygenate the electrolyte during all measurements. Diluted NaOH and HCl were used to

adjust the pH. It was important to make sure that the solution resistance for all measurements was the same. Before each measurement, EIS was recorded to assure that the solution resistance was consistent for all measurements and always within the range of $0.78 \pm 0.08 \Omega$.

7.5. Updated Mechanism Proposed for Modeling

Twenty kinetic rate constants are included in the scheme introduced by Keddam, et al. [37] (Figure 6). They used the numbers for kinetic rate constants that best fit both impedance and potentiodynamic data over the entire potential range [37]. As already noted, twenty constants give an extremely high level of freedom to the model and that is basically what they needed, a flexible enough model enabling them to capture all kinds of complex datasets over the entire range of experimental observations. However, there could well be another set of twenty numbers that could fit the data just as well if not better, and it is difficult to decide which ones are correct without some additional guidance by the physicality of the process. This is the objective of the present work to create a simpler model with a smaller number of adjustable constants that will be rooted in the physicochemical nature of the process. This should be feasible, since the region of our interest in corrosion studies is from OCP up to the transition region (or a bit above as shown as the shaded region in Figure 50), which is much narrower than what Keddam, *et al.* [37] used.



Figure 50. The range of interest for the current corrosion studies

Oftentimes, the anodic branch shows a nonlinear behavior due to the rapid dissolution and formation of the catalytic intermediates that speed up the dissolution rate [87, 121]. The active domain, which is the range of interest for corrosion modeling, is sometimes influenced by the transition region, more so under certain environmental conditions. Hence, it is important to also have the model capture the transition domain as well as the nonlinearity of the anodic branch. However, it seems unnecessary to model the anodic sweep far beyond the transition range (in the more positive direction). Within this context, the complex scheme shown in Figure 6 can be condensed to a simpler and more applicable version for several reasons:

1) Corrosion is occurring in the potential regions significantly more negative than where passivation occurs, and it will be assumed that there is no passive film formation at the electrode surface. Therefore, there is no need to cover the passivation potential region with the model and include this pathway (Path 3) into the model.

2) The objective of the present study is not to model the entire potential range (up to passivation). Only the active and transition regions, which are the domains near the corrosion potential, need to be taken into account for modeling the corrosion rate. So, it seems unessential to model either the entire potential range of pre-passivation or the passivation domain. As mentioned previously, the Transition Path and Pre-passivation *Path* (paths 2 and 3 in the mechanism shown in Figure 6) are very similar in nature, they are both catalytic paths, except that the numbers for the valence of the catalytic iron intermediates are different. In path 2, a chemisorbed monovalent iron is assumed, while path 3 expects the formation of a bivalent iron instead. It is proposed in this study that, by choosing only one of these two paths, one should be able to model the anodic potentiodynamic sweeps up to the transition domain and slightly above that. 3) Keddam, et al. [37] used a complicated scheme and arbitrary numbers for k_i values to fit the polarization curves as well as EIS data. This is not the objective in this research, as an attempt is made to develop an approach to estimate a smaller number of physically meaningful kinetic rate constants. There are twenty parameters in Keddam's multipath mechanism which makes it almost impossible to determine independent values for each of them according to a methodical approach. Additionally, according to the EIS studies done by Moradighadi et al. [42], this multipath scheme becomes even more complex in concentrated chloride solutions. Moradighadi et al. [42] reported that a fourth chloridebased adsorbed intermediate forms at the electrode surface in the concentrated chloridebased solutions. They claimed that a fourth dissolution path could be coupled with this three-pathway mechanism proceeding the dissolution of iron [42]. Thus, there is a need to shorten the complex mechanistic scheme to one with a lesser degree of freedom enabling the introduction of a systematic method for estimating the parameters and subsequently modeling the anodic sweeps.

A clearly defined mechanistic scheme with less complexity is needed to accurately describe and model the kinetics. A new two-path scheme, shown in Figure 51, is proposed in this study. In this scheme, the non-catalytic path is in parallel with only one catalytic path. Indeed, this idea combines two fundamental theories into a single one without any further complications. In this work, it has been hypothesized that using this scheme one can reasonably model the anodic potentiodynamic data and capture the nonlinearity of the anodic sweep over the potential ranges slightly above the transition region as shown in Figure 50. This simplified scheme is more pragmatic since it provides a platform based on which one can more easily model the steady-state kinetics. In addition, this platform enhances the capability of describing the influence of different environmental/metallurgical factors on anodic dissolution.



Figure 51. The theoretical scheme introduced in this study

An important point to mention is that two electrons are transferred during elementary step 4 (Figure 51). Transfer of two electrons during a single elementary step also took place in both Heusler's (Figure 5) and Keddam's (Figure 6) scheme. According to quantum theories, transfer of two electrons in one single step is less likely and this indicates that step 4 is not taking place as it is written in Figure 51. Although this step could potentially be broken down to other sub-elementary steps, for the sake of keeping this scheme less complicated, it is decided to consider step 4 with two electrons being transferred as a single building block. The objective in the present work was to understand how to couple two theories of non-catalytic and catalytic dissolution into a single scheme without adding unnecessary complications. Another point to mention is that all elementary steps in the theory presented herein (Figure 51) are electrochemical steps. Hence, it is reasonable to assume that their kinetics depend on potential.

7.6. Hypotheses

It has been hypothesized that using the simplified mechanistic scheme proposed in the present study (Figure 51) and by utilizing the potentiostatic procedure introduced previously, one should be able to model the anodic potentiodynamic sweeps over a variety of different experimental conditions and formulate a set of kinetic rate constants that is physically realistic. In addition, it is hypothesized that changes in pH and presence of CO₂ change the kinetics of the elementary steps, thereby influencing the overall rate of the anodic reactions.

7.7. Approach for Computing the Kinetic Rate Constants

7.7.1. Assumptions

A few assumptions have been made in this study. First, it has been assumed that no solid corrosion product layer or passive film is produced as the exposure time to the solution for a freshly polished specimen in all these experiments was short enough only to stabilize OCP before every measurement. In the experiments, the data points collected at 3-6 microseconds after polarization are used for computational purposes, obtained on a freshly exposed specimen at OCP. The second assumption is that any change due to the mass-transfer effect is negligible since the rotation rate was always kept high enough in the present study to eliminate possible diffusion-related limitations. In the present study, it was experimentally observed that at these high rotation rates, the current response did not change with rotation speed of the RCE. The third assumption is that the reaction rate for each elementary step (*i*) follows an exponential function of potential as described by Eq. 83 (Tafel behavior since all steps are electrochemical as shown in Figure 51), consistent with the Butler-Volmer equation:

$$k_i = k_{i,0} \exp\left(\frac{2.3E}{b_i}\right) \tag{83}$$

where $k_{0,i}$ is the kinetic rate constant k_i at the reference potential of zero *vs.* SHE reference electrode; b_i is the Tafel slope or the magnitude of the polarization that is needed to initiate that specific elementary step. Kinetic rate constant k_i is a function of potential; $k_{0,i}$, and b_i are independent of potential but they can change with pH, temperature, electrolyte types, *etc.*; b_i is different from the conventional known Tafel slope, as the latter one is typically defined for overall reaction while here it is defined for a single step. In the following discussion, 'kinetic rate constants' is referring to b_i and $k_{0,i}$. All potential and current density values will be reported in volts *vs.* SHE and A/m², respectively. It has also been assumed that k_2 (*Path 1*, Figure 51) is independent of pH, but it depends on the electrode material, anion, temperature, and CO₂ presence. This step is independent of pH since *OH*⁻ is excluded in step 2. A similar assumption (*i.e.*, k_2

independent of pH) was also made by Keddam, et al. [37]. k2 is more affected by characteristics of the crystal surface of the electrode (e.g., electrode material, arrangement, the surface density of metal atoms, the density of kinks, ad-sites, etc.) [37]. It is also assumed that there is a negligible contribution of oxygen reduction reaction as the test solution was always sparged with oxygen free N₂/CO₂ gas for at least 1 hour prior to each measurement to remove dissolved oxygen (< 3 ppb). Considering the scheme shown in Figure 51, there are five k_i (potential-dependent constants) and each contains two potential-independent variables ($k_{0,i}$, and b_i). It should be borne in mind that although $k_{0,i}$, and b_i are potential-independent, they depend on pH, CO₂, temperature, steel type, or other environmental conditions. Therefore, ten kinetic rate constants $(k_{0,1}, k_{0,2}, k_{0,3}, k_{0,-3}, k_{0,$ $k_{0,4}, b_1, b_2, b_3, b_{-3}, b_4$) need to be estimated in this study for a given experimental condition. Furthermore, it was assumed that the adsorption is the Langmuir type. In the present study, it is also assumed that CO₂ does not affect the chemical composition or nature of the intermediates/pathways and only influences the kinetic rate constants. The EIS studies done by Moradighadi et al. [42], have supported such an assumption, where introducing CO₂ did not affect the number of time constant or EIS characteristic loops [42].

7.7.2. Proposed Approach and Theory

In the mechanistic scheme presented in Figure 51, there are five k_i to be determined. Remember that k_i depends on potential and each k_i includes two kinetic rate constants ($k_{0,i}$, and b_i) that are independent of potential., therefore ten parameters need to be calculated for each environmental condition. Notice that all elementary steps in the

scheme presented (Figure 51) are charge transfer steps. Figure 52 represents the range of data points that were used to calculate a particular kinetic rate constant(s). The first step was to collect repeatable anodic potentiodynamic sweeps and specify the appropriate potential range of active, transition, or pre-passivation domains for subsequent potential perturbations. The blue boxes in Figure 52 (b) through (f) illustrate the range of data used to approximate k_1 , k_2 , k_3 , k_4 , and k_{-3} , respectively at a given fixed potential.



Figure 52. (*a*) Specifying the appropriate range for potential perturbation, and the range of data points used to calculate the kinetic rate constants (b) k_1 , (c) k_2 , (d) k_3 , (e) k_4 , and (f) k_{-3}

Table 17 summarizes the electrochemical technique, methodology, and mathematical correlation used to estimate the corresponding constant. The theory behind these mathematical expressions to compute k_i values will be explained in the following. By computing k_i at different overpotentials in a suitable potential range, one can approximate $k_{0,i}$, and b_i . k_1 and k_2 were obtained by perturbation of the system in the active dissolution range. Similarly, k_3 and k_4 were found by potentiostatic perturbation of the system in the transition range of potentials. Finally, k_{-3} was analytically estimated using the already calculated k_1 , k_2 , k_3 , and k_4 values and the data points taken from the experimental anodic sweeps.

Table 17. Summary of the proposed approach to estimate kinetic rate constants of eachelementary step

Parameter	Technique	Methodology	Approach for estimation
k_1	Potentiostatic	A set of transients in the active domain	$i_{t=0^+} \approx Fk_1$
k_2	Potentiostatic	A set of transients in the active domain	$\left. \frac{di}{dt} \right _{t=0^+} : k_2$
<i>k</i> 3	Potentiostatic	A set of transients in the transition domain	$i_{t=0^+} \approx 2Fk_3^*$
k_4	Sampled steady- state	A set of transients in the transition domain	$i_{st.st} \approx 2Fk_4$
<i>k</i> –3	Potentiodynamic	A set of data points from anodic polarization	$k_{-3}(E) = A + Bk_4$

The main challenge was to find a systematic approach based on known theory to calculate these ten constants, then insert these constants into the associated equations to reproduce the anodic sweeps. This is the key strength of the present approach. Let's assume that θ_1 is the fraction of the surface that is covered with chemisorbed non-catalytic $Fe(I)_{ads.}$ intermediate. Similarly, θ_2 is the fraction of the surface that is occupied

by a chemisorbed catalytic $Fe(II)_{ads}^*$ intermediate. θ_i is a function of time and potential, but at a fixed potential it's only a function of time ($\theta_i(t)$).

Estimation of k_l : Before applying a potential perturbation at OCP, the iron surface is almost entirely covered with hydrogen. With a positive perturbation in the potential of the iron surface, hydrogen desorption is achievable, but only at high overpotentials (> 60 mV vs. OCP) [37]. In the active domain, the non-catalytic path (Figure 51) is the dominant reaction pathway. By applying a positive potential perturbation, the electrons are pulled out of the WE leading to a quick "pile-up" of $Fe(I)_{ads}$ according to the first step (Eq. 71). Let's assume that θ_I is the fraction of the surface that is covered with chemisorbed non-catalytic $Fe(I)_{ads}$ intermediate. Similarly, θ_2 is the fraction of the surface that is occupied by a chemisorbed catalytic $Fe(II)_{ads}^*$ intermediate. θ_I is a function of time and potential, but at a fixed potential it's only a function of time ($\theta_I(t)$). Writing the charge balance equation, " $I - \theta_I$ " fraction of the surface is available for step 1 (Eq. 71) and " θ_I " fraction of the surface is available for step 2 (Eq. 72), hence the total current is given by:

$$\frac{i(t)}{F} = k_1(1 - \theta_1(t)) + k_2\theta_1(t)$$
(84)

At OCP the surface is completely covered by hydrogen and the surface coverage due to $Fe(I)_{ads}$ is almost negligible [37], therefore the initial coverage $\theta_I(t = 0) \approx 0$. Therefore, according to Eq. 84, the current response right after the potential perturbation at time $t = 0^+$ (~ at 6 microseconds) is approximately equal to Fk_I :

$$\frac{i(0^+)_{active}}{F} \approx k_1 \tag{85}$$

Since k_I is an exponential function of potential, a linear regression of k_I in a semilog plot provides the kinetic rate constants for the first elementary ($k_{0,I}$ and b_I). By plotting the natural logarithm of k_I vs. potential, the kinetic rate constants $k_{0,I}$ and b_I were obtained (Figure 53).



Figure 53. *Regression line used to estimate* $k_{0,1}$ *and* b_1

Estimation of k_2 : k_2 can be derived by writing a mass balance expression (Eq. 86) to describe the variation of θ_1 as a function of time. $Fe(I)_{ads}$ is produced in the first step (Eq. 71) and is consumed in the second step (Eq. 72), thus:

$$\beta \frac{d\theta_1}{dt} = k_1 (1 - \theta_1) - k_2 \theta_1 \tag{86}$$

where β is a constant, linking the fraction of the surface coverage, θ_1 , and the surface concentration of the chemisorbed species. By solving the first order differential Eq. 86, $\theta_1(t)$ can be expressed according to:

$$\theta_1(t) = \left(\frac{k_1}{k_1 + k_2}\right) \times \left\{1 - e^{-\left(\frac{k_1 + k_2}{\beta}\right)t}\right\}$$
(87)

From Eqs. (86 & 87) one obtains:

$$\frac{d(i(t))}{dt} = \frac{Fd\theta_1}{dt}(k_2 - k_1)$$
(88)

$$\frac{d\theta_1(t)}{dt} = \left(\frac{k_1}{\beta}\right) \times e^{-\left(\frac{k_1+k_2}{\beta}\right)t}$$
(89)

Substituting Eq. 89 into Eq. 88, and taking the natural logarithm of both sides, one obtains:

$$ln\left(\frac{di(t)}{dt}\right) = ln\left(\frac{Fk_1(k_2-k_1)}{\beta}\right) - \left(\frac{k_1+k_2}{\beta}\right)t$$
(90)

Therefore, by plotting $ln\left(\frac{di(t)}{dt}\right)$ as a function of time (for the time interval slightly after $t = 0^+$ and before the peak current) at a fixed potential and given that k_1 was already determined, k_2 can be calculated at a constant potential. The dependence of k_2 on potential was defined according to an exponential function, thus b_2 and $k_{0,2}$ can be obtained by plotting the natural logarithm of k_2 vs. potential (Figure 54).



Figure 54. Regression line used to estimate $k_{0,2}$ and b_2

Estimation of k_3 : To estimate k_3 , now we have to stimulate the system in the potential range of transition. In the transition range of a potential perturbation, the current

is not only coming from the non-catalytic pathway but also from the catalytic path as shown in Figure 51. Therefore, when writing a charge balance equation for the transition range, both θ_1 and θ_2 are involved in the production of current according to:

$$\frac{\iota(t)}{F} = 2k_3^*(1-\theta_2) - 2k_{-3}^*\theta_2 + 2k_4\theta_2 + k_2\theta_1$$
(91)

The net current in the potential ranges of the transition domain results from both step 1 and step 3 (see Figure 51). In this regard, the overall kinetics are under the control of steps 1 and 3. Therefore, the net rate is coming from these two steps 1 and 3. k_3^* is introduced as the harmonic average of both steps 1 and 3 and can be expressed as:

$$k_3^* = \left(\frac{1}{k_1} + \frac{1}{k_3}\right)^{-1} \tag{92}$$

According to the literature [67], the harmonic average is usually taken between two processes to indicate the consecutive nature of the ongoing phenomena. Before applying the external potential perturbation, at OCP the metal surface is completely covered by hydrogen and the surface coverage due to $Fe(I)_{ads}$ and $Fe(II)_{ads}$ * are negligible, therefore the initial coverage θ_I and θ_2 at t = 0 are assumed to be zero. Thus, according to Eq. 91, the current response right after the potential perturbation at time $t = 0^+$ (~ at 6 microseconds) is approximately equal to $2Fk_3^*$:

$$\frac{i(0^+)_{transition}}{F} \approx 2k_3^* \tag{93}$$

Having a set of transients at different potentials in the range of the transition domain, one can obtain k_3^* as a function of potential. Having k_3^* and given that $k_{0,1}$ and b_1 are already calculated, Eq. 94 can be used to obtain k_3 at different potentials:

$$k_3 = \left(\frac{1}{k_3^*} - \frac{1}{k_1}\right)^{-1} \tag{94}$$

Using regression analysis and by plotting the natural logarithm of $k_3 vs.$ potential, the kinetic rate constants for step 3 in Figure 51 ($k_{0,3}$ and b_3), can be estimated (Figure 55).



Figure 55. *Regression line used to estimate* $k_{0,3}$ *and* b_3

Estimation of k_4 : k_4 was estimated using sampled steady-state data points which is the current response when the transients reach a plateau (red data points shown in Figure 56).



Figure 56. Sampled steady-state analysis

Writing the charge balance equation from the scheme shown in Figure 51 we have:

$$\frac{i(t)}{F} = k_1(1 - \theta_1 - \theta_2) + (k_2 + k_3)\theta_1 + (2k_4 - k_{-3})\theta_2$$
(95)

From the mass balance equation for the chemisorbed entities $Fe(I)_{ads}$ and $Fe(II)_{ads}^*$, the time-dependence of θ_1 and θ_2 can be obtained through the following differential equations:

$$\beta \frac{d\theta_1}{dt} = k_1 (1 - \theta_1 - \theta_2) - (k_2 + k_3)\theta_1 + k_{-3}\theta_2 \tag{96}$$

$$\beta \frac{d\theta_2}{dt} = k_3 \theta_1 - k_{-3} \theta_2 \tag{98}$$

where at steady-state the constant values for the surface coverages (θ_1 and θ_2) vs. time make the first derivative of θ_i vs. time equal to zero:

$$\frac{d\theta_1}{dt} = 0 \quad \Rightarrow \quad \theta_{1,st.st} = \frac{k_1 k_{-3}}{k_1 k_3 + k_1 k_{-3} + k_2 k_{-3}} \tag{98}$$

$$\frac{d\theta_2}{dt} = 0 \quad \Rightarrow \theta_{2,st.st} = \frac{k_1 k_3}{k_1 k_3 + k_1 k_{-3} + k_2 k_{-3}} \tag{99}$$

Putting $\theta_{i,st.st}$ into Eq. 95, one can obtain the steady-state current density as:

$$i_{st.st} = \frac{2Fk_1(k_2k_{-3}+k_4k_3)}{k_1k_3+k_{-3}(k_1+k_2)} = 2Fk_2\theta_{1,stst} + 2Fk_4\theta_{2,stst}$$
(100)

By assuming that $k_{-3} \ll k_4$, Eq. 100 can be simplified to:

$$i_{sampled \ st.st} \approx 2Fk_4$$
 (101)

Thus, having a set of transients at different potentials in the range of the transition domain, one can obtain k_4 using sampled steady-state data. By plotting the natural logarithm of k_4 vs. potential, the kinetic rate constants for step 4 in Figure 51 ($k_{0,4}$ and b_4), can be estimated (Figure 57).



Figure 57. *The regression line used to estimate* $k_{0,4}$ *and* b_4

Estimation of k_{-3} : The last parameter that was computed is k_{-3} which is the reaction rate constant for the following quasi-reversible elementary step in the reverse direction.

$$Fe(I)_{ads.} \stackrel{k_3}{\leftrightarrow} Fe(II)^*_{ads.} + e^-$$
 (102)

 k_{-3} in the active range of potentials near transition tends to push the catalyst making step 3 in Figure 51, in the "backward" direction, resisting the imposed perturbation and

reducing the net current via this path. While, in the transition range, the current decreases at higher overpotentials, *i.e.*, the charge distribution at the surface is such that electrons tend to move in a backward direction in favor of k_{-3} . Therefore, the value of b_{-3} should be negative in the active domain and positive in the transition range of potential perturbation. An analytical approach was used to obtain k_{-3} using a set of data points taken from the potential ranges around the "*s-shape*" region of the anodic potentiodynamic sweeps. From the steady-state equation, k_{-3} can be written as a function of k_4 :

$$k_{-3}(E) = Bk_4 + A \tag{103}$$

where *A* and *B* are a function of potential and by rearranging Eq. 100, they can be expressed as:

$$A(E) = \frac{i_{st.st}k_1k_3}{2Fk_1k_2 - i_{st.st}(k_1 + k_2)}$$
(104)

$$B(E) = \frac{-2Fk_1k_3}{2Fk_1k_2 - i_{st,st}(k_1 + k_2)}$$
(105)

From $i_{st.st}$ taken from the experimental sweeps and using Eqs. (103–105), k_{-3} can be determined at different potentials. Given that k_{-3} was presumably an exponential function of potential, $k_{0, -3}$, and b_{-3} can be computed in the active and transition domains, separately using regression lines on a semi-logarithmic scale (Figure 58). For calculating k_{-3} in the transition region, similar steps were followed, and the net k_{-3} was estimated by superposing $k_{-3,active} + k_{-3,transition}$. As shown in Figure 59, 150 data points were always

taken from anodic polarization starting from +60 mV above OCP, and 60 data points were taken in the transition range to calculate $k_{-3,active}$ and $k_{-3,transition}$, respectively.



Figure 58. *Regression line used to estimate* $k_{0,-3}$ *and* b_{-3} *in (a) active and (b) transition*

domains



Figure 59. 150 data points in the active range and 60 data points in the transition range were always taken to calculate $k_{-3,active}$, and $k_{-3,transition}$, respectively

Estimation of $k_{0,a}$ and $b_{a,ov}$ in active and transition range of potentials for the overall reaction: To obtain an estimate of the $b_{a,ov}$ (anodic Tafel slope for the overall

reaction) and $k_{0,a}$ ($k_{a,ov}$ at E = 0 V vs. SHE), the sampled steady-state data point (Figure 56) was used. As shown in Figure 60, by plotting the $log(i_{st-st})$ vs. overpotential (η), $b_{a,ov}$ for the overall reaction can be obtained from the slope. It is assumed that the total number of electrons transferred during iron dissolution, n, is equal to 2. The anodic charge transfer coefficient (α_a) can be then estimated according to [122]:

$$\alpha_a = \frac{2.3RT}{Fb_{a,ov.}} \tag{106}$$

To estimate $k_{0,a}$ for the overall reaction at a given potential E_i , it has been assumed that the overall rate constant of anodic reaction ($k_{a,ov}$) is described according to [122]:

$$k_{a,ov.}(E_i) = \frac{(i_{st-st})_{sampled at E_i}}{F}$$
(107)

Having a set of sampled stead-state data at different potentials, $k_{0,a}$ can be found from the intercept of the regression line as depicted in the inset of Figure 60. Depending on the range of potential perturbation (active or transition), two different sets of $b_{a,ov}$ and $k_{0,a}$ will be calculated; one corresponds to the potential perturbation in the active and the other one relates to the transition state (Figure 60).



Figure 60. Regression line used to obtain $b_{a,ov}$ and $k_{0,a}$ in (a) active, and (b) transition range of potential for the overall anodic reaction

7.7.3. Uncertainty

In this study, every single measurement, including potentiostatic and potentiodynamic data, was repeated at least four times to ensure repeatability. Several kinetic rate constants, k_i , were estimated, and using the average value, k_{-i-avg} , in the model, reproduced the experimental potentiodynamic sweeps. Knowing the range of uncertainty associated with those parameters is important. Different algorithms were used to estimate the uncertainty such as $LINEST^4$ to estimate the uncertainty of slope and intercept (Figure 61 (a)), error propagation, or simple standard deviation of repeated data. In the case of having outlier data points, finding the uncertainty for each measurement, and taking the mean value gives the largest possible error (Figure 61 (b)).

⁴ Function in Excel.



Figure 61. *Estimating the uncertainty for (a) only repeatable data points and (b) all data points including the outlier ones*

It is essential to define the possible error range so that any particular parameter can be tuned within that error range to achieve the best fit.

7.8. Verification of the Proposed Approach & Model

A model, theory, hypothesis, or approach is valid if only it can reproduce various experimental patterns and different test conditions. In Section 7.8.1, the presented theory and methodology described in Sections 7.5 through 7.7 will be examined to find out how valid the described methodology was in terms of being able to reproduce the steady-state dissolution behavior of iron. Finally, in Sections 7.8.2 through 7.8.3, a detailed analysis will be done to discuss how exactly pH and CO₂ impact the kinetics of individual elementary steps.

7.8.1. Modeling

In the upcoming Section 7.8.1.1, the methodology detailed in Section 7.7.2 is followed to calculate the rate constants of the elementary steps during the anodic

dissolution of pure iron at different pH values in both N2-sparged and CO2-sparged media. In Section 7.8.1.1, first, the linear regressions and analytical plots that were used to obtain the rate parameters will be demonstrated. Then, the final acquired dataset of the kinetic rate constants will be summarized. At the end of Section 7.8.1.1, the final modeling output of the anodic sweeps using the obtained metrics (pure anodic, *i.e.*, excluding cathodic reactions) will be shown. Section 7.8.1.1, will basically discuss the surface reactions. Section 7.8.1.2 will focus on the solution, electrolyte thermodynamics, water chemistry, and basic speciation calculations for the homogenous equilibrium reactions in the sweet media (as summarized in Section 2.5). The current, due to the reduction of species in the electrolyte, will be modeled in 7.8.1.2 (charge/mass-transfer processes) to better approximate the current close to OCP. Finally, in Section 7.8.1.3, the net potentiodynamic sweeps will be modeled according to the mixed potential theory by taking the absolute value of the difference between anodic and cathodic currents ($i_{net} = |i_a|$ $(-i_c)$). The net anodic sweeps will be compared with the experiments to accomplish the final model verification.

7.8.1.1. Obtained Kinetic Rate Constants: Modeling the Anodic

Potentiodynamic Sweeps. First, we need to collect the reproducible experimental anodic potentiodynamic sweeps. Every measurement was repeated at least four times to ensure reproducibility.

Figure 62 shows the experimental anodic sweeps on iron in 2.9 wt.% NaCl at different solution pH in both N₂-sparged and CO₂-sparged environments.



Figure 62. Anodic polarization curves for iron in 2.9 wt.% NaCl (0.55 M) solution sparged with (a) 0.97 bar N_2 and (b) 0.97 bar CO_2 sparged: 0.5 mV/s

After sparging, the pH was adjusted using additions of HCl or NaOH. All sweeps were corrected for the effect of solution resistance.

In the next step, the suitable range of potential perturbation for the subsequent potentiostatic measurements should be specified. Table 18 summarizes the range of active and transition domains where the potential perturbation was carried out for potentiostatic measurements.

Table 18. Approximate range for potential perturbation (active or transition) for anodic

 dissolution of iron at different solution pH

Environment	pН	Active range (mV vs. OCP)	Transition range (mV vs. OCP)
Strong acid:	4	60 - 120	125 - 175
N ₂ -sparged	5	70 - 130	160 - 210
	6	100 - 300	310 - 360
Weak acid:	4	60 - 130	135 - 185
CO ₂ -sparged	5	60 - 110	120 - 170
	6	60 - 120	125 - 165

Figure 63 and Figure 64 illustrate the corresponding transients resulting from stimulating the iron in the active and transition regions, respectively in 2.9 wt.% NaCl at different solution pH in both strong and weak acid media. It should be kept in mind that transient data taken from the active (Figure 63) and transient domain (Figure 64) were used to calculate (k_1 , k_2) and (k_3 , k_4), respectively.



Figure 63. Potentiostatic transients of iron in the active potential range (a-c) in N_2 -sparged pH 4, 5, 6 and (d-f) CO₂-sparged media pH 4, 5, 6, respectively



Figure 64. Potentiostatic transients of iron in the transition potential range (a-c) in N_2 -sparged pH 4, 5, 6 and (d-f) CO₂-sparged media pH 4, 5, 6, respectively

<u>Calculating k_l </u>: k_l for iron in 2.9 wt.% NaCl solutions at different pH (for both strong and weak acids) were determined according to the procedure laid out in Section 7.7.2 and by using a set of transients in the active dissolution range (Figure 63). The second data point right after the potential perturbation (at t \approx 6.6 µs) was used to estimate k_l at a given applied potential within the range of active potential perturbations and $k_{0,l}$ and b_l were obtained from regression analysis in a semi-log plot. Figure 65 represents the transients at a time shorter than 0.02 milliseconds and the corresponding regression plots (the inset) to estimate $k_{0,l}$ and b_l at three different pH values of 4, 5, and 6 for both strong and weak acids.



Figure 65. Transient responses of iron at different potential perturbations in the active domain and analytical regression lines (insets) were used to compute $k_{0,1}$ and b_1 at (a–c) in N₂-sparged pH 4, 5, 6 and (d–f) CO₂-sparged media pH 4, 5, 6, respectively

<u>Calculating k_2 </u>: Figure 66 shows transients in the active range of potential perturbation and the corresponding regression lines used to obtain $k_{0,2}$ and b_2 for both strong and weak acid environments. k_2 is independent of pH and mainly depends on the characteristics of the crystal surface of the electrode itself rather than pH. Factors such as anions, electrode material, phase distribution at the electrode surface, arrangement and density of metal atoms, physical irregularity of the surface, crystal imperfections, the density of terrace, kink, and ad-sites, and any roughness due to machining, grinding, scratches can influence $k_{0,2}$ and b_2 [14]. A similar assumption (pH-independent k_2) was also made by Keddam, *et al.* [37].



Figure 66. Analytical plots and corresponding regressions lines to compute $k_{0,2}$ and b_2 in (a) N_2 -sparged and (b) CO₂-sparged media: 0.5 M NaCl solution

<u>Calculating k_3 </u>: To compute k_3 , the potential perturbations must be performed in the transition range of potentials. Moving from the active to transition domain, a current maximum appears in the anodic sweep which reflects itself as an "*s-shape*" response in anodic potentiodynamic sweeps. It has been reported that this current maximum only appears within a narrow range of pH and dissipates at more acidic or very alkaline media [35]. The appearance of this maximum mainly depends on the kinetics of the quasireversible step 3 (k_3/k_{-3}). Figure 67 illustrates the potentiostatic responses in the transition range of potentials and the corresponding regression lines to acquire $k_{0,3}$ and b_3 at three different pH values of 4, 5, and 6 for both strong and weak acids.



Figure 67. Transient responses of iron at different potential perturbations in the transition domain and analytical regression lines (insets) were used to compute $k_{0,3}$ and b_3 in (a–c) N₂-sparged pH 4, 5, 6, and (d–f) CO₂-sparged, pH 4, 5, 6, respectively

Through *Path (2)*, the current is mainly generated through the dissolution of $Fe(II)_{ads}^*$. However, the net charge at the potential perturbations close to the *s*-shape
region is coming from both step 1 and step 3 in Figure 51 (as explained in Section 7.7.2). In this regard, the overall kinetics are under the concurrent influence of steps 1 and 3.

<u>Calculating k_4 </u>: The kinetic rate constants of the fourth elementary step ($k_{0,4}$ and b_4) were estimated according to the methodology described in Section 7.7.2. Figure 68 shows the regression analysis used to obtain $k_{0,4}$ and b_4 at different pH values and in the presence and absence of CO₂-sparged.



Figure 68. Analytical regression lines used to compute $k_{0,4}$ and b_4 in (a-c) N₂-sparged

pH 4, 5, 6, and (d-f) CO₂-sparged, pH 4, 5, 6, respectively

<u>Calculating k_{-3} : k_{-3} in the active and transition range of potential was determined</u> using the analytical approach outlined in Section 7.7.2. Figure 69 and Figure 70 represent the regression analysis used to estimate the kinetic rate constants of step three in Figure 51, the backward direction in the active $(k_{0,-3,a}, b_{-3,a})$ and transition $(k_{0,-3,t}, b_{-3,t})$ ranges of potentials, respectively. The insets of Figure 69 represent the range of data points taken from anodic potentiodynamic sweeps (shown in orange color) for the corresponding analytical estimation of both $k_{-3,a}$ and $k_{-3,t}$. The way that the data points were sampled from the potentiodynamic data for subsequent analytical approximation of k_{-3} , was always the same and according to the method illustrated in Figure 59.



Figure 69. Analytical regression lines were used to compute $k_{0,-3,a}$, and $b_{-3,a}$ during iron dissolution in (a–c) N₂-sparged pH 4, 5, 6, and (d–f) CO₂-sparged, pH 4, 5, 6, respectively. The insets represent the range of data used for k_{-3} estimation (taken from anodic sweeps of iron)



Figure 70. Analytical regression lines were used to compute $k_{0,-3,t}$, and $b_{-3,t}$ during iron dissolution in (a–c) N₂-sparged pH 4, 5, 6, and (d–f) CO₂-sparged, pH 4, 5, 6, respectively

Table 19 summarizes the calculated kinetic rate constants using the

abovementioned transient approach for different experimental conditions. In this study, every single measurement was repeated at least four times. Several kinetic rate constants, k_i , are derived from experimental transients, and applying the average value, $k_{i,avg}$ (Table 19), in the model could reproduce the experimental potentiodynamic sweeps. Different algorithms were used to estimate the uncertainty associated with each computed parameter. It is essential to estimate the error range so that any particular parameter can be tuned within that range if needed. Parameters that are marked with a star (*) were not taken as average values but were slightly tuned within the error range to get a better fit. The anodic potentiodynamic sweeps were modeled in this study by inserting the data set listed in Table 19 into Eqs. (98–100) in Section 7.7.2. In Table 19, b_i is presented in V/dec. and $k_{0,i}$ is in mol.m⁻².s⁻¹.

Table 19. Summary of the rate constants at different pH values for pure iron derived from the transient measurements (25 °C)

Condition	k 0,1	bı	k 0,2	b2	k 0,3	b3	k0,-3,act.	b-3,act.	k0,-3,trams.	b-3,trans.	k 0,4	b 4
Fe, 25°C, pH4, N ₂	4.9×10 ⁻² *	0.12± 0.02	1.57 ×10-1	0.26± 0.09	1.03 ×10-3	0.34± 0.1	1.3 ×10 ⁻²⁰ *	-0.028*	1.63 ×10 ⁹	0.021	3.3 ×10-2	0.19± 0.02
Fe, 25°C, pH5, N ₂	5.3 ×10 ⁻² *	0.11± 0.03*	1.57 ×10 ⁻¹	0.26± 0.09	2.10 ×10-3	0.33± 0.03	4.1 ×10 ⁻¹⁷ *	-0.051*	1.30 ×105	0.035	3.1×10-2	0.19± 0.04
Fe, 25°C, pH6, N ₂	8.5 ×10 ⁻²	0.12± 0.06*	1.57 ×10-1	0.26± 0.09	9.26 ×10 ⁻³	0.33± 0.1	5.1 ×10-9	-0.058*	1.84 ×10 ²	0.023*	1.5 ×10-4*	0.19± 0.03
Fe, 25°C, pH4, CO 2	5.5 ×10-2	0.13± 0.02	1.63 ×10 ⁻¹	0.26± 0.09	1.29 ×10-3	0.31± 0.1	1.3 ×10 ⁻¹²	-0.064	1.37 ×105	0.028	1.95 ×10-2	0.24± 0.02*
Fe, 25°C, pH5, CO 2	2.5 ×10 ⁻¹ *	0.12± 0.03*	1.63 ×10 ⁻¹	0.26± 0.09	6.30 ×10 ⁻³	0.32± 0.2	1.1 ×10 ⁻¹¹ *	-0.075*	1.06×10 ⁹ *	0.027*	1.9×10 ⁻² *	0.28± 0.01*
Fe, 25°C, pH6, CO ₂	4.1×10°*	0.12± 0.02*	1.63 ×10 ⁻¹	0.135 ±0.09 *	2.50×101*	0.35± 0.2	5.5 ×10 ⁻⁶ *	-0.076*	1.55×10 ¹⁴ *	0.030	1.7×10-2*	0.29± 0.01*

To validate the introduced approach and the model developed for reproducing the anodic dissolution, Figure 71 compares the modeled sweeps with the experimental results. The gray curves represent the experimental data, and the black dashed lines show the model. The data pattern and the exact impact of CO_2 and pH on the trend of the rate constants for each elementary step will be discussed in detail in Section 7.8.2.



Figure 71. Comparison of the modeled (dashed black lines) vs. experimental (gray color curves) anodic sweeps of pure iron in $(a-c) N_2$ -sparged pH 4, 5, 6, and $(d-f) CO_2$ -sparged, pH 4, 5, 6, respectively

There is good consistency between the experiment and the modeled sweeps in all three regions of active, transition, and pre-passivation for different experimental conditions. This validates the accuracy of the introduced methodology for calculating the kinetic rate constants and subsequently modeling the anodic sweeps.

<u>Calculating $k_{0,a}$ and $b_{a,ov}$, for the overall anodic reaction in active and transition</u> <u>range of potentials—Effect of pH and CO₂</u>: The rate of elementary steps during iron dissolution was discussed so far to gather the required metrics for modeling the anodic sweeps. In this section, a quantitative interpretation of the effect of CO₂ and pH on the rate of the overall reaction (Eq. 6) is carried out, according to the procedure explained in Section 7.7.2. The anodic Tafel slope for the overall reaction ($b_{a,ov}$) were determined at different environmental conditions from the slope $i_{st-st} vs. \eta$ in a semi-logarithmic scale. Figure 72 and Figure 73 show the regression lines to determine the $b_{a,ov}$ in the potential range of active and transition, respectively. The rate constant for the overall reaction at E = 0 V vs. SHE ($k_{0,a}$) was obtained from the intercept of $ln(k_{a,ov})$ vs. potential plots (insets of Figure 72 and Figure 73).



Figure 72. *Regression analysis for determining* $b_{a,ov}$, and $k_{0,a}$ *for pure iron in active range in* (*a*–*c*) *N*₂-*sparged pH* 4, 5, 6, *and* (*d*–*f*) *CO*₂-*sparged*, *pH* 4, 5, 6, *respectively*



Figure 73. Regression analysis for determining $b_{a,ov}$ and $k_{0,a}$ for pure iron in transition range in (*a*–*c*) N_2 -sparged pH 4, 5, 6, and (*d*–*f*) CO₂-sparged, pH 4, 5, 6, respectively

Table 20 presents the summary statistics of obtained values of $b_{a,ov}$, $k_{0,a}$, and α_a at different experimental conditions in both active and transition ranges of potentials.

Potential		pH 4			pH5			pH6		
range	Environment	k _{0,a} (mol/m².s)	b _{a,ov.} (mV/dec)	α_{a}	k _{0,a} (mol/m².s)	b _{a,ov.} (mV/dec)	α_{a}	k _{0,a} (mol/m².s)	b _{a,ov.} (mV/dec)	α _a
Active	N ₂ -sparged	5.84	44.0	1.34	7.32	43.1	1.37	0.043	67.1	0.89
domain	CO ₂ -sparged	9.45	41.9	1.41	141.7	37.4	1.58	65.79	41.0	1.44
Transition	N2-sparged	0.052	91.7	0.65	0.023	91.7	0.65	0.014	94.0	0.63
domain	CO ₂ -sparged	0.042	99.9	0.59	0.62	64.8	0.92	3.65	53.7	1.10

dissolution at different environmental conditions in active and transition domains

To better visualize the trends of changes in the data sets summarized in Table 20, the bar plots of $b_{a,ov}$, $k_{0,a}$, and α_a at three different pH values are depicted in Figure 74 and Figure 75 for the active and transition range of potentials, respectively.



Figure 74. Variation of (a) $k_{0, a}$, (b) $b_{a,ov}$, and (c) α_a for the overall anodic reaction of

iron in the active domain at different pH (25 $^{\circ}$ C)



Figure 75. Variation of (a) $k_{0,a}$, (b) $b_{a,ov}$, and (c) α_a for the overall anodic reaction of

iron in the transition domain at different pH (25 °C)

It is important to bear in mind that by increasing $k_{0,a}$, decreasing $b_{a,ov}$ or increasing α_a all lead to an enhancement of the kinetics. Alteration of $b_{a,ov}$ or α_a indicates the likelihood of a slight shift in the electron tunneling pathways – but not necessarily a change of the reaction mechanism in terms of the nature of the elementary sequences (as discussed in Section) [123]. Comparing Figure 74 (a) and Figure 75 (a), a higher $k_{0,a}$ was obtained in the presence of CO₂ in both active and transition ranges. This indicates that CO₂ enhances the kinetics, especially at pH 5 and 6 this enhancement is more notable. This conclusion could also be inferred from Figure 74 (c) and Figure 75 (c) where a meaningful shift of α_a especially at pH 5 and 6 is detected due to the presence of carbonate/bicarbonate buffers. Numerous studies have shown a similar observation where CO₂ exacerbates the kinetics of the overall anodic reaction [45,61,90, 124].

Bockris' theory (with the experimental $b_{a,ov}$ of about 30–40 mV/dec. at around room temperature) has been frequently considered as the dominant mechanism even in the presence of CO₂ [50,52, 63]. As shown in Figure 74 (b), CO₂ does not significantly impact $b_{a,ov}$ in the active dissolution range at pH 4 and 5 which indicates that CO₂ does not directly influence the mechanistic pathway in the active range. Regardless of the presence or the absence of carbonate/bicarbonate buffers, $b_{a,ov}$ is always around 40 mV/dec. which is in agreement with Bockris' mechanism [20], which is usually more trustworthy at low overpotentials (active domain) and in low pH media [104]. However, as seen in Figure 74 (b), starting from pH 6, a 38% decrease in $b_{a,ov}$ (from ~67 mV/dec. to ~41 mV/dec.) and an increase of α_a from 0.89 to 1.44 (Figure 74 (c)) implies that the role of CO₂ in speeding up the kinetics becomes more notable. Still, under this more alkaline

condition, we believe that CO₂ neither directly acts over the surface nor shifts the mechanistic path. This view further supports the previous findings by Almeida, et al. [49] who claimed that even in the presence of strong anions such as Cl^{-} or SO_4^{2-} , OH^{-} are still the first predominant adsorbed ions on iron and weak acids such as carbonic acid thermodynamically could never directly act on the iron surface. We argue that CO₂ contribution in escalating the iron dissolution (increasing $k_{0,a}$) is mainly due to its capability of maintaining a constant level of local H^+ concentration at the surface. This idea can be reinforced as a few studies have also shown an enhancement of the active dissolution kinetics due to the buildup and chemisorption of hydrogen at the surface [125]. Additionally, this claim could also be backed up by our earlier observations in Section 6.6.1.2, where the pile-up of H^+ at the surface was accompanied by superpolarization and a momentary jump of the signal due to the fast rate of dissolution at the early stages. The trend of data shown in Figure 74 (a) and Figure 75 (a) further support the abovementioned inference, as at higher pH of 5 and 6 when there is H^+ deficiency, the buffering role of carbonic acid would become more crucial, and distinguishable (increase of $k_{0,a}$ becomes more significant at higher pH). As seen in Figure 75 (b), in the transition range in less acidic media at pH 5 and 6, the CO₂ effect becomes more noteworthy as a 30% decrease in $b_{a,ov}$ (from ~90 mV/dec. to ~60 mV/dec.) is observed under these slightly more alkaline conditions. Comparing Figure 74 and Figure 75, it can be noticed that under the same environmental conditions the $k_{0,a}$ in the transition range is much lower than that in the active range. Additionally, observing a greater $b_{a,ov}$ and a smaller α_a in the transition domain as compared to the active one

(compare Figure 74 (b & c) with Figure 75 (b & c)) is also consistent with the argument that a kinetic retardation phenomenon is taking place in the transition range that decelerates the overall anodic reaction. This retardation basically relates to the aforesaid *s-shape* region of the sweeps where a slight current decay appeared in the anodic potentiodynamic sweeps.

Although an enhancement of the reaction rate for anodic dissolution with respect to OH^- are seen up to pH 5 in all test conditions (see data in Table 20), a change in such dependency occurs starting from pH 6 where a sluggishness of the reaction rate was observed under all experimental conditions (for both the active and transition states). In contrast to the fundamental assumptions made by Bockris [20] or Heusler [21] about the first or second order of rate dependency on OH^- , it has been argued that such a direct proportionality to OH^- is more legitimate for more acidic media (particularly when pH is less than or equal to 4) [73, 106]. This is due to approaching saturation of the surface with OH^- , and therefore the dependence drops off [106].

7.8.1.2. Water Chemistry and the Cathodic Reactions. To model the anodic sweeps over the entire range of potentials in the vicinity of OCP, the effect of cathodic reaction is also needed to be taken into account since the measured currents on polarization curves are actually the net values. Figure 76 compares the cathodic potentiodynamic sweeps of pure iron in 2.9 wt.% NaCl in both strong and weak acids at different solution pH values.



Figure 76. Experimental cathodic potentiodynamic sweeps for pure iron in 2.9 wt.% NaCl (0.55 M) solution sparged with (a) 0.97 bar N_2 and (b) 0.97 bar CO_2 at different pH values, T = 25 °C, scan rate: 0.5 mV/sec

A similar method of math computation as implemented in ICMT's FREECORPTM software [126], was followed to model the cathodic current density (i_c) by assuming the ideal solution situation. A few of the empirical equations and the rate expressions used for modeling the aqueous chemistry and describing the equilibrium constants of hydration/dissociation reactions (the reactions were listed in Section 2.5) are presented below in Table 21.

Table 21. Summary of the equations, constants, and reference values used to model the

Name	Equations	Constants/Ref. values
Empirical correlation s to calculate equilibriu m constants	$\begin{array}{lll} & K_{sol} = \frac{14.5}{1.00258} \times 10^{-(2.27+5.65\times10^{-3}T_f - 8.06\times10^{-6}T_f^2 + 0.075I} \\ & K_{hyd} = 2.58\times10^{-3} \\ & K_{ca} = 387.6\times \\ & 10^{-(6.41-1.594\times10^{-3}T_f + 8.52\times10^{-6}T_f^2 - 3.07\times10^{-5}p - 0.4772I^{0.5} + 0.1181} \\ & K_{bi} = \\ & 10^{-(10.61-4.97\times10^{-3}T_f + 1.331\times10^{-5}T_f^2 - 2.624\times10^{-5}p - 1.66I^{0.5} + 0.3466} \\ & K_{wa} = 10^{-(29.3868-0.0737549T_k + 7.47881\times10^{-5}T_k^2)} \end{array}$	 <i>T_f</i>: <i>Temperature in</i>°F For equilibrium constants and the corresponding reactions in Section 2.5
H ⁺ reduction	$ \begin{array}{l} \succ I = 0.5 \sum_{i} c_{i} z_{i}^{2} \\ \hline i_{H}^{-1} = i_{\alpha,H}^{-1} + i_{lim,H}^{-1} \\ \Rightarrow i_{\alpha,H}^{-1} = i_{0,H}^{-1} + i_{lim,H}^{-\eta} \\ \hline i_{\alpha,H}^{-1} = i_{0,H}^{-1} \times 10^{-\eta} / b_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline b_{c}^{-1} = 2.303 RT / F \alpha_{c} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} pH - \frac{2.303 RT}{2F} log p_{H_{2}} \\ \hline c_{rev,H}^{-1} = \frac{-2.303 RT}{F} r_{ref} r_{ref} \\ \hline c_{rev,H}^{-1} = F k_{m,H} + c_{H_{1}} \\ \hline c_{rev,H_{1}}^{-1} = F k_{m,H_{1}} \\ \hline c_{rev,H_{1}}^{-1} $	• $T_k: Temperature in K$ • $T_c: Temperature in °C$ • $i_0^{ref} = 0.03 A/m^2$ • $T_{ref} = 293 K$ • $c_{H^{+,ref}} = 10^{-4} mol/L$ • $\Delta H = 30 \frac{kJ}{mol}$ • $D_{ref,H^+} = 9.31 \times 10^{-9} \frac{m^2}{s}$ • $\mu_{ref} = 1.002 \frac{kg}{m.s}$
H ₂ O reduction	$ i_{H_20} = i_{0,H_20} \times 10^{-\eta/b_c} $ $ i_{0,H_20} = i_0^{ref} \left({}^{C_H +}/{}_{C_H +,ref} \right)^{-0.5} \times e^{\frac{\Delta H}{R} \left(T^{-1} - T_{ref}^{-1} \right)} $	• $T_{ref} = 293 K$ • $i_0^{ref} = 2 \times 10^{-5} \frac{A}{m^2}$ • $c_{H^{+,ref}} = 10^{-4} mol/L$ • $\Delta H = 30 \frac{kJ}{mol}$
H ₂ CO ₃ reduction	$ \begin{split} & i_{H_{2}CO_{3}}^{-1} = i_{\alpha,H_{2}CO_{3}}^{-1} + i_{lim,H_{2}CO_{3}}^{-1} \\ & \downarrow i_{\alpha,H_{2}CO_{3}} = i_{0,H_{2}CO_{3}} \times 10^{-\eta/b_{c}} \\ & \downarrow b_{c} = 2.303RT/F_{\alpha_{c}} , E_{rev} = \frac{-2.303RT}{F}pH - \frac{2.303RT}{2F}logp_{H_{2}} \\ & \downarrow i_{0,H_{2}CO_{3}} = i_{0}^{ref} \left({}^{CH_{2}CO_{3}}/c_{H_{2}CO_{3},ref} \right)^{0.5} \left({}^{C}H^{+}/c_{H^{+},ref} \right)^{-0.5} \times e^{\frac{\Delta H}{R}(T^{-1} - T_{ref}^{-1})} \\ & \downarrow i_{lim,H_{2}CO_{3}} = Fc_{CO_{2}}(D_{H_{2}CO_{3}}K_{hyd}k_{hyd}^{f})^{0.5} \\ & k_{hvd}^{f} = 10^{329.85 - 110.541 \times \log(T_{K} - 17265.4/T_{K})} \end{split} $	• T_c : Temperature in K • $i_0^{ref} = 0.014 \ A/m^2$ • $T_{ref} = 293 \ K$ • $C_{H_2CO_{3,ref}} = 10^{-4} \ mol/L$ • $\Delta H = 50 \ kJ/mol$ • $D_{ref,H_2CO_3} = 2 \times 10^{-9} \ m^2/s$

cathodic reactions [126]

Figure 77 represents the final modeling results of the cathodic sweeps for iron in 2.9 wt.% NaCl solution at different concentrations in both strong and weak acid environments.



Figure 77. Modeled cathodic potentiodynamic sweeps for pure iron in 2.9 wt.% NaCl (0.55 M) solution sparged with (a) 0.97 bar N_2 and (b) 0.97 bar CO_2 at different pH values, T = 25 °C, scan rate: 0.5 mV/sec

Comparing Figure 76 with Figure 77, there is an acceptable level of agreement between experimental data and model predictions in terms of the value of OCP and the range of the limiting current density (~ $3-7 \text{ A/m}^2$). The present dissertation did not aim to engage with developing an elaborate model for the cathodic reactions, as the focus is on the anodic sweeps. The abovementioned practice was done only because the net anodic sweep intrinsically possesses the influence of cathodic formulations in it ($i_{net,a} = |i_a - i_c|$), particularly close to the OCP. Thus, we also needed to include an approximate estimation of the cathodic current to make the correction and capture the entire anodic sweeps at the potential ranges equal to or above OCP (Section 7.8.1.3).

7.8.1.3. Net Anodic Current. As just mentioned, the measured values in the polarization curves are in fact the net values. In other words, the measured net anodic sweep is the difference between the anodic and the cathodic current [8]:

$$i_{net,a} = |i_a - i_c| \tag{108}$$

where $i_{net,a}$ is the net anodic current over the entire range of potential from OCP to more positive values that also encompass the influence of cathodic reactions. i_c is the pure cathodic current density defined by the equations in Section 7.8.1.2. Similarly, i_a is the pure anodic current density described according to the equations presented in Sections 7.7.2 and 7.8.1.1. To obtain the net anodic sweeps, the pure anodic and cathodic current densities were modeled according to the data set listed in Table 19 and Table 21, respectively. After incorporating the effect of the cathodic reactions, in some cases, a few of the kinetic rate constants listed in Table 19 were further slightly tuned to obtain a better match with experimental sweeps (bolded and marked with ‡). The updated Table 22 represents the input dataset needed to reproduce the anodic sweep over the entire range of potentials (from OCP to more positive potentials). In Table 22, b_i is presented in V/dec. and $k_{0,i}$ is in mol.m⁻².s⁻¹.

Table 22. Summary of the rate constants at different test conditions to model net anodic

Condition	k 0,1	b 1	k0,2	b2	k 0,3	b3	k0,-3,act.	b-3,act.	k0,-3,trams.	b-3,trans.	k 0,4	b 4
Fe, pH4, N ₂	4.9×10-2	0.12± 0.02	1.57 ×10 ⁻¹	0.26± 0.09	1.03 ×10-3	0.34± 0.1	1.3 ×10 ⁻²⁰	-0.028	1.63 ×10 ⁹	0.021	3.3 ×10-2	0.19± 0.02
Fe, pH5, N ₂	5.3 ×10 ⁻²	0.12± 0.03‡	1.57 ×10 ⁻¹	0.26± 0.09	2.10 ×10-3	0.33± 0.03	4.1 ×10 ⁻¹⁷	-0.051	1.30 ×10 ⁵	0.035	3.1×10-2	0.19± 0.04
Fe, pH6, N ₂	8.5 ×10 ⁻²	0.12± 0.06	1.57 ×10 ⁻¹	0.26± 0.09	9.26 ×10 ⁻³	0.33± 0.1	5.1 ×10-9	-0.058	1.84 ×10 ²	0.023	1.5 ×10-4	0.19± 0.03
Fe, pH4, CO ₂	6.5 ×10 ⁻² ‡	0.12± 0.02‡	1.63 ×10 ⁻¹	0.26± 0.09	1.29 ×10-3	0.31± 0.1	1.3 ×10 ⁻¹²	-0.064	1.37 ×10 ⁵	0.028	1.95 ×10-2	0.24± 0.02
Fe, pH5, CO ₂	2.5 ×10 ⁻¹	0.11± 0.03‡	1.63 ×10 ⁻¹	0.26± 0.09	6.30 ×10 ⁻³	0.32± 0.2	1.1 ×10 ⁻¹¹	-0.075	5×10 ⁸ ‡	0.027	1.9×10-2	0.28± 0.01
Fe, pH6, CO ₂	4.1 ×10°	0.1± 0.02‡	1.63 ×10 ⁻¹	0.135 ±0.09	2.50×10 ¹	0.35± 0.2	5.5 ×10-6	-0.076	1.00×10 ¹⁴ ‡	0.030	1.7×10-2	0.29± 0.01

current during iron dissolution (25 °C)

To quicken the model fitting and the parametric computations, MATLAB R2022a software was utilized. To distinguish strong from weak acid conditions, a simple binary prompt was created in MATLAB R2022a. The final modeling results of the net anodic sweep after implementing the input variables (Table 22) to the equations described in Sections 7.7.2, are shown in Figure 78. The comparison between the modeled (dashed blue lines) *vs.* the experimental (red solid lines) net anodic sweeps shows a reasonable match between the model and experiment at different environmental conditions.



anodic sweeps of pure iron in (a–c) N₂-sparged pH 4, 5, 6, and (d–f) CO₂-sparged, pH 4, 5, 6, respectively

The corrosion rate of iron in the model was also predicted and mentioned in Figure 78 according to the following Eq. 109 [127]:

$$CR = C \times i_{corr.} \tag{109}$$

where *CR* and $i_{corr.}$ are corrosion rate in mm/y and the corrosion current density in A/m², respectively. *C* is a material-dependent factor and for iron or steel is equal to 1.155.

7.8.2. Effect of pH and CO₂ on the Kinetics of the Elementary Steps

No previous work has investigated the impact of pH and CO₂ on the kinetics of the individual elementary reactions within the theoretical framework presented in this study (Figure 79).



Figure 79. The theoretical scheme introduced in this study (repetition of Figure 51)

As mentioned in section 7.5, it is important to keep in mind that although step 4 in Figure 79 could potentially be broken down to other sub-elementary steps, for the sake of keeping this scheme less complicated, step 4 with two electrons being transferred is considered as a single building block. The objective in the present work was to understand how to couple two theories of non-catalytic and catalytic dissolution into a single scheme without adding unnecessary complications. Another point to mention is that all elementary steps in the theory presented herein (Figure 79) are electrochemical steps. Therefore, it is reasonable to assume that their kinetics depend on potentialIn this section, further interpretation of the kinetic rate constants obtained in Section 7.8.1.1, will be carried out so that the readers could readily recognize the exact influence of pH and CO₂ on the hidden trend of the data presented in Table 19. As discussed in Section 7.7.1, it was presumed that the kinetics of non-catalytic dissolution of $Fe(I)_{ads.}$ ($k_{0,2}$) do not depend on pH. A similar assumption was also made by Keddam, *et al.* [37]. As shown in Figure 80, in strong acids with increasing pH, no remarkable change in the kinetics of $Fe(I)_{ads.}$ formation ($k_{0,1}$) occurred and $k_{0,1}$ was always in a range of $6.2 \times 10^{-2} \pm 0.02$ mol/m².s. However, in the presence of CO₂, increasing pH from 4 to pH 6 could significantly increase $k_{0,1}$ from 0.055 to 4.1 (~ 65 times). The impact of CO₂ on $k_{0,1}$ enhancement was observed more clearly at higher pH. In strong acids, a slight increase of $k_{0,1}$ with pH was observed, but the increment in the case of weak acids was marked. This finding is consistent with those of Keddam, *et al.* [37], who reported a shift of $k_{0,1}$ with pH in strong acids.



Figure 80. Effect of pH and CO₂ on $k_{0,1}$ (kinetic of Fe(I)_{ads.} formation) at 25 °C





Figure 81. Effect of pH and CO₂ on kinetics of $Fe(I)_{ads.}$ conversion to $Fe(II)_{ads.}^*$ in (a) forward direction ($k_{0,3}$), (b) backward direction in the active domain ($k_{0,-3a}$), and (c) backward direction in the transition domain ($k_{0,-3t}$) at 25 °C

Although the effect of CO₂ is shown to increase the rate of $Fe(I)_{ads.}$ conversion to $Fe(II)_{ads.}^*$ in both forward and backward directions, its contribution in accelerating this step in the reverse direction is dominant. This influence becomes more significant at pH

6, while at pH 4 and 5 a slighter increase of $k_{0,-3}$ due to CO₂ is seen. Interestingly, a similar trend in terms of the influence of CO₂ was also seen in the case of $k_{0,1}$ (Figure 80), where $k_{0,1}$ augmentation was more marked at higher pH. Taken together, it seems that the impact of CO₂ on the variation of $k_{0,1}$, $k_{0,3}$, and $k_{0,-3}$ becomes more substantial as we go to higher pH. This could lead to observing a more discernible impact of CO₂ on anodic sweeps as the solution becomes less acidic (as shown in Figure 82).



Figure 82. Effect of CO_2 on experimental and modeled (black solid lines) anodic sweeps for iron in (a) pH 4, (b) pH 5, and (c) pH 6 at 25 °C

From the data in Figure 80 and Figure 81 it is apparent that as pH was changed or CO₂ was introduced, the change of the kinetic rate constants related to the transition path

 $(i.e., Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$ equilibrium) was more marked than other elementary steps (*i.e.*, steps 1, 2, and 4). Augmentation of $k_{0,3}$ with pH in strong acids was also in agreement with what was reported by Keddam, *et al.* [37]. In strong acids, there is a decreasing trend of $k_{0,-3}$ in the transition range of potentials ($k_{0,-3t}$), while a reverse increasing trend for $k_{0,-3t}$ is seen in the case of weak acids (Figure 81 (c)). It seems that the role of CO₂ on $k_{0,-3t}$ is critical and requires further elaboration and justification.

To better identify the effect of the $k_{0,3}$ and $k_{0,-3}$ on the "s-shape" curvature of the sweeps Figure 83 illustrates a few sets of modeled anodic sweeps for different input parameters. As shown in Figure 83 (a), increasing $k_{0,3}$ moves the sweeps toward higher current densities and intensifies the appearance of the "s-shape" transition domain, while increasing $k_{0,-3a}$ has apparently a reverse effect. By increasing $k_{0,-3a}$, the nose area of the sweep starts to disappear. This is basically because the creation of the catalytic species on the surface is slowed down. These results suggest that when step 3 (in Figure 79) is favored in the forward direction (*i.e.*, dominant conversion of $Fe(I)_{ads.}$ to $Fe(II)_{ads.}^*$), the higher surface coverage of catalytic $Fe(II)_{ads.}^*$ intermediate leads to a more noticeable twist of the sweep. In other words, the more step 3 (in Figure 79) is derived in the forward direction, the more remarkable "s-shape" behavior is seen owing to a rapid formation of catalytic $Fe(II)_{ads.}^*$. Neither $k_{0,3}$ nor $k_{0,-3}$ has any impact on the prepassivation range. It is noteworthy that similar to $k_{0,-3a}$, increasing $k_{0,-3t}$ also retards the sweeps toward the lower currents but without affecting the characteristics of the sweeps in the active domain. In contrast to $k_{0,-3a}$, increment of $k_{0,-3t}$ does not fade the "s-shape"

feature, instead, it tends to reposition the entire transition range and move it toward lower overpotentials and current densities.



Figure 83. Modeled anodic sweeps for different input variables of (a) $k_{0,3}$, (b) $k_{0,-3a}$, and (c) $k_{0,-3t}$ (other input variables for modeling remained unchanged as $k_{0,1} = 4.12 \times 10^{0}$, $b_{1} = 0.10$, $k_{0,2} = 1.63 \times 10^{-1}$, $b_{2} = 0.135$, $k_{0,4} = 1.7 \times 10^{-2}$, $b_{4} = 0.287$ for pH 6: weak acid, 25 °C)

As seen in Figure 81 (c), in weak acids the enhancement of $k_{0,-3t}$ with pH is substantial, *i.e.*, Path 2 is suppressed in weak acid. Furthermore, by increasing $k_{0,-3t}$ a

shrinkage of the transition segment of the sweep is seen (Figure 83 (c)). The shrinkage of the transition domain observed in the experimental sweeps (Figure 82 (c)) actually stems from the marked increment of $k_{0,-3t}$ in the presence of CO₂. This effect was not detected in the case of strong acids.

The bar plot in Figure 84 represents the effect of pH and CO₂ on the kinetics of catalytic dissolution of iron ($k_{0,4}$) at 25 °C. The presence of CO₂ was not observed to influence the rate of catalytic dissolution over the pH range from 4 to 6, but a noticeable decrease in the rate of this step was observed in strong acids only at pH 6. A sudden decrease of $k_{0,4}$ could be noted as a distinct semi-passivation nose in the anodic sweep seen at pH 6 in strong acid (See Figure 62 (a) and Figure 82). This is consistent with those of Keddam, *et al.* [37], who also reported a decreasing trend for $k_{0,4}$ with increasing pH in strong acids.



Figure 84. Effect of pH and CO₂ on $k_{0,4}$ (kinetic of catalytic iron dissolution) at 25 °C

Figure 85 shows how changing $k_{0,4}$ could influence the semi-passivation feature of the anodic sweep at 25 °C.



Figure 85. Modeled anodic sweeps for different input variables of $k_{0,4}$ ($k_{0,1} = 8.5 \times 10^{-2}$, $b_1 = 0.121$, $k_{0,2} = 1.57 \times 10^{-1}$, $b_2 = 0.258$, $k_{0,3} = 9.2 \times 10^{-3}$, $b_3 = 0.33$, $k_{0,-3a} = 5.08 \times 10^{-9}$, $b_{-3,a} = -0.058$, $k_{0,-3t} = 1.84 \times 10^2$, $b_{-3,t} = 0.023$ for pH 6: strong acid, 25 °C)

By increasing $k_{0,4}$ the nose of the sweeps tends to disappear since higher $k_{0,4}$ derives step 4 in favor of more catalytic dissolution of iron, which in turn leads to a slighter twist due to the passivation. During the experimental measurements, a marked change in the feature of the anodic sweeps in the form of a segment with a very large Tafel slope followed by a significant maximum was noticed only in strong acids with a pH equal to 6 (Figure 82 (c) and Figure 62 (a)). Observing a sector of the sweep with a high anodic Tafel slope could stem from the formation of an impending passivation layer at this high level of pH [13, 107]. This huge shift of behavior at 6 (or 5.5) is explainable

according to the variation of $k_{0,4}$ as shown in Figure 84. As seen in Figure 84, $k_{0,4}$ remains almost unaffected under different conditions, except at pH 6 in strong acids where a sudden drop of $k_{0,4}$ occurs.

To summarize, Table 23 highlights the key information concerning the effect of pH and CO₂ on the kinetics of the elementary steps.

Table 23. Summary of the effect of pH and CO_2 on the kinetics of the elementary steps

	Step 1	Step 2	Step 3	Step -3	Step 4
CO ₂	Affected by CO2	No effect	Significantly affected by CO ₂	Significantly affected by CO ₂	No effect
рН	No effect	No effect	Slightly affected by pH	Significantly affected by pH	Not affected by pH. A sudden drop was observed at pH 6 in strong acid

Step 1: Fe(I)ads. formation

Step 2: Non-catalytic dissolution of Fe(I)ads.

Step 3/-3: Fe(I)ads. conversion to Fe(II)ads.*

Step 4: Catalytic iron dissolution

As shown in Table 23, the effect of CO_2 and pH on elementary steps 1 and 3 (in Figure 79) are more noteworthy. It could be seen from the data in Table 19 that b_i or Tafel value of the individual steps remained almost unaffected at different pH in both strong and weak acid environments. Table 24 represents the summary of the average b_i values at different experimental conditions at 25 °C. These b_{ave} values were calculated by averaging all b_i at three different pH 4, 5, and 6 for strong and weak acids.

	b 1	b ₂	b 3	b -3,a	b -3,t	b 4
b _{ave.}	0.122	0.257	0.330	-0.058	0.027	0.23
(V/dec.)	±0.01	±0.01	±0.02	±0.01	±0.005	±0.05

Table 24. Average Tafel values among all experimental conditions at 25 °C

The relative errors for b_i values as shown in Table 24, are insignificant implying that although pH and CO₂ affect the kinetics of the steps by altering $k_{0,i}$ values, they do not change the reaction path of individual steps. A possible explanation for the slight change of b_i observed under certain experimental conditions could stem from a slight change of β factor [7,37, 112]. From Section 7.7.2, β was a constant linking the fraction of the surface coverage to the surface concentration of the chemisorbed species [37].

7.8.3. Effect of pH and CO₂ on Formation of Non-Catalytic/Catalytic Intermediates

In this section, it will be discussed how the pH and CO₂ can influence the isotherms of θ_1 (fraction of surface coverage with non-catalytic $Fe(I)_{ads}$) and θ_2 (fraction of surface coverage with catalytic $Fe(II)_{ads}^*$). The steady-state isotherms of θ_1 and θ_2 were simulated using Eqs. (98 & 99), respectively (see Section 7.7.2) and using the kinetic rate constants listed in Table 22 at different experimental conditions. To better understand the origin of the appearance of the "*s-shape*" region in the anodic potentiodynamic sweeps, the modeled anodic sweep and the corresponding variation of θ_1 and θ_2 on a shared potential-axis plot is shown in Figure 86 for pure iron dissolution in weak acid (pH 4, 25 °C).



Figure 86. (a) Modeled polarization curve (b) the corresponding variation of θ_1 and θ_2 during iron dissolution at pH 4 in weak acid (25 °C) in the present study, and (c) comparison with the isotherms θ_i reported by Keddam in strong acid pH 5 [37]

A few important conclusions could be made from Figure 86:

• θ_1 increases initially implying that the non-catalytic complex of $Fe(I)_{ads}$ is produced firstly as potential is changed in the more positive direction. This is the first intermediate forming at the surface, which is consistent with Bockris' mechanism [20]. Subsequently, it reaches a maximum (Max θ_1). Max θ_1 is coincident with an inflection point in the anodic sweep. At positive enough overpotentials, the catalytic $Fe(II)_{ads}^*$ intermediate (θ_2) "kicks in". When the contribution of θ_1 becomes negligible compared to θ_2 , a retardation in the current density is obtained (initiation of the transition domain in anodic sweeps, *i.e.*, *s-shape* region).

• The transition domain of the anodic polarization (Max I) takes place when the surface coverage of the catalytic $Fe(II)_{ads}^*$ intermediate is maximum (Max θ_2). In addition, Max θ_2 is coincident with Min θ_1 , indicating that the current decay in the transition domain (*i.e.*, *s-shape* or Max I) occurs once the coverage with catalytic $Fe(II)_{ads}^*$ is maximum and the coverage with non-catalytic is $Fe(I)_{ads}$ minimum. The more intense drop of θ_1 (deeper Min θ_1), the more noticeable the "*s-shape*" nose will appear in the anodic sweeps. Taken together, this suggests that the transition domain occurs due to the buildup of the catalytic $Fe(II)_{ads}^*$ intermediate once the surface coverage of non-catalytic $Fe(I)_{ads}$ becomes negligible compared to it.

• The intersection point of θ_1 and θ_2 at high enough potentials is coincident with the initiation of the pre-passivation region in the anodic polarization. In the other words, the pre-passivation range is due to the repression of $Fe(II)_{ads}^*$ intermediate at high enough overpotentials.

• About the variation of θ_1 as a function of potential, as it is seen in Figure 86 (b), it seems like at Min θ_1 , θ_1 starts to "take over" and increase again to compensate for the decrease in θ_2 . Remember that only two intermediates were included in the model to

reduce the unnecessary complication of the theory. So, this increase in θ_1 could mean that another third intermediate is increasing its coverage, which is in this model captured as an increase in θ_1 . Comparing the variation of θ_1 and θ_2 with what was reported by Keddam [37]. for three intermediates (θ_1 , θ_2 , and θ_3 in Figure 86 (c)), θ_1 in Figure 86 (b) denotes the θ_1 ' (the red solid line in Figure 86 (c)). In another word, the lack of θ_3 (as hypothesized by Keddam [37]) is compensated by θ_1 in our model. Both viewpoints are legitimate, consistent, and based on identical perspectives except that the present one is based on a systematic approximation for kinetic rate constants.

Figure 87 shows the effect of pH on the variation of θ_1 and θ_2 as a function of the electrode potential for iron at 25 °C in weak acid.



Figure 87. *Variation of* θ_1 *(solid lines) and* θ_2 *(dashed lines) as a function of potential at different solution pH values for pure iron in (a) strong and (b) weak acid (25 °C)*

The Min θ_1 points are shallower in weak acid as compared to strong acid indicating that the current retardation in the transition range of the anodic sweeps is less

significant when the solution is sparged with CO₂. In other words, in weak acids, the tendency for the formation of $Fe(II)_{ads}^*$ is less than that in strong acids. This conclusion can also be made by comparing the full width at half maximum (FWHM) of θ_2 , when the *FWHM* of θ_2 in strong acids is greater than those in weak acids. The shrinkage of the transition domain by increasing the pH in weak acids (see the polarization curves in Figure 62) stems from θ_l increment at higher pH (Figure 87 (b)). As pH increases, the potential of Max peak θ_2 (Min θ_1) shifts to more negative values, thereby shifting the Max I transition toward negative potentials. Furthermore, by increasing pH in weak acids, the slight retardation of θ_2 is coinciding with the lesser drop of θ_1 , both leading to the disappearance of the transition range in the weak acids at higher pH. To better identify the influence of CO₂, Figure 88 illustrates the effect of CO₂ on the behavior of θ_1 and θ_2 at three different pH values. Regardless of solution pH, θ_1 in weak acids is always greater than that in strong acids, indicating that the tendency for the formation of noncatalytic $Fe(I)_{ads}$ increases as the solution is sparged with CO₂. The increment of θ_I due to CO₂, increases as the solution pH increases. A drop of Max θ_2 due to CO₂ is noticeable in all pH values. Additionally, the drop becomes more remarkable as pH increases. These findings are consistent with our results and discussions presented in Section 7.8.2, where the role of CO₂ became more marked at higher pH. It would be helpful to again recall and compare the following kinetic rate constants presented in Section 7.8.1.3, to better recognize such a substantial impact of CO₂ at pH 6 (Table 25).

Table 25. Effect of CO_2 on the kinetic rate constants of steps 1 and 3 (in Figure 79)

obtained from the experiment (Section 7.8.1.3)

Condition k0,1		k 0,3	k 0,-3,act.	K0,-3,trams.	k 0,4
Fe, pH6, N ₂	8.5 ×10 ⁻²	9.26 ×10 ⁻³	5.1 ×10 ⁻⁹	1.84×10^{2}	1.5×10^{-4}
Fe, pH6, CO ₂	4.1 ×10 ⁰	2.50×10 ¹	5.5 ×10 ⁻⁶	1.00×10^{14}	1.7×10^{-2}

Step 1: $Fe+OH \rightarrow Fe(I)_{ads.} + e^-$

Step 3/-3: $Fe(I)_{ads.} \rightleftharpoons Fe(II)_{ads.} *+e^-$

Step 4: $Fe+Fe(II)_{ads.} * \rightarrow Fe(II)+Fe(II)_{ads.} * + 2e^{-1}$



Figure 88. Influence of CO_2 on θ_1 (solid lines) and θ_2 (dashed lines) at (a) pH 4, (b) pH 5, and (c) pH 6 for pure iron at 25 °C

 CO_2 increased the rate of $Fe(I)_{ads}$ formation, which led to the shift of current in the active range of the anodic sweeps as seen in Figure 82 (c). At the same time, in the

presence of CO₂, $k_{0,4}$ increased drastically, which means an enhancement of the current in the transition and pre-passivation region of the sweeps is expected (as seen in Figure 82 (c)). CO₂ also boosted the kinetics of the elementary step 3 (in Figure 79) in both forward and backward directions, however, its contribution in pushing step 3 (in Figure 79) in the reverse direction dominates. A possible explanation for this could be achieved by recalling the nature of $Fe(I)_{ads}$ and $Fe(II)_{ads}^*$ species and the plausible buffering effect of carbonic acid as follows. According to the literature [13] and our discussions in Chapter 5, the most thermodynamically feasible intermediates that could represent $Fe(I)_{ads}$ and $Fe(II)_{ads}^*$ complexes are $FeOH_{ads}$ and $Fe(OH)_{2,ads}$, respectively. Thus, another way of writing step 3 (in Figure 79) in the reverse direction would be:

$$Fe(OH)_{2,ads} + H^+ + e^{-} \xrightarrow{\kappa_{0,-3}} FeOH_{ads} + H_2O$$
(110)

After the dissolution of CO₂ in the electrolyte, the homogeneous dissociation of H_2CO_3 can provide a reservoir for H^+ [128], thereby providing more H^+ ions in access for this step (Eq. 110). In this study, the possible effect of the mass transfer of H^+ ions on the kinetics of the reaction is assumed to be negligible within the range of our experimental measurements.

Taken together, these results suggest that the effect of CO_2 on enhancing the kinetics of anodic dissolution is explainable according to four key facts:

• The role of CO₂ in accelerating the formation of non-catalytic *Fe*(*I*)_{*ads*} (step 1 in Figure 79).

• The buffering nature of carbonic acid and its subsequent impact on suppressing the catalytic Path 2 in Figure 79 (i.e., less generation of $Fe(II)_{ads.}^*$).
• Its effect in increasing $k_{0,4}$. This effect is discernible only at high enough pH conditions (usually greater than 5.5 or 6).

• Although this mechanistic impact of CO₂ on the kinetics of the iron dissolution always remains the same, its effect becomes more discernible at higher pH.

• The transition and so called "*s-shape*" region of the anodic potentiodynamic sweep is mainly due to the formation of $Fe(II)_{ads}^*$. CO₂ retards the formation of $Fe(II)_{ads}^*$, by forcing the elementary step 3 ($Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$) in the reverse direction, thereby shrinking the transition range of the anodic sweeps.

7.9. Summary

In this chapter, a systematic methodology was introduced to first discretize the overall reaction of anodic dissolution into a few elementary steps, then approximate the kinetic rate constants for the individual step. This led to the establishment of a database used for modeling the anodic potentiodynamic sweeps. A reasonable consistency between the model and experimental sweeps under different experimental conditions was obtained, which validates the legitimacy of the presented approach and the corresponding kinetic database. According to the quantitative analysis accomplished by relying on the abovementioned database, the following conclusions can be drawn:

The shrinkage, expansion, location, and general feature of the "s-shape" region in the anodic sweep are controlled mainly by the kinetic of Fe(I)_{ads.} ↔ Fe(II)_{ads.}* equilibrium. The transition and so-called "s-shape" region of the anodic potentiodynamic sweep is mainly due to the formation of Fe(II)_{ads}*.

- Although the effect of CO₂ is shown to increase the rate of *Fe(I)_{ads.}* conversion to *Fe(II)_{ads.}** in both forward and backward directions, its contribution in forcing this step in the reverse direction dominated. In other words, CO₂ suppressed the catalytic Path 2 (*i.e.*, it decelerated the formation of *Fe(II)_{ads.}**). This effect seems to be related to the buffering nature of carbonic acid.
- A short summary of the effect of pH ??
- The current decay in the transition domain (*i.e.*, *s-shape* or Max I) occurred when the coverage with catalytic *Fe(II)_{ads}*^{*} is maximum and the coverage with noncatalytic is *Fe(I)_{ads}* minimum. In other words, the *s-shape* appearance stems from the formation of catalytic *Fe(II)_{ads}*^{*}.
- Regardless of the solution pH, θ₁ in weak acids was always greater than that in strong acids, indicating that the tendency for the formation of non-catalytic *Fe(I)_{ads}* increases as the solution is sparged with CO₂.

Chapter 8: Effect of Temperature and Electrode Materials on Anodic Dissolution in CO₂ Environments

8.1. Introduction

In this chapter, a similar methodology described in Chapter 7 is followed to investigate the influence of temperature and steel types on the kinetics of iron dissolution. The same procedure based on the transient analysis as explained in Chapter 7, is employed to determine the rate constants of the elementary steps (Figure 79). Then, the steady-state anodic polarizations of pure iron at different temperatures were modeled using the extracted rate constants. Similarly, the steady-state potentiodynamic sweeps for X65 and 2% Cr steel were modeled using the kinetic data set extracted from transient measurements.

Very little is known about the impact of the temperature and steel type on the kinetics of individual elementary steps and the mechanistic aspects of the anodic dissolution process. Several researchers have reported the temperature dependence of the electrode kinetic factors such as the Tafel slope, symmetry factor, and charge transfer coefficient during iron anodic dissolution [32,64, 129]. Generally, the kinetics of reactions enhances at elevated temperatures, while literature has emerged that offers contradictory findings about the effect of temperature [32, 64]. A considerable amount of literature has been published on the effect of temperature on the rate of the overall reaction without discussing the influence on the reaction sequence of the elementary steps. This indicates that a better understanding of the temperature effect on the mechanism of anodic dissolution needs to be developed.

Additionally, more complexity regarding the reaction mechanism is expected in the case of steel containing alloying elements because a higher number of complex interactions could take place between surface intermediates [39, 40]. Researchers working with Ingham used *in situ* synchrotron X-ray diffraction analysis and, by applying the Avrami expression of crystal growth, successfully modeled the anodic corrosion of steel in CO₂ environments [130–136]. They claimed that the main role of Cr is through introducing Cr^{3+} into the solution which can decrease the FeCO₃ supersaturation factor, thereby catalyzing the siderite nucleation and providing a more protective and adherent corrosion product layer in sweet environments [132]. According to the literature [39,40,137, 138], the dissolution mechanism for the steels with less than 7–10 wt.% alloying element content is similar to that of pure iron, whereas for steels containing more than 7-10 wt.% of alloying elements, a different mechanistic scheme other than that presented in Figure 79 should be applied. For steels with high enough Cr contents (usually > 7 %), Keddam, et al., [39] reported a reaction model of dissolution-passivation based on the interaction between the surface species of iron and chromium [39]. In this scheme, two additional non-catalytic intermediates, namely, Cr(I)ads. and Cr(II)ads., are introduced to the mechanism. These adsorbed species could block the iron pre-passive dissolution according to [39]:

$$i_{blocking} = k_4 \theta_2 (1 - \theta_3^{0.5}) \tag{111}$$

_ _

where θ_3 is the surface coverage with $Cr(II)_{ads.}$. According to the chemical composition of the specimens used in our case (see Table 26), the summation of wt.% of all alloying elements is less than 4 wt.%, therefore, a mechanistic model similar to that for pure iron could be applied for X65, and also 2% Cr steel. However, when alloying element "*A*" is added to iron in a content greater than 7 wt.%, one might need to also incorporate the following elementary steps (Figure 89) in charge balance and mass balance expressions [39, 40].

$$A(I)_{ads} \xrightarrow{k_6} A(II)_{sol} + e^-$$

$$A \xrightarrow{k_5} A(I)_{ads} + e^- \longrightarrow A(I)_{ads} \xrightarrow{k_7} A(II)_{ads} + e^-$$

Figure 89. *The scheme that needs to be incorporated into the model when the content of the alloying element "A" is more than 7% [39]*

Since the concentration of the alloying elements for the specimens used in this study is less than 4 wt.%, a similar scheme presented in Figure 79 and an identical methodology described for pure iron in Chapter 7 is still applicable. Additionally, experiments were conducted at moderate enough temperatures (<45 °C) to ensure no corrosion product layer is formed. Therefore, the proposed mechanistic model is expected to be suitable for investigating the behavior of dissolution within the range of temperatures and for the steel types tested herein. This chapter aims to elucidate the effect of temperature and steel type on the mechanism of iron dissolution through a similar analytical approach as laid out in Chapter 7.

8.2. Objectives

The major objectives of this chapter are to:

- Follow the same style of interpretation and analysis described in Chapter 7 to understand the effect of temperature and steel type on the mechanism of iron anodic dissolution.
- Develop mathematical functions for modeling purposes under different experimental conditions and to discuss the possible source of error and improvement for the introduced models. This function helps us to replace the lookup table data (*e.g.*, Table 22) with simplified functions necessary for modeling the anodic polarization curves.

8.3. Experimental Method

A 2-liter glass cell with a RCE as a working electrode was employed. A ringshaped platinum-coated titanium mesh counter electrode was used for completing the circuit to allow the charge to flow, and an Ag/AgCl reference electrode was used with respect to which all potentials were measured. The ring-shaped counter electrode was used to provide a more symmetric current distribution around the rotating WE. An overview of the experimental setup and test matrix is shown in Figure 90.

<u>A</u>	Demonster	Com I'llow		
3 P	Parameter	Condition		
		25		
	T (± 0.5 °C)	35		
		45		
		Sparged with 0.97 bar N ₂		
	Environment	Sparged with 0.97 bar		
		CO ₂		
		2.9 wt.% (~0.55 M) NaCl		
	Electrolyte	$(R_s \sim 0.78 {\pm} 0.08~\Omega$ for all		
		measurements)		
	рН (±0.02) °С	4.00		
	Test set-up	2L glass cell		
	Motor rotation speed	2000		
		RCE- Pure iron		
	Specimens	RCE- X65		
		RCE- 2% Cr steel		

Figure 90. Overview of the RCE experimental setup and test matrix

Table 26 summarizes the chemical composition of the RCE specimens used in this study.

I able 20	able 20. Chemical composition of KCE specimens										
Steel	Cr	С	Mn	Ni	Si	Mo	Р	v	Al	S	Fe
(wt.%)											
X65	0.25	0.13	1.16	0.29	0.26	0.16	0.009	0.047	-	0.009	balance
2% Cr	1.9	0.042	1.4	0.308	0.254	-	0.008	-	0.022	<	balance
steel										0.003	

 Table 26. Chemical composition of RCE specimens

All experiments and the test procedure were accomplished according to the process explained in Chapter 4. Potentiodynamic sweeps and potentiostatic data with a high sampling rate (~3 microseconds per data point) were conducted using a Gamry potentiostat Reference 600. All potentiodynamic sweeps presented in this work were

corrected for the effect of solution resistance (*iR-drop*). It was important to enhance the speed setting of the potentiostat/galvanostat instrument to be able to capture the data points with a very high sampling rate (in a few microseconds). Each test was repeated at least four times to reduce the statistical uncertainty. Uncertainty for all measurements is reported in this study. All RCE specimens were polished up to 1200-grit, rinsed with deionized water and isopropanol alcohol, then dried with nitrogen gas before every experiment. High-purity N₂ or CO₂ gas was sparged continuously through the test solution to deoxygenate the electrolyte during all measurements, and in the latter case saturate the electrolyte with carbonic species. Diluted NaOH and HCl were used to adjust the pH. Before each measurement, EIS was recorded to assure that the solution resistance was consistent for all measurements and always within the range of $0.78 \pm 0.08 \Omega$.

8.4. Results and Discussion

8.4.1. Modeling

In this section, a similar procedure as described in Section 7.8.1 is followed to first extract the kinetic rate constants during the anodic dissolution of iron and a few types of steel at different temperatures. Then, using the obtained kinetic rate constants, the pure anodic sweeps will be modeled. In Section 8.4.1.3, the net anodic current will be reproduced after incorporating the cathodic reactions into the model. Finally, the model verification will be done to assess the reliability of the proposed methodology in modeling the anodic potentiodynamic sweeps for iron, X65 steel and 2% Cr steel at different temperatures.

8.4.1.1. Obtained Kinetic Rate Constants: Modeling the Anodic

Potentiodynamic Sweeps. First, reproducible experimental anodic potentiodynamic sweeps required collection and analysis. Every measurement was repeated at least four times to ensure reproducibility. Figure 91 shows the experimental anodic sweeps of iron at different temperatures in both N₂- and CO₂-sparged environments. The anodic polarization curves are displaced towards more negative potentials as the temperature increases from 25 °C to 45 °C. Furthermore, the current density increases with increasing temperature at a fixed potential in the active range of potentials. All sweeps were corrected for the effect of solution resistance.



Figure 91. Anodic sweeps for pure iron in 0.55 M NaCl solution sparged with 0.97 bar (a) N_2 and (b) CO_2 at different temperatures, pH = 4, scan rate: 0.5 mV/sec

In the next step, the suitable range of potential perturbation for the subsequent potentiostatic measurements should be specified. Table 27 summarizes the range of active and transition domains where the potential perturbation was carried out.

Table 27. Approximate range for potential perturbation (active or transition) for anodic

Environment	T (°C)	Active range (mV vs. OCP)	Transition range (mV vs. OCP)
Strong acid:	25	60 - 120	125 - 175
N ₂ -sparged	35	60 - 110	120 - 180
	45	60 - 100	110 - 180
Weak acid:	25	60 - 130	135 – 185
CO ₂ -sparged	35	60 - 120	130 - 190
	45	60 - 110	120 - 190

dissolution of iron at different temperatures in both strong and weak acids (pH 4)

Figure 92 represents the reproducible anodic sweeps for different materials in 0.5 M NaCl solution at 25 °C (pH = 4) for both strong and weak acids.



Figure 92. Anodic potentiodynamic sweeps for different materials in 0.55 M NaCl solution sparged with 0.97 bar (a) N_2 and (b) CO_2 , pH = 4, T = 25 °C, scan rate: 0.5 mV/sec

Similarly, the range of active and transition domains where the potential perturbation was carried out is summarized in Table 28. As seen in Figure 92, at higher contents of Cr, the current maximum (Max I) decreases drastically during the alloy dissolution, disappearing the "*s-shape*" transition range.

Environment	Material	Active range (mV vs. OCP)	Transition range (mV vs. OCP)
Strong acid:	Pure Fe	60 - 120	125 – 175
N ₂ -sparged	X65	60 - 120	130 - 170
	1.9 % Cr	70 - 110	120 - 170
Weak acid:	Pure Fe	60 - 130	135 - 185
CO ₂ -sparged	X65	70 - 120	130 - 170
	1.9 % Cr	70 - 110	120 - 170

Table 28. Approximate range for potential perturbation (active or transition) for anodic dissolution for different materials in different environments, T = 25 °C, pH 4

A similar analysis and methodology described in Section 7.7.2 and utilized in Section 7.8.1.1, was followed to estimate the kinetic rate constants for elementary steps at different temperatures for different materials. The corresponding transient data, analytical plots, and regression analysis are presented in Appendix C. Table 29 summarized the computed kinetic rate constants at different temperatures for different steel types at pH 4.

Condition	k _{0,1}	b1	k _{0,2}	b ₂	k _{0,3}	b3	k0,-3,act.	b-3,act.	k0,-3,trams.	b-3,trans.	k _{0,4}	b4
Fe, 25°C, N ₂	4.9×10-2	0.12± 0.02	1.57 ×10-1	0.26± 0.09	1.03 ×10-3	0.34± 0.1	1.3 ×10 ⁻²⁰ *	-0.028*	1.63 ×109	0.021	3.3 ×10-2	0.19± 0.02
Fe, 35°C, N ₂	1.3 ×10-1	0.12± 0.03	1.4×10-1	0.116 ±0.08	9.94 ×10 ⁻⁴	0.39± 0.03	1.21 ×10-20	-0.029	1.65 ×10 ⁹	0.0225	2.56×10-2	0.25± 0.04*
Fe, 45°C, N ₂	5.9 ×10-1*	0.11± 0.06*	3.81 ×102*	0.112 ±0.09	8.97 ×10-4	0.47± 0.1	7.64 ×10 ⁻¹⁴	-0.056	6.75 ×103	0.042	7.15 ×10-1*	0.25± 0.03*
Fe, 25°C, CO ₂	5.5 ×10-2	0.13± 0.02	1.63 ×10-1	0.26± 0.09	1.29 ×10-3	0.31± 0.1	1.3 ×10-12	-0.064	1.37 ×105	0.028	1.95 ×10-2	0.24± 0.02*
Fe, 35°C, CO ₂	1.4×10-1*	0.12± 0.03*	6.54 ×10-1	0.184 ±0.09	9.30 ×10-4	0.436 ±0.2	1.21 ×10-12	-0.066	3.34×105	0.0229	2.61 ×10-2	0.27± 0.01*
Fe, 45°C, CO ₂	7.2 ×10-1*	0.1± 0.02*	2.52 ×10º	0.147 ±0.09	8.27×10-4	0.494 ±0.2	1.0×10-12*	-0.059	6.79×101	0.0606	7.5 ×10-1*	0.24± 0.01
X65, 25 °C, N ₂	9 ×10-2*	0.12± 0.03	8 ×10-2*	0.26± 0.09*	5.82 ×10-3	0.173 ±0.07	1.52 ×10-12	-0.064	4.74×107	0.0244	7.10×10-2	0.165± 0.02*
X65, 25 °C, CO ₂	1.4×10-1*	0.11± 0.02	9.58 ×10-2*	0.27± 0.09*	5.96 ×10-3	0.181 ±0.07	1.11 ×10-10	-0.104*	1.75×109	0.021	6.70×10-2	0.157 ±0.02
2% Cr, 25 °C, N ₂	1.4×10-1*	0.11± 0.01	1.66 ×10-1	0.26± 0.09*	3.92×10-4	0.397 ±0.1	6.38 ×10-14	-0.045	2.32×10 ²	0.0383	3.8×10-2	0.171± 0.01*
2% Cr, 25 °C, CO ₂	2.30 ×10-1*	0.1± 0.03	1.9×10-1	0.25± 0.09	5.83×10-4	0.434 ±0.2	2.56 ×10-11	-0.076*	2.64×103	0.0367	6.22 ×10-2	0.184± 0.01*

Table 29. Summary of the kinetic rate constants for dissolution of Fe, X65, and 2% Cr at

different temperatures (pH 4)

Figure 93 and Figure 94 compare the modeled sweeps with the experimental results. The gray curves represent the experimental data, and the black dashed lines show the model. The exact impact of temperature and steel type on the variation of the rate constants of the elementary step will be discussed in detail in Sections 8.4.2 and 8.4.3, respectively. There is good consistency between the experiment and the modeled sweeps in all three regions of active, transition, and pre-passivation for different experimental conditions. This validates the applicability of the methodology described in Chapter 7 for calculating the kinetic rate constants and subsequent modeling of the anodic sweeps, not only at different pH values for pure iron but also at various temperatures for different materials.



Figure 93. Comparison of the modeled (dashed black lines) vs. experimental (gray color curves) anodic sweeps of pure iron in $(a-c) N_2$ -sparged 25 °C, 35 °C, 45 °C, and $(d-f) CO_2$ -sparged 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 94. Comparison of the modeled (dashed black lines) vs. experimental (gray color curves) anodic sweeps for $(a-c) N_2$ -sparged Fe, X65, 2% Cr steel, and $(d-f) CO_2$ -sparged Fe, X65, 2% Cr steel, respectively (pH 4, 25 °C)

Calculating $k_{0,a}$ and $b_{a,ov}$ in active and transition range of potentials for the overall anodic reaction—Effect of Temperature: A similar analysis that was detailed in Section 7.7.2 (and was applied in Section 7.8.1.1) was followed to estimate the kinetic rate constants of the overall reaction at different temperatures for different steels. The corresponding transient data, analytical plots, and regression analysis are presented in Appendix C. Table 30 represents the influence of temperature on $b_{a,ov}$, $k_{0,a}$, and α_a (in the active ranges of potentials). The corresponding bar plot in Figure 95 shows the variation of kinetic rate constants for the overall reaction as a function of temperature.

Table 30. Effect of temperature on $b_{a,ov}$, $k_{0,a}$, and α_a for the overall anodic reaction of iron dissolution at pH 4

		25 °C		35 °C	45 °C				
Temperature	k _{0,a} (mol/m ² .s)	b _{a,ov.} (mV/dec)	αa	k _{0,a} (mol/m ² .s)	b _{a,ov.} (mV/dec)	αa	k _{0,a} (mol/m ² .s)	b _{a,ov.} (mV/dec)	αa
N ₂ -sparged	5.84	44	1.34	2.06	52.9	1.15	16.18	46.2	1.36
CO ₂ -sparged	9.45	41.9	1.41	4.63	49.0	1.25	2.93	55.5	1.14



Figure 95. Variation of (a) $k_{0, a}$, (b) $b_{a,ov}$, and (c) α_a for the overall anodic reaction of iron in the active domain at different temperatures (pH 4)

As shown in Figure 95, at different temperatures, the CO₂ increases $k_{0,a}$, while a reverse trend takes place at 45 °C. A sudden drop of $k_{0,a}$ at higher temperature is not really physical and might be due to the initiation of a process that could passivate the surface. Further investigation is needed to better understand such a decreasing trend in $k_{0,a}$ by increasing temperature. The highest $k_{0,a}$ was obtained in strong acids at 45 °C. Additionally, considering the data listed in Table 30, at all temperatures the anodic Tafel slope and the anodic charge transfer coefficient (α_a) for the overall reaction are close to about 48±5 mV/dec. and 1.27±0.1, respectively, which is consistent with the theory proposed by Bockris, *et al.* [20]. These values were determined based on the following equation for calculating the charge transfer coefficient described in Section 5.5:

$$\alpha_a = \frac{n_b + \nu n_r}{\nu} - n_r \beta \tag{112}$$

The magnitude of n_b , v, n_r , and β for the reaction sequence of Bockris' are equal to 1, 1, 1, and 0.5, respectively (when the reactions are written in the reduction style), therefore:

$$\alpha_a = \frac{n_b + \nu n_r}{\nu} - n_r \beta = \frac{1 + 1 \times 1}{1} - 1 \times 0.5 = 1.5$$
(113)

$$|b_{a,ov.}| = \frac{2.3RT}{\alpha_a F} = \frac{2.3RT}{1.5F} \sim 40 \frac{mV}{dec}$$
 (114)

Table 31 represents the influence of steel type on $b_{a,ov}$, $k_{0,a}$, and α_a (in the active ranges of potentials). The corresponding bar plot in Figure 96 shows the variation of kinetic rate constants for the overall reaction for different steel types.

(25	°C)
(

		Fe			X65	2% Cr			
Steel type	k _{0,a} (mol/m ² .s)	b _{a,ov.} (mV/dec)	αa	k _{0,a} (mol/m ² .s)	b _{a,ov.} (mV/dec)	αa	k _{0,a} (mol/m ² .s)	b _{a,ov.} (mV/dec)	αa
N ₂ - sparged	5.84	44	1.34	2.19	45.5	1.30	9.70	38.6	1.53
CO ₂ - sparged	9.45	41.9	1.41	4.05	43.4	1.36	1.78	46.0	1.28



Figure 96. Variation of (a) $k_{0,a}$, (b) $b_{a,ov}$, and (c) α_a for the overall anodic reaction for different materials in the active domain at 25 °C (pH 4)

As seen in Figure 96 (a), for pure iron and X65, $k_{0,a}$ in weak acid is greater than that for strong acid. In contrast, for 2% Cr steel, the $k_{0,a}$ in strong acid is greater than that in weak acid. This might be related to the hydrolysis reactions of Cr^{3+} at higher Cr contents and the buffering feature of carbonic acid as a weak acid [139]. Further investigations need to be carried out to understand such an effect. The anodic Tafel slope and the anodic charge transfer coefficient for X65 and 2% Cr steels are about 43±3 mV/dec. and 1.37±0.1, respectively. This indicates that for steels with small amounts of alloying elements (normally when the content of alloying elements is less than 7 wt.% [39,137, 138]), Bockris' theory [20] is still an acceptable mechanism that could reasonably capture the overall reaction kinetics.

8.4.1.2. Cathodic Reactions. Figure 97 and Figure 98 represent the experimental cathodic potentiodynamic sweeps at different temperatures and for different steel types, respectively.



Figure 97. Cathodic potentiodynamic sweeps for pure iron in 0.55 M NaCl solution sparged with 0.97 bar (a) N_2 and (b) CO_2 at different temperatures, pH = 4, scan rate: 0.5 mV/sec



Figure 98. *Cathodic potentiodynamic sweeps for different materials in 0.55 M NaCl* solution sparged with 0.97 bar (a) N_2 and (b) CO_2 , pH = 4, scan rate: 0.5 mV/sec

Presumably, the models for the cathodic reaction do not depend on steel type, therefore, the cathodic sweeps were modeled only at different temperatures. The cathodic sweeps were reproduced according to the mathematical correlations described in Section 7.8.1.2. Figure 99 shows the modeled anodic sweeps at different temperatures at pH 4.



Figure 99. Modeled cathodic potentiodynamic sweeps for pure iron in 2.9 wt.% NaCl (0.55 M) solution sparged with (a) 0.97 bar N_2 and (b) 0.97 bar CO_2 at different temperatures, pH 4, scan rate: 0.5 mV/sec

Comparing Figure 97 and Figure 99, there is an acceptable level of agreement between experimental data and model predictions. The present dissertation did not aim to engage with developing an elaborate model for the cathodic reactions, as the focus is the anodic sweeps. The abovementioned practice was done only because the net anodic sweep always carry the influence of cathodic formulations therein ($i_{net,a} = |i_a - i_c|$), particularly significant close to OCP. Thus, there is also a need to include an approximate estimation of the cathodic current to correct the anodic sweeps at the potential ranges equal to or above OCP (Section 8.4.1.3).

8.4.1.3. Net Anodic Current. As just stated, the measured values in the polarization curves are in fact the net values. In other words, the net anodic sweep is the difference between the anodic and the cathodic current [8]:

$$i_{net,a} = |i_a - i_c| \tag{115}$$

where $i_{net,a}$ is the net anodic current over the entire range of potential from OCP to more positive values that also encompass the influence of cathodic reactions. Parameter i_c is the pure cathodic current density defined by the equations in Section 7.8.1.2. Similarly, i_a is the pure anodic current density (Section 8.4.1.1). To obtain the net anodic sweeps, the pure cathodic and anodic current densities were modeled according to the data sets listed in Table 21 and Table 29, respectively. After incorporating the effect of the cathodic reactions, in some cases, a few of the kinetic rate constants listed in Table 29 were just slightly tuned to obtain a better match with experimental sweeps (bolded and marked with ‡). The updated Table 32 represents the input dataset needed to reproduce the anodic sweep over the entire range of potentials (from OCP and above that). In Table 32, b_i is presented in V/dec. and $k_{0,i}$ is in mol.m⁻².s⁻¹.

Table 32. Summary of the rate constants for Fe, X65, and 2% Cr steel at different

temperatures to mo	del	net ar	odic	current a	luring	iron c	lissol	lution ((pH	[[] 4])
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Condition	k 0,1	bı	k 0,2	b2	k 0,3	b3	k0,-3,act.	b-3,act.	k0,-3,trams.	b -3,trans.	k 0,4	b4
Fe, 25°C, N2	4.9 ×10 ⁻²	0.12± 0.02	1.57 ×10 ⁻¹	0.26± 0.09	1.03 ×10 ⁻³	0.34± 0.1	1.3 ×10 ⁻²⁰	-0.028	1.63 ×10 ⁹	0.021	3.3 ×10 ⁻²	0.19± 0.02
Fe, 35°C, N2	1.3 ×10 ⁻¹	0.12± 0.03	1.4×10 ⁻¹	0.116 ±0.08	9.94 ×10 ⁻⁴	0.39± 0.03	1.21 ×10 ⁻²⁰	-0.029	1.65 ×10 ⁹	0.0225	2.56×10-2	0.25± 0.04
Fe, 45°C, N2	5.9 ×10 ⁻¹	0.11± 0.06	3.81 ×10 ²	0.112 ±0.09	8.97 ×10 ⁻⁴	0.47± 0.1	7.64 ×10 ⁻¹⁴	-0.056	6.75 ×10 ³	0.042	7.15 ×10 ⁻¹	0.25± 0.03
Fe, 25°C, CO ₂	6.5 ×10 ⁻² ‡	0.12± 0.02‡	1.63 ×10 ⁻¹	0.26± 0.09	1.29 ×10 ⁻³	0.31± 0.1	1.3 ×10 ⁻¹²	-0.064	1.37 ×10 ⁵	0.028	1.95 ×10-2	0.24± 0.02
Fe, 35°C, CO ₂	1.4 ×10 ⁻¹	0.12± 0.03	6.54 ×10 ⁻¹	0.184 ±0.09	9.30 ×10 ⁻⁴	0.436 ±0.2	1.21 ×10 ⁻¹²	-0.066	3.34×10 ⁵	0.0229	2.61 ×10 ⁻²	0.27± 0.01
Fe, 45°C, CO ₂	7.2 ×10 ⁻¹	0.1± 0.02	2.52 ×10 ⁰	0.147 ±0.09	8.27×10 ⁻⁴	0.494 ±0.2	1.0 ×10 ⁻¹²	-0.059	6.79×101	0.0606	7.5 ×10 ⁻¹	0.24± 0.01
X65, 25 °C, N ₂	1 ×10 ⁻¹ ‡	0.115± 0.03‡	8 ×10 ⁻²	0.26± 0.09	5.82 ×10 ⁻³	0.173 ±0.07	1.52 ×10 ⁻¹²	-0.064	3×10 ⁷ ‡	0.0244	7.10 ×10 ⁻²	0.165± 0.02
X65, 25 °C, CO ₂	1.2 ×10 ⁻¹ ‡	0.11± 0.02	9.58 ×10 ⁻²	0.27± 0.09	5.96 ×10 ⁻³	0.181 ±0.07	1.11 ×10 ⁻¹⁰	-0.104	1×10°‡	0.021	6.70×10 ⁻²	0.157 ±0.02
2% Cr, 25 °C, N ₂	1.4 ×10 ⁻¹	0.11± 0.01	1.66 ×10-1	0.26± 0.09	3.92×10 ⁻⁴	0.397 ±0.1	6.38 ×10 ⁻¹⁴	-0.045	2.32×10 ²	0.0383	3.8 ×10 ⁻²	0.171± 0.01
2% Cr, 25 °C, CO ₂	2.30 ×10-1	0.1± 0.03	1.9 ×10-1	0.25± 0.09	5.83×10-4	0.434 ±0.2	2.56 ×10 ⁻¹¹	-0.076	2.64×103	0.0367	6.22 ×10 ⁻²	0.184± 0.01

The final modeling results of the net anodic sweep after implementing the input variables (Table 32) to the Eq. 100 are shown in Figure 100 and Figure 101. The comparison between the modeled (dashed blue lines) *vs.* the experimental (red solid lines) net anodic sweeps for different steels at various temperatures shows a reasonable match between the model and experiment.



Figure 100. Comparison of the modeled (blue lines) vs. experimental (red curves) net anodic sweeps of pure iron in NaCl solution at different temperatures in $(a-c) N_2$ sparged and $(d-f) CO_2$ -sparged environment (pH 4)



Figure 101. Comparison of the modeled (blue lines) vs. experimental (red curves) net anodic sweeps for different materials in 2.9 wt.% NaCl solution (a-c) N₂-sparged, and (d-f) CO₂-sparged (pH 4)

8.4.2. Effect of Temperature on the Kinetics of the Elementary Steps

In this section, further interpretation of the kinetic rate constants obtained in Section 8.4.1.1, will be carried out so that readers can readily recognize the exact influence of temperature on the trend of the rate constants presented in Table 29. Figure 102 (a) and (b) represent the effect of temperature on $k_{0,1}$ and $k_{0,2}$, respectively.



Figure 102. Effect of temperature on (a) $k_{0,1}$ (kinetic of $Fe(I)_{ads.}$ formation) and (b) $k_{0,2}$ (non-catalytic dissolution of $Fe(I)_{ads.}$) at pH 4 for pure iron

As seen in Figure 102 (a), the higher temperature increased the rate of $Fe(I)_{ads.}$ formation in both strong and weak acid media. Furthermore, the rate of non-catalytic dissolution of $Fe(I)_{ads.}$ increased at higher temperatures (Figure 102 (b)). The enhancement of $k_{0,2}$ at higher temperatures in strong acids was more significant than that in weak acids. Figure 103 shows the impact of temperature on the kinetics of $Fe(I)_{ads.}$ conversion to $Fe(II)_{ads.}^*$ in both forward and backward directions in strong and weak acid media.



Figure 103. Effect of temperature on the kinetic of $Fe(I)_{ads.}$ conversion to $Fe(II)_{ads.}^*$ in (a) forward direction $(k_{0,3})$, (b) backward direction in the active domain $(k_{0,-3a})$, and (c) backward direction in the transition domain $(k_{0,-3t})$ at pH 4 for pure iron

The change in temperature from 25 °C to 45 °C seems to not influence the conversion of Fe(I)_{ads.} to Fe(II)_{ads.} * in the forward direction ($k_{0,3}$). In addition, the reaction rate of this step in the backward direction ($k_{0,-3}$) remained unaffected by temperature except at 45 °C. An unusual drop of $k_{0,-3}$ is seen at 45 °C (Figure 103 (c)). A possible explanation for this might be that there is a slight change in the mechanism of the elementary step 3 at higher temperatures (starting from 45 °C). The bar plot in Figure 104

represents the effect of temperature on the kinetics of catalytic dissolution of iron ($k_{0,4}$) at pH 4 for both strong and weak acids.



Figure 104. *Effect of temperature on* $k_{0,4}$ *(kinetic of catalytic iron dissolution) at pH4 for pure iron*

As shown in Figure 104, the kinetics of the catalytic dissolution (k_4) increase as temperature increases (especially at 45 °C). Table 33 shows how temperature affects the rate of each elementary step. As the temperature increased, the increase of k_2 and k_4 were more noticeable than other elementary steps in Figure 51 (*i.e.*, 1 and 3). In other words, the higher temperature increased the rate of both non-catalytic (step 2 in Figure 51) and catalytic dissolutions (step 2 in Figure 51) paths. Higher temperature slightly increased k_1 as well, but the effect on k_1 was less notable than that for k_2 or k_4 .

Table 33. Summary of the effect of temperature on the kinetics of the elementary steps in

	Step 1	Step 2	Step 3	Step -3	Step 4
Temperature	Slightly affected	Significantly affected	Unaffected	Not affected by temperature. Only a sudden shift observed at 45 °C in strong acid	Significantly affected

 N_2 or CO_2 -sparged media

Step 1: Fe(I)_{ads} formation Step 2: Non-catalytic dissolution of Fe(I)ads. Step 3/-3: Fe(I)_{ads}, conversion to Fe(II)_{ads}.*

Step 4: Catalytic iron dissolution

8.4.3. Effect of Electrode Materials on the Kinetics of the Elementary Steps

Alloying elements can remarkably modify the kinetics of iron dissolution [39, 40]. The chemical composition of steel can change the kinetic rate constants of the elementary steps as seen in Table 29. From the data listed in Table 29, it could be seen that the rate constants for the elementary steps 1, 2 and 4 remained almost unaffected for the different steels. However, the alloying elements could influence the catalytic pathway by mainly affecting the $Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$ step in both forward and reverse directions (Figure 105). This conclusion could also be drawn by comparing the b_l or Tafel values of the elementary steps listed in Table 29 for different steels, where the highest variance corresponded to b_l values for elementary step 3. A possible explanation is that by changing the chemical composition of the steel, a slight change of the reaction path for elementary step 3 could take place that shifts the rate constants for elementary step 3 more significantly than other steps.



forward direction $(k_{0,3})$, (b) backward direction in the active domain $(k_{0,-3a})$, and (c) backward direction in the transition domain $(k_{0,-3t})$ at pH 4, 25 °C

The surface species of the alloying elements can interact with $Fe(I)_{ads.}$ and $Fe(II)_{ads.}^*$, thereby modifying the kinetics of $Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$ conversion. Indeed, it has been reported that the key role of alloying elements is through their active interaction with adsorbed iron intermediates, *i.e.*, $Fe(I)_{ads.}$ and $Fe(II)_{ads.}^*$ [39, 40]. The influence of alloying elements on $k_{0,3}$ and $k_{0,-3}$ can be explained by the fact that they change steadystate θ_I and θ_2 isotherms. In the following section, the impact of steel type on θ_I and θ_2 isotherms will be discussed.

8.4.4. Effect of Electrode Materials on Formation of Non-Catalytic/Catalytic Intermediates

In this section, it is discussed how the type of steel can influence the isotherms of θ_1 (fraction of surface coverage with non-catalytic $Fe(I)_{ads}$) and θ_2 (fraction of surface coverage with catalytic $Fe(II)_{ads}^*$). The steady-state isotherms θ_1 and θ_2 were simulated using Eqs. (98 & 99), respectively (see Section 7.7.2), and using the kinetic rate constants provided in Table 32 at pH 4 (25 °C). Figure 106 shows the variation of θ_1 and θ_2 isotherms for different steel types on both strong and weak acids at pH 4 and 25 °C.



Figure 106. *Variation of* θ_1 *(solid lines) and* θ_2 *(dashed lines) as a function of potential for pure iron, X65, and 3% Cr steel in (a) strong and (b) weak acid (pH 4, 25 °C)*

It has been claimed that for low anodic overpotentials, the behavior of steel is similar to that of pure iron [39]. For all materials, Min θ_1 coincides with Max θ_2 , where the transition region of the anodic sweep or "*s-shape*" region begins. In both strong and weak acids, the appearance of the Min θ_1 drop for pure iron is more intense than those for X65 and 2% Cr steels. This indicates that the tendency for the formation of catalytic $Fe(II)_{ads}^*$ species for pure iron is more than that for X65 and 2% Cr steels. Therefore, it is expected that there is a more noticeable "*s-shape*" transition in the case of iron (as seen in potentiodynamic sweeps shown in Figure 92). As seen in Figure 106 (b), in weak acid media, the Min θ_1 for 2% Cr steel is the shallowest, implying that the transition domain for this steel should be imperceptible (as seen in Figure 92 (b)). Alloying elements could modify the interaction between the adsorbed intermediates since in the presence of Cr and Mo, additional surface species are expected. This could lead to a change in the adsorption isotherms θ_1 and θ_2 [39, 40]. It has been claimed that Cr-containing species such $Cr(I)_{ads}$ and $Cr(II)_{ads}$ can block the pre-passive dissolution path of iron, thus drastically hindering the catalytic dissolution path (*i.e.*, step 4 in the scheme presented in Figure 79) [39]. This is actually the basic reason for the retardation of the current density for 2% Cr steel as compared to pure iron and X65 steel in the pre-passivation domain (Figure 92).

8.5. Simplified Mechanistic Model for Anodic Iron Dissolution

So far, the modeling of the anodic sweeps was conducted according to a few sets of lookup table data (Table 22 and Table 32). In this section, mathematical functions are introduced considering select rudimentary mechanistic aspects (*e.g.*, a linear dependence of reaction rate on solution bulk pH on a semi-log plot or the exponential dependence of rate constant on temperature, or Arrhenius behavior). These expressions usually are used to serve as predictive methods to reasonably extrapolate/predict the observations beyond the range of tested conditions or when little is known about the fundamental aspects of a particular system.

Considering the variation of the parameters k_i and b_i listed in Table 22 (Section 7.8.1.3) and Table 32 (Section 8.4.1.3), it was found that each environmental condition (pH, CO₂, or temperature) influences the kinetics of one or two particular elementary steps more significantly. An initial assumption can be made that the environmental condition, *Y*, (pH, CO₂, or temperature) influences the kinetic rate constants of the elementary step X (k_x) more than it does the other steps. In this section, a few *f*(*Y*) functions will be introduced to define the dependency of k_x on Y. *f*(*Y*) functions are defined to predict k_x , and certainly, the uncertainty associated with each regression must be taken into consideration. Therefore, it is necessary to hold fixed those k_i parameters with the least dependency on *Y*. This way, by decreasing the size of the training dataset, the degree of freedom will be reduced but the penalty that will remain in turn is optimizing the level of accuracy in our ultimate predictive model [140]. Recalling the discussions in Sections 7.8.2 and 8.4.2, Table 34 summarizes the key elementary steps whose kinetics rate constants k_i , was affected by varying the environmental factor *Y*.

Y	Step 1	Step 2	Step 3	Step -3	Step 4
CO ₂	Significantly	N/A	Significantly	Significantly	N/A
pН	N/A	N/A	Slightly	Significantly	Not affected by pH. A sudden drop was observed at pH 6 in strong acid
Т	Slightly	Significantly	N/A	Not affected by temperature. A sudden shift observed at 45 °C in strong acid	Significantly

elementary steps

Step 1: Fe(I)ads. formation

Step 2: Non-catalytic dissolution of Fe(I)ads.

Step 3/-3: Fe(I)ads. conversion to Fe(II)ads. *

Step 4: Catalytic iron dissolution N/A: No effect

Referring to the dataset summarized in Table 22 (Section 7.8.1.3) and Table 32 (Section 8.4.1.3), it is noteworthy that further deviations of k_x as a function of environmental parameters *Y* are negligible, therefore, they can be retained at fixed values close to their averages (Table 35). The notation f(pH) or f(T) indicates that the variable shows a dependency on the corresponding environmental factor *Y*, subsequently, a mathematical correlation is required to describe such functionality.

Y	Media	<i>k</i> _{0,1}	b 1	<i>k</i> _{0,2}	b ₂	<i>k</i> _{0,3}	b 3	k 0,-3a	b -3,a	k _{0,-3t}	b -3,t	<i>k</i> _{0,4}	b 4
pН	N ₂	6.23×10 ⁻²	0.12	1.57×10-1	0.258	f(pH)	0.33	f(pH)	-0.055	f(pH)	0.022	3.2×10 ⁻²	0.19
	CO ₂	f(pH)	0.112	1.63×10-1	0.256	f(pH)	0.316	1×10-11	-0.071	f(pH)	0.028	1.9×10 ⁻²	0.28
Т	N ₂	f(T)	0.12	f(T)	f(T)	1.5×10-3	f(T)	1×10 ⁻¹³	-0.055	4×10 ⁸	0.022	f(T)	0.19
	CO ₂	9×10-2	0.112	<i>f(T)</i>	f(T)	1.29×10-3	0.316	1×10 ⁻¹¹	-0.071	1×10 ⁵	f(T)	f(T)	0.28

Table 35. Dependent and independent variables and the input dataset for modeling of the

anodic sweeps in strong and weak acids

An Arrhenius-type correlation is expected for f(T), while f(pH) is oftentimes described according to a linear dependence of rate on pH in a semi-logarithmic scale [1, 27,30, 141]. Additionally, a linear dependency between b_i and temperature is expected from theory [8]. Table 36 provides the functions used for modeling. The regression analysis and the corresponding uncertainty associated with each function are presented in Appendix D. The least squares regression, the residual sum, Pearson's r number⁵ (further away from zero shows a better fit), and R-squared for each f(Y) function were estimated using OriginPro 2023 software, according to the following equations:

Slope uncertainty:
$$S_{slp} = \sqrt{\frac{S_r^2}{\sum (x_i - \bar{x})^2}}$$
 (116)

Slope intercept:
$$S_{intcpt} = \sqrt{\frac{S_r^2 \sum x_i^2}{n \sum (x_i - \bar{x})^2}}$$
 (117)

$$Pearson's \ r \ number = \frac{\sum(x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum(x_i - \bar{x})^2 \sum(y_i - \bar{y})^2}}$$
(118)

$$R - Squared = \frac{\Sigma(\tilde{y}_{l} - \bar{y})^{2}}{\Sigma(y_{l} - \bar{y})^{2}}$$
(119)

⁵ - It can take values between -1 and 1

Y	Media	k _{0,1}	ko,2	<i>b</i> 2	ko,3	b₃	k0,-3a	k0,-31	<i>Ъ-3,t</i>	k0,4
Hq	N2-sparged	I	ı	I	10 ^{0.39526,pH-4.39471}	1	10-2.65051. <i>pH</i> -2.31053	10 ^{3.69897.pH-6.29416}	I	I
	CO ₂ -sparged	10 ^{0.42934.pH-2.75831}	ı	ı	10 ^{0.66909.} <i>pH</i> -5.56027	-	-	10 ³ <i>pH</i> -7.01525	-	
Temperature	N ₂ -sparged	$e^{-7447.08681}+22.17741$	$e^{-37137.95191}_{T}$ +122.58228	-0.0079T + 2.61372	-	0.00705T - 1.77446	-	-	-	$e^{-8688.55606}+25.68995$
	CO ₂ -sparged	I	$e^{-16598.42428}$ +53.82449	-0.00583T + 1.98974					0.000516667T - 0.12515	$e^{-24015.74579}_{T}$ +76.6108

Table 36. Equations used for modeling the anodic sweeps in strong and weak acids

The anodic sweeps were modeled by incorporating functions listed in Table 36 into Eq. 100 presented in Section 7.7.2 to replicate the steady-state current density.





Figure 107. *Comparison of the modeling results using lookup table data and the simplified functions for pure iron in weak acid at 25 °C at pH (a) 4, (b) 5, and (c) 6*

Figure 108 compares the modeled *vs.* experimental sweeps at different pH values for both strong and weak acids. Figure 109 represents the one-by-one comparison of the modeled sweep *vs.* the experimental measurement.



Figure 108. (a and b) modeled anodic sweeps and (c and d) experimental sweeps for pure iron in 2.9 wt.% NaCl (0.55 M) solution sparged with 0.97 bar N_2 or CO_2 at different pH values, T = 25 °C, scan rate: 0.5 mV/sec. The inset shows the zoom for a detailed comparison


Figure 109. *Comparison between model output (blue) and experimental sweeps (red) for pure iron in 2.9 wt.% NaCl, at* T = 25 °C

A reasonable match between modeled sweeps and the experiment was obtained in the case of the weak acid, however, the simplified functions do not reproduce a reasonable fit for the case of strong acids at pH greater than 5.25. Figure 110 and Figure 111 represent the modeling results for steady-state dissolution of iron at different temperatures using the mathematical correlations summarized in Table 36.



Figure 110. (a and b) modeled anodic sweeps and (c and d) experimental sweeps for pure iron in NaCl solution ($R_s \sim 0.78\pm0.08 \ \Omega$) solution sparged with 0.97 bar N_2 or CO_2 at different temperatures, pH = 4, scan rate: 0.5 mV/sec



Figure 111. Comparison between model output (blue) and experimental sweeps (red) for pure iron in NaCl solution ($R_s \sim 0.78\pm0.08 \ \Omega$) in (a–c) N₂-sparged 25 °C, 35 °C, 45 °C, and (d–f) CO₂-sparged, 25 °C, 35 °C, 45 °C, respectively (pH 4)

As seen in Figure 111, at higher temperatures there is a mismatch between the model and the experiment, especially in the transition and pre-passivation domains. In the following section, the possible sources of error and the model improvement will be discussed.

8.5.1. Source of Error, Limitations, and Model Improvement

The models have normally unavoidable limitations and restricted accuracy under certain conditions. In this section, the plausible sources of uncertainty associated with the simplified models presented in Section 8.5 and their limitations will be discussed for future developments. Model output usually has inherent inaccuracies. Extrapolation and interpolation outside of the ranges of experiments can provide valuable insight into the possible model limitations. A mismatch might occur when the input variable is selected far outside of the range of the experimental testation. A few examples of such extrapolation/interpolation attempts are presented in Appendix E, to identify the points of the weakness of the simplified model presented in Section 8.5. Some of the possible sources of error and model improvement are listed below.

- The mass transfer and therefore the buffering effect of the carbonic acid was not included in the model. In other words, it was assumed that the anodic dissolution is not controlled by the diffusion of the species toward the electrode surface. Indeed, the experiments were conducted at high enough rotation rates for RCE specimens to eliminate the limitation due to the mass transfer. One might need to examine the stagnant or lower RCE rotation speed conditions to assess the possible impact of mass transfer.
- The underlying assumption of the isotherm Langmuir type which assumes a homogeneous surface and a monolayer of adsorbent might be simplistic under certain experimental conditions. Therefore, other adsorption models such as Freundlich, Temkin, Dubinin–Radushkevich, Harkins–Jura, and Halsey might lead to more precise predictions under certain experimental conditions.
- The model presented herein takes the bulk pH since the mass-transfer limitations were excluded in our model. Using the surface pH as the model input might result in a more accurate prediction, especially at higher bulk pH.
- The theory used for our modeling (Figure 79), is a simplified and adapted twopathway version of a much more complex scheme with three pathways (Keddam *et al.* [37]) or four pathways (Moradighadi *et al.* [42]).

- The lack of a substantial amount of test data might make a model biased. Therefore, testation under a much wider range of experimental conditions would make a model more comprehensive.
- As the input condition moves away from the test conditions, less accurate predictions are expected (see Appendix E). A stronger physical model might improve the model's accuracy. For example, the potential-dependent charge transfer coefficient is explainable based on Marcus' theory [142], while the non-linearity of the anodic polarization curves might not be directly explainable based on Butler-Volmer and Tafel's law.
- Larger error propagation is expected in the case of a model with a large number of input parameters (each parameter has its uncertainty).
- The direct reduction mechanism of carbonic acid was applied in this study to replicate the cathodic reaction. However, this view has evolved over time, especially after the studies done by Kahyarian *et al.* [67–69], who reported that the "buffering effect" of the weak acid is the governing mechanism that can significantly influence the kinetics and thermodynamics of the cathodic reactions. The buffering mechanism can provide more accurate predictions for the cathodic reactions in the weak acid media. It is important to bear in mind that although using either mechanism for cathodic, would not affect the introduced models for the anodic, instead, it mainly affects the cathodic polarization sweeps.

8.6. Summary

- A similar methodology as described in Chapter 7 was followed to investigate the influence of temperature and steel types on the kinetics of iron dissolution. Using the proposed approach in Chapter 7 the steady-state anodic polarization curves were modeled for pure iron at different temperatures as well as for a few types of steel.
- As the temperature increased the increase of k_2 and k_4 was more noticeable than in other elementary steps. In other words, the higher temperature increased the rate of both non-catalytic and catalytic dissolutions (k_2 and k_4), while other elementary steps remained almost unaffected. In other words, the change of temperature had a greater impact on k_2 and k_4 values than other kinetic rate constants. Furthermore, it was found that higher temperatures slightly increased k_1 (the formation of $Fe(I)_{ads.}$). ??
- ➤ Alloying elements influenced the catalytic pathway by mainly affecting step 3, *i.e.*, $Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$ conversion. In the other words, the change of material had a greater impact on k_3 and k_{-3} values than other kinetic rate constants.
- Mathematical functions were introduced to replace the previously obtained lookup table for modeling the anodic polarization sweeps. Using these simplified correlations, the anodic potentiodynamic sweeps were successfully modeled for pure iron at different temperatures and pH values in both strong and weak acid media. A reasonable match between the model and the experiment was obtained in the case of the weak acid, while the predictions were less precise in the case of the strong acid at pH higher than about 5.25. The possible sources of error and model improvement were discussed for future development.

Chapter 9: Conclusions and Future Work

9.1. Conclusions

In this dissertation, the aim was to better understand the mechanism of iron anodic dissolution at different experimental conditions and to assess the role of CO₂. Through the present study, the following conclusions can be drawn:

- A quantitative analysis of iron dissolution in strong acid in a potential range in the proximity of its OCP led to the articulation of a revised narrative of the Bockris' mechanism for iron dissolution. Thirty-eight different pathways were investigated, and the theoretical predictions for each were compared with the observations. It was found that $FeOH_{ads.}$ is always the first produced intermediate at the electrode surface during iron dissolution. This agrees well with the fundamental mechanistic theory as described by Bockris. According to this theory, in the vicinity of OCP, the dominant adsorbed intermediate that controls the dissolution of iron is most likely $FeOH_{ads.}$ and the dissolution of $FeOH_{ads.}$ to the $Fe(II)_{sol.}$ is the predominant pathway in the potential range close to the OCP.
- The semi-quantitative analysis based on potentiostatic data in the potential ranges close to OCP indicated that the dissolved CO₂ did not notably affect the current density in the active dissolution range, while its effect in the transition and prepassivation ranges of the sweeps was marked. In addition, based on the galvanostatic analysis it was found that CO₂ retarded the adsorption of intermediates by destabilizing surface species.

- A systematic methodology was introduced to first discretize the overall reaction of anodic dissolution into a few elementary steps, then approximate the kinetic rate constants for this individual step. This led to the establishment of a database used for modeling the anodic potentiodynamic sweeps. A reasonable consistency between the model and experimental sweeps under different experimental conditions was obtained, which validated the legitimacy of the presented approach and the corresponding kinetic database.
- As pH was changed or CO₂ was introduced, the change of the kinetic rate constants related to the transition path (*i.e.*, *Fe(I)_{ads.}* ↔ *Fe(II)_{ads.}* * equilibrium) was more marked than other elementary steps. In addition, the impact of CO₂ on the variation of k_{0,1}, k_{0,3}, and k_{0,-3} became more substantial at higher pH. In actuality, this was the fundamental reason for observing a more discernible effect of CO₂ on the feature of the anodic sweeps as the solution became less acidic.
- > The shrinkage, expansion, location, and general feature of the "s-shape" region in the anodic sweep were controlled mainly by the kinetic of $Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$ equilibrium.
- ➤ The effect of CO₂ on enhancing the kinetics of anodic dissolution was explainable according to a few key facts: a) the role of CO₂ in accelerating the formation of noncatalytic $Fe(I)_{ads}$, b) the buffering nature of carbonic acid and its impact on accelerating step 3 (*i.e.*, $Fe(I)_{ads}$. \leftrightarrow $Fe(II)_{ads}$.^{*}) in the reverse direction, and c) its effect in increasing $k_{0,4}$ (this effect was discernible only at high enough pH conditions).

- ▶ Based on the qualitative interpretations accomplished to understand the influence of CO₂ and pH on the θ_1 and θ_2 isotherms it was found that the current decay in the transition domain (*i.e.*, *s-shape* or Max I) occurred when the coverage with catalytic $Fe(II)_{ads}^*$ is maximum and the coverage with non-catalytic is $Fe(I)_{ads}$ minimum. In other words, the *s-shape* appearance stems from the formation of catalytic $Fe(II)_{ads}^*$.
- > CO₂ suppressed the catalytic Path 2, i.e., it decelerated the formation of $Fe(II)_{ads}^*$.
- As the temperature increased the increase of k_2 and k_4 was more noticeable than in other elementary steps. In other words, the higher temperature increased the rate of both non-catalytic and catalytic dissolutions (k_2 and k_4), while other elementary steps remained almost unaffected.
- ➤ Alloying elements influenced the catalytic pathway by mainly affecting step 3, *i.e.*, $Fe(I)_{ads.} \leftrightarrow Fe(II)_{ads.}^*$ conversion; the change of material had a greater impact on k_3 and k_{-3} values than other kinetic rate constants.
- Mathematical functions were introduced for modeling the anodic polarization sweeps. Using these correlations, the anodic potentiodynamic sweeps were successfully modeled for pure iron at different temperatures and pH values in both strong and weak acid media. A reasonable match between the model and the experiment was obtained in the case of the weak acid, while the predictions were less precise in the case of the strong acid at pH higher than about 5.25. Further investigations need to be carried out to improve the model predictions according to the discussion provided in Section 8.5.1 and the recommendations provided in Section 9.2.

9.2. Future Scope and Recommendations

Some recommendations for future work are listed below:

- The majority of the transient or steady-state experiments were done at pH 4 and 25 °C. A more substantial amount of data at a wider range of experimental conditions should be conducted, for example, a pH range of 5–7 at elevated temperatures, *e.g.*, 35 °C 60 °C.
- In this study, it was assumed that the mass-transfer effect is negligible; any limitations due to mass-transfer may need to be considered. It was experimentally observed that increasing the rotation speed for the RCE specimen beyond 2000 rpm did not significantly influence the anodic sweeps (see Figure 138 in Appendix E). Hence, selecting 2000 rpm was reasonable to minimize the possible mass-transfer effects.
- The nature of the catalytic step 4 has the potential for further investigations since transfer of two electrons at once is physically less likely. In the present study, for the sake of keeping the scheme less complicated, catalytic step 4 (with two electrons transferred) was not further broken down to other sub-elementary steps. Obtaining a few unusually small charge transfer coefficients indicated that those steps could potentially be further broken down.
- The influence of NaCl concentration (or other cation/anion combinations) might need to be incorporated into the model. At high concentrations of chloride ions, the thermodynamics of non-ideal situations should be taken into account.

- Only two types of steel, *i.e.*, X65 and 2% Cr, were investigated in the present work. To better recognize the influence of alloying elements a wider range of materials should be examined. For example, testing 1% Cr, 2% Cr, 3% Cr, 4% Cr, and 5% Cr steels would offer important insights into the effect of Cr on the mechanism of iron dissolution.
- The influence of material microstructure on the mechanism of iron anodic dissolution was not assessed in this study. The impact of metallurgical properties such as phase distribution, grain size, microstructure, heat treatment processes, *etc.*, would be good to investigate in future studies.
- All experiments were accomplished at a partial pressure of 0.97 bar CO₂. It is recommended to also conduct experiments at intermediate and higher partial pressures of CO₂ to examine if this has any impact on the transient response and reaction mechanism.
- A more accurate model for the cathodic reaction may need to be used since the cathodic model used herein works based on the direct reduction of carbonic acid, *i.e.*, the buffering effect of CO₂ on the cathodic reaction was ignored.

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Appendix A: Comparison of Data Acquisition Speed for Different Potentiostat/Galvanostat Instruments

In this section, data acquisition speed is compared for three cell test systems available at ICMT, *i.e.*, SOLARTRON 1470E, VersaSTAT3, and GAMRY 600. In this study, it was needed to collect the transient response in the time domain as fast as possible to obtain information about the element. By Fourier transforms of the transients in the time domain, one can obtain the response in the frequency domain and the Nyquist plots. The ability of an instrument for the high-speed acquisition of clean and smooth transients in the time domain depends on its capability to capture the Nyquist data points at high frequencies. In other words, the less noisy Nyquist plots, the faster the instrument can collect the transients in the time domain. Figure 112 compares the current transients for different potentiostat instruments at a fixed applied potential of 100 mV vs. OCP. The corresponding Nyquist plots after applying the Fourier transform are also shown in this Figure 112. The transient and the corresponding Nyquist plot are only showing up smoother for the GAMRY potentiostat instrument. This indicates that the capability of GAMRY for high-speed data acquisitions is better than that of SOLARTRON 1470E or VersaSATAT3.



Figure 112. *Current transient response and the corresponding Nyquist after Fourier transform for (a, b) Solartron 1470E, (c, d) VersaSTAT3, (e, f) GAMRY, respectively*

Appendix B: Proposed Mechanistic Pathways for Iron Dissolution: Calculation of

Butler-Volmer Calculations and the Kinetic Consequences

Mechanism (b):

$$Fe + H_20 \leftrightarrow FeOH_{ads.} + H^+ + e^-$$

$$FeOH_{ads.} \leftrightarrow FeOH^+ + e^-$$

$$FeOH^+ + Fe \xrightarrow{rds} Fe_2OH^+$$

$$Fe_2OH^+ \leftrightarrow Fe^{2+} + FeOH_{as.} + e^-$$

$$FeOH_{ads.} + H^+ \leftrightarrow Fe^{2+} + H_2O + e^-$$

For this mechanism, $n_{f}^{b} = 2$, $n_{b}^{b} = 2$, $v^{b} = 1$, $n_{r}^{b} = 0$ and thus:

$$|b_c^b| = \left| \left(\frac{dE_c^b}{dlogi_c^b} \right)_c \right| = \frac{2.3RT}{\left(\frac{n_f^b}{v^b} + n_r^b \beta^b \right)_F} = \frac{2.3RT}{2F}$$

$$|b_a^b| = \left| \left(\frac{dE_a^b}{dlog i_a^b} \right)_a \right| = \frac{2.3RT}{\left(\frac{n_b^b + \nu^b n_r^b}{\nu^b} - n_r^b \beta^b \right)_F} = \frac{2.3RT}{2F}$$

Writing the law of mass action for the *rds* step:

$$\tilde{\nu}_b - \vec{\nu}_b = k^b_{-3} C_{FeOH^+} - k^b_3 C_{Fe_2OH^+}$$
(120)

Writing the law of mass action for other equilibrium steps:

$$k_{-1}^{b}(1-\theta_{FeOH})e^{(1-\beta)F\eta/RT} = k_{1}^{b}\theta_{FeOH}C_{H^{+}}e^{-\beta F\eta/RT} \rightarrow k_{-1}^{b}e^{(1-\beta)F\eta/RT} = k_{1}^{b}(1-\theta_{FeOH})\frac{K_{w}}{C_{OH^{-}}}e^{-\beta F\eta/RT} \rightarrow \theta_{FeOH} = \frac{C_{OH^{-}}}{K_{w}K_{1}^{b}}e^{F\eta/RT}$$
(121)

$$k_{-2}^b \theta_{FeOH} e^{(1-\beta)F\eta/RT} = k_2^b C_{FeOH^+} (1-\theta_{FeOH}) e^{-\beta F\eta/RT}$$
(122)

$$C_{FeOH^+} = \frac{\theta_{FeOH}}{K_2^b} e^{F\eta/RT}$$
(123)

$$C_{FeOH^+} = \frac{1}{K_1^b K_2^b K_W} C_{OH^-} e^{2F\eta/RT}$$
(124)

$$k_{-4}^{b}(1-\theta_{FeOH})C_{Fe_{2}OH}+e^{(1-\beta)F\eta/RT} = k_{4}^{b}C_{Fe^{2}}+\theta_{FeOH}e^{-\beta F\eta/RT} \rightarrow$$

$$C_{Fe_{2}OH}+=K_{4}^{b}C_{Fe^{2}}+\theta_{FeOH}e^{-F\eta/RT} \qquad (125)$$

$$k_{-5}^{b}\theta_{FeOH}C_{H}+e^{(1-\beta)F\eta/RT} = k_{5}^{b}C_{Fe^{2}}+(1-\theta_{FeOH})e^{-\beta F\eta/RT} \rightarrow$$

$$\theta_{FeOH}=\frac{K_{5}^{b}}{K_{w}}C_{Fe^{2}}+C_{OH}-e^{-F\eta/RT} \qquad (126)$$

$$C_{Fe_2OH^+} = \frac{K_4^b K_5^b}{K_w} C_{OH^-} C_{Fe^{2+}}^2 e^{-2F\eta/RT} \quad \longrightarrow \quad$$

Considering Eq. 120, then:

$$\dot{\nu}_b - \vec{\nu}_b = k_{-3}^b \frac{1}{K_1^b K_2^b K_W} C_{OH^-} e^{2F\eta/RT} - k_3^b \frac{K_4^b K_5^b}{K_W} C_{OH^-} C_{Fe^{2+}}^2 e^{-2F\eta/RT}$$
(127)

Placing $\overleftarrow{k}_b = k_{-3}^b \frac{1}{\kappa_1^b \kappa_2^b \kappa_w}$ and $\vec{k}_b = k_3^b \frac{\kappa_4^b \kappa_5^b}{\kappa_w}$, the following Butler-Volmer equation will

be obtained for mechanism (b):

$$r^{b} = \overleftarrow{k}_{b} C_{OH} - e^{2F\eta/RT} - \vec{k}_{b} C_{OH} - C_{Fe^{2+}}^{2} e^{-2F\eta/RT}$$
(128)

During the anodic dissolution of iron, in the backward direction, the dependency of current *vs.* overpotential can be expressed as:

$$\bar{r}^b = \bar{k}_b C_{OH^-} e^{2F\eta/RT} \tag{129}$$

For this mechanism p_{OH-} and E_{OH-} are theoretically obtained as:

$$p_{OH^{-}}^{b} = \left(\frac{\partial \tilde{r}^{b}}{\partial \ln c_{OH^{-}}}\right)_{C_{Fe2+}} = 1$$

$$E_{OH^{-}}^{b} = \left(\frac{\partial (E_{corr.})}{\partial \log (c_{OH^{-}})}\right)_{C_{Fe2+}}^{b} = -2.3 \left(\frac{p_{OH^{-}+1}^{b}}{\alpha_{a}^{b} + \alpha_{c}^{b}}\right)_{F}^{RT} = -2.3 \left(\frac{1+1}{2+2}\right)_{F}^{RT} = -0.03 \, V/dec.$$

Mechanism (c):

 $Fe + OH^{-} \xrightarrow{rds} FeOH^{+} + 2e^{-}$ $FeOH^{+} \leftrightarrow Fe^{2+} + OH^{-}$ For this mechanism, $n_f^c = 0$, $n_b^c = 0$, $v^c = 1$, $n_r^c = 2$ and therefore b_c^c and b_a^c can be obtained as:

$$|b_c^c| = \frac{2.3RT}{\left(\frac{n_f^c}{\nu^c} + n_r^c \beta^c\right)F} = \frac{2.3RT}{F}$$
$$|b_a^c| = \frac{2.3RT}{\left(\frac{n_b^c + \nu^c n_r^c}{\nu^c} - n_r^c \beta^c\right)F} = \frac{2.3RT}{F}$$

Similar to the procedure that was followed for mechanisms (a) and (b), one could determine the theoretical Butler-Volmer equation for all proposed pathways. When more than one electron is involved in the *rds*, instead of β or $1-\beta$, α_a and α_c should be used for writing the Butler-Volmer equation for *rds*.

$$i^{c} = 2F\{k_{-1}^{c}C_{OH^{-}}e^{\alpha_{a}F\eta/RT} - k_{1}^{c}C_{FeOH^{+}}e^{-\alpha_{c}F\eta/RT}\}$$

$$k_{-2}^{c}C_{FeOH^{+}} = k_{2}^{c}C_{Fe^{2+}}C_{OH^{-}} \rightarrow C_{FeOH^{+}} = K_{2}^{c}C_{Fe^{2+}}C_{OH^{-}} \rightarrow$$

$$i^{c} = 2F\{k_{-1}^{c}C_{OH^{-}}e^{\alpha_{a}F\eta/RT} - k_{1}^{c}K_{2}^{c}C_{Fe^{2+}}C_{OH^{-}}e^{-\alpha_{c}F\eta/RT}\}$$
(130)
(131)

Placing $\tilde{k}_c = k_{-1}^c$ and $\vec{k}_c = k_1^c K_2^c$, the following Butler-Volmer equation will be obtained for mechanism (c):

$$i^{c} = 2F\{\bar{k}_{c}C_{OH^{-}}e^{\alpha_{a}F\eta/RT} - \vec{k}_{c}C_{Fe^{2+}}C_{OH^{-}}e^{-\alpha_{c}F\eta/RT}\}$$
(132)

According to the calculated values of $\alpha_a = \alpha_c = 1$

$$i^{c} = 2F\{\vec{k}_{c}C_{OH^{-}}e^{F\eta/RT} - \vec{k}_{c}C_{Fe^{2+}}C_{OH^{-}}e^{-F\eta/RT}\}$$
(133)

During the anodic dissolution of iron, in the backward direction, the dependency of current *vs*. overpotential can be expressed as:

$$\tilde{\iota}^c = 2F \tilde{k}_c C_{OH^-} e^{F \eta_c/RT} \tag{134}$$

For this mechanism p_{OH-} and E_{OH-} are theoretically obtained as:

$$p_{OH^{-}}^{c} = \left(\frac{\partial \ln i_{0,a}}{\partial \ln C_{OH^{-}}}\right)_{C_{Fe2+}} = 1$$

$$i_{a,Fe}^{c} = i_{c,H}^{c} \rightarrow 2F \overleftarrow{k}_{c} C_{OH^{-}} e^{\alpha_{a}^{c}F(E-E_{corr})/RT} = 2F \overrightarrow{k}_{e} C_{Fe^{2+}} C_{OH^{-}} e^{-\alpha_{c}^{c}F(E-E_{corr})/RT} \rightarrow$$

$$E_{OH^{-}}^{c} = \left(\frac{\partial (E_{corr.})}{\partial \log (C_{OH^{-}})}\right)_{C_{Fe2+}}^{c} = -2.3 \left(\frac{p_{OH^{-}+1}^{c}}{\alpha_{a}^{c}+\alpha_{c}^{c}}\right) \frac{RT}{F} = -2.3 \left(\frac{1+1}{1+1}\right) \frac{RT}{F} = -0.06 \text{ V/dec.}$$

Mechanism (d):

$$Fe + OH^{-} \leftrightarrow FeOH_{ads.} + e^{-}$$

$$FeOH_{ads.} + OH^{-} \xrightarrow{rds} FeO_{ads.} + H_{2}O + e^{-}$$

$$FeO_{ads.} + OH^{-} \leftrightarrow HFeO_{2}^{-}$$

$$HFeO_{2}^{-} + H_{2}O \leftrightarrow Fe(OH)_{2,ads} + OH^{-}$$

$$Fe(OH)_{2,ads} \leftrightarrow Fe^{2+} + 2OH^{-}$$

For this case, $n^d_f = 0$, $n^d_b = 1$, $v^d = 1$, $n^d_r = 1$ and therefore:

$$|b_{c}^{d}| = \frac{2.3RT}{\left(\frac{n_{f}^{d}}{\nu^{d}} + n_{r}^{d}\beta^{d}\right)_{F}} = \frac{2.3RT}{0.5F}$$

$$|b_{a}^{d}| = \frac{2.3RT}{\left(\frac{n_{b}^{d} + \nu^{d}n_{r}^{d}}{\nu^{d}} - n_{r}^{d}\beta^{d}\right)_{F}} = \frac{2.3RT}{1.5F}$$

$$i^{d} = 2F\{(1 - \theta_{FeO})k_{-2}^{d}\theta_{FeOH}C_{OH} - e^{(1 - \beta)F\eta/RT} - k_{2}^{d}\theta_{FeO}e^{-\beta F\eta/RT}\}$$

$$k_{-1}^{d}(1 - \theta_{FeOH})C_{OH} - e^{(1 - \beta)F\eta/RT} = k_{1}^{d}\theta_{FeOH}e^{-\beta F\eta/RT} \rightarrow \frac{1 - \theta_{FeOH}}{\theta_{FeOH}} = \frac{K_{1}^{d}}{c_{OH}^{-}}e^{-F\eta/RT}$$
(135)

Assuming $\theta_{FeOH} \ll 1$:

$$\rightarrow \theta_{FeOH} = \frac{C_{OH^-}}{K_1^d} e^{F\eta/RT}$$
(137)

$$k_{-3}^{d}\theta_{FeO}C_{OH} - e^{(1-\beta)F\eta/RT} = k_{3}^{d}(1-\theta_{FeO})C_{HFeO_{2}} - e^{-\beta F\eta/RT} \rightarrow \frac{\theta_{FeO}}{1-\theta_{FeO}} = \frac{K_{3}^{d}}{c_{OH}}C_{HFeO_{2}} - e^{-F\eta/RT}$$
(138)

Assuming $\theta_{FeO} \ll 1$:

$$\theta_{FeO} = \frac{K_3^d}{C_{OH^-}} C_{HFeO_2} e^{-F\eta/RT}$$
(139)

$$k_{-4}^d C_{HFeO_2} (1 - \theta_{Fe(OH)_2}) e^{(1-\beta)F\eta/RT} = k_4^d \theta_{Fe(OH)_2} C_{OH} e^{-\beta F\eta/T} \rightarrow$$

$$\frac{1 - \theta_{Fe(OH)_2}}{\theta_{Fe(OH)_2}} = \frac{K_4^d}{C_{HFeO_2}} C_{OH} - e^{-F\eta/RT}$$
(140)

Assuming $\theta_{Fe(OH)_2} \ll 1$:

$$\theta_{Fe(OH)_2} = \frac{c_{HFeO_2}}{c_{OH} - K_4^d} e^{F\eta/RT}$$
(141)

$$k_{-5}^{d}\theta_{Fe(OH)_2}e^{(1-\beta)F\eta/RT} = k_5^{d}(1-\theta_{Fe(OH)_2})C_{OH}-C_{Fe^{2+}}e^{-\beta F\eta/RT} \rightarrow \frac{\theta_{Fe(OH)_2}}{2} = K_5^{d}C \qquad C_{-21}e^{-F\eta/RT} \qquad (142)$$

$$\frac{\theta_{Fe(OH)_2}}{1 - \theta_{Fe(OH)_2}} = K_5^d C_{OH^-} C_{Fe^{2+}} e^{-F\eta/RT}$$
(142)

Assuming $\theta_{Fe(OH)_2} \ll 1$:

$$\theta_{Fe(OH)_2} = K_5^d C_{OH^-} C_{Fe^{2+}} e^{-F\eta/RT}$$
(143)

From Eqs. (140–143):

$$\frac{C_{HFeO_2}}{C_{OH}-K_4^d} e^{F\eta/RT} = K_5^d C_{OH} - C_{Fe^{2+}} e^{-F\eta/RT} \rightarrow C_{HFeO_2} - K_4^d K_5^d (C_{OH})^2 C_{Fe^{2+}} e^{-2F\eta/RT} \qquad (144)$$

Inserting Eq. 144 in Eq. 139:

$$\theta_{FeO} = \frac{K_3^d}{c_{OH^-}} C_{HFeO_2} e^{-F\eta/RT} = K_3^d K_4^d K_5^d C_{OH^-} C_{Fe^{2+}} e^{-3F\eta/RT}$$
(145)

Inserting Eqs. (137 & 145) in Eq. 135 and assuming $\theta_{FeO} \ll 1$:

$$i^{d} = 2F\{(1 - \theta_{FeO})k_{-2}^{d}\theta_{FeOH}C_{OH} - e^{\frac{(1 - \beta)F\eta}{RT}} - k_{2}^{d}\theta_{FeO}e^{-\frac{\beta F\eta}{RT}}\} = 2F\{k_{-2}^{d}\frac{(C_{OH})^{2}}{K_{1}^{d}}e^{(2 - \beta)F\eta/RT} - k_{2}^{d}K_{3}^{d}K_{4}^{d}K_{5}^{d}C_{OH} - C_{Fe^{2}}e^{-3F\eta/RT}e^{-\beta F\eta/RT}\}$$
(146)

Placing $\vec{k}_d = k_{-2}^d \frac{1}{K_1^d}$ and $\vec{k}_d = k_2^d K_3^d K_4^d K_5^d$, and assuming $\beta = 0.5$, the following Butler-

Volmer equation will be obtained for mechanism (e):

$$i^{d} = 2F\{\vec{k}_{d}(C_{OH^{-}})^{2}e^{\frac{1.5F\eta}{RT}} - \vec{k}_{d}C_{OH^{-}}C_{Fe^{2}} + e^{-\frac{3.5F\eta}{RT}}\}$$
(147)

During the anodic dissolution of iron, in the backward direction, the dependency of current *vs.* overpotential can be expressed as:

$$\tilde{\iota}^{d} = 2F \tilde{k}_{d} (C_{OH^{-}})^{2} e^{1.5F \eta_{d}/RT}$$
(148)

For this mechanism p_{OH-} and E_{OH-} are theoretically obtained as:

$$p_{OH^{-}}^{d} = \left(\frac{\partial \ln i_{0,a}}{\partial \ln C_{OH^{-}}}\right)_{C_{Fe2+}} = 2$$

$$i_{a,Fe}^{d} = i_{c,H}^{d} \rightarrow 2F \overleftarrow{k}_{d} C_{OH^{-}} e^{\alpha_{a}^{d}F(E-E_{corr})/RT} = 2F \overrightarrow{k}_{d} C_{Fe^{2+}} C_{OH^{-}} e^{-\alpha_{c}^{d}F(E-E_{corr})/RT} \rightarrow$$

$$E_{OH^{-}}^{d} = \left(\frac{\partial (E_{corr.})}{\partial \log (C_{OH^{-}})}\right)_{C_{Fe2+}}^{d} = -2.3 \left(\frac{p_{OH^{-}+1}^{d}}{\alpha_{a}^{d}+\alpha_{c}^{d}}\right)_{F}^{RT} = -2.3 \left(\frac{2+1}{1.5+0.5}\right)_{F}^{RT} = -0.09$$

Mechanism (e), (Bockris):

$$Fe + H_2 0 \leftrightarrow FeOH_{ads.} + H^+ + e^-$$

$$FeOH_{ads.} \xrightarrow{rds} FeOH^+ + e^-$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2 O$$

For this scheme, $n_f^e = 0$, $n_b^e = 1$, $v^e = 1$, $n_r^e = 1$ and hence:

$$\begin{aligned} |b_{c}^{e}| &= \frac{2.3RT}{\left(\frac{n_{f}^{e}}{\nu^{e}} + n_{r}^{e}\beta^{e}\right)F} = \frac{2.3RT}{0.5F} \\ |b_{a}^{e}| &= \frac{2.3RT}{\left(\frac{n_{b}^{e} + \nu^{e}n_{r}^{e}}{\nu^{e}} - n_{r}^{e}\beta^{e}\right)F} = \frac{2.3RT}{1.5F} \end{aligned}$$

To obtain the theoretical Butler-Volmer equation for this pathway, the correction factor due to the adsorption of the $FeOH_{ads.}$ should be taken into account during *rds*. Steps one

and three are at equilibrium, which means their forward and backward reaction rates are equal. The only step which has contributes to the rate of the overall reaction is *rds*. Step

$$i_e = 2F(\bar{\iota} - \bar{\iota}) = 2F\{k_{-2}^e \theta_{FeOH} e^{(1-\beta)F\eta/RT} - k_2^e C_{FeOH^+} (1-\theta_{FeOH}) e^{-\beta F\eta/RT}\}$$
(149)

After re-arranging all steps in the cathodic direction and writing the law of mass action at equilibrium for step 1 yields:

$$\nu_1^e = \nu_{-1}^e \longrightarrow k_{-1}^e (1 - \theta_{FeOH}) e^{(1 - \beta)F\eta/RT} = k_1^e C_{H^+} \theta_{FeOH} e^{-\beta F\eta/RT} \longrightarrow$$

$$\frac{\theta_{FeOH}}{1 - \theta_{FeOH}} = \frac{1}{K_1^e} (C_{H^+})^{-1} e^{F\eta/RT}$$
(150)

By assuming $1 - \theta_{FeOH} \approx 1$, the following equation is obtained:

$$\theta_{FeOH} = \frac{1}{K_1^e} (C_{H^+})^{-1} e^{F\eta/RT}$$
(151)

where $K_i = \frac{k_i}{k_{-i}}$ always.

Introducing the equilibrium constant (K_w) for the formation of the water as, $C^{H+}C^{OH-}$:

$$\theta_{FeOH} = \frac{1}{K_1^e K_W} C_{OH} - e^{F\eta/RT}$$
(152)

To obtain the concentration term for C_{FeOH+} , it is necessary to write the law of mass action for step. There is no electron transferred in this step 3, hence, there is no need to involve the exponential function of dependency of current on overpotential (according to Butler-Volmer), hence:

$$k_{-3}^{e}C_{FeOH} + C_{H^{+}} = k_{3}^{e}C_{Fe^{2+}} \rightarrow C_{FeOH^{+}} = K_{3}^{e}\frac{C_{Fe^{2+}}}{C_{H^{+}}} = \frac{K_{3}^{e}}{K_{w}}C_{Fe^{2+}}C_{OH^{-}}$$
(153)

Inserting expressions for C_{FeOH^+} and θ_{FeOH} in Eq. 149, the predicted theoretical Butler-Volmer equation will be obtained as:

$$i^{e} = 2F \times \left\{ k_{-2}^{e} \frac{1}{K_{1}^{e} K_{w}} C_{OH^{-}} e^{F\eta/RT} e^{(1-\beta)F\eta/RT} - k_{2}^{e} \frac{K_{3}^{e}}{K_{w}} C_{Fe^{2+}} C_{OH^{-}} (1-\theta_{FeOH}) e^{-\beta F\eta/RT} \right\}$$
(154)

Placing $\dot{k}_e = k_{-2}^e \frac{1}{\kappa_1^e \kappa_w}$ and $\vec{k}_e = k_2^e \frac{\kappa_3^e}{\kappa_w}$, and assuming $\beta = 0.5$, the following Butler-

Volmer equation will be obtained for mechanism (e):

$$i^{e} = 2F\{\vec{k}_{e}C_{OH} - e^{1.5F\eta_{e}/RT} - \vec{k}_{e}C_{Fe^{2+}}C_{OH} - e^{-0.5F\eta_{e}/RT}\}$$
(155)

During the anodic dissolution of iron, in the backward direction, the dependency of current *vs*. overpotential can be expressed as:

$$\tilde{\iota}^e = 2F \tilde{k}_e C_{OH^-} e^{1.5F \eta_e/RT}$$
(156)

For this mechanism p_{OH-} and E_{OH-} are theoretically obtained as:

$$p_{OH^{-}}^{e} = \left(\frac{\partial \ln i_{0,a}}{\partial \ln C_{OH^{-}}}\right)_{C_{Fe2+}} = 1$$

$$i_{a,Fe}^{e} = i_{c,H}^{e} \rightarrow 2F \overleftarrow{k}_{e} C_{OH^{-}} e^{\alpha_{a}^{e}F(E-E_{corr})/RT} = 2F \overrightarrow{k}_{e} C_{Fe^{2+}} C_{OH^{-}} e^{-\alpha_{c}^{e}F(E-E_{corr})/RT} \rightarrow E_{OH^{-}}^{e} = \left(\frac{\partial (E_{corr.})}{\partial \log (C_{OH^{-}})}\right)_{C_{Fe2+}}^{e} = -2.3 \left(\frac{p_{OH^{-}+1}^{e}}{\alpha_{a}^{e}+\alpha_{c}^{e}}\right)_{F}^{RT} = -2.3 \left(\frac{1+1}{1.5+0.5}\right)_{F}^{RT} = -0.06 \text{ V/dec}$$

Mechanism (f), (Heusler):

 $Fe + H_20 \leftrightarrow FeOH_{ads.} + H^+ + e^ Fe + FeOH_{ads.} \leftrightarrow Fe(FeOH)_{ads.}$ $Fe(FeOH)_{ads.} + OH^- \xrightarrow{rds} FeOH^+ + FeOH_{ads.} + 2e^ FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$

In this case, $n_f^f = 0$, $n_b^f = 1$, $v^f = 1$, $n_r^f = 2$ and therefore:

$$\left|b_{c}^{f}\right| = \frac{2.3RT}{\left(\frac{n_{f}^{f}}{\nu^{f}} + n_{r}^{f}\beta^{f}\right)F} = \frac{2.3RT}{F}$$

$$\left|b_{a}^{f}\right| = \frac{2.3RT}{\left(\frac{n_{b}^{f} + \nu^{f} n_{r}^{f}}{\nu^{f}} - n_{r}^{f} \beta^{f}\right)F} = \frac{2.3RT}{2F}$$

When more than one electron is involved in the *rds*, instead of β use α for writing the Butler-Volmer equation for the *rds*.

$$i^{f} = 2F \left\{ k_{-3}^{f} (1 - \theta_{FeOH}) \theta_{Fe(FeOH)} C_{OH} - e^{\alpha_{a} F \eta/RT} - k_{3}^{f} \theta_{FeOH} (1 - \theta_{Fe(FeOH)}) C_{FeOH} + e^{-\alpha_{c} F \eta/RT} \right\}$$
(157)

Using other equilibrium steps:

$$\theta_{FeOH} = \frac{1}{\kappa_w \kappa_1^f} C_{OH^-} e^{F\eta/RT}$$
(158)

$$\theta_{Fe(FeOH)} = \frac{\theta_{FeOH}}{\kappa_2^f} \tag{159}$$

$$C_{FeOH^+} = K_4^f \frac{C_{Fe^{2+}}}{C_{H^+}} = \frac{K_4^f}{K_w} C_{Fe^{2+}} C_{OH^-}$$
(160)

Inserting these expressions in Eq. 157 and assuming $\theta_{FeOH} \ll 1$ and $\theta_{Fe(FeOH)} \ll 1$:

$$i^{f} = 2F \times \left\{ k_{-3}^{f} \frac{1}{K_{w} K_{2}^{f} K_{1}^{f}} (C_{OH^{-}})^{2} e^{a_{a}^{\prime} F \eta / RT} - k_{3}^{f} \frac{1}{K_{w} K_{1}^{f}} e^{F \eta / RT} \frac{K_{4}^{f}}{K_{w}} (C_{OH^{-}})^{2} C_{Fe^{2+}} e^{-a_{c}^{\prime} F \eta / RT} \right\}$$
(161)

Placing $\overleftarrow{k}_f = k_{-3}^f \frac{1}{K_w K_2^f K_1^f}$ and $\overrightarrow{k}_f = k_3^f \frac{K_4^f}{(K_w)^2 K_1^f}$, the following Butler-Volmer equation

will be obtained for mechanism (f):

$$i^{f} = 2F\{\vec{k}_{f}(C_{OH^{-}})^{2}e^{2F\eta_{f}/RT} - \vec{k}_{f}(C_{OH^{-}})^{2}C_{Fe^{2}}e^{-F\eta_{f}/RT}\}$$
(162)

During the anodic dissolution of iron, in the backward direction, the dependency of current *vs.* overpotential can be expressed as:

$$\tilde{\iota}^f = 2F \tilde{k}_f (\mathcal{C}_{OH^-})^2 e^{2F\eta_f/RT}$$
(163)
For this mechanism p_{OH^-} and E_{OH^-} are theoretically obtained as:

$$p_{OH^{-}}^{f} = \left(\frac{\partial lni_{0,a}}{\partial lnC_{OH^{-}}}\right)_{C_{Fe2+}} = 2$$

$$i_{a,Fe}^{f} = i_{c,H}^{f} \rightarrow 2F \overleftarrow{k}_{f} C_{OH^{-}} e^{\alpha_{a}^{f}F(E-E_{corr})/RT} = 2F \overrightarrow{k}_{e} C_{Fe^{2+}} C_{OH^{-}} e^{-\alpha_{c}^{f}F(E-E_{corr})/RT} \rightarrow$$

$$E_{OH^{-}}^{f} = \left(\frac{\partial (E_{corr.})}{\partial \log (C_{OH^{-}})}\right)_{C_{Fe2+}}^{f} = -2.3 \left(\frac{p_{OH^{-}+1}^{f}}{\alpha_{a}^{f}+\alpha_{c}^{f}}\right)_{F}^{RT} = -2.3 \left(\frac{2+1}{2+1}\right)_{F}^{RT} = -0.06$$

Mechanism (g):

$$Fe + FeOH_{ads.} + OH^{-} \leftrightarrow (FeOH)_{2,ads.} + e^{-}$$

$$(FeOH)_{2,ads.} \leftrightarrow (FeOH)_{2}^{+} + e^{-}$$

$$(FeOH)_{2}^{+} \xrightarrow{rds} FeOH^{+} + FeOH_{ads.}$$

$$FeOH^{+} \leftrightarrow Fe^{2+} + OH^{-}$$

For this scheme, $n_f^g = 0$, $n_b^g = 2$, $v_f^g = 1$, $n_r^g = 1$ and thus:

$$\begin{vmatrix} b_{c}^{g} \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_{f}^{g}}{r_{f}^{g}} + n_{r}^{g}\beta^{g}\right)_{F}} = \frac{2.3RT}{0.5F}$$

$$\begin{vmatrix} b_{a}^{g} \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_{b}^{g} + \nu^{g}n_{r}^{g}}{\nu^{f}} - n_{r}^{g}\beta^{g}\right)_{F}} = \frac{2.3RT}{2.5F}$$

$$\frac{\theta_{FeOH}}{\theta_{(FeOH)_{2}}} = \frac{K_{1}^{g}}{C_{OH^{-}}}e^{-F\eta/RT}$$
(164)

$$C_{(FeOH)_{2}^{+}} = (K_{2}^{g})^{-1} \theta_{(FeOH)_{2}} e^{F\eta/RI}$$
(165)

$$C_{FeOH^+} = K_4^g C_{Fe^{2+}} C_{OH^-}$$
(166)

$$\theta_{FeOH} = \frac{K_1^g K_2^g}{C_{OH^-}} C_{(FeOH)_2^+} e^{-2F\eta/RT}$$
(167)

$$C_{(FeOH)_{2}^{+}} = (K_{1}^{g}K_{2}^{g})^{-1}C_{OH} - \theta_{FeOH}e^{F\eta/RT}$$
(168)

$$r^{g} = \overleftarrow{k}_{g} e^{-\frac{F\eta_{f}}{RT}} - \vec{k}_{g} \frac{\left(C_{FeOH}^{+}\right)^{2}}{C_{OH}^{-}} e^{-\frac{2F\eta_{f}}{RT}} = \overleftarrow{k}_{g} e^{-\frac{F\eta_{f}}{RT}} - \vec{k}_{g}' (C_{Fe^{2+}})^{2} C_{OH}^{-} e^{-\frac{2F\eta_{f}}{RT}}$$
(169)

$$r^{g} = \overleftarrow{k}_{g} e^{\frac{2.5F\eta_{f}}{RT}} - \vec{k}_{g}' (C_{Fe^{2+}})^{2} C_{OH} - e^{-\frac{0.5F\eta_{f}}{RT}}$$
(170)

During the anodic dissolution of iron, in the backward direction, the dependency of current *vs.* overpotential can be expressed as:

$$\tilde{\iota}^g = \overleftarrow{k}_g e^{\frac{2.5F\eta_f}{RT}}$$
(171)

For this mechanism p_{OH^-} and E_{OH^-} are theoretically obtained as:

$$p_{OH^{-}}^{g} = \left(\frac{\partial \ln i_{0,a}}{\partial \ln C_{OH^{-}}}\right)_{C_{Fe2+}} = 0$$

$$i_{a,Fe}^{g} = i_{c,H}^{g} \rightarrow 2F \overleftarrow{k}_{g} C_{OH^{-}} e^{\alpha_{a}^{g} F(E-E_{corr})/RT} = 2F \overrightarrow{k}_{g} C_{Fe^{2+}} C_{OH^{-}} e^{-\alpha_{c}^{g} F(E-E_{corr})/RT} \rightarrow E_{OH^{-}}^{g} = \left(\frac{\partial (E_{corr.})}{\partial \log (C_{OH^{-}})}\right)_{C_{Fe2+}}^{g} = -2.3 \left(\frac{p_{OH^{-}}^{g}+1}{\alpha_{a}^{g}+\alpha_{c}^{f}}\right)_{F}^{RT} = -2.3 \left(\frac{0+1}{2.5+0.5}\right)_{F}^{RT} = -0.02 \text{ V/dec.}$$

Mechanism (h):

$$\begin{aligned} Fe + FeOH_{ads.} + OH^{-} \xrightarrow{rds} (FeOH)_{2,ads.} + e^{-} \\ (FeOH)_{2,ads.} &\leftrightarrow (FeOH)_{2}^{+} + e^{-} \\ (FeOH)_{2}^{+} &\leftrightarrow HFe_{2}O_{2}^{+} + H^{+} + e^{-} \\ HFe_{2}O_{2}^{+} + H^{+} &\leftrightarrow 2FeOH^{+} \\ 2FeOH^{+} + 2H^{+} &\leftrightarrow 2Fe^{2+} + 2H_{2}O \\ \text{In this case, } n^{h}_{f} = 2, n^{h}_{b} = 0, v^{h} = 1, n^{h}_{r} = 1 \text{ and therefore:} \end{aligned}$$

$$|b_{c}^{h}| = \frac{2.3RT}{\left(\frac{n_{f}^{h}}{\nu^{h}} + n_{r}^{h}\beta^{h}\right)F} = \frac{2.3RT}{2.5F}$$
$$|b_{a}^{h}| = \frac{2.3RT}{\left(\frac{n_{b}^{h} + \nu^{h}n_{r}^{h}}{\nu^{h}} - n_{r}^{h}\beta^{h}\right)F} = \frac{2.3RT}{0.5F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{h} = 2F \{ i^{h}_{0,a} e^{0.5F\eta_{h}/RT} - i^{h}_{0,c} e^{-2.5F\eta_{h}/RT} \}$$

$$p^{h}_{OH^{-}} = 1$$

$$E^{h}_{OH^{-}} = -0.04 \text{ V/dec.}$$
(172)

Mechanism (i):

$$Fe + H_2 O \xrightarrow{rds} FeO_{ads.} + 2H^+ + 2e^-$$

$$FeO_{ads.} + OH^- \leftrightarrow HFeO_2^-$$

$$HFeO_2^- + H^+ \leftrightarrow Fe(OH)_{2,ads}$$

$$Fe(OH)_{2,ads} \leftrightarrow Fe^{2+} + 2OH^-$$

In this case, $n_{f}^{i} = 0$, $n_{b}^{i} = 0$, $v^{i} = 1$, $n_{r}^{i} = 2$ and therefore:

$$\begin{vmatrix} b_c^i \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_f^i}{\nu^h} + n_r^i \beta^i\right)F} = \frac{2.3RT}{F}$$
$$\begin{vmatrix} b_a^i \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_b^i + \nu^i n_r^i}{\nu^i} - n_r^i \beta^i\right)F} = \frac{2.3RT}{F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{i} = 2F \{ i^{i}_{0,a} e^{F\eta_{i}/RT} - i^{i}_{0,c} e^{-F\eta_{i}/RT} \}$$

$$p^{i}_{OH^{-}} = 0$$

$$E^{i}_{OH^{-}} = -0.03 \text{ V/dec.}$$
Mechanism (j):
(173)

$$Fe + H_2 O \xrightarrow{rds} FeO_{ads.} + 2H^+ + 2e^-$$

 $FeO_{ads.} + OH^{-} \leftrightarrow HFeO_{2}^{-}$ $HFeO_{2}^{-} + H^{+} \leftrightarrow FeOH^{+} + OH^{-}$ $FeOH^{+} + H^{+} \leftrightarrow Fe^{2+} + H_{2}O$

For this case, $n_f^i = 0$, $n_b^i = 0$, $v^j = 1$, $n_r^j = 2$ and hence:

$$\begin{vmatrix} b_c^j \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_f^j}{\nu^j} + n_r^j \beta^j\right)F} = \frac{2.3RT}{F}$$
$$\begin{vmatrix} b_a^j \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_b^j + \nu^j n_r^j}{\nu^j} - n_r^j \beta^j\right)F} = \frac{2.3RT}{F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{j} = 2F\{i_{0,a}^{j}e^{F\eta_{j}/RT} - i_{0,c}^{j}e^{-F\eta_{j}/RT}\}$$
(174)

$$p_{OH^{-}}^{j} = 0$$

$$E_{OH^{-}}^{j} = -0.03 \text{ V/dec.}$$

Mechanism (k):

$$Fe + 20H^{-} \leftrightarrow Fe(OH)_{2,ads.} + 2e^{-}$$

$$Fe(OH)_{2,ads.} \xrightarrow{rds} Fe(OH)_{2}^{+} + e^{-}$$

$$Fe(OH)_{2}^{+} \leftrightarrow FeO(OH)_{ads.} + H^{+}$$

$$FeO(OH)_{ads.} \leftrightarrow FeOH_{ads.} + \frac{1}{2}O_{2}$$

$$FeOH_{ads.} \leftrightarrow FeOH^{+} + e^{-}$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

For this mechanism, $n_{f}^{k} = 1$, $n_{b}^{k} = 2$, $v^{k} = 1$, $n_{r}^{k} = 1$ and therefore:

$$|b_{c}^{k}| = \frac{2.3RT}{\left(\frac{n_{f}^{k}}{\nu^{k}} + n_{r}^{k}\beta^{k}\right)F} = \frac{2.3RT}{1.5F}$$
$$|b_{a}^{k}| = \frac{2.3RT}{\left(\frac{n_{b}^{k} + \nu^{k}n_{r}^{k}}{\nu^{k}} - n_{r}^{k}\beta^{k}\right)F} = \frac{2.3RT}{2.5F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{k} = 2F \{ i_{0,a}^{k} e^{2.5F \eta_{k}/RT} - i_{0,c}^{k} e^{-1.5F \eta_{k}/RT} \}$$

$$p_{OH^{-}}^{k} = 2$$

$$E_{OH^{-}}^{k} = -0.045 \text{ V/dec.}$$
(175)

Mechanism (l):

$$2Fe + H_20 \leftrightarrow Fe_2H_20^+ + e^-$$

$$Fe_2H_20^+ \leftrightarrow Fe_2(0H)^+ + H^+ + e^-$$

$$Fe_2(0H)^+ \xrightarrow{rds} Fe^{2+} + Fe0H_{ads.} + e^-$$

$$Fe0H_{ads.} + H^+ \leftrightarrow Fe^{2+} + H_20 + e^-$$

For this mechanism, $n_f^l = 1$, $n_b^l = 2$, $v^l = 1$, $n_r^l = 1$ and hence:

$$|b_c^l| = \frac{2.3RT}{\left(\frac{n_f^l}{\nu^l} + n_r^l\beta^l\right)F} = \frac{2.3RT}{1.5F}$$

$$|b_{a}^{l}| = \frac{2.3RT}{\left(\frac{n_{b}^{l} + \nu^{l}n_{r}^{l}}{\nu^{l}} - n_{r}^{l}\beta^{l}\right)F} = \frac{2.3RT}{2.5F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{l} = 2F \left\{ i^{l}_{0,a} e^{2.5F\eta_{l}/RT} - i^{l}_{0,c} e^{-1.5F\eta_{l}/RT} \right\}$$
(176)

$$p_{OH^-}^l = 1$$

 $E_{OH^-}^l = -0.03 \text{ V/dec.}$

Mechanism (m):

$$2Fe + H_2 0 \leftrightarrow Fe_2 H_2 0^+ + e^-$$

$$Fe_2 H_2 0^+ + 0H^- \xrightarrow{rds} 2Fe 0 H_{ads.} + H^+ + e^-$$

$$2Fe 0 H_{ads.} \leftrightarrow 2Fe 0H^+ + 2e^-$$

$$2Fe 0H^+ + 2H^+ \leftrightarrow 2Fe^{2+} + 2H_2 0$$

In this case, $n^m_f = 2$, $n^m_b = 1$, $v^m = 1$, $n^m_r = 1$ and therefore:

$$\begin{aligned} |b_{c}^{m}| &= \frac{2.3RT}{\left(\frac{n_{f}^{m}}{\nu^{m}} + n_{r}^{m}\beta^{m}\right)F} = \frac{2.3RT}{2.5F} \\ |b_{a}^{m}| &= \frac{2.3RT}{\left(\frac{n_{b}^{m} + \nu^{m}n_{r}^{m}}{\nu^{m}} - n_{r}^{m}\beta^{m}\right)F} = \frac{2.3RT}{1.5F} \end{aligned}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH^-} and E_{OH^-} for this mechanism will be obtained as:

$$i^{m} = 2F \{ i^{m}_{0,a} e^{F\eta_{m}/RT} - i^{m}_{0,c} e^{-1.5F\eta_{m}/RT} \}$$

$$p^{m}_{OH^{-}} = 1$$
(177)

 $E_{OH^-}^m = -0.03 \text{ V/dec.}$

Mechanism (n):

$$Fe + H_2 0 \leftrightarrow FeO(OH)_{ads.}$$

$$FeO(OH)_{ads.} \leftrightarrow FeOH_{ads.} + \frac{1}{2}O_2$$

$$FeOH_{ads.} \xrightarrow{rds} FeOH^+ + e^-$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

For this scheme, $n_f^n = 0$, $n_b^n = 0$, $v^n = 1$, $n_r^n = 1$ and hence:

$$|b_{c}^{n}| = \frac{2.3RT}{\left(\frac{n_{f}^{n}}{\nu^{n}} + n_{r}^{n}\beta^{n}\right)F} = \frac{2.3RT}{0.5F}$$
$$|b_{a}^{n}| = \frac{2.3RT}{\left(\frac{n_{b}^{n} + \nu^{n}n_{r}^{n}}{\nu^{n}} - n_{r}^{n}\beta^{n}\right)F} = \frac{2.3RT}{0.5F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{n} = 2F \{ i^{n}_{0,a} e^{0.5F\eta_{n}/RT} - i^{n}_{0,c} e^{-0.5F\eta_{m}/RT} \}$$
(178)

$$p^{n}_{OH^{-}} = 0$$

$$E^{n}_{OH^{-}} = -0.06 \text{ V/dec.}$$

Mechanism (o):

$$Fe + 2H_{0}O \Leftrightarrow Fe(OH)_{0}^{+} + H_{0} + e^{-}$$

$$Fe^{(0H)_{2}^{+}} \xrightarrow{rds} Fe^{(0H)_{2}^{-}} + H^{+}$$

$$2Fe^{(0H)_{ads.}} + 2H^{+} \leftrightarrow (Fe^{0H})_{2}^{+} + H^{2}^{0} + Fe^{2+} + \frac{1}{2}O_{2}^{+} + e^{-}$$

For this case, $n^o_f = 1$, $n^o_b = 1$, $v^o = 1$, $n^o_r = 0$ and therefore:

$$\begin{aligned} |b_{c}^{0}| &= \frac{2.3RT}{\left(\frac{n_{f}^{0}}{v^{0}} + n_{r}^{0}\beta^{0}\right)F} = \frac{2.3RT}{F} \\ |b_{a}^{0}| &= \frac{2.3RT}{\left(\frac{n_{b}^{0} + v - n_{r}^{0}}{v^{0}} - n_{r}^{0}\beta^{0}\right)F} = \frac{2.3RT}{F} \\ i^{o} &= 2F\left\{i_{0,a}^{o}e^{F\eta_{o}/RT} - i_{0,c}^{o}e^{-F\eta_{o}/RT}\right\} \\ p_{OH^{-}}^{o} &= 0 \\ E_{OH^{-}}^{o} &= -0.03 \text{ V/dec.} \end{aligned}$$
(179)

Mechanism (p):

$$Fe + H_2 0 \leftrightarrow H_2 Fe0^{2+} + 2e^{-}$$

$$H_2 Fe0^{2+} \xrightarrow{rds} Fe0_{ads.} + 2H^{+}$$

$$Fe0_{ads.} + H_2 0 \leftrightarrow Fe(0H)_2^{+} + e^{-}$$

$$Fe(0H)_2^{+} \leftrightarrow Fe0H^{+} + H^{+} + \frac{1}{2}O_2 + e^{-}$$

$$Fe0H^{+} + H^{+} \leftrightarrow Fe^{2+} + H_2 0$$

For this mechanism, $n_f^p = 2$, $n_b^p = 2$, $v^p = 1$, $n_r^p = 0$ and thus:

$$\begin{vmatrix} b_c^p \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_f^p}{\nu^p} + n_r^p \beta^p\right)F} = \frac{2.3RT}{2F}$$
$$\begin{vmatrix} b_a^p \end{vmatrix} = \frac{2.3RT}{\left(\frac{n_b^p + \nu^p n_r^p}{\nu^p} - n_r^p \beta^p\right)F} = \frac{2.3RT}{2F}$$

Following the same mathematical computation, the final expressions of the Butler-Volmer equation, p_{OH^-} and E_{OH^-} for this mechanism will be obtained as:

$$i^{p} = 2F\{i^{p}_{0,a}e^{2F\eta_{p}/RI} - i^{p}_{0,c}e^{-2F\eta_{p}/RI}\}$$
(180)
$$p^{p}_{0H^{-}} = 0$$

$$E^{p}_{0H^{-}} = -0.015 \text{ V/dec.}$$
Mechanism (q):

$$Fe + H_{0} \leftrightarrow H_{0}Fe^{Q^{2+}} + 2e^{-}$$

$$Fe^{2} + H_{2}O \leftrightarrow H_{2}FeO^{2} + 2e^{2}$$

$$H_{2}FeO^{2+} \xrightarrow{rds} FeOH^{+} + H^{+}$$

$$FeOH^{+} + H^{+} \leftrightarrow Fe^{2+} + H_{2}O$$

In this case, $n_f^q = 0$, $n_b^q = 2$, $v_f^q = 1$, $n_r^q = 0$ and thus:

$$\begin{aligned} \left| b_{c}^{q} \right| &= \frac{2.3RT}{\left(\frac{n_{f}^{q}}{\nu^{q}} + n_{r}^{q}\beta^{q}\right)_{F}} = \frac{2.3RT}{0 \times F} \rightarrow \infty \quad (N/A) \\ \left| b_{a}^{q} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{q} + \nu^{q}n_{r}^{q}}{\nu^{q}} - n_{r}^{q}\beta^{q}\right)_{F}} = \frac{2.3RT}{2F} \\ p_{OH^{-}}^{q} &= 0 \\ E_{OH^{-}}^{q} &= -0.03 \text{ V/dec.} \\ \underline{Mechanism (r)}: \\ Fe + OH^{-} \leftrightarrow FeOH^{+} + 2e^{-} \\ Fe + FeOH^{+} + H_{2}O \xrightarrow{rds} HFe_{2}O_{2}^{+} + 2H^{+} + 2e^{-} \end{aligned}$$

$$HFe_2O_2^+ \leftrightarrow FeO_{ads.} + FeOH^+$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

In this case, $n_f^r = 0$, $n_b^r = 2$, $v^r = 1$, $n_r^r = 2$ and thus:

$$\begin{aligned} |b_c^r| &= \frac{2.3RT}{\left(\frac{n_f^r}{\nu^r} + n_r^r \beta^r\right)F} = \frac{2.3RT}{F} \\ |b_a^r| &= \frac{2.3RT}{\left(\frac{n_b^r + \nu^r n_r^r}{\nu^r} - n_r^r \beta^r\right)F} = \frac{2.3RT}{3F} \end{aligned}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{r} = 2F\{i^{r}_{0,a}e^{3F\eta_{r}/RT} - i^{r}_{0,c}e^{-F\eta_{r}/RT}\}$$

$$p^{r}_{0H^{-}} = 1$$

$$E^{r}_{0H^{-}} = -0.03 \text{ V/dec.}$$
(181)

Mechanism (s):

$$Fe + 20H^- \leftrightarrow Fe(0H)_{2,ads.} + 2e^-$$

$$2Fe(OH)_{2,ads.} \xrightarrow{rds} Fe(OH)_{2,ads.} + Fe(OH)_{2}^{+} + e^{-}$$
$$Fe(OH)_{2}^{+} \leftrightarrow FeOH^{+} + H^{+} + \frac{1}{2}O_{2} + e^{-}$$

 $FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$

For this mechanism, $n_f^s = 1$, $n_b^s = 2$, $v^s = 1$, $n_r^s = 1$ and hence:

$$|b_{c}^{s}| = \frac{2.3RT}{\left(\frac{n_{f}^{s}}{\nu^{s}} + n_{r}^{s}\beta^{s}\right)F} = \frac{2.3RT}{1.5F}$$
$$|b_{a}^{s}| = \frac{2.3RT}{\left(\frac{n_{b}^{s} + \nu^{s}n_{r}^{s}}{\nu^{s}} - n_{r}^{s}\beta^{s}\right)F} = \frac{2.3RT}{2.5F}$$

Following the same mathematical computation, the final expressions for the Butler-

Volmer equation, p_{OH-} and E_{OH-} for this mechanism will be obtained as:

$$i^{s} = 2F \{ i^{s}_{0,a} e^{2.5F\eta_{s}/RT} - i^{s}_{0,c} e^{-1.5F\eta_{s}/RT} \}$$
(182)

$$p^{s}_{OH^{-}} = 4$$

$$E^{s}_{OH^{-}} = -0.075 \text{ V/dec.}$$

$$\underline{\text{Mechanism (a'):}}$$

$$Fe + OH^{-} + FeOH_{ads.} \leftrightarrow (FeOH)_{2,ads} + e^{-}$$

$$(FeOH)_{2,ads} \xrightarrow{rds} FeOH_{ad.} + FeOH^{+}_{ads.} + e$$

$$FeOH^{+}_{ads.} \xrightarrow{des} FeOH^{+}$$

 $FeOH_{ads.} \leftrightarrow FeOH^+ + e^-$

 $FeOH^+ \leftrightarrow Fe^{2+} + OH^-$

In this case, $n^{a'_{f}} = 1$, $n^{a'_{b}} = 2$, $v^{a'} = 1$, $n^{a'_{r}} = 0$ and hence at 303 K:

$$|b_c^{a'}| = \left| \left(\frac{dE_c^{a'}}{dlogi_c^{a'}} \right)_c \right| = \frac{2.3RT}{\left(\frac{n_f^{a'}}{\nu^{a'}} + n_r^{a'}\beta^{a'} \right)_F} = 0.06 \text{ V/dec.}$$

$$|b_a^{a'}| = \left| \left(\frac{dE_a^{a'}}{dlog i_a^{a'}} \right)_a \right| = \frac{2.3RT}{\left(\frac{n_b^{a'} + \nu^{a'} n_r^{a'}}{\nu^{a'}} - n_r^{a'} \beta^{a'} \right)_F} = 0.03 \text{ V/dec}$$

 $p^{a\prime}_{OH^-}=0.5$

 $E_{OH^-}^{a'} = -0.03 \text{ V/dec.}$

Mechanism (b'):

 $Fe + H_2 0 \leftrightarrow FeOH_{ads.} + H^+ + e^ FeOH_{ads.} \leftrightarrow FeOH^+ + e^ FeOH^+ + Fe \xrightarrow{rds} Fe_2 OH^+_{ads}$ $Fe_2 OH^+_{ads} \xrightarrow{des} Fe_2 OH^+$ $Fe_2 OH^+ \leftrightarrow Fe^{2+} + FeOH_{ads.} + e^ FeOH_{ads.} + H^+ \leftrightarrow Fe^{2+} + H_2 O + e^-$

For this case, $n^{b'}_{f} = 2$, $n^{b'}_{b} = 2$, $v^{b'} = 1$, $n^{b'}_{r} = 0$ and therefore at 303 K:

$$|b_c^{b'}| = \left| \left(\frac{dE_c^{b'}}{dlog i_c^{b'}} \right)_c \right| = \frac{2.3RT}{\left(\frac{n_f^{b'}}{\nu^{b'}} + n_r^{b'} \beta^{b'} \right)_F} = 0.03 \text{ V/dec.}$$

$$|b_a^{b'}| = \left| \left(\frac{dE_a^{b'}}{dlog i_a^{b'}} \right)_a \right| = \frac{2.3RT}{\left(\frac{n_b^{b'} + \nu^{b'} n_r^{b'}}{\nu^{b'}} - n_r^{b'} \beta^{b'} \right)_F} = 0.03 \text{ V/dec.}$$

 $p_{OH^-}^{b'} = 1$ $E_{OH^-}^{b'} = -0.03 \text{ V/dec.}$

Mechanism (c'):

$$Fe + OH^{-} \xrightarrow{rds} FeOH^{+}_{ads.} + 2e^{-}$$

$$FeOH^{+}_{ads.} \xrightarrow{des} FeOH^{+}$$

$$FeOH^{+} \leftrightarrow Fe^{2+} + OH^{-}$$

In this case, $n^{c'}_{f} = 0$, $n^{c'}_{b} = 2$, $v^{c'} = 1$, $n^{c'}_{r} = 0$ and thus at 303 K:

$$|b_{c}^{c'}| = \frac{2.3RT}{\left(\frac{n_{f}^{c'}}{v^{c_{f}}} + n_{r}^{c'}\beta^{c'}\right)F} = \infty \qquad (N/A)$$
$$|b_{a}^{c'}| = \frac{2.3RT}{\left(\frac{n_{b}^{c'} + v^{c'}n_{r}^{c'}}{v^{c}} - n_{r}^{c'}\beta^{c'}\right)F} = 0.03 \text{ V/dec}$$

 $p_{OH^{-}}^{c'} = 1$

 $E_{OH^-}^{c'} = -0.06 \text{ V/dec.}$

Mechanism (d'):

$$\begin{split} Fe + OH^{-} &\leftrightarrow FeOH_{ads.} + e^{-} \\ FeOH_{ads.} + OH^{-} \stackrel{rds}{\rightarrow} FeO_{ads.} + H_{2}O + e^{-} \\ FeO_{ads.} + OH^{-} &\leftrightarrow HFeO_{2}^{-} \\ HFeO_{2}^{-} \underset{ads.}{\overset{des}{\rightarrow}} HFeO_{2}^{-} \\ HFeO_{2}^{-} + H_{2}O &\leftrightarrow Fe(OH)_{2,ads.} + OH^{-} \\ Fe(OH)_{2,ads.} &\leftrightarrow Fe^{2+} + 2OH^{-} \end{split}$$

For this case, $n^{d'}_{f} = 0$, $n^{d'}_{b} = 2$, $v^{d'} = 1$, $n^{d'}_{r} = 0$ and therefore at 303 K:

$$|b_c^{d\prime}| = \frac{2.3RT}{\left(\frac{n_f^{d\prime}}{\nu^{d\prime}} + n_r^{d\prime}\beta^{d\prime}\right)_F} = \infty \quad (N/A)$$

$$|b_a^{d'}| = \frac{2.3RT}{\left(\frac{n_b^{d'} + \nu^{d'} n_r^{d'}}{\nu^d} - n_r^{d'} \beta^{d'}\right)_F} = 0.03 \text{ V/dec.}$$

 $p_{OH^-}^{d\prime}=3$

 $E_{OH^-}^{d'} = -0.12 \text{ V/dec.}$

Mechanism (e'), (branched version of Bockris):

 $Fe + H_2 0 \leftrightarrow FeOH_{ads.} + H^+ + e^ FeOH_{ads.} \xrightarrow{rds} FeOH_{ads.}^+ + e^ FeOH_{ads.}^+ \xrightarrow{des} FeOH^+$ $FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$

In this mechanism, $n^{e'}_{f} = 0$, $n^{e'}_{b} = 2$, $v^{e'} = 1$, $n^{e'}_{r} = 0$ and therefore at 303 K:

$$|b_{c}^{e'}| = \frac{2.3RT}{\left(\frac{n_{f}^{e'}}{v^{e'}} + n_{r}^{e'}\beta^{e_{\prime}}\right)F} = \infty \text{ (N/A)}$$
$$|b_{a}^{e'}| = \frac{2.3RT}{\left(\frac{e!}{v^{e'}} + n_{r}^{e'}\beta^{e_{\prime}}\right)F} = 0.03 \text{ V}$$

$$|b_a^{e'}| = \frac{2.3RT}{\left(\frac{n_b^{e'} + \nu^{e'} n_r^{e'}}{\nu^{e'}} - n_r^{e'} \beta^{e'}\right)^F} = 0.03 \text{ V/dec.}$$

 $p^{e\prime}_{OH^-}=1$

$$E_{OH^-}^{e'} = -0.06 \text{ V/dec.}$$

Mechanism (f'), (branched version of Heusler):

$$Fe + H_20 \leftrightarrow FeOH_{ads.} + H^+ + e^-$$

$$Fe + FeOH_{ads.} \leftrightarrow Fe(FeOH)$$

$$Fe(FeOH) + OH^- \xrightarrow{rds} FeOH_{ads.}^+ + FeOH_{ads.} + 2e^-$$

$$FeOH_{ads.}^+ \xrightarrow{des} FeOH^+$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

In this case, $n_{f}^{r} = 0$, $n_{b}^{f} = 3$, $v_{r}^{r} = 1$, $n_{r}^{r} = 0$ and thus at 303 K:

$$\begin{split} \left| b_{c}^{f'} \right| &= \frac{2.3RT}{\left(\frac{n_{f'}^{f'}}{v^{f'}} + n_{r}^{f'}\beta^{f'} \right)^{F}} = \infty \text{ (N/A)} \\ \left| b_{a}^{f'} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{f'} + v^{f'}n_{r}^{f'}}{v^{f}} - n_{r}^{f'}\beta^{f'} \right)^{F}} = 0.02 \text{ V/dec.} \end{split}$$

$$p_{OH^-}^{f'} = 1$$

 $E_{OH^-}^{f'} = -0.04 \text{ V/dec.}$

Mechanism (g'):

$$Fe + FeOH_{ads.} + OH^{-} \leftrightarrow (FeOH)_{2,ads.} + e^{-}$$

$$(FeOH)_{2,ads.} \leftrightarrow (FeOH)_{2,ads}^{+} + e^{-}$$

$$(FeOH)_{2,ads}^{+} \xrightarrow{rds} FeOH_{ads.}^{+} + FeOH_{ads.}$$

$$FeOH_{ads.}^{+} \xrightarrow{des} FeOH^{+}$$

$$FeOH^{+} \leftrightarrow Fe^{2+} + OH^{-}$$
For this machanism $u_{s}^{g'} = 0$ $u_{s}^{g'} = 2$ $u_{s}^{g'} = 1$ $u_{s}^{g'}$

For this mechanism, $n^{g'}_{f} = 0$, $n^{g'}_{b} = 2$, $v^{g'} = 1$, $n^{g'}_{r} = 0$ and therefore at 303 K:

$$\begin{aligned} \left| b_{c}^{g'} \right| &= \frac{2.3RT}{\left(\frac{n_{f}^{g'}}{v^{g'}} + n_{r}^{g'}\beta^{g'} \right)^{F}} = \infty \text{ (N/A)} \\ \left| b_{a}^{g'} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{g'} + v^{g}n_{r}^{g'}}{v^{g'}} - n_{r}^{g'}\beta^{g'} \right)^{F}} = 0.03 \text{ V/dec.} \\ p_{OH^{-}}^{g'} &= 1 \\ E_{OH^{-}}^{g'} &= -0.06 \text{ V/dec.} \end{aligned}$$
Mechanism (h'):

$$Fe + FeOH_{ads.} + OH^{-} \xrightarrow{rds} (FeOH)_{2,ads.} + e^{-}$$

$$(FeOH)_{2,ads.} \leftrightarrow (FeOH)_{2,ads.}^{+} + e^{-}$$

$$(FeOH)_{2,ads.}^{+} \xrightarrow{des} (FeOH)_{2}^{+}$$

$$(FeOH)_{2}^{+} \leftrightarrow HFe_{2}O_{2}^{+} + H^{+} + e^{-}$$

$$HFe_{2}O_{2}^{+} + H^{+} \leftrightarrow 2FeOH^{+}$$

$2FeOH^+ + 2H^+ \leftrightarrow 2Fe^{2+} + 2H_2O$

For this case, $n^{h'}_{f} = 1$, $n^{h'}_{b} = 2$, $v^{h'} = 1$, $n^{h'}_{r} = 0$ and therefore at 303 K:

$$|b_c^{h\prime}| = \frac{2.3RT}{\left(\frac{n_f^{h\prime}}{v^{h}\prime} + n_r^{h\prime}\beta^{h\prime}\right)_F} = -0.06 \text{ V/dec}$$

$$|b_a^{h'}| = \frac{2.3RT}{\left(\frac{n_b^{h'} + \nu^{h'} n_r^{h'}}{\nu^{h'}} - n_r^{h'} \beta^{h'}\right)F} = 0.03 \text{ V/dec.}$$

 $p^{h\prime}_{OH^-}=1$

$$E_{OH^-}^{h'} = -0.04 \text{ V/dec.}$$

Mechanism (i'):

 $Fe + H_2 O \xrightarrow{rds} FeO_{ads.} + 2H^+ + 2e^ FeO_{ads.} + OH^- \leftrightarrow HFeO_2^-_{ads.}$ $HFeO_2^-_{ads.} \xrightarrow{des} HFeO_2^ HFeO_2^- + H^+ \leftrightarrow Fe(OH)_{2,ads.}$ $Fe(OH)_{2,ads.} \leftrightarrow Fe^{2+} + 2OH^-$

For this mechanism, $n_{f}^{i'} = 0$, $n_{b}^{i'} = 2$, $v_{f}^{i'} = 1$, $n_{r}^{i'} = 0$ and therefore at 303 K:

$$\begin{aligned} \left| b_{c}^{i\prime} \right| &= \frac{2.3RT}{\left(\frac{n_{f}^{i\prime}}{\nu h} + n_{r}^{i\prime} \beta^{i\prime} \right)_{F}} = \infty \text{ (N/A)} \\ \left| b_{a}^{i\prime} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{i\prime} + \nu^{i\prime} n_{r}^{i\prime}}{\nu^{l}} - n_{r}^{i\prime} \beta^{i\prime} \right)_{F}} = 0.03 \text{ V/dec.} \\ p_{OH^{-}}^{i\prime} &= 3 \\ E_{OH^{-}}^{i\prime} &= -0.12 \text{ V/dec.} \end{aligned}$$

Mechanism (j'):

$$Fe + H_2O \xrightarrow{rds} FeO_{ads.} + 2H^+ + 2e^-$$

$$FeO_{ads.} + OH^- \leftrightarrow HFeO_2^-_{ads.}$$

$$HFeO_2^-_{ads.} \xrightarrow{des} HFeO_2^-$$

$$HFeO_2^- + H^+ \leftrightarrow FeOH^+ + OH^-$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

In this case, $n^{j'}_{f} = 0$, $n^{j'}_{b} = 2$, $v^{j'} = 1$, $n^{j'}_{r} = 0$ and thus at 303 K:

$$\begin{aligned} \left| b_{c}^{j'} \right| &= \frac{2.3RT}{\left(\frac{n_{f}^{j'}}{v^{j}} + n_{r}^{j'}\beta^{j'}\right)^{F}} = \infty \quad (N/A) \\ \left| b_{a}^{j'} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{j'} + v^{j}n_{r}^{j'}}{v^{j}} - n_{r}^{j'}\beta^{j'}\right)^{F}} = 0.03 \text{ V/dec.} \\ p_{OH^{-}}^{j'} &= 3 \\ E_{OH^{-}}^{j'} &= -0.12 \text{ V/dec.} \\ \underline{Mechanism (k^{*}):} \\ Fe + 2OH^{-} \leftrightarrow Fe(OH)_{2,ads.} + 2e^{-} \\ Fe(OH)_{2,ads.} \xrightarrow{rds} Fe(OH)_{2}^{+} + e^{-} \\ Fe(OH)_{2}^{+} &\leftrightarrow FeO(OH)_{ads.} + H^{+} \end{aligned}$$

$$FeO(OH)_{ads.} \leftrightarrow FeOH_{ads.} + \frac{1}{2}O_2$$

$$FeOH_{ads.} \leftrightarrow FeOH_{ads.}^{+} + e^{-}$$

$$FeOH_{ads.}^{+} \xrightarrow{des} FeOH^{+}$$

 $FeOH^{+} + H^{+} \leftrightarrow Fe^{2+} + H_2O$

In this case, $n^{k'_f} = 0$, $n^{k'_b} = 4$, $v^{k'} = 1$, $n^{k'_r} = 0$ and thus at 303 K:

$$|b_{c}^{k'}| = \frac{2.3RT}{\left(\frac{n_{f}^{k'}}{\nu^{k'}} + n_{r}^{k'}\beta^{k'}\right)F} = \infty \text{ (N/A)}$$
$$|b_{a}^{k'}| = \frac{2.3RT}{\left(\frac{n_{b}^{k'} + \nu^{k'}n_{r}^{k'}}{\nu^{k'}} - n_{r}^{k'}\beta^{k'}\right)F} = 0.015 \text{ V/dec.}$$

 $p_{OH^-}^{k\prime}=3$

 $E_{OH^-}^{k\prime} = -0.06 \text{ V/dec.}$

Mechanism (l'):

$$2Fe + H_2 O \leftrightarrow Fe_2 H_2 O^+_{ads.} + e^-$$

$$Fe_2 H_2 O^+_{ads.} \xrightarrow{des} Fe_2 H_2 O^+$$

$$Fe_2 H_2 O^+ \leftrightarrow Fe_2 (OH)^+ + H^+ + e^-$$

$$Fe_2 (OH)^+ \xrightarrow{rds} Fe^{2+} + FeOH_{ads.} + e^-$$

$$FeOH_{ads.} + H^+ \leftrightarrow Fe^{2+} + H_2 O + e^-$$

In this case, $n_{f}^{l'} = 3$, $n_{b}^{l'} = 1$, $v_{f}^{l'} = 1$, $n_{r}^{l'} = 0$ and therefore at 303 K:

$$|b_c^{l\prime}| = \frac{2.3RT}{\left(\frac{n_f^{l\prime}}{\nu^l} + n_r^{l\prime}\beta^{l\prime}\right)_F} = 0.02 \text{ V/dec.}$$

$$|b_a^{l\prime}| = \frac{2.3RT}{\left(\frac{n_b^{l\prime} + \nu^{l\prime} n_r^{l\prime}}{\nu^l} - n_r^{l\prime} \beta^{l\prime}\right)^F} = 0.06 \text{ V/dec.}$$

$$p_{OH^-}^{l\prime}=0$$

 $E_{OH^-}^{l\prime} = -0.015 \text{ V/dec.}$

Mechanism (m'):

$$2Fe + H_2O \leftrightarrow Fe_2H_2O^+ + e^-$$

$$Fe_{2}H_{2}O^{+} + OH^{-} \xrightarrow{rds} 2FeOH_{ads.} + H^{+} + e^{-}$$

$$2FeOH_{ads.} \leftrightarrow 2FeOH_{ads.}^{+} + 2e^{-}$$

$$2FeOH_{ads.}^{+} \xrightarrow{des} 2FeOH^{+}$$

$$2FeOH^{+} + 2H^{+} \leftrightarrow 2Fe^{2+} + 2H_{2}O$$
In this case, $n^{m'}{}_{f} = 0$, $n^{m'}{}_{b} = 4$, $v^{m'} = 2$, $n^{m'}{}_{r} = 0$ and thus at 303 K:

$$|b_c^{m\prime}| = \frac{2.3RT}{\left(\frac{n_f^{m\prime}}{\nu^{m\prime}} + n_r^{m\prime}\beta^{m\prime}\right)^F} = \infty (N/A)$$

$$|b_a^{m'}| = \frac{2.3RT}{\left(\frac{n_b^{m'} + \nu^{m'} n_r^{m'}}{\nu^{m'}} - n_r^{m'} \beta^{m'}\right)F} = 0.03 \text{ V/dec.}$$

$$p_{OH^{-}}^{m'} = 2$$

$$E_{OH^-}^{m'} = -0.09 \text{ V/dec.}$$

Mechanism (n'):

$$Fe + H_2 0 \leftrightarrow FeO(OH)_{ads.}$$

$$FeO(OH)_{ads.} \leftrightarrow FeOH_{ads.} + \frac{1}{2}O_2$$

$$FeOH_{ads.} \xrightarrow{rds} FeOH_{ads.}^+ + e^-$$

$$FeOH_{ads.}^+ \xrightarrow{des} FeOH^+$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

For this mechanism, $n'_{f} = 0$, $n'_{b} = 1$, v' = 1, $n'_{r} = 0$ and thus at 303 K:

$$\begin{aligned} |b_{c}^{n\prime}| &= \frac{2.3RT}{\left(\frac{n_{f}^{n\prime}}{\nu^{n\prime}} + n_{r}^{n\prime}\beta^{n\prime}\right)F} = \infty \quad (N/A) \\ |b_{a}^{n\prime}| &= \frac{2.3RT}{\left(\frac{n_{b}^{n\prime} + \nu^{n\prime}n_{r}^{n\prime}}{\nu^{n\prime}} - n_{r}^{n\prime}\beta^{n\prime}\right)F} = 0.06 \text{ V/dec.} \end{aligned}$$

$$p_{OH^-}^{n\prime} = 0$$

 $E_{OH^-}^{n\prime} = -0.06 \text{ V/dec.}$

Mechanism (o'):

$$Fe + 2H_20 \leftrightarrow Fe(OH)_2^{+}_{ads.} + H_2 + e^{-}$$

$$Fe(OH)_2^{+}_{ads.} \xrightarrow{des} Fe(OH)_2^{+}$$

$$Fe(OH)_2^{+} \xrightarrow{rds} FeO(OH)_{ads.} + H^{+}$$

$$2FeO(OH)_{ads.} + 2H^{+} \leftrightarrow (FeOH)_2^{+} + H_2O + Fe^{2+} + \frac{1}{2}O_2 + e^{-}$$

In this mechanism, $n^{o'}_{f} = 1$, $n^{o'}_{b} = 1$, $v^{o'} = 1$, $n^{o'}_{r} = 0$ and thus at 303 K:

$$\begin{aligned} |b_{c}^{0'}| &= \frac{2.3RT}{\left(\frac{n_{f}^{0'}}{\nu^{0'}} + n_{r}^{0'}\beta^{0'}\right)F} = 0.06 \quad \text{V/dec.} \\ |b_{a}^{0'}| &= \frac{2.3RT}{\left(\frac{n_{b}^{0'} + \nu^{0'}n_{r}^{0'}}{\nu^{0'}} - n_{r}^{0'}\beta^{0'}\right)F} = 0.06 \text{ V/dec.} \\ p_{OH^{-}}^{0'} &= 0 \\ E_{OH^{-}}^{0'} &= -0.03 \text{ V/dec.} \end{aligned}$$

Mechanism (p'):

$$Fe + H_2 0 \leftrightarrow H_2 FeO^{2+} + 2e^{-}$$

$$H_2 FeO^{2+} \xrightarrow{rds} FeO_{ads.} + 2H^{+}$$

$$FeO_{ads.} + H_2 0 \leftrightarrow Fe(OH)_2^{+}_{ads.} + e^{-}$$

$$Fe(OH)_2^{+}_{ads.} \xrightarrow{des} Fe(OH)_2^{+}$$

$$Fe(OH)_2^{+} \leftrightarrow FeOH^{+} + H^{+} + \frac{1}{2}O_2 + e^{-}$$

$$FeOH^{+} + H^{+} \leftrightarrow Fe^{2+} + H_2O$$

In this mechanism, $n^{p'}_{f} = 1$, $n^{p'}_{b} = 3$, $v^{p'} = 1$, $n^{p'}_{r} = 0$ and therefore at 303 K:

$$\begin{aligned} \left| b_{c}^{p\prime} \right| &= \frac{2.3RT}{\left(\frac{n_{f}^{p\prime}}{v^{p\prime}} + n_{r}^{p\prime} \beta^{p\prime} \right)^{F}} = 0.06 \text{ V/dec.} \\ \left| b_{a}^{p\prime} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{p\prime} + v^{p\prime} n_{r}^{p\prime}}{v^{p\prime}} - n_{r}^{p\prime} \beta^{p\prime} \right)^{F}} = 0.02 \text{ V/dec.} \\ p_{OH^{-}}^{p\prime} &= 2 \\ E_{OH^{-}}^{p\prime} &= -0.045 \text{ V/dec.} \end{aligned}$$

Mechanism (q'):

$$Fe + H_2 0 \leftrightarrow H_2 Fe 0^{2+} + 2e^{-}$$
$$H_2 Fe 0^{2+} \xrightarrow{rds} Fe 0 H_{ads.}^{+} + H^{+}$$
$$Fe 0 H_{ads.}^{+} \xrightarrow{des} Fe 0 H^{+}$$
$$Fe 0 H^{+} + H^{+} \leftrightarrow Fe^{2+} + H_2 0$$

In this case, $n^{q'}_{f} = 0$, $n^{q'}_{b} = 2$, $v^{q'} = 1$, $n^{q'}_{r} = 0$ and therefore at 303 K:

$$\begin{aligned} \left| b_{c}^{q'} \right| &= \frac{2.3RT}{\left(\frac{n_{f}^{q'}}{\nu^{q'}} + n_{r}^{q'}\beta^{q'} \right)_{F}} = \infty \quad (N/A) \\ \left| b_{a}^{q'} \right| &= \frac{2.3RT}{\left(\frac{n_{b}^{q'} + \nu^{q'}n_{r}^{q'}}{\nu^{q'}} - n_{r}^{q'}\beta^{q'} \right)_{F}} = 0.03 \text{ V/dec.} \end{aligned}$$

$$p_{OH^{-}}^{q'} &= 0$$

$$E_{OH^-}^{q'} = -0.03 \text{ V/dec.}$$

Mechanism (r'):

$$Fe + OH^{-} \leftrightarrow FeOH^{+} + 2e^{-}$$
$$Fe + FeOH^{+} + H_2O \xrightarrow{rds} HFe_2O_2^{+} + 2H^{+} + 2e^{-}$$

- $HFe_2O_2^+ \leftrightarrow FeO_{ads.} + FeOH_{ads.}^+$
- $FeOH_{ads.}^{+} \xrightarrow{des} FeOH^{+}$ $FeOH^{+} + H^{+} \leftrightarrow Fe^{2+} + H_2O$

In this case, $n_{f}^{r'} = 0$, $n_{b}^{r'} = 4$, $v_{f}^{r'} = 1$, $n_{f}^{r'} = 0$ and therefore at 303 K:

$$|b_{c}^{r'}| = \frac{2.3RT}{\left(\frac{n_{f}^{r'}}{\nu^{r'}} + n_{r}^{r'}\beta^{r'}\right)F} = \infty \quad (N/A)$$
$$|b_{a}^{r'}| = \frac{2.3RT}{\left(\frac{n_{b}^{r'} + \nu^{r'}n_{r}^{r'}}{\nu^{r}} - n_{r}^{r'}\beta^{r'}\right)F} = 0.015 \text{ V/dec.}$$
$$p_{OH^{-}}^{r'} = 3$$

$$E_{OH^-}^{r\prime} = -0.03 \text{ V/dec.}$$

Mechanism (s'):

$$Fe + 20H^{-} \leftrightarrow Fe(0H)_{2,ads.} + 2e^{-}$$

$$2Fe(0H)_{2,ads.} \xrightarrow{rds} Fe(0H)_{2,ads.} + Fe(0H)^{+}_{2} + e^{-}$$

$$Fe(0H)_{2}^{+} \leftrightarrow FeOH_{ads.}^{+} + H^{+} + \frac{1}{2}O_{2} + e^{-}$$

$$FeOH_{ads.}^{+} \xrightarrow{des} FeOH^{+}$$

$$FeOH^+ + H^+ \leftrightarrow Fe^{2+} + H_2O$$

In this mechanism, $n^{s'}_{f} = 0$, $n^{s'}_{b} = 4$, $v^{s'} = 1$, $n^{s'}_{r} = 0$ and thus at 303 K:

$$|b_c^{s\prime}| = \frac{2.3RT}{\left(\frac{n_f^{s\prime}}{\nu^{s\prime}} + n_r^{s\prime}\beta^{s\prime}\right)F} = \infty \quad (N/A)$$

$$|b_a^{s'}| = \frac{2.3RT}{\left(\frac{n_b^{s'} + \nu^{s'} n_r^{s'}}{\nu^{s'}} - n_r^{s'} \beta^{s'}\right)F} = 0.015 \text{ V/dec.}$$

$$p_{OH^-}^{s'} = 3$$
 , $E_{OH^-}^{s'} = -0.06 \text{ V/dec.}$

Appendix C: Transient Data, Analytical Plots, and Regression Analysis Used to Estimate the Kinetic Parameters of the Elementary Steps for Different Materials at Different Temperatures



Figure 113. Potentiostatic transients of iron in the active potential range (a-c) in N_2 -sparged at 25 °C, 35 °C, 45 °C and (d-f) CO₂-sparged media at 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 114. Potentiostatic transients of different materials in the active potential range (a-c) in N_2 -sparged and (d-f) CO₂-sparged media at 25 °C (pH 4)



Figure 115. Potentiostatic transients of iron in the transition potential range (a-c) in N_2 -

sparged at 25 °C, 35 °C, 45 °C and (*d*−*f*) CO₂-sparged media at 25 °C, 35 °C, 45 °C, respectively (*pH* 4)



Figure 116. Potentiostatic transients of different materials in the transition potential range (a-c) in N₂-sparged and (d-f) CO₂-sparged media at 25 °C (pH 4)



Figure 117. Transient responses of iron at different potential perturbations in the active domain and analytical regression lines (insets) were used to compute $k_{0,1}$ and b_1 at (a–c) in N_2 -sparged at 25 °C, 35 °C, 45 °C and (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 118. Transient responses of different materials at different potential perturbations in the active domain and analytical regression lines (insets) were used to compute $k_{0,1}$ and b_1 at (a–c) in N₂-sparged and (d–f) CO₂-sparged media, respectively (25 °C, pH 4)



Figure 119. Analytical plots and corresponding regressions lines to compute $k_{0,2}$ and b_2 for pure iron in (a–c) in N₂-sparged at 25 °C, 35 °C, 45 °C and (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C media, respectively (pH 4)



Figure 120. Analytical plots and corresponding regressions lines to compute $k_{0,2}$ and b_2 for different materials in (a-c) in N_2 -sparged and (d-f) CO₂-sparged media (25 °C, pH 4)



Figure 121. Transient responses of pure iron at different potential perturbations in the transition domain and analytical regression lines (insets) were used to compute $k_{0,3}$ and b_3 in (a–c) N₂-sparged at 25 °C, 35 °C, 45 °C (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 122. Transient responses of different materials at potential perturbations in the transition domain and analytical regression lines (insets) were used to compute $k_{0,3}$ and b_3 for different materials in (a–c) N₂-sparged and (d–f) CO₂-sparged media (25 °C, pH 4)



Figure 123. Analytical regression lines used to compute $k_{0,4}$ and b_4 in (a–c) N₂-sparged at 25 °C, 35 °C, 45 °C, and (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 124. Analytical regression lines used to compute $k_{0,4}$ and b_4 for different materials in (*a*–*c*) N_2 -sparged and (*d*–*f*) CO₂-sparged media (25 °C, pH 4)



Figure 125. Analytical regression lines were used to compute $k_{0,-3,a}$, and $b_{-3,a}$ during iron dissolution in (a–c) N₂-sparged at 25 °C, 35 °C, 45 °C, and (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C, respectively. The insets represent the range of data used for k_{-3} estimation (taken from anodic sweeps of iron)



Figure 126. Analytical regression lines were used to compute $k_{0,-3,a}$, and $b_{-3,a}$ for different materials in (a-c) N_2 -sparged and (d-f) CO_2 -sparged (pH 4, 25 °C). The insets represent the range of data used for k_{-3} estimation (taken from anodic sweeps of iron)



Figure 127. Analytical regression lines were used to compute $k_{0,-3,t}$, and $b_{-3,t}$ during iron dissolution in (a–c) N₂-sparged at 25 °C, 35 °C, 45 °C, and (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C, respectively


Figure 128. Analytical regression lines were used to compute $k_{0,-3,t}$, and $b_{-3,t}$ for different materials in (a–c) N₂-sparged and (d–f) CO₂-sparged media (25 °C, pH 4)



Figure 129. Regression analysis for determining $b_{a,ov}$, and $k_{0,a}$ for pure iron in active range in (*a*-*c*) N_2 -sparged at 25 °C, 35 °C, 45 °C, and (*d*-*f*) CO_2 -sparged at 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 130. Regression analysis for determining $b_{a,ov}$, and $k_{0,a}$ for different materials in active range in (a–c) N₂-sparged, and (d–f) CO₂-sparged media (pH 4, 25 °C)



Figure 131. Regression analysis for determining $b_{a,ov}$, and $k_{0,a}$ for pure iron in transition range in (a–c) N₂-sparged at 25 °C, 35 °C, 45 °C, and (d–f) CO₂-sparged at 25 °C, 35 °C, 45 °C, respectively (pH 4)



Figure 132. Regression analysis for determining $b_{a,ov}$, and $k_{0,a}$ for different materials in transition range in (a–c) N₂-sparged, and (d–f) CO₂-sparged media (pH 4, 25 °C)



the Anodic Sweeps

Figure 133. Regression analysis used to obtain the simplified functions for predicting (a) $k_{0,3}$, (b) $k_{0,-3a}$, and (c) $k_{0,-3t}$ as a function of pH in strong acid (25 °C)



Figure 134. Regression analysis used to obtain the simplified functions for predicting (a) $k_{0,1}$, (b) $k_{0,2}$, (c) $k_{0,4}$, (d) b_2 , and (e) b_3 as a function of temperature in strong acid (pH 4)



Figure 135. Regression analysis used to obtain the simplified functions for predicting (a) $k_{0,1}$, (b) $k_{0,3}$, and (c) $k_{0,-3t}$ as a function of pH in weak acid (25 °C)



Figure 136. Regression analysis used to obtain the simplified functions for predicting (a) $k_{0,2}$, (b) $k_{0,4}$, (c) b_2 , and (d) b_{-3t} as a function of temperature in weak acid (pH 4)



Appendix E: Possible Point of Error for the Simplified Anodic Model

Figure 137. Possible Point of error for the simplified models of anodic dissolution of iron presented in Section 8.5 (y axis: E vs. SHE in V and x axis: i in A/m^2)



Figure 138. Effect of rpm on the anodic sweeps for pure iron RCE at different trials



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