

MOLECULAR MODELING OF **CORROSION PROCESSES**

Scientific Development and
Engineering Applications

EDITED BY

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PREFACE

Molecular modeling and computational materials science have the potential to transform the way chemicals and materials are synthesized and built by providing a “virtual laboratory” for the testing of materials properties, including their response to the environment, before engaging in any of the financial, safety, or environmental risks that accompany the bench-top synthesis of a new material. Furthermore, a sophisticated virtual laboratory can be used to predict the behavior of materials currently in service in new environments, or modifications of old environments, providing scientists and engineers with an additional tool for risk assessment prior to making changes in operating procedures or conditions. Finally, molecular modeling and computational materials science provide a “third eye” into the mechanisms of materials transformation that occur in the nanoscale world, the fundamental landscape in which many materials/environment effects take place, but only few contemporary measurement techniques can access, and even then, only under well-controlled conditions. For these reasons, the modern virtual laboratory is bringing about a scientific revolution, and each day new publications appear in the literature, illustrating how molecular modeling uncovers unprecedented insights into the inner workings of processes in both chemistry and materials science or predict, for the first time, the properties of new compounds.

Some of these papers are tackling the difficult problem of materials corrosion. Corrosion, at its core, is the exchange and reaction of electrons, atoms, or molecules between a material and its environment; and hence, it is highly

predisposed to a molecular modeling approach. Yet, corrosion, despite its ubiquity and long history of study, remains a fiercely challenging problem. It bridges topics of metallurgy; solid-state physics; and physical, inorganic, and organic chemistry. It is controlled by processes that occur not only at the atomic length scale, but at the nanoscale, mesoscale, microscale, and beyond. Corrosion may be a fleeting, transient event, but lifetimes of materials must often be assessed for years, decades, or millennia. But it is also an urgent problem—corrosion costs industrial and agrarian economies hundreds of billions of dollars each year, some have estimated trillions, creating along with it significant human and environmental costs—and, therefore, demands the best of our scientific theoretical and experimental efforts to be applied. This book highlights some of the areas in which molecular modeling and computational materials science have been applied to this endeavor, and tries to shine a light ahead toward future fields of application in corrosion science and to the techniques that still need to be developed to take us there.

Two of the biggest challenges facing the molecular modeler in any field of inquiry are “which technique do I use?”, and “how do I simplify my complex materials system into the key thousand or so atoms that represent the active site of interest?” This book, therefore, provides a number of case studies that demonstrate how scientists over the past few years have found answers to these questions, and at what success they arrived. Some of the time- and length-scales surrounding corrosion phenomena are too big for a simplistic atomistic approach; but by judicious choice of representation or the use of multiscale modeling, reasonable approximations can be obtained and an important complementary viewpoint to the field of experimental corrosion science provided.

As a consequence, this is a book that should be read by students interested in beginning a career in corrosion modeling, by corrosion scientists eager to add another tool to their research group, by researchers already engaged in modeling but not yet aware of the opportunities that exist in the world of corrosion, or by project leaders in industry who may be curious about investing in molecular modeling research but uncertain as to what value such a project could provide. Through interacting over the years with professionals in each of these categories, it became apparent that a resource of this nature was in demand, and could help encourage the growth of modeling efforts in the field of corrosion science.

Two recent workshop series have been initiated that have also greatly helped to promote the use of molecular modeling to critical corrosion problems facing industry today: the Quantitative Micro-Nano workshops in stress corrosion cracking, principally organized by Dr. Roger W. Staehle, and the International Winter School on Corrosion Modeling, co-organized by one of the editors of this book, Dr. Philippe Marcus. Both of these events have worked to foster a sense of community amongst those scientists who commonly think about corrosion science problems from an atoms and bonds viewpoint, experimentally and theoretically.

The first chapter of this book was inspired by the presentations given by Professors Julian Gale, Philippe Marcus, and Christopher (Chris) Taylor at the Winter School, which was held in Saclay, France, in December 2012.

The remainder of the book was assembled through soliciting contributions from colleagues who we have come to know through workshops, conferences, and academic collaborations over the years. Their hard work on these

chapters is gratefully acknowledged. Thanks to all the contributors the present volume spans topics ranging from the initial stages of oxidation of metal surfaces through to the kinetic simulation of metal dissolution, and the mechanisms of inhibition through to hydrogen embrittlement. Their collective breadth of expertise speaks to the necessity of engaging experts across the fields of chemistry, physics, and materials science and engineering for the challenges corrosion presents.

The editors would like to personally thank colleagues who have provided encouragement along the road to completing this volume: Rob Kelly and Matthew Neurock at the University of Virginia, Scott Lillard at the University of Akron; Rudy Buchheit and Jerry Frankel at the Ohio State University; and Mark Paffett at Los Alamos National Laboratory.

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AN INTRODUCTION TO CORROSION MECHANISMS AND MODELS

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1.1 INTRODUCTION

The history of mankind is distinguished by the pronounced effort to understand the processes of nature and to manipulate these processes for the improvement of the human condition and survivability. One remarkable instance of this effort can be found in the realm of materials engineering; here, advances have been so significant that historical eras are frequently named by the materials that characterized them: the Stone Age, Bronze Age, and Iron Age [1]. Materials engineers in our present age have a significant number of alloy components and fabrication techniques at their disposal. Consequently, there is a vast range of properties for which materials can

be tailor-made, based on considerations such as materials lifetime, strength, ductility, and temperature range. In the world of metals, corrosion is an ever-present concern, and there are an often bewildering number of modes via which materials failure by corrosion may occur, such as localized corrosion (pitting), stress corrosion cracking, galvanic corrosion, crevice corrosion, uniform corrosion, or hydrogen embrittlement [2]. As in past ages, corrosion scientists and engineers of today must confront such problems by conceptualizing the modes *via* which these effects may occur, leading to direct testing of these hypotheses through a combination of modeling and experiment. Ultimately, the objective is to provide solutions, such as ever more durable materials and/or processes for current and future applications.

In the precomputation era, materials modeling was restricted to mechanical (i.e., physical, tangible) models, hypothetical *Gedanken* experiments, or analytic calculations based on the continuous phenomena known to materials physics. However, it is known that physicochemical processes such as corrosion ultimately occur as discrete, atomistic events that involve the making, breaking, or rearrangement of bonds between atoms, such as dissolution, substitution, and diffusion. To date, kinetic models for these processes have been fitted to experimental data in an effort to understand their relative importance and hence develop predictive models for corrosion rates. However, the ability to extrapolate such models to as yet unstudied conditions, in which case the mechanisms of corrosion may be subtly (or drastically) changed, is hindered by the lack of a first-principles justification for the values obtained from such fitting experiments. Empirical *rules of thumb* may be useful in, for example, identifying the relative importance of such alloying ingredients as chromium, molybdenum, or nitrogen

to the corrosion resistance of a series of iron-based alloys under a given set of conditions [3]. However, such rules do not provide the fundamental insights as to the mechanism *via* which these effects occur, as would be necessary to significantly advance materials development. In an age where the ability to control materials design at the nanoscale is beginning to appear feasible, it is important to develop the theoretical tools to guide such low-level design effects and to reach levels of corrosion resistance optimization previously considered unthinkable.

Molecular modeling provides the ability to simulate and analyze hypothetical processes at the atomic level [4]. Such models have been used extensively in the realm of chemistry [4, 5], as well as in solid-state physics and materials science [6, 7]. Now, we have progressed to the point where the conjunction between chemistry and solid-state physics, namely, interfacial science, is also being tackled by such methods [8]. While heterogeneous catalysis initially dominated this particular application of molecular modeling to interfacial systems, the field of corrosion has recently been attracting more and more attention. This increase in interest can be seen from the analysis in [Figure 1.1](#), which shows that the current interest in applying molecular modeling techniques (highlighted here as *molecular dynamics* and *density functional theory (DFT)*) to problems in corrosion science is roughly equivalent to the surge of interest that spurred the application of these techniques to problems in catalysis at the beginning of the twenty-first century.

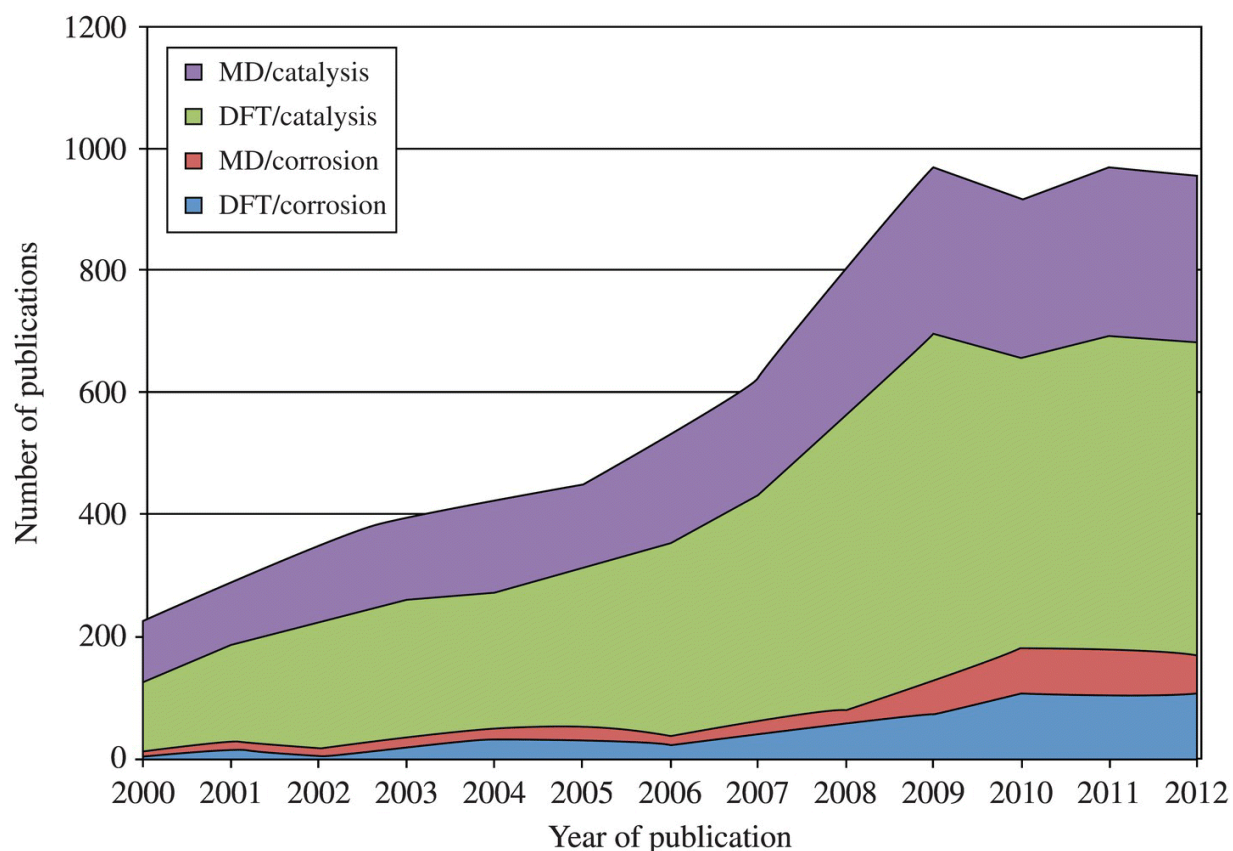


FIGURE 1.1 Number of peer-reviewed publications with topics *molecular dynamics* or *density functional theory* combined with either *catalysis* or *corrosion*. .

Data obtained from the Web of Knowledge database by Thomson Reuters, 2013. <https://access.webofknowledge.com/>

Molecular modeling of corrosion, by definition, requires the construction of a model system, which consists of atoms and molecules, that is as faithful as possible a representation of the corroding system of interest. Since corroding systems contain an extraordinary degree of complexity—encompassing features such as: the microstructure of the material; the elemental composition; multiple phases including metals, alloys, and oxides; surface-solute-solvent interactions; and electrochemical interfaces—the construction of an appropriate model therefore requires an advanced understanding of corrosion mechanisms. As shown in [Figure 1.2](#), interfacial processes

such as corrosion lie at the intersection of chemistry and materials science. A particular challenge for molecular modeling is that, at least for present computers, only a finite number of atoms and molecules (somewhere between dozens and, at best, billions) can be simulated [9-11]. Thus, one must be especially judicious in choosing the representation of the corroding system (recall that even a billion atoms of Fe weigh $<1 \times 10^{-10}$ mg). The challenge is, therefore, significant; how does one model a macroscopic and inherently multiscale process such as corrosion using molecular modeling techniques? Approaches to tackle this challenge form the scope of this book. We begin in this chapter by introducing a series of corrosion mechanisms and then discuss the principal modeling techniques used to represent and simulate these systems from the molecular perspective.

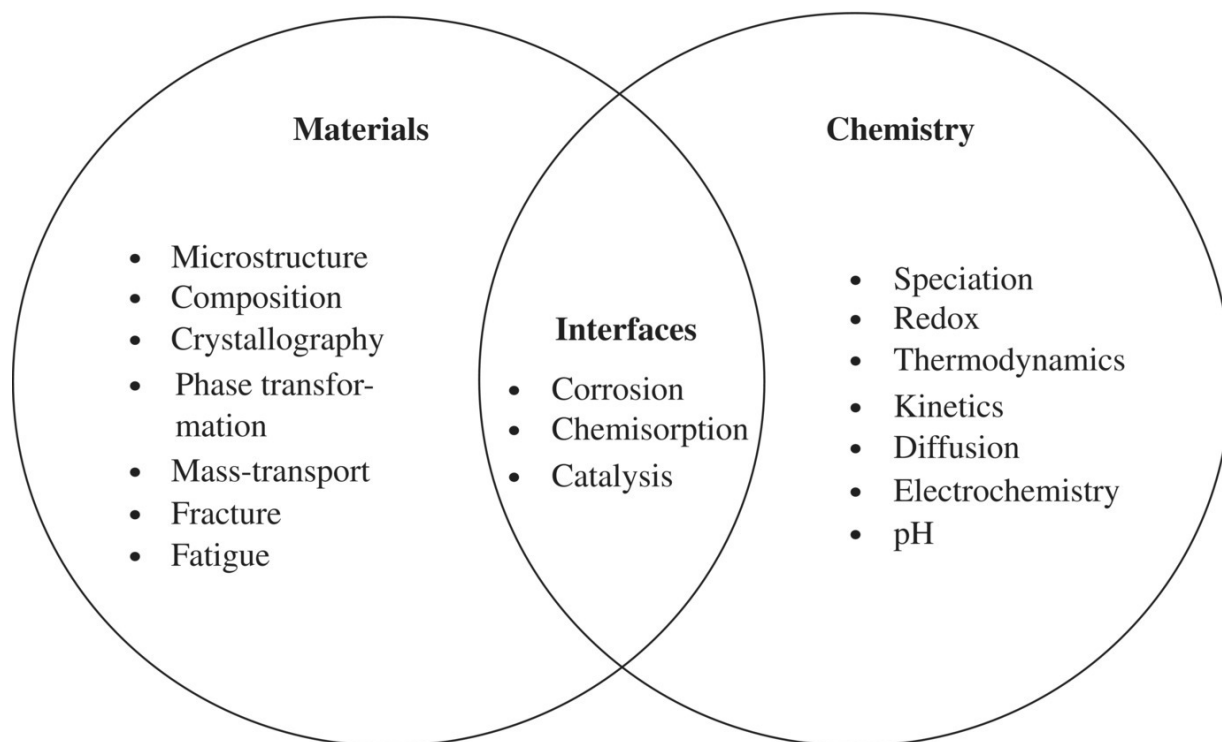


Figure 1.2 Interfacial problems, such as corrosion, occur at the intersection between materials science and chemistry.

1.2 MECHANISMS IN CORROSION SCIENCE

The conversion of metals back into their native oxide forms, or some similarly preferred thermodynamic state, can take many forms and can be exacerbated by various chemical or environmental conditions. Thus, corrosion itself has no single mechanism of action [12]. Various mechanisms have been proposed to account for effects such as atmospheric corrosion [13-15], chloride-induced pitting [16-25], sulfidation [26-40], acidic dissolution, crevice corrosion [13, 41-44], stress corrosion cracking [45-49], ammoniacal attack [18, 19, 23-25, 29-31, 33, 50], and so on. In order to make the following discussion as general as possible and to avoid going into detail regarding some of the more specific corrosion instances that will be addressed in later chapters, we here take the liberty of dividing corrosion processes into a number of sequential (although they often occur in parallel) steps, each of which may be subject to chemical and/or environmental modification. By categorizing the leading causes and mechanistic pathways of corrosion in this way, we will then show how, in each case, molecular modeling could feasibly be applied to provide greater insights into the fundamental processes and hence guide next-generation corrosion mitigation strategies and the design of corrosion-resistant materials.

The Collins English Dictionary [51] defines corrosion as:

a process in which a solid, especially a metal, is eaten away and changed by a chemical action, as in the oxidation of iron in the presence of water by an electrolytic process.

Corrosion is a chemical process that occurs at the solid/environment interface, that is, at the external or internal surface of a material where it meets a fluid

(gaseous or solvent) phase. The sciences appropriate to the study of this process include: surface science; electrochemistry; physical, inorganic, and analytical chemistry; physics; materials science; metallurgy; and, finally, theory, which encompasses both modeling and simulation. The chief reactions that contribute to aqueous corrosion are electrochemical in nature and, for this reason, can be broken down into anodic metal dissolution and the corresponding cathodic reactions of hydrogen evolution and oxygen reduction [3]. Factors that may affect these reactions, and thus the overall process of corrosion, include the structure and composition of the bulk solid phase, as well as the composition of the electrolyte and the changes that these subsystems undergo during the process of corrosion.

This breakdown is given further elaboration in the list of topics that accompanies the Venn diagram in [Figure 1.2](#). Small changes in materials microstructure, alloy composition, and mass-transport pathways (such as the *short-circuit* diffusion routes in passive oxide films) [52–57] can be particularly significant for the overall corrosion properties of the material. Similarly, phase transformations that occur as a function of temperature, or the impurity content at either grain boundaries or in the bulk, may again affect the resilience of a material to corrosion, especially when the material is also placed under mechanical strain (such as in instances of stress corrosion cracking). Even factors such as the materials texture [58], grain-boundary engineering [55, 59, 60], and the crystallographic orientations that are exposed at the surface can affect its reaction with the environment.

From the chemistry side, the environmental conditions can be highly important. The pH may affect speciation of organic or mineral acid moieties, thus changing their propensity for surface reaction. Variations in the electrode

potential (that can be induced galvanically, from the materials side, or chemically, via ionic concentration gradients in the electrolyte) can play a large role in biasing a system toward or away from passivation. The myriad of physical and chemical interactions that go into surface adsorption, bond breaking and bond formation, and solvation by the solution play a continuous role in mediating the overall thermodynamics and kinetics of corrosion reactions [61, 62]. Chemical species, such as inhibitors, can be introduced to bias the surface chemistry such that corrosion kinetics are subdued, whereas other chemical species (such as halides) can accelerate them [25b, c, 32, 38, 63, 64].

These two features of corrosion—materials control and environmental control—meet in the very processes that occur at the interface, which is the critical region where corrosion reactions take place, but is also the least understood [65–68]. Hence, there is a strong motivation for developing the theoretical framework via which these reactions can be simulated, predicted, and, ultimately, controlled.

1.2.1 Thermodynamics and Pourbaix Diagrams

The starting point for the scientific understanding of chemical processes is thermodynamics. For a metal subject to aqueous, that is, electrochemical, corrosion, the scheme introduced by Marcel Pourbaix provides the framework for a first assessment of materials stability [69]. Pourbaix considered that the Gibbs free energy associated with an electrochemical reaction is a function of two key variables: the electrode potential and the pH. These two variables can be used to define the Gibbs free energy of the dissolution, oxidation, hydroxylation, and hydride reactions. Since these are the primary products of corrosion under aqueous conditions, a broad range of corrosion phenomena can be

surveyed visually with Pourbaix's approach. This visual aspect is conveyed via the *Pourbaix potential-pH diagram*—a phase diagram that outlines the most stable phase (as defined by the phase with the lowest Gibbs free energy) in the two-dimensional space limited by reasonable values that can be expected for the pH and potential (typically between -2 and $+2$ V vs. normal hydrogen electrode (NHE) and pH 0-14). As an example, the Pourbaix diagram for iron is provided in [Figure 1.3](#).

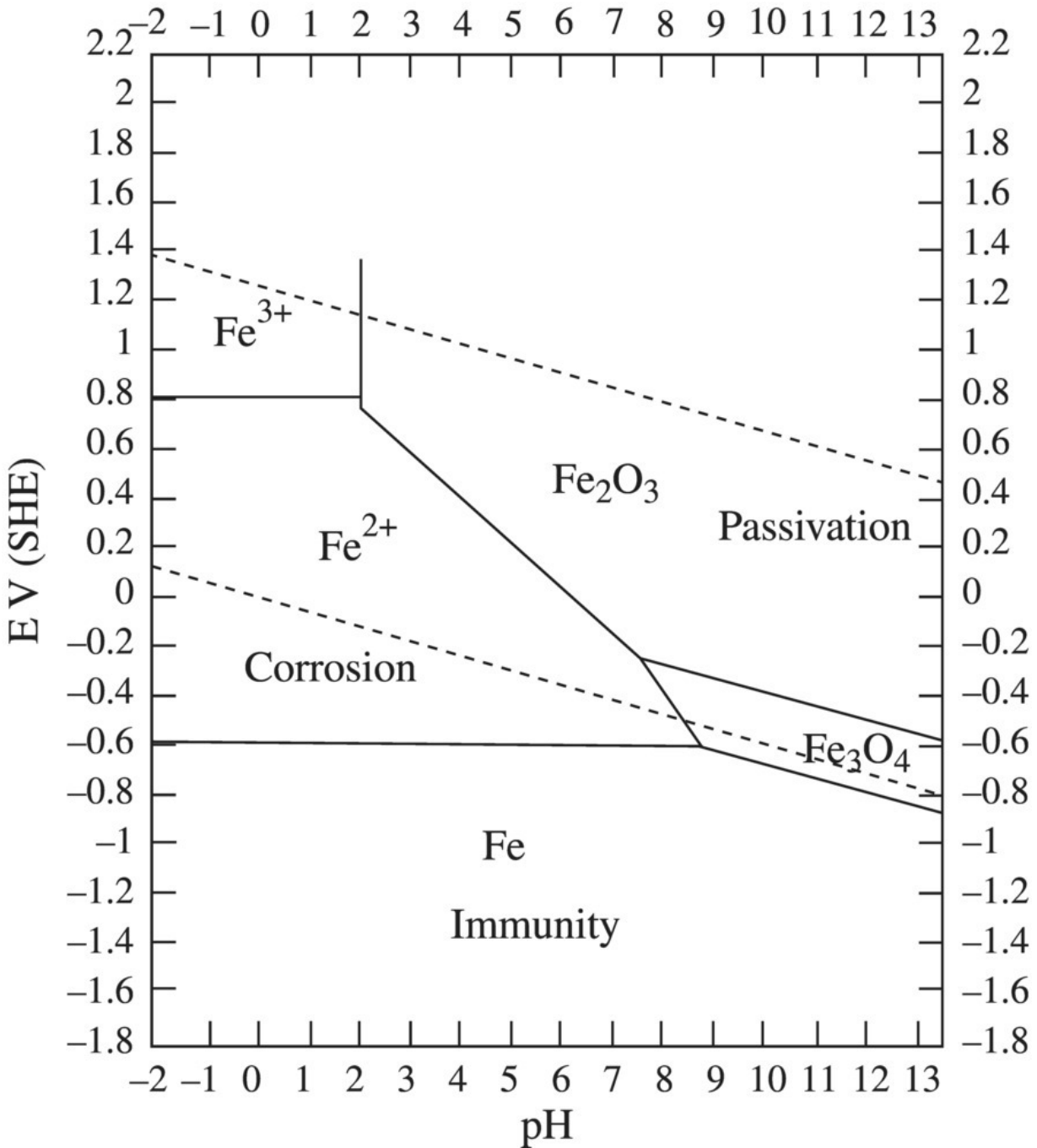
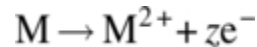


FIGURE 1.3 The Pourbaix diagram for iron. .

Adapted from Strehblow and Marcus [70]

The electrochemical model for corrosion breaks the process down into anodic and cathodic *half-cell* reactions, each having their own equations, which may include:

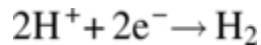
For dissolution:



For oxygen reduction:



For hydrogen reduction:



Reactions that involve a number of protons or hydroxide ions being exchanged are dependent upon pH, via the equation [71]

$$\Delta G = \Delta G^0 \pm 2.303mRT\text{pH}$$

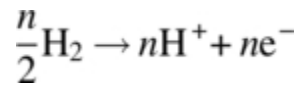
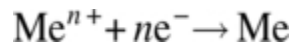
where m is the number of protons exchanged in the reaction and the \pm depends on whether protons are produced or consumed, respectively. T is the temperature, R is the ideal gas constant, and ΔG^0 is the standard Gibbs free energy (activity $a = 1$, pressures of gases $p = 1 \text{ atm} = 1.013 \text{ bar}$).

Reactions that involve the loss or gain of electrons (oxidation or reduction, respectively) are dependent upon the potential. The reaction free energy varies with potential according to the equation [70]

$$\Delta G = -nFE$$

where n is the number of electrons consumed for the cathodic direction of the reaction, that is, the reduction process, and ΔG the related change of the Gibbs free energy. The counter reaction for the production of the electrons is by convention the oxidation of hydrogen gas to hydrogen ions for the standard hydrogen electrode with a

hydrogen pressure of $p(\text{H}_2) = 1 \text{ atm} = 1.013 \text{ bar}$ and a hydrogen ion activity of $a(\text{H}^+) = 1$. The following two equations give an example for the reduction of metal ions Me^{n+} and the compensating hydrogen oxidation:



For a reactive metal like iron, the discussed electrodeposition associated to hydrogen oxidation is not possible with a strongly positive ΔG . The reverse process, that is, iron dissolution associated to hydrogen evolution, is the spontaneous reaction with a very negative ΔG . E is the electrode potential measured against the standard hydrogen electrode. With $a = 1$ for all activities and $p = 1 \text{ atm}$ for gas pressures, the electrode potential equals its standard value $E = E^0$ for the electrochemical reaction of interest. For these conditions the relation $\Delta G^0 = -nFE^0$ holds with the standard Gibbs free energy change ΔG^0 holds. The standard electrode potentials E^0 are listed for all metal-metal-ion and redox electrodes [71b] similar to the standard Gibbs free energy ΔG^0 of electrochemical reactions. For Fe dissolution to Fe^{2+} , the electrode potential equals $E^0 = -0.44 \text{ V}$, a relatively negative value for a reactive metal.

Reactions that are only dependent upon pH are represented in the Pourbaix diagrams by vertical lines. Reactions that are only dependent upon potential are marked as horizontal lines. Reactions that involve both will have some slope that depends jointly upon the ratio between proton/hydroxide activities and electron transfer coefficients, in which case both of the above equations have to be applied.

As seen in [Figure 1.3](#), the typical Pourbaix diagram consists of three regions, corresponding to immunity (the metallic phase has the lowest free energy), passivation (the oxide phase has the lowest free energy), and corrosion (either the metal cation phase is most stable or the soluble hydroxides/oxyanions). The electrochemical boundaries associated with the oxidation and reduction of water are also typically shown as boundary points within these diagrams via the use of dotted or dashed lines.

As described in more detail in subsequent chapters of this book, the Pourbaix principle has been extended to include adsorbed surface phases and other variables, including the presence of sulfides or chlorides [62, 73–76]. The analog for high-temperature corrosion by gaseous agents is the Ellingham diagram, in which the free energy associated with oxidation reactions is plotted against temperature [77]. However, as with any thermodynamic analysis, one should keep in mind that the kinetics often play a crucial role in the observed behavior. For instance, Anderko and Shuler's study of iron sulfide phases indicated that many metastable phases are significant and should be displayed in the practical Pourbaix diagram due to the slow kinetics associated with the formation of the most stable thermodynamic phase [78].

1.2.2 Electrode Kinetics

While thermodynamics provides a starting point, kinetics is essential for providing any corrosion model of practical utility. The term *electrode kinetics* is often used as, in the electrochemical paradigm, the oxidation and reduction occur at independent sites, which can be considered as separate electrodes marking a solid/electrolyte interface at which the half-cell reactions take place. In the case of chemical corrosion, these half-cell reactions can take place at the same location, in which case there is no external

current flow between the half-reaction centers, but instead, direct charge transfer between the reactants via electronic contact at the same metal site.

The electrode potential exerts a powerful control over corrosion kinetics, just as the chemical potential or the electrochemical potential does in thermodynamics. The deviation of the electrode potential E from its equilibrium value E_{eq} given by the Nernst equation, the so-called overvoltage $\eta = E - E_{\text{eq}}$, is the driving force for the kinetics of the electrode process. This kinetic control can be broken down into the following categories:

1. Transport of reactants and products, controlled by the diffusion overvoltage
2. Chemical reaction rates, controlled by the reaction overvoltage
3. Adsorption and desorption on the electrode surface with charge transfer, controlled by the charge transfer overvoltage

The charge transfer overvoltage is fairly well understood in terms of the Butler-Volmer equation: [71a]

$$i = i_0 \left(e^{\alpha z F \eta / RT} - e^{-(1-\alpha) z F \eta / RT} \right)$$

where z is the number of elementary charges of the species passing the electrode-electrolyte interface ($z = -1$ for an electron, $z \geq +1$ for a metal cation), α is the transfer coefficient, and η is the overpotential, which marks the deviation of the electrode potential from the equilibrium potential for the reaction being considered. F is Faraday's constant. Inspection of this equation shows that, for large positive overpotentials, the first exponential dominates, whereas, for large negative overpotentials, the second

exponential is more critical. In these two cases, one can show that the overpotential should be linear with respect to the log of the current density. This relation is known as the Tafel equation.

In the limit of small overpotentials ($\eta \sim 0$), the Butler-Volmer equation can be linearized to yield the charge transfer resistance (R_{CT}):

$$i = \frac{i_0 z F \eta_{CT}}{RT}$$

$$\eta_{CT} = i R_{CT}$$

$$R_{CT} = \frac{RT}{i_0 z F}$$

Observed deviations from this behavior can be attributed to the interference of diffusion control.

Mass-transport (i.e., diffusion or electromigration) effects are particularly acute in the cases of cracking, pitting, and crevice corrosion, whereby occlusion effects can create highly concentrated solutions that move an otherwise stable system into regions of thermodynamic instability at the local level [13, 14, 41-43, 79-82]. When porous films or particular solution flow conditions exist, mass-transport effects should also be taken into account [83, 84].

Molecular dynamics and Monte Carlo simulations of interfaces over the past few decades have provided some insight into the concentration gradients that occur close to the electrochemical interface [85-91], and these, coupled with computational fluid dynamics simulations, can indicate the extent to which mass-transport effects can dominate an overall corrosion scenario [92].

At the same time, surface effects can be strongly dependent upon local species that adsorb on the exposed

surface and thereby modify in a direct way the rates of those chemical reactions that contribute to a given corrosion pathway. When comparing mass-transport effects to surface phenomena, therefore, such scenarios should also be taken into account. Researchers in the field of heterogeneous catalysis, for example, have applied molecular modeling to understand the effects by which environmental species and/or reaction by-products can poison certain reaction pathways and favor others [93]. In the world of corrosion, certain species are suspected to promote hydrogen uptake by metals [45, 94-98] and, in other cases, to inhibit surface passivation [99-102]. The tools that have been successfully applied to assess such surface processes in the field of catalysis can and have been applied to similar problems in corrosion science [65, 93, 103-108].

1.2.3 Metal Dissolution

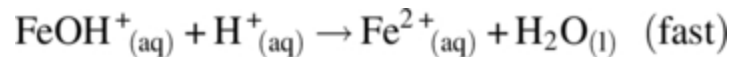
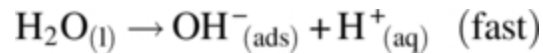
The most quintessential element of corrosion is the loss of mass from a structural component, which may be embodied by the generic metal dissolution reaction:



The metal may be directly passing from a bare metal surface into an aqueous solution [109-111] or passing through an oxide (alternatively, sulfide, chloride, etc.) film via point defect-mediated mass transport [112], among other mechanisms. This reaction may be accelerated (or, potentially, retarded) by the complexation of the surface metal atoms by species in the environment. For instance, sulfur, hydroxide, or chloride could form bonds with the surface atoms on a bare metal surface, thereby weakening the metal/surface bonds and facilitating the corrosion reaction [25b, c, 113]. Some atomistically resolved investigations of this process suggest that the

surface structure provides a high degree of control, leading to such features as surface faceting and crystallographic pitting [25b, c, 113b, 114].

In the case of iron dissolution, the following reactions are believed to play a role according to K.E. Heusler:



Thus, surface adsorption of water and subsequent dissociation and reaction with surface iron adatoms form a complete mechanism for dissolution [114b]. In addition to experimental investigations of reaction kinetics and surface characterization, molecular modeling can play a key role in assessing the various aspects associated with these mechanisms. The Butler-Volmer framework also provides a means for assessing the role of overpotential in affecting the overall rate of reaction [71a].

Thermodynamically, dissolution should occur whenever the free energy of the solvated metal ion at a given concentration is lower than the free energy of the atom in the metal, plus the thermodynamic potential of the electrons exchanged during the reaction via the standard hydrogen electrode. Such thermodynamic conditions are summarized in the series of potential-pH phase diagrams that have been extensively collated by Pourbaix [69]. Even in cases where a metal is covered by a thin protective oxide, deleterious corrosion effects can arise from the dissolution of metal atoms directly exposed by virtue of

cracks or pores in the protective film. The dissolution of metal atoms at the bare metal/solution interface, and also at the oxide/solution interface, requires the metal atoms to traverse the so-called electrochemical double layer [71a]. This concept, arising from electrochemistry, is based on a potential difference between the metal and the solution, due to aligned water dipoles, the ionic strength of the solution, and any bias existing on the metal [89, 115-121]. Dissolution of metal atoms, therefore, involves the breaking of cohesive forces between the metal atom and its neighbors in the solid state, electron transfer resulting in an ion formation (it is presently unclear exactly when this step occurs) [109-111], the formation of a solvation sphere around the nascent metal ion, and the movement of the ion through the potential gradient existing at this *double layer* ([Fig. 1.4](#)) [110]. Clearly, such a process involves a number of atomistic events that are sensitive to several highly localized environmental parameters that are amenable to a molecular modeling analysis.

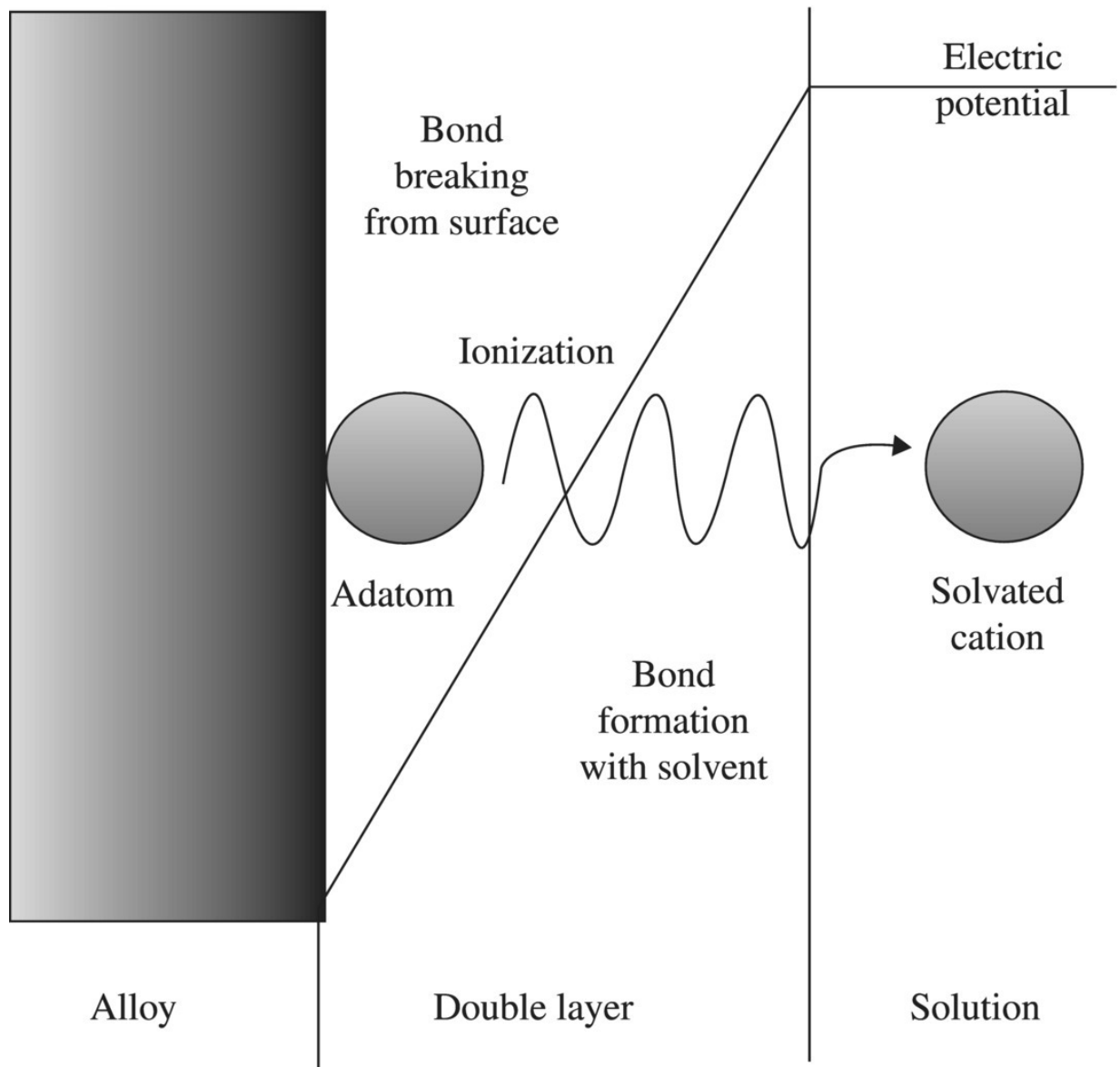
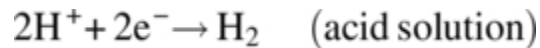


FIGURE 1.4 Schematic of the transport of a metal atom across the electrochemical double layer (from left to right).

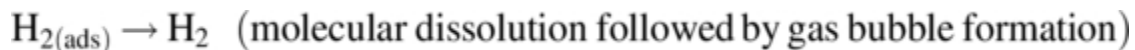
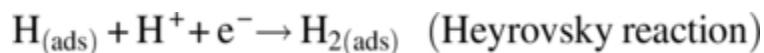
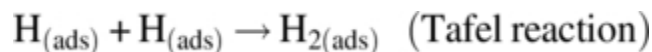
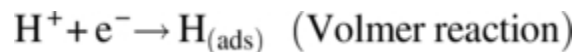
1.2.4 Hydrogen Evolution and Oxygen Reduction

Since aqueous corrosion is often electrochemical in nature, the reactions that lead to loss of metal via dissolution require a cathodic counterpart, which is often either hydrogen evolution or oxygen reduction [3]. Hydrogen evolution involves the reduction of a proton (or a

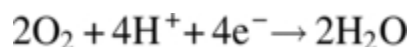
hydronium ion, i.e., a proton within a water molecule) to form molecular H₂:



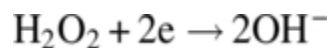
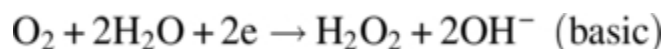
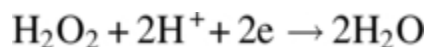
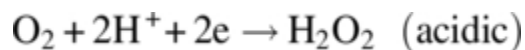
The hydrogen evolution reaction in acid solution has been broken down into the following steps:



In experimental reality, the presence of oxygen is found to greatly accelerate the rate of corrosion, which is due to the action of oxygen as an oxidant via the oxygen reduction reaction. The overall reaction is expressed as



The reaction steps differ in acidic and basic reactions, namely,



The oxygen reduction reaction has received a large amount of attention recently, from both modeling and experimental investigations, due to its importance in the development of fuel cell systems [74, 103, 122–125]. The rate of corrosion reactions may be controlled by either the anodic or cathodic process, depending upon which of the two half-cell reactions is rate limiting. This combination is elaborated further in the following text.

1.2.5 The Mixed Potential Model for Corrosion

In the electrochemical mechanism of corrosion, the metal dissolution—which involves the loss of electrons vis-à-vis oxidation—must be accompanied by a cathodic reaction that consumes electrons, which is typically oxygen or proton or water reduction. According to the Butler-Volmer equation, the current density for the anodic reaction varies according to

$$i_a = i_{a,0} e^{zF(E-E_{0,a})/RT}$$

A similar expression exists for the cathodic reaction:

$$i_c = i_{c,0} e^{-zF(E-E_{0,c})/RT}$$

Here, $E_{0,a}$ and $E_{0,c}$ are the equilibrium potentials for the anodic and cathodic process, respectively, and $i_{a,0}$ and $i_{c,0}$ are the respective current densities at these potentials. In a corroding system, where both reactions are occurring simultaneously, the total current is the difference of these terms:

$$i = i_a - i_c = i_{a,0} e^{zF(E-E_{0,a})/RT} - i_{c,0} e^{-zF(E-E_{0,c})/RT}$$

Under open-circuit conditions (i.e., when the metal surface is not connected to an external potentiostat), the net

current $i_a - i_c$ will be zero, and the electrode potential E will adjust according to the corrosion potential, E_{corr} . In this case, the corrosion current density (i.e., the current density associated with the loss of metal) is $i_a = i_c = i_{\text{corr}}$.

In the limit of large anodic polarization, π , relative to the open-circuit potential E_{corr} , the variation of current with potential will be log-linear and vice versa for large cathodic potentials (relative to open-circuit potential). This behavior can be modeled by the semilogarithmic Tafel equations:

$$\log i = \log i_a + \frac{\pi}{b_a} \quad (\text{large anodic potential, } \pi)$$

$$\log |i| = \log i_c - \frac{\pi}{b_c} \quad (\text{large cathodic potential, } \pi)$$

The corrosion potential can then be found by extrapolating the linear portions of these two equations in the plot of log current density versus potential.

The variation in current with potential implies that there exists an electrochemical resistance that results from the coupling of anodic and cathodic reactions. Following from the expressions for the corrosion current density, as given earlier, this *polarization resistance* R_p can be obtained from the equations:

$$i = i_{\text{corr}} \left(\frac{\exp \pi \ln 10}{b_a} - \exp \pi \ln 10 \right)$$

$$\frac{1}{R_p} = \left(\frac{di}{d\pi} \right)_{\pi \rightarrow 0} = i_{\text{corr}} \left(\frac{\ln 10}{b_a} - \frac{\ln 10}{b_c} \right)$$

$$R_p = \frac{b_a b_c}{\ln 10 (b_a + b_c) i_{\text{corr}}}$$

These equations, therefore, allow the experimentalist to extract fundamental quantities from a mixed potential system in order to understand aspects of the decoupled anodic and cathodic reactions.

1.2.6 Selective Dissolution of Alloys

Since most structural metals are, in fact, alloys, it is necessary to consider how metals corrode when found in combination. A classic system here, amenable to detailed investigation due to the nobility of the components, is the AuCu alloy system [126]. These alloys are characterized by a very low dissolution current at potentials that are positive with respect to the Cu/Cu²⁺ equilibrium potential, but negative with respect to the Au/Au³⁺ electrode. There exists a critical potential E_{cr} , however, above which the dissolution current increases sharply. This critical potential increases with the Au content of the alloy [127]. The general mechanism proposed for this phenomenon is that above the Cu/Cu²⁺ potential surface, copper atoms may dissolve, but as they do, they leave Au enriched at the metal surface. Therefore, continued Cu dissolution is blocked by Au atoms that cap the surface. When the critical potential is reached, the steep increase in current is due to the fast Cu corrosion current density corresponding to the high overpotential for Cu dissolution. The stress corrosion cracking of brass in ammonia-rich environments presents another example of this failure mode, caused by the loss of Zn from the alloy as a result of selective dealloying [128, 129].

1.2.7 Passivity of Metals and Alloys

In addition to dissolution, reaction of solution or atmospheric constituents with the metal very often results in the formation of a surface film, most commonly a metal oxide, that can be as thin as a nanometer (i.e., a few atomic layers) [112, 129b, c, 130–136]. The rate of formation of this passive film and the rate at which it dissolves into solution ultimately determine the stability of the material in its environment. In this way, iron, which is thermodynamically stable only in a small region of the Pourbaix diagram (see [Fig. 1.3](#)), can be usefully employed over a significantly wider range of conditions due to the extremely slow dissolution kinetics of the passivating oxide film. Passive film stability has been described mechanistically via several models, including the *high-field* and *point defect* models, which attribute the overall stability to kinetic factors such as the migration of vacancies or other oxide defects through the thickness of the film, as a function of the electric potential across the film [112, 129b, c, 137, 138]. Other important mechanistic details include the transfer of metal ions from the underlying metal substrate to the oxide film and the interfacial chemistry occurring between the oxide film and the solution itself. Localized corrosion may also occur when particular defects in the oxide are subject to a preferential attack from species such as chloride in the environment [25b, c, 137, 138]. Such pathways and their associated kinetic parameters could be directly assessed from first-principles and molecular modeling techniques, although a complete analysis of the many pathways and interfacial transitions remains a significant challenge. Metal surfaces exposed to aqueous solution or water vapor may have a compound passive film, which consists of an outermost hydroxide or oxyhydroxide and an inner layer oxide. Further complexities arise due to composition gradients in the material and the relative oxidation strengths of different alloy components [129b, c].

The electrochemical behavior of passivation is such that as the potential increases from the cathodic direction, one first encounters the *active region* in which typical current densities may be up to 100 mA/cm^2 and more. This corresponds to free corrosion of the metal, before a protective oxide or oxyhydroxide film forms. As the potential becomes increasingly anodic, the current density diminishes, down to $1 \text{ }\mu\text{A/cm}^2$, as the corrosion product film lowers the rate at which corrosion can occur. This is the region of passivity. It can extend over several hundred mV. Beyond this region lies the transpassive film: oxygen evolution and transpassive dissolution can occur on semiconducting passive films. For more inert materials (Al and the valve metals, Zr, Hf, etc.), the passive region can extend to a larger range of anodic potentials due to the insulating nature of the oxide films that severely retard ion mass transport and electron transfer across the passive layer.

Localized corrosion can occur in the otherwise passive region of potentials. In the case of localized corrosion, the passive film is locally breached, due to mechanical or chemical compromise of the oxide film or structural defects, such as grain boundaries, triple points, surfacing dislocations, or intermetallic phases such as carbide and/or sulfides. Localized corrosion manifests itself in the plot of corrosion current versus electrode potential (the polarization curve) as *noisy* peaks in the passivation region, due to the stochastic nature of this mode of corrosion.

1.2.8 Inhibition of Corrosion

The corrosion rate of metals may be reduced by the addition of inorganic or organic compounds, called inhibitors, to their environment [139]. The inhibitor efficiency is defined as the relative reduction of the