

# Contents

<b>1</b>	<b>Societal Aspects of Corrosion</b>	<b>1</b>
	We Live in a Metals-Based Society	1
	Why Study Corrosion?	1
	Corrosion and Human Life and Safety	1
	Economics of Corrosion	4
	Corrosion and the Conservation of Materials	5
	The Study of Corrosion	6
	Corrosion Science vs. Corrosion Engineering	8
	Challenges for Today's Corrosion Scientist	9
	Problems	10
	References	10
<b>2</b>	<b>Getting Started on the Basics</b>	<b>13</b>
	Introduction	13
	What is Corrosion?	13
	Physical Processes of Degradation	13
	Environmentally Assisted Degradation Processes	14
	Electrochemical Reactions	15
	Half-Cell Reactions	15
	Anodic Reactions	15
	Cathodic Reactions	16
	Coupled Electrochemical Reactions	17
	A Note About Atmospheric Corrosion	18
	Secondary Effects of Cathodic Reactions	19
	Three Simple Properties of Solutions	21
	The Faraday and Faraday's Law	23
	Units for Corrosion Rates	24
	Uniform vs. Localized Corrosion	25
	The Eight Forms of Corrosion	27
	Problems	28
	References	31
<b>3</b>	<b>Charged Interfaces</b>	<b>33</b>
	Introduction	33
	Electrolytes	33
	The Interior of an Electrolyte	33
	Interfaces	35

Encountering an Interface . . . . .	35
The Solution/Air Interface . . . . .	36
The Metal/Solution Interface . . . . .	37
Metal Ions in Two Different Chemical Environments . . . . .	38
The Electrical Double Layer . . . . .	39
The Gouy–Chapman Model of the Electrical Double Layer . . . . .	40
The Electrostatic Potential and Potential Difference . . . . .	40
The Stern Model of the Electrical Double Layer . . . . .	41
The Bockris–Devanathan–Müller Model of the Electrical Double Layer . . . . .	42
Significance of the Electrical Double Layer to Corrosion . . . . .	43
Electrode Potentials . . . . .	44
The Potential Difference Across a Metal/Solution Interface . . . . .	44
Relative Electrode Potentials . . . . .	45
The Electromotive Force Series . . . . .	46
Reference Electrodes for the Laboratory and the Field . . . . .	48
Measurement of Electrode Potentials . . . . .	52
Problems . . . . .	53
References . . . . .	55
<b>4 A Brief Review of Thermodynamics . . . . .</b>	<b>57</b>
Introduction . . . . .	57
Thermodynamic State Functions . . . . .	57
Internal Energy . . . . .	57
Entropy . . . . .	58
Enthalpy . . . . .	59
Helmholtz and Gibbs Free Energies . . . . .	59
Free Energy and Spontaneity . . . . .	60
Relationships Between Thermodynamic Functions . . . . .	61
The Chemical Potential and Standard States . . . . .	63
More About the Chemical Potential . . . . .	63
A Note About Units for $\Delta G^\circ$ or $\Delta G$ . . . . .	64
The Free Energy and Electrode Potentials . . . . .	65
The Nernst Equation . . . . .	66
Standard Free Energy Change and the Equilibrium Constant . . . . .	67
A Quandary – The Sign of Electrode Potentials . . . . .	68
Factors Affecting Electrode Potentials . . . . .	69
Problems . . . . .	70
References . . . . .	72
<b>5 Thermodynamics of Corrosion: Electrochemical Cells and Galvanic Corrosion . . . . .</b>	<b>73</b>
Introduction . . . . .	73
Electrochemical Cells . . . . .	73
Electrochemical Cells on the Same Surface . . . . .	75
Galvanic Corrosion . . . . .	76
Galvanic Series . . . . .	76
Cathodic Protection . . . . .	79
Two Types of Metallic Coatings . . . . .	80
Titanium Coatings on Steel: A Research Study . . . . .	82

Protection Against Galvanic Corrosion . . . . .	83
Differential Concentration Cells . . . . .	84
Metal Ion Concentration Cells . . . . .	84
Oxygen Concentration Cells . . . . .	86
The Evans Water Drop Experiment . . . . .	88
Waterline Corrosion . . . . .	88
Crevice Corrosion: A Preview . . . . .	89
Problems . . . . .	89
References . . . . .	93
<b>6 Thermodynamics of Corrosion: Pourbaix Diagrams . . . . .</b>	<b>95</b>
Introduction . . . . .	95
Pourbaix Diagram for Aluminum . . . . .	96
Construction of the Pourbaix Diagram for Aluminum . . . . .	96
Comparison of Thermodynamic and Kinetic Data for Aluminum . . . . .	101
Pourbaix Diagram for Water . . . . .	101
Pourbaix Diagrams for Other Metals . . . . .	103
Pourbaix Diagram for Zinc . . . . .	103
Pourbaix Diagram for Iron . . . . .	103
Pourbaix Diagrams for Additional Metals . . . . .	106
Applications of Pourbaix Diagrams to Corrosion . . . . .	108
Limitations of Pourbaix Diagrams . . . . .	111
Pourbaix Diagrams for Alloys . . . . .	111
Pourbaix Diagrams at Elevated Temperatures . . . . .	112
Problems . . . . .	114
References . . . . .	116
<b>7 Kinetics of Corrosion . . . . .</b>	<b>119</b>
Introduction . . . . .	119
Units for Corrosion Rates . . . . .	119
Methods of Determining Corrosion Rates . . . . .	119
Weight Loss Method . . . . .	120
Weight Gain Method . . . . .	120
Chemical Analysis of Solution . . . . .	121
Gasometric Techniques . . . . .	122
Thickness Measurements . . . . .	124
Electrical Resistance Method . . . . .	124
Inert Marker Method . . . . .	124
Electrochemical Techniques . . . . .	126
Electrochemical Polarization . . . . .	127
Anodic and Cathodic Polarization . . . . .	127
Visualization of Cathodic Polarization . . . . .	127
Visualization of Anodic Polarization . . . . .	128
Ohmic Polarization . . . . .	130
Electrode Kinetics for Activation Polarization . . . . .	131
Absolute Reaction Rate Theory . . . . .	131
Electrode Kinetics for Non-Corroding Metals . . . . .	132
How to Plot Polarization Curves? . . . . .	136
The Tafel Equation . . . . .	138

Reversible and Irreversible Potentials . . . . .	139
Mixed Potential Theory (Wagner and Traud) . . . . .	140
Electrode Kinetic Parameters . . . . .	144
Applications of Mixed Potential Theory . . . . .	146
Metals in Acid Solutions . . . . .	146
Tafel Extrapolation . . . . .	148
Verification of Corrosion Rates Obtained by Tafel Extrapolation . . . . .	150
Cathodic Protection of Iron in Acids . . . . .	150
Effect of the Cathodic Reaction . . . . .	154
Effect of Cathode Area on Galvanic Corrosion . . . . .	154
Multiple Oxidation–Reduction Reactions . . . . .	156
Anodic or Cathodic Control . . . . .	158
The Linear Polarization Method (Stern and Geary) . . . . .	159
Advantages and Possible Errors for the Linear Polarization Technique . . . . .	162
Applications of the Linear Polarization Technique . . . . .	163
Small-Amplitude Cyclic Voltammetry . . . . .	164
Experimental Techniques for Determination of Polarization Curves . . . . .	165
Electrode Samples . . . . .	165
Electrode Holders . . . . .	166
Electrochemical Cells . . . . .	167
Instrumentation and Procedures . . . . .	168
Problems . . . . .	169
References . . . . .	173
<b>8 Concentration Polarization and Diffusion . . . . .</b>	<b>177</b>
Introduction . . . . .	177
Where Oxygen Reduction Occurs . . . . .	177
Concentration Polarization in Current Density–Potential Plots . . . . .	178
Solubility and Diffusion . . . . .	179
Solubility of Oxygen in Aqueous Solutions . . . . .	179
Fick’s First Law of Diffusion . . . . .	181
Diffusion and Random Walks . . . . .	183
Electrode Kinetics for Concentration Polarization . . . . .	186
Concentration Profile Near an Electrode Surface . . . . .	186
Limiting Diffusion Current Density . . . . .	187
Diffusion Layer vs. The Diffuse Layer . . . . .	189
Current–Potential Relationship for Concentration Polarization . . . . .	189
Wagner–Traud Theory for Concentration Polarization . . . . .	191
Effect of Environmental Factors on Concentration Polarization and Corrosion . . . . .	192
Effect of Oxygen Concentration . . . . .	193
Effect of Solution Velocity . . . . .	194
Effect of Temperature . . . . .	196
Further Applications of Concentration Polarization Curves . . . . .	197
Cathodic Protection . . . . .	197
Area Effects in Galvanic Corrosion . . . . .	199
Linear Polarization . . . . .	199
Concentration Polarization in Acid Solutions . . . . .	200
Combined Activation and Concentration Polarization . . . . .	202

The Rotating Disc Electrode . . . . .	202
Problems . . . . .	205
References . . . . .	208
<b>9 Passivity . . . . .</b>	<b>209</b>
Introduction . . . . .	209
Aluminum: An Example . . . . .	209
What is Passivity? . . . . .	210
Early History of Passivity . . . . .	210
Thickness of Passive Oxide Films . . . . .	210
Purpose of This Chapter . . . . .	211
Electrochemical Basis for Passivity . . . . .	211
Theories of Passivity . . . . .	215
Adsorption Theory . . . . .	215
Oxide Film Theory . . . . .	216
Film Sequence Theory . . . . .	218
Surface Analysis Techniques for the Examination of Passive Films . . . . .	218
X-ray Photoelectron Spectroscopy (XPS) . . . . .	220
X-ray Absorption Spectroscopy . . . . .	222
Scanning Tunneling Microscopy . . . . .	223
Models for the Passive Oxide Film on Iron . . . . .	224
Bilayer Model . . . . .	224
Hydrous Oxide Model . . . . .	227
Bipolar-Fixed Charge Model . . . . .	228
Spinel/Defect Model . . . . .	229
What Do These Various Models Mean? . . . . .	230
Passive Oxide Films on Aluminum . . . . .	230
Air-Formed Oxide Films . . . . .	231
Films Formed in Aqueous Solutions . . . . .	231
Properties of Passive Oxide Films . . . . .	232
Thickness . . . . .	233
Electronic and Ionic Conductivity . . . . .	233
Chemical Stability . . . . .	233
Mechanical Properties . . . . .	234
Structure of Passive Films . . . . .	235
Passivity in Binary Alloys . . . . .	237
Electron Configuration Theory . . . . .	238
Oxide Film Properties . . . . .	241
Percolation Theory . . . . .	242
Graph Theory Model . . . . .	243
Passivity in Stainless Steels . . . . .	249
Electrochemical Aspects . . . . .	250
Composition of Passive Films on Stainless Steels . . . . .	252
Passivity by Alloying with Noble Metals . . . . .	254
Anodic Protection . . . . .	255
Problems . . . . .	257
References . . . . .	260

<b>10 Crevice Corrosion and Pitting</b>	263
Introduction	263
Crevice Corrosion	263
Initiation of Crevice Corrosion	264
Propagation of Crevice Corrosion	269
Crevice Corrosion Testing	272
Area Effects in Crevice Corrosion	274
Protection Against Crevice Corrosion	275
Pitting	277
Critical Pitting Potential	278
Experimental Determination of Pitting Potentials	280
Effect of Chloride Ions on the Pitting Potential	282
Effect of Inhibitors on the Pitting Potential	283
Mechanism of Pit Initiation	283
Mechanism of Pit Propagation	286
Protection Potential	288
Metastable Pits and Repassivation	290
Experimental Pourbaix Diagrams for Pitting	291
Effect of Molybdenum on the Pitting of Stainless Steels	293
Effect of Sulfide Inclusions on the Pitting of Stainless Steels	294
Effect of Temperature	294
Protection Against Pitting	296
Pitting of Aluminum	297
Occluded Corrosion Cells	300
Occluded Corrosion Cell (OCC) on Iron	301
Occluded Corrosion Cells on Copper and Aluminum	303
Differences Between Pitting and Crevice Corrosion	306
Detection of Corrosion Pits	306
Problems	308
References	311
<b>11 Mechanically Assisted Corrosion</b>	315
Introduction	315
Stress-Corrosion Cracking	318
Mechanical Metallurgy	318
Characteristics of Stress-Corrosion Cracking	319
Stages of Stress-Corrosion Cracking	320
Fracture Mechanics and SCC	323
SCC Testing	331
Interpretation of SCC Test Data	334
Metallurgical Effects in SCC	335
Environmental Effects on SCC	336
Mechanisms of SCC	339
Protection Against Stress-Corrosion Cracking	345
Corrosion Fatigue	346
Corrosion Fatigue Data	347
Protection Against Corrosion Fatigue	348
Cavitation Corrosion	349

Erosion Corrosion and Fretting Corrosion . . . . .	352
Problems . . . . .	353
References . . . . .	354
<b>12 Corrosion Inhibitors . . . . .</b>	<b>357</b>
Introduction . . . . .	357
Types of Inhibitors . . . . .	359
Acidic Solutions . . . . .	360
Chemisorption of Inhibitors . . . . .	361
Effect of Inhibitor Concentration . . . . .	362
Chemical Factors in the Effectiveness of Chemisorbed Inhibitors . . . . .	363
Involvement of Water . . . . .	367
Competitive vs. Co-operative Adsorption . . . . .	369
Effect of the Electrical Double Layer . . . . .	370
The Potential of Zero Charge . . . . .	372
Effect of Molecular Structure . . . . .	373
Adsorption Isotherms . . . . .	376
Nearly Neutral Solutions . . . . .	379
Effect of Oxide Films . . . . .	379
Chelating Compounds as Corrosion Inhibitors . . . . .	380
Chromates and Chromate Replacements . . . . .	381
Inhibition of Localized Corrosion . . . . .	382
Pitting Corrosion . . . . .	382
Crevice Corrosion . . . . .	386
Stress-Corrosion Cracking and Corrosion Fatigue . . . . .	387
New Approaches to Corrosion Inhibition . . . . .	389
Biological Molecules . . . . .	390
Langmuir–Blodgett Films and Self-assembled Monolayers . . . . .	393
Vapor-Phase Inhibitors . . . . .	396
Problems . . . . .	398
References . . . . .	400
<b>13 Corrosion Under Organic Coatings . . . . .</b>	<b>403</b>
Introduction . . . . .	403
Paints and Organic Coatings . . . . .	404
Underfilm Corrosion . . . . .	405
Water Permeation into an Organic Coating . . . . .	406
Permeation of Oxygen and Ions into an Organic Coating . . . . .	410
Breakdown of an Organic Coating . . . . .	411
Adhesion of Organic Coatings . . . . .	412
Improved Corrosion Prevention by Coatings . . . . .	416
Filiform Corrosion . . . . .	417
Corrosion Tests for Organic Coatings . . . . .	419
Accelerated Tests . . . . .	419
Cathodic Delamination . . . . .	419
AC Impedance Techniques – A Brief Comment . . . . .	422
Recent Directions and New Challenges . . . . .	422
Problems . . . . .	423
References . . . . .	425

<b>14 AC Impedance</b>	427
Introduction	427
Relaxation Processes	427
Experimental Setup	429
Complex Numbers and AC Circuit Analysis	430
The Metal/Solution Interface	431
Impedance Analysis	432
Additional Methods of Plotting Impedance Data	434
Multiple Time Constants and the Effect of Diffusion	436
Kramers–Kronig Transforms	437
Application to Corrosion Inhibition	438
Organic Coatings	441
Oxide Films and Surface Treatments	446
Concluding Remarks	449
Problems	449
References	451
<b>15 High-Temperature Gaseous Oxidation</b>	453
Introduction	453
Thermodynamics of High-Temperature Oxidation	453
Ellingham Diagrams	454
Equilibrium Pressure of Oxygen	455
Theory of High-Temperature Oxidation	456
Oxidation Rate Laws	457
Linear Rate Law	458
Parabolic Rate Law	459
Logarithmic Rate Law	460
Comparison of Rate Laws	460
The Wagner Mechanism and the Parabolic Rate Law	460
Effect of Temperature on the Oxidation Rate	463
Defect Nature of Oxides	463
Semiconductor Nature of Oxides	465
Hauffe Rules for Oxidation	466
Effect of Oxygen Pressure on Parabolic Rate Constants	471
Non-uniformity of Oxide Films	472
Protective vs. Non-protective Oxides	473
Pilling–Bedworth Ratio	473
Properties of Protective High-Temperature Oxides	473
Problems	474
References	475
<b>16 Selected Topics in Corrosion Science</b>	477
Introduction	477
Electrode Kinetics of Iron Dissolution in Acids	477
Bockris–Kelly Mechanism	478
Heusler Mechanism	480
Reconciliation of the Two Mechanisms	481
Additional Work on Electrode Kinetics	482
Distribution of Current and Potential	483



Laplace's Equation . . . . .	483
Circular Corrosion Cells . . . . .	483
Parametric Study . . . . .	486
Application to the Experiments of Rozenfeld and Pavluts kaya . . . . .	488
Large Structures and Scaling Rules . . . . .	489
Modeling of the Cathodic Protection System of a Ship . . . . .	491
Scaling Rules . . . . .	492
Acid–Base Properties of Oxide Films . . . . .	494
Surface Hydroxyl Groups . . . . .	494
Nature of Acidic and Basic Surface Sites . . . . .	495
Isoelectric Points of Oxides . . . . .	495
Surface Charge and Pitting . . . . .	497
Pitting Potential of Aluminum as a Function of pH . . . . .	498
Surface Modification by Directed Energy Beams . . . . .	499
Ion Implantation and Related Processes . . . . .	499
Applications of Ion Implantation . . . . .	501
Laser-Surface Processing Techniques . . . . .	505
Applications of Laser-Surface Processing . . . . .	507
Comparison of Ion Implantation and Laser–Surface Processing . . . . .	509
Problems . . . . .	510
References . . . . .	512
<b>17 Beneficial Aspects of Corrosion . . . . .</b>	<b>515</b>
Introduction . . . . .	515
Rust Is Beautiful . . . . .	515
Copper Patinas Are Also Beautiful . . . . .	515
Cathodic Protection . . . . .	517
Electrochemical Machining . . . . .	517
Metal Cleaning . . . . .	517
Etching . . . . .	517
Batteries . . . . .	517
Passivity . . . . .	517
Anodizing . . . . .	518
Titanium Jewelry and Art . . . . .	518
Caution to Inexperienced Artisans: . . . . .	518
References . . . . .	518
<b>Answers to Selected Problems . . . . .</b>	<b>521</b>
Chapter 2 . . . . .	521
Chapter 3 . . . . .	521
Chapter 4 . . . . .	522
Chapter 5 . . . . .	522
Chapter 6 . . . . .	523
Chapter 7 . . . . .	524
Chapter 8 . . . . .	524
Chapter 9 . . . . .	524
Chapter 10 . . . . .	525
Chapter 11 . . . . .	526
Chapter 12 . . . . .	526

Chapter 13 . . . . .	527
Chapter 14 . . . . .	528
Chapter 15 . . . . .	528
Chapter 16 . . . . .	528
<b>Appendix A: Some Properties of Various Elemental Metals . . . . .</b>	<b>531</b>
<b>Appendix B: Thermodynamic Relationships for Use in Constructing Pourbaix</b>	
<b>Diagrams at High Temperatures . . . . .</b>	<b>533</b>
References . . . . .	534
<b>Appendix C: Relationship Between the Rate Constant and the Activation</b>	
<b>Energy for a Chemical Reaction . . . . .</b>	<b>535</b>
<b>Appendix D: Random Walks in Two Dimensions . . . . .</b>	<b>537</b>
<b>Appendix E: Uhlig's Explanation for the Flade Potential on Iron . . . . .</b>	<b>541</b>
<b>Appendix F: Calculation of the Randic Index <math>X(G)</math> for the Passive Film</b>	
<b>on Fe–Cr Alloys . . . . .</b>	<b>543</b>
References . . . . .	545
<b>Appendix G: Acid Dissociation Constants <math>pK_a</math> of Bases and the Base Strength . . . . .</b>	<b>547</b>
<b>Appendix H: The Langmuir Adsorption Isotherm . . . . .</b>	<b>549</b>
<b>Appendix I: The Temkin Adsorption Isotherm . . . . .</b>	<b>551</b>
<b>Appendix J: The Temkin Adsorption Isotherm for a Charged Interface . . . . .</b>	<b>553</b>
<b>Appendix K: Effect of Coating Thickness on the Transmission Rate</b>	
<b>of a Molecule Permeating Through a Free-Standing Organic Coating . . . . .</b>	<b>557</b>
<b>Appendix L: The Impedance for a Capacitor . . . . .</b>	<b>559</b>
Reference . . . . .	559
<b>Appendix M: Use of L'Hospital's Rule to Evaluate <math> Z </math> for the Metal/Solution</b>	
<b>Interface for Large Values of Angular Frequency <math>\omega</math> . . . . .</b>	<b>561</b>
<b>Appendix N: Derivation of the Arc Chord Equation for Cole–Cole plots . . . . .</b>	<b>563</b>
References . . . . .	565
<b>Appendix O: Laplace's Equation . . . . .</b>	<b>567</b>
Reference . . . . .	569
<b>Index . . . . .</b>	<b>571</b>

<http://www.springer.com/978-1-4419-0454-6>

Introduction to Corrosion Science

McCafferty, E.

2010, X, 302 p. 501 illus., 1 illus. in color., Hardcover

ISBN: 978-1-4419-0454-6