Contents

Preface xiii
Author xvii

Chapter 1 Introduction 1

1.1 Colloidal Domain 2
1.2 Interfaces Are Closely Related to Colloids 4
1.3 Colloid and Interface Science in a Historical Perspective 4
1.4 Classification of Colloidal Systems 6
Suggestions for Further Reading 8

Chapter 2 Colloidal Particles: Shapes and Size Distributions 9

2.1 Shapes 10
2.2 Particle Size Distributions 10
2.3 Average Molar Mass 14
2.4 Specific Surface Area 16
Exercises 17
Suggestions for Further Reading 18

Chapter 3 Some Thermodynamic Principles and Relations, with Special Attention to Interfaces 19

3.1 Energy, Work, and Heat: The First Law of Thermodynamics 20
3.2 The Second Law of Thermodynamics: Entropy 21
3.3 Reversible Processes: Definition of Intensive Variables 22
3.4 Introduction of Other Functions of State: Maxwell Relations 23
3.5 Molar Properties and Partial Molar Properties: Dependence of the Chemical Potential on Temperature, Pressure, and Composition of the System 25
3.6 Criteria for Equilibrium: Osmotic Pressure 27
3.7 Phase Equilibria, Partitioning, Solubilization, and Chemical Equilibrium 30
3.7.1 Phase Equilibria 30
3.7.2 Partitioning and Solubilization 31
3.7.3 Chemical Equilibrium 32
3.8 Entropy of Mixing 32
3.9 Excess Nature of Interfacial Thermodynamic Quantities: The Gibbs Dividing Plane 33

3.10 Gibbs–Duhem Relation 38
3.11 Gibbs Adsorption Equation 38
3.12 Some Applications of the Gibbs Adsorption Equation 40
3.12.1 Adsorption of (Ionic) Surfactants 40
3.12.2 Adsorption of (Bio)polymers 41
3.12.3 Adsorption of Uncharged Compounds at a Charged Interface 42
3.13 Nonideal Mixtures 43
Exercises 44
Suggestions for Further Reading 45

Chapter 4 Water 47

4.1 Phenomenological Aspects of Water 48
4.2 Molecular Properties of Water 52
4.3 Water as a Solvent 54
4.3.1 Electrolytes 55
4.3.2 Noncharged Components 56
Exercises 59
Suggestions for Further Reading 60

Chapter 5 Interfacial Tension 61

5.1 Interfacial Tension: Phenomenological Aspects 62
5.2 Interfacial Tension as a Force: Mechanical Definition of Interfacial Tension 63
5.3 Interfacial Tension as an Interfacial (Gibbs) Energy: Thermodynamic Definition of Interfacial Tension 64
5.4 Operational Restrictions of Interfacial Tension 67
5.4.1 Interfacial Tension of Solids 67
5.4.2 Constant Composition 67
5.4.3 Dynamic Interfacial Tension 68
5.5 Interfacial Tension and the Works of Cohesion and Adhesion 68
5.6 Molecular Interpretation of Interfacial Tension 69
5.6.1 Nearest-Neighbor Interactions 69
5.6.2 Relations between Interfacial Tension $\gamma^{\alpha\beta}$ and Surface Tensions γ^{α} and γ^{β} 72
Exercises 75
Suggestions for Further Reading 77

Chapter 6 Curvature and Capillarity 79

6.1 Capillary Pressure: The Young–Laplace Equation 80
6.1.1 Radii of Curvature 82
6.2 Some Consequences of Capillary Pressure 84

6.3 Curvature and Chemical Potential: Kelvin's Law and Ostwald's Law 87
6.4 Curvature and Nucleation 90
Exercises 92
Suggestions for Further Reading 94

Chapter 7 Monolayers at Fluid Interfaces 95

7.1 The Interfacial Pressure 97
7.2 Gibbs and Langmuir's Monolayers: Equations of State 98
7.3 Formation of Monolayers 98
7.4 Pressure–Area Isotherms of Langmuir's Monolayers: Two-Dimensional Phases 100
7.4.1 Influence of the Temperature on the π(A) Isotherm 103
7.5 Transfer of Monolayers to Solid Surfaces: Langmuir–Blodgett and Langmuir–Schaefer Films 105
7.6 Covalent Organic Monolayers 108
7.6.1 Alkyl Thiols on Noble Metals 108
7.6.2 Alkyl Silanes on Oxides 108
7.6.3 Alkenes on Silicon and Silica 109
Exercises 109
Suggestions for Further Reading 111

Chapter 8 Wetting of Solid Surfaces 113

8.1 Contact Angle: Equation of Young and Dupré 114
8.2 Some Complications in the Establishment of the Contact Angle: Hysteresis, Surface Heterogeneity, and Roughness 115
8.3 Wetting and Adhesion: Determination of Surface Polarity 117
8.4 Approximation of the Surface Tension of a Solid: The Critical Surface Tension of Wetting 119
8.4.1 Zisman Method 119
8.4.2 Wu Method 120
8.5 Wetting by Solutions Containing Surfactants 121
8.6 Capillary Penetration 121
8.7 Some Practical Applications and Implications of Wetting: Impregnation, Flotation, Pickering Stabilization, and Cleansing 123
8.7.1 Impregnation 123
8.7.2 Flotation 124
8.7.3 Pickering Stabilization 125
8.7.4 Cleansing 126
Exercises 127
Suggestions for Further Reading 129

Chapter 9 Electrochemistry of Interfaces 131

9.1 Electric Charge 132
9.2 Electric Potential 138
9.3 The Gibbs Energy of an Electrical Double Layer 139
9.4 Models for the Electrical Double Layer 141
9.4.1 The Molecular Condenser 141
9.4.2 The Diffuse Double Layer 142
9.4.3 The Gouy–Chapman–Stern Model 145
9.5 Donnan Effect, Donnan Equilibrium, Colloidal Osmotic Pressure, and Membrane Potential 148
Exercises 152
Suggestions for Further Reading 154

Chapter 10 Electrokinetic Phenomena 155

10.1 The Plane of Shear: The Zeta Potential 156
10.2 Derivation of the Zeta Potential from Electrokinetic Phenomena 157
10.2.1 Electroosmosis 157
10.2.2 Electrophoresis 160
10.2.3 Streaming Current and Streaming Potential 162
10.3 Some Complications in Deriving the Zeta Potential 164
10.3.1 Surface Conduction 165
10.3.2 Viscoelectric Effect 165
10.3.3 Permeable Surface Layer Containing Fixed Charges 167
10.4 Interpretation of the Zeta Potential 169
10.5 Applications of Electrokinetic Phenomena 170
Exercises 172
Suggestions for Further Reading 174

Chapter 11 Self-Assembly of Amphiphilic Molecules 175

11.1 Self-Assembly as Phase Separation 177
11.2 Different Types of Self-Assembled Structures 179
11.3 Aggregation as a "Start–Stop" Process: Size and Shape of Self-Assembled Structures 181
11.4 Mass Action Model for Micellization 184
11.5 Factors That Influence the Critical Micelle Concentration 187
11.6 Bilayer Structures 188
11.7 Reverse Micelles 191
11.8 Microemulsions 193
11.9 Self-Assembled Structures in Applications 196
Exercises 198
Suggestions for Further Reading 200

Chapter 12 Polymers 201

12.1 Polymers in Solution 203
12.2 Conformations of Dissolved Polymer Molecules 206
12.3 Coil-Like Polymer Conformations 207
12.4 Semi-Dilute and Concentrated Polymer Solutions 210
12.5 Polyelectrolytes 211
12.6 Phase Separations in Polymer Solutions: Complex Coacervation 214
12.6.1 Polyelectrolyte Multilayers 216
12.6.2 Complex Coacervate Core Micelles 217
12.7 Polymer–Surfactant 219
12.8 Polymer Gels 220
Exercises 223
Suggestions for Further Reading 224

Chapter 13 Proteins 225

13.1 The Amino Acids in Proteins 226
13.2 The Three-Dimensional Structure of Protein Molecules in Aqueous Solution 231
13.3 Noncovalent Interactions That Determine the Structure of a Protein Molecule in Water 235
13.3.1 Hydrophobic Interaction 236
13.3.2 Electrostatic Interactions 237
13.3.2.1 Ion-Pair Formation 237
13.3.2.2 Charge Distribution 238
13.3.3 Dipolar Interactions 240
13.3.4 Dispersion Interactions 241
13.3.5 Hydrogen Bonding 242
13.3.6 Bond Lengths and Angles 243
13.4 Stability of Protein Structure in Aqueous Solution 243
13.5 Thermodynamic Analysis of Protein Structure Stability 245
13.6 Reversibility of Protein Denaturation: Aggregation of Unfolded Protein Molecules 250
Exercises 251
Suggestions for Further Reading 253

Chapter 14 Adsorption 255

14.1 Adsorbent–Adsorbate Interactions 257
14.2 Adsorption Kinetics 259
14.2.1 Transport toward the Interface 259
14.2.2 Interaction with the Interface: Attachment and Detachment 259
14.3 Adsorption Equilibrium 261
14.3.1 Configuration Entropy 262

14.3.2 Interaction Entropy 263
14.3.3 Nearest-Neighbor Interactions 265
14.3.4 Cooperativity 267
14.3.5 Adsorption of Ions 268
14.4 Binding of Ligands 270
14.5 Applications of Adsorption 272
Exercises 273
Suggestions for Further Reading 275

Chapter 15 Adsorption of (Bio)Polymers, with Special Emphasis on Globular Proteins 277

15.1 Adsorption Kinetics 279
15.2 Morphology of the Interface 285
15.3 Relaxation of the Adsorbed Molecule 285
15.4 Adsorption Affinity: Adsorption Isotherm 286
15.4.1 Polymers 286
15.4.2 Polyelectrolytes 288
15.5 Driving Forces for Adsorption of Globular Proteins 290
15.5.1 Interaction between Electrical Double Layers 291
15.5.2 Dispersion Interaction 293
15.5.3 Changes in the State of Hydration 294
15.5.4 Rearrangements in the Protein Structure 295
15.6 Reversibility of the Protein Adsorption Process: Desorption and Exchange 296
15.7 Competitive Protein Adsorption 298
Exercises 299
Suggestions for Further Reading 302

Chapter 16 Stability of Lyophobic Colloids against Aggregation 305

16.1 Forces Operating between Colloidal Particles 307
16.1.1 London–van der Waals Forces or Dispersion Forces 307
16.1.2 Electrical Double Layer Forces 310
16.1.3 Short-Range Forces 314
16.2 DLVO Theory of Colloid Stability 315
16.2.1 Critical Coagulation Concentration 317
16.3 Influence of Polymers on Colloidal Stability 319
16.3.1 Nonadsorbing Polymers: Depletion Flocculation 319
16.3.2 Adsorbing Polymers: Bridging Flocculation and Steric Stabilization 321
16.4 Aggregation Kinetics 324
16.5 Morphology of Colloidal Aggregates 328
Exercises 330
Suggestions for Further Reading 333

Chapter 17 Rheology, with Special Attention to Dispersions and Interfaces 335

17.1 Rheological Properties 338
17.1.1 Compression at All Sides 338
17.1.2 Elongation in One Direction 339
17.1.3 Shear 339
17.2 Classification of Materials Based on Their Rheological Behavior 341
17.2.1 Time-Independent Behavior 341
17.2.2 Time-Dependent Behavior 342
17.3 Viscosity of Diluted Liquid Dispersions 344
17.3.1 Compact Particles 344
17.3.2 Uncharged Polymers 347
17.3.3 Polyelectrolytes 348
17.4 Interfacial Rheology 350
17.4.1 Dilation or Compression 350
17.4.2 Shear 351
Exercises 353
Suggestions for Further Reading 355

Chapter 18 Emulsions and Foams 357

18.1 Phenomenological Aspects 358
18.2 Emulsification and Foaming 359
18.3 Emulsion and Foam Stability 361
18.3.1 Sedimentation and Creaming 362
18.3.2 Drainage 363
18.3.3 Aggregation 365
18.3.4 Disproportionation 365
18.3.5 Coalescence 368
18.4 Modulation of the Coarseness and Stability of Emulsions and Foams 371
Exercises 372
Suggestions for Further Reading 373

Chapter 19 Physicochemical Properties of Biological Membranes 375

19.1 Structure and Dynamics of Biomembranes 377
19.2 Electrochemical Properties of Biomembranes 379
19.3 Transport in Biological Membranes 381
19.4 Transmembrane Potential 386
Exercises 388
Suggestions for Further Reading 390

Chapter 20 Bioadhesion 391

20.1 A Qualitative Description of Biofilm Formation 393
20.2 Biological Surfaces 395

20.3 Physicochemical Models for Cell Deposition and Adhesion 397
20.3.1 Capillarity 397
20.3.2 Stability of Lyophobic Colloids 398
20.3.3 Balance of Interfacial Tensions: The Wetting Approach 401
20.4 Surface Modification to Reduce (Bio)Adhesion 402
20.4.1 Positively Charged Surfaces 402
20.4.2 Low Surface Free Energy Coatings 403
20.4.3 Polymer Brush Coatings 403
20.5 General Thermodynamic Analysis of Particle Adhesion 406
Exercises 409
Suggestions for Further Reading 410

Appendix: Solutions to Exercises 413

Index 467