Contents

Pref	ace to	the Third Edition	ii
Ack	nowle	dgments	vi
Pref	ace to	the Second Edition	ix
Pref	ace to	the First Edition	X
1.	Coll	oid and Surface Chemistry: Scope and Variables	1
	1.1	Introduction	1
	1.2	The Importance of the Surface for Small Particles	6
	1.3	Classification of Colloids Based on Affinity to Carrier Fluid	10
	1.4	Concept of Stability of Colloidal Systems	14
	1.5	Some Physical Characteristics of Colloids	19
	1.6	Some Classical and Emerging Experimental Tools	38
	1.7	An Overview of the Book	56
		Review Questions	57
		References	57
		Problems	59
2.	Sedi	imentation and Diffusion and Their Equilibrium	62
	2.1	Introduction	62
	2.2	Sedimentation: Some Basic Considerations	65
	2.3	Gravitational Sedimentation	67
	2.4	Centrifugal Sedimentation	74
	2.5	Diffusion	78
	2.6	Brownian Motion and Diffusion	85
	2.7	The Random Coil and Random Walk Statistics	94
	2.8	Equilibrium Between Sedimentation and Diffusion	98
		Review Questions	101
		References Problems	101 102
		Problems	102
3.	Solu	tion Thermodynamics: Osmotic and Donnan Equilibria	105
	3.1	Introduction	105
	3.2	Osmotic Pressure: Thermodynamic Foundations	108
	3.3	Osmometry: Some Applications	114
	3.4	Statistical Foundations of Solution Thermodynamics	120
	3.5	Osmotic Equilibrium in Charged Systems	132
	26	Same Applications of Osmatic Phenomena	120

xvi	Contents
^*'	

		Review Questions	140
		References	141
		Problems	142
4.	The Rheology of Dispersions		145
	4.1	Introduction	145
	4.2	Newton's Law of Viscosity	148
	4.3	Concentric-Cylinder and Cone-and-Plate Viscometers	150
	4.4	The Poiseuille Equation and Capillary Viscometers	154
	4.5	The Equation of Motion: The Navier-Stokes Equation	158
	4.6	Einstein's Theory of Viscosity of Dispersions	161
	4.7	Deviations from the Einstein Model	168
	4.8	Non-Newtonian Behavior	174
	4.9	Viscosity of Polymer Solutions	181
		Review Questions	188
		References	188
		Problems	189
5.	Stati	c and Dynamic Light Scattering and Other Radiation Scattering	193
	5.1	Introduction	193
	5.2	Interaction of Radiation with Matter	196
	5.3	Scattering by Small Particles: Theory of Rayleigh Scattering	202
	5.4	Experimental Aspects of Light Scattering	207
	5.5	Extension to Larger Particles and to Intraparticle Interference Effects	213
	5.6	Interference Effects and Structure of Particles	223
	5.7	Scattering by Large, Absorbing Particles	229
	5.8	Dynamic Light Scattering	236
		Review Questions	242
		References	243
6.	Surf	References	243
6.	Surf 6.1	References Problems	243 244
6.		References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look	243 244 248
6.	6.1	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy	243 244 248 248
6.	6.1 6.2	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity	243 244 248 248 251
6.	6.1 6.2 6.3	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation:	243 244 248 248 251 255
6.	6.1 6.2 6.3 6.4 6.5	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation	243 244 248 248 251 255 257
6.	6.1 6.2 6.3 6.4	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting	243 244 248 248 251 255
6.	6.1 6.2 6.3 6.4 6.5	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena	243 244 248 248 251 255 257 261
6.	6.1 6.2 6.3 6.4 6.5 6.6	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications	243 244 248 248 251 255 257 261 265
6.	6.1 6.2 6.3 6.4 6.5 6.6	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two	243 244 248 248 251 255 257 261 265 272
6.	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders	243 244 248 248 251 255 257 261 265 272 276
6.	6.1 6.2 6.3 6.4 6.5 6.6	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders Molecular Interpretation of Surface Tension	243 244 248 248 251 255 257 261 265 272 276 283
6.	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders Molecular Interpretation of Surface Tension Review Questions	243 244 248 248 251 255 257 261 265 272 276 283 286
6.	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders Molecular Interpretation of Surface Tension	243 244 248 248 251 255 257 261 265 272 276 283 286 291
6 .	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9 6.10	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders Molecular Interpretation of Surface Tension Review Questions References Problems	243 244 248 248 251 255 257 261 265 272 276 283 286 291 293
	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9 6.10	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders Molecular Interpretation of Surface Tension Review Questions References Problems orption from Solution and Monolayer Formation	243 244 248 248 251 255 257 261 265 272 276 283 286 291
	6.1 6.2 6.3 6.4 6.5 6.6 6.7 6.8 6.9 6.10	References Problems ace Tension and Contact Angle: Application to Pure Substances Introduction Surface Tension and Contact Angle: A First Look Thermodynamics of Surfaces: Surface Tension as Surface Free Energy Surface Tension: Implications for Curved Interfaces and Capillarity Effects of Curved Interfaces on Phase Equilibria and Nucleation: The Kelvin Equation Surface Tension and Contact Angle: Their Relation to Wetting and Spreading Phenomena Contact Angles: Some Complications Measuring Surface Tension and Contact Angle: Round Two Contact of Liquids with Porous Solids and Powders Molecular Interpretation of Surface Tension Review Questions References Problems	243 244 248 248 251 255 257 261 265 272 276 283 286 291 293

Cor	ntents		xvi
	7.3	Experimental Measurement of Film Pressure	304
	7.4	Results of Film Balance Studies	308
	7.5	Viscous Behavior of Two-Dimensional Phases	318
	7.6	Applications of Monolayers and Monolayer Concepts	320
	7.7	Adsorption from Solution: Thermodynamics	323
	7.8	The Gibbs Equation: Experimental Results	327
	7.9	Adsorption on Solid Surfaces	331
	7.10	Applications of Adsorption from Solution	338
	7.11	Adsorption in the Presence of an Applied Potential	343
		Review Questions	348
		References	348
		Problems	349
8.	Coll	oidal Structures in Surfactant Solutions: Association Colloids	355
	8.1	Introduction	355
	8.2	Surfactants in Solution: Experimental Observations and Models	357
	8.3	Structure of Micelles Melocular Applications of Sunfactores Backing County Local	362
	8.4	Molecular Architecture of Surfactants, Packing Considerations, and Shapes of Micelles	367
	8.5	Critical Micelle Concentration and the Thermodynamics of Micellization	370
	8.6	Solubilization	375
	8.7	Catalysis by Micelles	380
	8.8	Reverse Micelles	386
	8.9	Emulsions and Microemulsions	389
	8.10	Some Applications of Microemulsions	392
	8.11	Biological Membranes	395
		Review Questions	398
		References	399
		Problems	399
9.	Adso	orption at Gas-Solid Interfaces	405
	9.1	Introduction	405
	9.2	Experimental and Theoretical Treatments of Adsorption: An Overview	409
	9.3	Thermodynamics of Adsorption: Phenomenological Perspective	413
	9.4	Thermodynamics of Adsorption: A Statistical Perspective Multilayer Adsorption: The Brunauer-Emmett-Teller Equation	419
	9.5 9.6	Energetics of Adsorption	425 433
	9.0 9.7	Adsorption in Porous Solids	436
	9.8	Adsorption on Crystal Surfaces	439
	9.9	Metal Surfaces and Heterogeneous Catalysis	451
	7.7	Review Questions	455
		References	456
		Problems	456
10.	van d	er Waals Forces	462
	10.1	Introduction	462
	10.2	van der Waals Forces and Their Importance in Colloid and	
		Surface Chemistry	464
	10.3	Molecular Interactions and Power Laws	467
	10.4	Molecular Origins and the Macroscopic Implications of	
		van der Waals Forces	471

Contents

	10.5 10.6 10.7 10.8	van der Waals Forces Between Large Particles and Over Large Distances Calculating van der Waals Forces Between Macroscopic Bodies Theories of van der Waals Forces Based on Bulk Properties Effect of the Medium on the van der Waals Attraction Review Questions References Problems	479 483 486 490 495 495 496
11.	The E	lectrical Double Layer and Double-Layer Interactions	499
	11.1	Introduction	499
	11.2	Surface Charges and Electrical Double Layer: Background	502
	11.3	The Capacitor Model of the Double Layer	504
	11.4	The Diffuse Double Layer: The Debye-Hückel Approximation	508
	11.5	The Debye-Hückel Approximation: Results	512
	11.6	The Electrical Double Layer: Gouy-Chapman Theory	516
	11.7	Overlapping Double Layers and Interparticle Repulsion	520
	11.8	"Not-Quite-Indifferent" Electrolytes: Stern Adsorption	527
		Review Questions References	530 530
		Problems	531
12.	Electi	rophoresis and Other Electrokinetic Phenomena	534
	12.1	Introduction	534
	12.2	Mobilities of Small Ions and Macroions in Electric Fields: A Comparison	536
	12.3	Zeta Potential: Thick Electrical Double Layers	538
	12.4	Zeta Potential: Thin Electrical Double Layers	544
	12.5	Zeta Potential: General Theory for Spherical Particles	546
	12.6	Electroosmosis	550
	12.7	Streaming Potential	553
	12.8	The Surface of Shear and Viscoelectric Effect	555
	12.9	Experimental Aspects of Electrophoresis	559
	12.10	Determining the Surface Charge from Electrokinetic Measurements	565
	12.11	Applications of Electrokinetic Phenomena	567
		Review Questions References	570
		Problems	570 571
13.	Elect	rostatic and Polymer-Induced Colloid Stability	575
	13.1	Introduction	575
	13.2	Interparticle Forces and the Structure and Stability of Dispersions	578
	13.3	The Derjaguin-Landau-Verwey-Overbeek Theory of Colloid Stability	585
	13.4	Theory of Coagulation in Dilute Dispersions	592
	13.5	Polymer-Colloid Mixtures: A Phenomenological Perspective	604
	13.6	Polymer-Induced Forces	610
	13.7	Steric Stabilization: A Model for the Initial Encounter	614
		Review Questions	619
		References	620
		Problems	621

Contents		xix
Appendix A:	Examples of Expansions Encountered in This Book Reference	625 625
Appendix B:	Units: CGS-SI Interconversions References	626 626
Appendix C:	Statistics of Discrete and Continuous Distributions of Data	631
	C.1 Introduction	631
	C.2 Discrete Distributions	631
	C.3 Theoretical Distribution Functions	634
	References	637
Appendix D:	List of Worked-Out Examples	638
Index		641