

CONTENT

	Page
Chapter One—Clay Suspensions and Colloidal Systems in General	1
I. The Colloidal Solution of a Clay in Water	1
A. Observations with the Naked Eye	1
B. Observations in the Ordinary-Light Microscope	2
C. Observations in the Ultramicroscope	2
D. Observations with the Electron Microscope	6
E. X-Ray Diffraction Patterns of Clays	9
F. Electron Diffraction Patterns of Clay Particles	9
II. Particle Interaction	9
III. Terminology in Colloid Chemistry	12
IV. Classification of Colloidal Systems	13
Reference	15
Chapter Two—Properties of Hydrophobic Sols	16
I. Settling, Aging, and Flocculation	16
A. Settling	16
B. Aging	17
C. Flocculation (Particle Agglomeration)	17
II. The Origin of the Electric Charge of the Particles	17
III. The Preparation of a Stable Hydrophobic Sol	20
A. Condensation Method	21
B. Dispersion Method	21
C. Cleaning of the Sols	22
IV. Flocculation of Sols by Electrolytes	23
V. Reversal of Particle Charge—Irrregular Flocculation Series	25
VI. Counter-Ion Exchange	27
VII. Gelation—A Special Case of Flocculation	28
References	29
Chapter Three—The Theory of the Stability of Hydrophobic Sols	30
I. Configuration of the Electric Double Layer	30
II. Effect of Electrolytes on the Configuration of the Electric Double Layer	35
III. The Balance of Repulsive and Attractive Forces on Particle Approach	37
A. The Electric Double-Layer Repulsion	37
B. The van der Waals Attraction	37
IV. The Summation of Repulsion and Attraction	39
V. The Net Interaction Curve and Sol Stability	40
References	43
Chapter Four—Successes of the Theory of Stability	45
I. Stability, Flocculation, and the Schulze-Hardy Rule	45
II. Limits of Particle Size	46
III. Flocculation by Water-Miscible Organic Solvents	47
IV. Direct Evidence of Long-Range Particle Interaction : Schiller Layers and Tactoids	47
A. Schiller Layers	47
B. Tactoid Formation	48
V. Counter-Ion Exchange	49
References	49
Chapter Five—Further Theories	51
I. Stern's Model of the Double Layer and Other Refinements	51
II. The Hydration Theory of Stability and Its Fallacies	53
III. The "Critical Zeta Potential"	55
IV. "Entropy" Stabilization	56
References	57
Chapter Six—Clay Mineralogy	59
I. Structural Principles	59

II. Montmorillonites (Expanding Three-Layer Clays)	66
III. Illites (Nonexpanding Three-Layer Clays)	70
IV. Kaolinites (Two-Layer Clays)	71
V. Chlorites	72
VI. Attapulgitite (Palygorskite)	72
VII. Mixed-Layer Clays	73
VIII. Differential Thermal Analysis of Clays (DTA)	73
IX. Size and Shape of Clay Particles	76
A. Direct Method—Ultramicroscopical Counting	76
B. Indirect Methods	77
C. Factors Determining Particle Size and Shape in the Genesis and Diagenesis Of Clay Minerals	78
X. Determination of the Surface Area of Clays	79
A. Computation from the Particle Dimensions	79
B. Computation from the Crystallographic Cell Dimensions	79
C. Direct Determination from Vapor-Adsorption Data	80
XI. Density of Charge of the Surface	80
XII. Conclusions	81
References	82
Chapter Seven—Electric Double-Layer Structure and Stability of Clay Suspensions	89
I. Electric Double-Layer Structure	89
A. The Double-Layer on the Flat Unit-Layer Surface	89
B. The Double-Layer on the Edge Surfaces of Clay Plates	90
II. Flocculation and Gelation	93
A. Modes of Particle Association	93
B. Clay Flocculation and the Schulze-Hardy Rule	95
C. Particle Association and Flow Properties	90
D. Argumentation	101
E. Further Experimental Support	103
1. The Structure of the Pure Gel	103
2. Criterion for Face-to-Face Association (“aggregation”)	104
F. Particle Association in Dilute Sols and Spontaneous Swelling of Montmorillonites	104
1. Particle Association in Dilute sols	104
2. Spontaneous Swelling of Montmorillonites	105
G. Deflocculation of Clay Suspensions	106
References	107
Chapter Eight—Peptization of Clay Suspensions	109
I. Peptization (Deflocculation) by Special Inorganic Salts	109
II. The Mechanism of Peptization	111
III. Activity Reduction and Ion Exchange in Clay Peptization	115
A. Cation Activity Reduction	116
B. Ion Exchange	116
IV. Peptization by Alkali	117
References	119
Chapter Nine—Technological Applications of Stability Control	120
I. Sedimentation and Stability	120
A. Principles	120
B. Applications	123
1. Separation of Dispersed Solids from a Suspension	123
2. Sedimentation Geology	124
3. Paints	124
4. Preparation of Thin Surface Coatings	124
5. Soils	124
II. Filtration of Suspensions and Stability	124
A. Principles	124
B. Applications	125
1. Analytical Chemistry	125

2. Management of Clay-Containing Soils	125
3. Permeability of Porous Formations	126
4. Conditioning of Drilling Fluids	127
5. Ceramics	129
III. Rheology and Stability of Suspensions	129
A. Terminology	129
B. Measurements of Flow Properties	133
C. Rheological Properties of Suspensions	135
1. Dilute Sols and Suspensions	135
2. Effect of particle Interaction on the Flow Properties of Suspensions	136
3. Thixotropy and Rheopexy	137
D. Applications	139
1. Drilling Fluids	139
2. Paints	143
3. Paper Filler and Coatings	144
E. Rheological Properties of Sediments	144
IV. Clay-Water Relationships: Swelling and Compaction in Soil Engineering and Sedimentary Geology	146
A. Short Range Particle Interaction—Swelling Due to Surface Hydration Energy	148
B. Long Range Particle Interaction—“Osmotic Swelling” or Electrical Double-Layer Repulsion	149

References

152

Chapter Ten—Interaction of Clays and Organic Compounds	155
I. Introduction	155
A. Terminology	155
B. Wetting	156
C. Classification	156
D. X-Ray Observations	157
E. Adsorption Measurements	159
II. Compounds with Low to Moderate Molecular Weights	160
A. Organic Anions—Specifically Tannates	160
1. Effect of Tannates on Clay Suspensions	160
2. Application of Tannates in “Red Muds” and “Lime Red Muds”	161
B. Organic Cations—Specifically Amine Salts	165
C. Polar Organic Compounds	167
III. Macromolecular Compounds	168
A. Polyelectrolytes	168
1. Effect of Polyelectrolytes on Clay Suspensions	169
2. The Mechanism of the Protective and Sensitizing Action	170
3. Applications	172
B. Nonionic Polymers	174
1. Interaction with Clay Suspensions	174
2. Applications	174
IV. Chemical Reaction Products of Clays and Organic Compounds	175
A. Reactions Involving Silanol Groups	175
B. Interlayer Reactions in Nonswelling Minerals	176
C. Color Reactions	176
V. Emulsions Containing Dispersed Clays	177
A. Applications	178
VI. Clay Dispersions in Oil	179
A. Applications	180
VII. Summary of Particle Interaction	181
A. Factors Promoting Deflocculation	181
1. Electric Double-Layer Repulsion	181
2. “Entropic” Repulsion	181
3. Short-Range Hydration or “Lyosphere” Repulsion	181
4. Born Repulsion	181
B. Factors Promoting Flocculation	182
1. van der Waals Attraction	182
2. Electrostatic Attraction	182
3. Bridging of Particles by Polyfunctional Long-Chain Compounds	182

4. Bridging of Particles by a Second Immiscible Liquid Component	182
References	183
Chapter Eleven—Electrokinetic and Electrochemical Properties of Clay-Water Systems	188
I. Electrokinetic Phenomena	189
A. Surface Conductance	189
B. Electrophoresis	192
C. Electrophoresis	193
D. Streaming Potentials	194
E. Electrokinetic Phenomena in Porous Media	194
II. Electrochemistry of Dispersed Systems	196
A. Ion Activities and pH Measurements	196
1. Degree of Dissociation and Ion Activity in Electrolyte Solutions	196
2. Determination of Ion Activities in Solutions	197
3. The pH Scale and Measurements of pH in Electrolyte Solutions	198
4. Measurement of pH in Sols and Suspensions	199
5. “Degree of Dissociation” and “Cation Activities” in Clay Suspensions	202
B. Membrane Potentials	205
References	208
Synopsis	210
Appendix I—Note on the Preparation of Clay Suspensions	239
References	242
Appendix II—Miscellaneous Computed Data for Montmorillonites	244
A. Total Layer Surface Area and Surface Charge Density	244
B. Average Particle Distance in Suspensions of Clays Parallel and Cubic Stacking Of the plates	245
C. Formula Computation from Chemical Analysis	248
References	249
Appendix III—Electric Double-Layer Computations	251
A. The Single Flat Double Layer	251
1. Potential and Charge Distribution in a Single Flat Double Layer According To the Gouy theory	251
2. Potential and Charge Distribution in a Flat Double Layer According to the Stern Model	256
3. Corrections of the Gouy Theory According to Bolt	259
B. Interacting Flat Double Layers	260
1. Potential and Charge Distribution between Interacting Flat Double Layers According to the Gouy Model	260
2. Potential and Charge Distribution between Interacting Surfaces with Stern-Type Double Layers	263
C. Force and Energy of Interaction of Two Flat Double Layers	267
1. Repulsive Energy of Double Layers of Constant Potential Derived from the Free-Energy Change	267
2. Direct Computation of the Interaction Force between Flat Double Layers	267
3. Interaction Energy of Stern Double Layers	267
D. Cation-Exchange Capacity and Negative Adsorption	270
E. Cation-Exchange Equilibrium	273
1. Monovalent Cation Exchange	273
2. Monovalent-Divalent Ion Exchange	274
F. Summary of Gouy Double-Layer Formulas	275
1. Symbols and Values	275
2. Single Gouy Double Layer	276
3. Interacting Gouy Double Layers	277
4. Interaction Force and Energy	279
References	279

Appendix IV—van der Waals Attraction Energy between Two Unit Layers	280
Appendix V—Clay Literature	282
Books, Monographs, Reviews	282
Periodic Publications	284
Author Index	289
Subject Index	295