

PRINCIPLES *of* **SOIL CHEMISTRY**

Third Edition, Revised and Expanded

Kim H. Tan

*Department of Crop and Soil Sciences
The University of Georgia
Athens, Georgia*



MARCEL DEKKER, INC.

NEW YORK • BASEL • HONG KONG

CONTENTS

Preface to the Third Edition	v
Preface to the Second Edition	xi
Preface to the First Edition	xv
Chapter 1 REVIEW OF BASIC CHEMICAL PRINCIPLES	1
1.1 Atom and Atomic Structure	1
1.2 Particle Accelerators or Synchrotrons	2
1.3 Elementary Particles	4
1.3.1 Quarks	5
1.3.2 Leptons	5
1.3.3 Neutrinos	6
1.3.4 Force Carriers	7
1.4 Atomic Model of Rutherford and Bohr	7
1.5 Atomic Masses and Weights	9
1.5.1 Mass	9
1.5.2 Weight	9
1.6 Atomic Mass and Atomic Mass Number	10
1.6.1 Atomic Mass Unit	10
1.7 Atomic Number	12
1.8 Atomic Weights	12
1.9 Avogadro's Number	13

1.10	Atomic Orbital	13
1.11	Atomic Radius	13
1.12	Valence	14
1.13	Equivalent Weight	15
1.13.1	Acid-Base Titrations	16
1.13.2	Precipitation and Complex Reactions	16
1.13.3	Oxidation-Reduction Reactions	17
1.14	Chemical Units	19
1.14.1	Normality	19
1.14.2	Molarity, Molality, and Formality	19
1.14.3	Mole Fraction	20
1.15	Isotopes	21
1.16	Radioactivity	21
1.17	Half-Life of Radioactive Material and Carbon Dating	22
Chapter 2 ELECTROCHEMICAL CELLS AND CHEMICAL POTENTIALS		24
2.1	Electrochemical Cells and Electrode Potential	24
2.2	Electron Activity	29
2.2.1	Electron Activity in the Biochemical Cycle	32
2.3	Relationship between Electron Activity and Electrode Potential	33
2.4	Redox Reaction Limits in Soils and E_h -pH Relation	35
2.4.1	pe-pH Relation	36
2.4.2	Importance of E_h -pH or pe-pH Relations in Soil and Biological Systems	38
2.4.3	Constancy in E_h -pH or pe-pH Relation	39
2.5	rH Concept	40
2.5.1	Relationship between rH and pe-pH	42
2.6	Chemical Potentials and Their Application in Ion Uptake by Plants	43
2.6.1	Chemical Potential	43
2.6.2	Equilibrium Potential	45
2.6.3	Membrane or Donnan Potential	46

Chapter 3 SOIL COMPOSITION, SOIL AIR, AND SOIL SOLUTION	49
3.1 Soil Composition	49
3.2 Soil Air	51
3.2.1 Characterization of Soil Air Quality	52
3.2.2 Humidity of Soil Air	53
3.3 Concept and Importance of Soil Solution	55
3.3.1 Approximations of Soil Solution	56
3.3.2 Effect of the Gas Phase on the Soil Solution	56
3.4 Chemistry of Soil Water	58
3.5 Oxygen Demand of Water	60
3.5.1 Importance of Oxygen Demand in the Environment	61
3.6 Soil-Water Energy Concepts	62
3.6.1 Water Potential (ψ_w)	63
3.6.2 Relationship of Water Potential and Chemical Potential of Water	64
3.6.3 Total Soil Water Potential (Ψ)	65
3.6.4 Matric Potential (ψ_m)	66
3.6.5 Pressure Potential (ψ_p)	66
3.6.6 Osmotic Potential (ψ_o)	67
3.6.7 Gravitational Potential (ψ_g)	67
3.6.8 Units of Soil Water Potential	67
3.6.9 Relationship between ψ_w and Water Content and Relative Humidity	69
3.7 Plant-Soil-Water Energy Relation	70
3.8 Law of Mass Action and Equilibrium Constant	72
3.9 Solubility Product	74
3.10 Dissociation of Water	76
3.11 Dissociation of Strong Electrolytes	77
3.12 Dissociation of Weak Electrolytes	79
3.13 The Henderson-Hasselbalch Equation	80
3.13.1 Application of the Henderson-Hasselbalch Concept	81
3.14 The Equilibrium Constant and Ion Pairs	83
3.15 The Exchange Constant and Ion Exchange	84
3.16 Relationship between Equilibrium Constant and Cell or Electrode Potential	85
3.17 Equilibrium Constant and Free Energy Relationship	86

3.18	Equilibrium Constant and Electron Activity	88
3.19	Activity and Standard State	90
3.20	Debye-Hueckel Theory and Activity Coefficients	92
3.21	Ionic Strength	93
Chapter 4	COLLOIDAL CHEMISTRY OF ORGANIC SOIL CONSTITUENTS	97
4.1	The Colloidal System	97
4.2	The Organic Components	98
4.3	Soil Humus	99
4.4	Carbohydrates	101
4.4.1	Properties of Carbohydrates and Their Accumulation in Soils	104
4.4.2	Effect of Carbohydrates on Soil Properties	105
4.4.3	Importance of Carbohydrates in the Environment	106
4.5	Amino Acids and Protein	108
4.5.1	Colloidal Chemistry of Amino Acids	110
4.6	Lipids	113
4.6.1	Colloidal Chemistry and Importance of Lipids in Soils	114
4.7	Nucleic Acids	116
4.7.1	Colloidal Properties and Importance of Nucleic Acids in Soils	117
4.8	Lignins	117
4.8.1	Colloidal Chemistry and Importance of Lignins in Soils	121
4.9	Humic Matter	122
4.9.1	Definitions and Terminology	122
4.9.2	Types of Humic Matter	124
4.9.3	Extraction and Isolation of Humic Substances from Soils and Water	126
4.9.4	Chemical Characterization and Composition	128
4.9.5	Colloidal Chemistry and Reactions	134
4.9.6	Colloidal Properties and Potentiometric Titrations of Humic Acid	136
4.9.7	Chromatography of Humic Substances	138
4.9.8	Molecular Weights of Humic Compounds	143

4.9.9	Spectral Characteristics of Humic Compounds	146
4.9.10	Electron Microscopy of Humic Matter	159
4.9.11	Structural Chemistry of Humic Acids	162
4.9.12	Agricultural, Industrial, and Environmental Importance of Humic Acids	172

Chapter 5	COLLOIDAL CHEMISTRY OF INORGANIC SOIL CONSTITUENTS	177
5.1	The Clay Fraction of Soils	177
5.2	Structural Chemistry of Clay Minerals	181
5.2.1	The Unit Cell and Crystal Lattice	181
5.2.2	The Structure of Silicate Clays	183
5.2.3	Kaolinite Group (1:1 Layer Clays)	185
5.2.4	Halloysite (1:1 Layer Clays)	187
5.2.5	Smectite Group (2:1 Expanding Layer Clays)	190
5.2.6	Illites (Nonexpanding 2:1 Layer Clays)	193
5.2.7	Vermiculites	194
5.2.8	Chlorites (2:2 Layer Clay)	197
5.2.9	Mixed-Layer Clays	199
5.2.10	Silica Minerals	200
5.2.11	Iron and Aluminum Hydrous Oxide Clays	202
5.2.12	Amorphous Clays, Allophane, and Imogolite	207
5.3	The Identification of Clay Minerals	213
5.3.1	Differential Thermal Analysis (DTA)	213
5.3.2	X-ray Diffraction Analysis	218
5.3.3	Infrared Spectroscopy	229
5.4	Surface Chemistry of Soil Clays	236
5.5	Surface Areas	238
5.6	Origin of Negative Charge in Soil Clays	240
5.6.1	Isomorphous Substitution	241
5.6.2	Dissociation of Exposed Hydroxyl Groups	243
5.7	Positive Charges and Zero Point of Charge	245
5.8	The Use of ΔpH in the Determination of Negative or Positive Charges	246
5.9	Surface Potential	247
5.10	Electric Double Layer	248
5.10.1	Helmholtz Double-Layer Theory	249

5.10.2	Gouy-Chapman Double-Layer Theory	250
5.10.3	Effect of Electrolytes on the Thickness of the Diffuse Double Layer	251
5.10.4	Effect of Valency of Cations on the Thickness of the Diffuse Double Layer	252
5.10.5	Limitations to the Gouy-Chapman Diffuse Double-Layer Theory	253
5.10.6	Stern Double-Layer Theory	253
5.10.7	Triple-Layer Theory	254
5.11	Zeta Potential	255
5.11.1	Effect of Electrolytes on Zeta Potential	255
5.12	The Electric Double Layer and Stability of Clays	257
5.13	The Effect of Flocculation and Dispersion on Plant Growth	258
Chapter 6 ADSORPTION IN SOILS		260
6.1	Types of Adsorption	261
6.2	Adsorption Characteristics	262
6.3	Forces of Adsorption	264
6.3.1	Physical Forces	264
6.3.2	Chemical Forces	265
6.3.3	Hydrogen Bonding	266
6.3.4	Hydrophobic Bonding	266
6.3.5	Electrostatic Bonding	266
6.3.6	Coordination Reaction	267
6.3.7	Ligand Exchange	268
6.4	Adsorption Isotherms	268
6.4.1	Freundlich Equation	269
6.4.2	Langmuir Equation	271
6.4.3	Brunauer, Emmett, and Teller (BET) Equation	273
6.4.4	Gibbs Equation	274
6.5	Adsorption of Water	275
6.5.1	Adsorption of Water by Silicate and Hydrous Oxide Clays	276
6.5.2	Adsorption of Water by Organic Matter	280
6.6	Plant-Soil-Water Energy Relation	281
6.7	Adsorption of Organic Compounds	284

6.7.1 Physico-Chemical Properties of Organic Substances Influencing Adsorption	287
6.7.2 Interlayer Adsorption and Molecular Orientation of Organic Compounds	288
6.7.3 Effect of Molecular Size on Adsorption	290
6.7.4 Nature of Adsorption Isotherms	292
6.8 Interparticle Attraction	292
Chapter 7 CATION EXCHANGE	295
7.1 Adsorption of Cations by Soil Colloids	295
7.2 Cation Exchange Reactions	296
7.3 Cation Exchange Capacity	300
7.4 The Exchanging Powers of Cations	304
7.5 The Ionic Composition of the Exchange Complex	304
7.6 Empirical Equations of Cation Exchange	307
7.6.1 The Freundlich Equation	307
7.6.2 The Langmuir-Vageler Equation	308
7.7 Mass Action Law Equations of Cation Exchange	309
7.7.1 Kerr's Equation	309
7.7.2 Vanselow's Equation	310
7.8 Kinetic Equations of Cation Exchange	311
7.9 Thermodynamic Equations of Cation Exchange	312
7.9.1 Quantity/Intensity (Q/I) Relation	313
7.10 Cation Exchange Equation Based on the Donnan Theory	317
7.10.1 Donnan Equilibrium Law	317
7.10.2 Donnan Equation of Cation Exchange	318
7.11 Cation Exchange Equation of Eriksson	320
7.12 Cation Exchange Equation According to the Diffuse Double-Layer Theory	320
7.13 Schofield's Ratio Law	321
7.14 Fixation of Cations	323
7.15 Base Saturation	324
7.16 Adsorption and Exchange of Cations by Soil Organic Matter	326

Chapter 8 ANION EXCHANGE	327
8.1 Positive Charges	327
8.2 Adsorption of Anions by Soil Colloids	330
8.2.1 Nonspecific Adsorption	331
8.2.2 Specific Adsorption	334
8.3 Phosphate Retention and Fixation	336
8.3.1 Phosphate Retention	336
8.3.2 Phosphate Fixation in Acid Soils	338
8.3.3 Phosphate Fixation in Alkaline Soils	340
8.4 Biological Fixation of Phosphate	342
8.4.1 Immobilization of Phosphates	344
8.4.2 Interaction of Phosphates with Humic Acids and other Organic Acids	346
8.5 Soil Reaction and Availability of Inorganic Phosphates	348
8.6 Prediction of Phosphate Ion Concentration According to Schofield's Ratio Law	352
8.7 The Phosphate Potential	353
8.7.1 Chemical Potential of Phosphate	354
8.7.2 Electrochemical Potential of Phosphate	354
8.7.3 Schofield's Phosphate Potential	356
Chapter 9 SOIL REACTION	357
9.1 Definition and Importance	357
9.2 Acid-Base Chemistry	359
9.2.1 Arrhenius Concept	359
9.2.2 Brønsted-Lowry Concept	360
9.2.3 Lewis Concept	361
9.2.4 Application in Soils	362
9.3 Formulation of Soil Acidity and Alkalinity	363
9.3.1 Soil pH	363
9.3.2 Acidity Constant	364
9.3.3 Acid Strength and Ion Pairs	365
9.4 Concepts of Soil Acidity	366
9.4.1 Soil pH Range	366
9.4.2 Active versus Potential Acidity	368
9.4.3 Nonselective and Preferential Adsorption of Hydrogen Ions by Soils	370

9.5	The Role of Aluminum in Soil Acidity	371
9.6	The Role of Fertilizers, Sulfur, Pyrite, N-fixation, and Acid Rain in Soil Acidity	375
9.6.1	Ammonium Fertilizers	375
9.6.2	Phosphate Fertilizers	377
9.6.3	Elemental S	377
9.6.4	Pyrite (FeS_2)	378
9.6.5	Biological Nitrogen Fixation	379
9.6.6	Acid Precipitation	379
9.7	Buffering Capacity of Soils	382
9.8	Electrometric Measurement of Soil pH	383
9.8.1	Measurement of pH in a Water Extract	384
9.8.2	Measurement of pH in a Soil Suspension	385
9.8.3	Measurement of pH in a KCl Solution	385
9.8.4	Measurement of pH in a CaCl_2 Solution	385
9.9	Suspension Effect in Soil pH Measurement	386
9.10	Lime Potential	386
9.11	The Need for Acidic Soil Reactions	387
9.12	Soil Reactions in Saline and Sodic Soils	388
9.12.1	Salinization	388
9.12.2	Sodication and Alkalinization	388
9.13	Chemical Characterization of Saline and Sodic Soils	389
9.14	Effect of Salinization and Sodication on Plant Growth	390
9.15	Irrigation of Saline and Sodic Soils	392
9.15.1	Salinity Hazard	392
9.15.2	Hazard of Sodication	393
9.16	Salt Balance and Leaching Ratio	393
9.17	Irrigation-Induced Salinization and Sodication	394
Chapter 10	SOIL CHEMISTRY AND SOIL FORMATION	395
10.1	Weathering Processes	395
10.2	Stability and Weathering of Soil Minerals	397
10.2.1	Crystal Chemistry and Mineral Properties	397
10.2.2	Coordination Theory and Pauling's Rules	397
10.2.3	Stability of Minerals and Bond Strength	402
10.3	Weathering of Feldspars and the Silica Potential	405
10.4	Weathering of Kaolinite and the Gibbsite Potential	406

10.5	Stability and Phase Relationships of Soil Minerals	407
10.6	Biological and Biochemical Weathering	409
10.6.1	Biological Weathering	409
10.6.2	Biochemical Weathering	411
10.7	Soil Formation Processes	414
10.7.1	Desilicification	414
10.7.2	Translocation of Clays	417
10.7.3	Translocation of Aluminum and Iron	418
10.8	Oxidation and Reduction Reaction in Soils	424
10.8.1	Redox Potentials	425
10.8.2	Application of Redox Potentials in Soils	426
10.8.3	Stability of Iron Oxides and Hydroxides	429
10.8.4	Activity of Reduction Products	430
Chapter 11 CHEMISTRY OF SOIL–ORGANIC MATTER INTERACTION		431
11.1	Complex Formation and Chelation	431
11.1.1	Soil Organic Compounds	434
11.1.2	Effectiveness of Organic Acids in Chelation	435
11.2	Metal–Organic Complex Reaction	436
11.2.1	Stability Constants	436
11.3	Clay–Organic Compound Complexes	438
11.3.1	Complex Formation with Organic Anions	438
11.3.2	Complex Formation with Organic Cations	441
11.3.3	Complex Formation with Amphoteric Organic Compounds	443
11.3.4	Complex Formation with Nonionic Organic Compounds	444
11.4	Complex Formation and Mobility of Soil Constituents	446
11.4.1	Metal Mobility	446
11.5	Stability Diagram of Metal Chelates	449
11.6	Complex Formation and Clay Mobility	450
11.7	Complex Formation and Soil Fertility	450
11.7.1	Complex Formation and Soil Physical Characteristics	450
11.7.2	Complex Formation and Soil Chemical Characteristics	452

11.7.3 Complex Formation and Soil Biological Characteristics	453
Appendix A Fundamental Constants	457
Appendix B Greek Alphabet	459
Appendix C Periodic Classification of Elements	461
Appendix D X-ray Diffraction 2θ d-Spacing Conversion Table	463
Appendix E System International (SI) Units	465
References and Additional Readings	469
Subject Index	495