

CONTENTS

Symbols	xvii
1 Introduction	1
1.1 Dynamic Equilibria in Soils,	2
1.2 Intensity and Capacity Factors,	4
1.3 Elemental Composition of Soils,	6
References,	8
Problems,	9
2 Methods of Handling Chemical Equilibria	10
2.1 Equilibrium Constants,	11
2.2 Concentration Versus Activity Constants,	12
2.3 Ionic Strength,	12
2.4 Activity Coefficients,	13
2.5 Debye–Hückel Equations,	13
2.6 Activity Coefficients from Electrical Conductivities,	16
2.7 Transforming Equilibrium Constants,	18
2.8 Equilibrium Constants from Thermodynamic Data,	21
2.9 Redox Relationships,	23
2.10 $pe + pH$,	23
2.11 E° versus $\log K^\circ$,	26
2.12 pe versus Eh ,	27

2.13 Redox Measurements in Natural Environments	28
References,	30
Problems,	31
3 Aluminum	34
3.1 Solubility of Aluminum Oxides and Hydroxides,	35
3.2 Solubility of Aluminum Sulfates,	38
3.3 Hydrolysis of Al^{3+}	39
3.4 Fluoride Complexes of Aluminum,	41
3.5 Other Aluminum Complexes,	43
3.6 Estimating Al^{3+} Activity,	45
3.7 Redox Relationships of Aluminum,	46
3.9 Exchangeable Aluminum,	47
References,	48
Problems,	49
4 Silica	50
4.1 Forms of Silica in Soils,	51
4.2 Silicate Species in Solution,	53
References,	54
Problems,	55
5 Aluminosilicate Minerals	56
5.1 Unsubstituted Aluminosilicates,	57
5.2 Sodium Aluminosilicates,	62
5.3 Potassium Aluminosilicates,	65
5.4 Calcium Aluminosilicates,	66
5.5 Magnesium Aluminosilicates,	68
5.6 Summary Stability Diagrams for Aluminosilicates,	71
5.7 Controls of Al^{3+} Activity in Soils,	73
5.8 General Discussion of Aluminosilicates,	75
References,	76
Problems,	77
6 Carbonate Equilibria	78
6.1 The $\text{CO}_2\text{—H}_2\text{O}$ System,	79
6.2 The $\text{CO}_2\text{—Soil}$ System,	84
References,	84
Problems,	84

7 Calcium	86
7.1 Calcium Silicates and Aluminosilicates,	87
7.2 Other Calcium Minerals,	93
7.3 Complexes of Calcium in Solution,	95
7.4 Redox Relationships of Calcium,	98
7.5 The $\text{CaCO}_3\text{—CO}_2\text{—H}_2\text{O}$ System,	98
7.6 The Phase Rule,	101
7.7 The $\text{CO}_2\text{—H}_2\text{O}$ System,	102
7.8 The $\text{CaO—CO}_2\text{—H}_2\text{O}$ System,	102
7.9 The $\text{CaO—CO}_2\text{—H}_2\text{O—H}_2\text{SO}_4$ System,	102
Problems,	103
8 Magnesium	105
8.1 Solubility of Magnesium Silicates,	106
8.2 Magnesium Aluminosilicates,	112
8.3 Oxides, Hydroxides, Carbonates, and Sulfates,	113
8.4 Magnesium Complexes in Solution,	114
8.5 Effect of Redox on Magnesium,	116
Problems,	116
9 Sodium and Potassium	118
9.1 Solubility of Sodium Minerals,	119
9.2 Solubility of Potassium Minerals,	123
9.3 Complexes of Sodium and Potassium,	125
9.4 Redox Relationships,	126
Problems,	127
10 Iron	128
10.1 Solubility of Fe(III) Oxides in Soils,	129
10.2 Other Fe(III) Minerals,	133
10.3 Hydrolysis of Fe(III),	134
10.4 Fe(III) Complexes in Soils,	136
10.5 Effect of Redox on Fe(II) Solubility,	139
10.6 Effect of Redox on the Stability of Iron Minerals,	141
10.7 Hydrolysis and Complexes of Fe(II),	146
References,	148
Problems,	149

11 Manganese	150
11.1 Effect of Redox and pH on Manganese Solubility,	151
11.2 Solution Species of Manganese,	157
References,	160
Problems,	160
12 Phosphates	162
12.1 Orthophosphoric Acid,	163
12.2 Aluminum Phosphates,	169
12.3 Iron Phosphates,	173
12.4 Effect of Redox on the Stability of Iron and Aluminum Phosphates,	177
12.5 Solubility of Calcium Phosphates,	180
12.6 Effect of Redox on the Stability of Calcium Phosphates,	185
12.7 Solubility of Magnesium Phosphates,	186
12.8 Manganese Phosphates,	187
12.9 Other Orthophosphates,	189
12.10 Reduced Forms of Phosphorus,	189
12.11 Stability of Polyphosphates in Soils,	190
12.12 Orthophosphate Complexes in Solution,	195
12.13 Reactions of Phosphate Fertilizer with Soils,	197
References,	204
Problems,	205
13 Zinc	210
13.1 Oxidation State of Zinc	211
13.2 Solubility of Zinc Minerals in Soils,	211
13.3 Zinc Species in Solution,	216
References,	219
Problems,	219
14 Copper	221
14.1 Solubility of Cu(II) Minerals in Soils,	222
14.2 Hydrolysis and Solution Complexes of Cu(II),	228
14.3 Effect of Redox on Copper,	231
14.4 Complexes of Cu(I),	234
References,	235
Problems.	236

15	Chelate Equilibria	238
15.1	Metal Chelates and Their Stability Constants,	239
15.2	Development of Stability-pH Diagrams for Chelates,	244
15.3	Effect of Redox on Metal Chelate Stability,	252
15.4	Chelation in Hydroponics,	256
15.5	Use of Chelates to Estimate Metal Ion Activities in Soils,	259
15.6	Use of Chelating Agents as Soil Tests,	261
15.7	Natural Chelates in Soils,	263
	References,	264
	Problems,	265
16	Nitrogen	267
16.1	Oxidation States of Nitrogen,	268
16.2	Equilibrium Between Atmospheric N_2 and O_2 ,	269
16.3	Effect of Redox on Nitrogen Stability,	272
	References,	279
	Problems,	280
17	Sulfur	281
17.1	Effect of Redox on Sulfur Speciation,	282
17.2	Dissociation of Sulfur Acids,	287
17.3	Formation of Elemental Sulfur in Soils,	288
17.4	Formation of Metal Sulfides,	290
17.5	Effect of Sulfides on Metal Solubilities,	295
	References,	297
	Problems,	297
18	Silver	299
18.1	Effect of Redox on the Stability of Silver Minerals,	300
18.2	Solubility of Silver Halides and Sulfides,	304
18.3	Stability of Other Silver Minerals,	306
18.4	Stability of Silver Halide Complexes,	308
18.5	Hydrolysis Species and Other Silver Complexes,	310
	References,	313
	Problems,	313

19 Cadmium	315
19.1 Oxidation States of Cadmium in Soils,	316
19.2 Cadmium Minerals in Soils,	316
19.3 Hydrolysis Species of Cd(II),	321
19.4 Halide and Ammonia Complexes of Cadmium,	322
19.5 Other Cadmium Complexes,	323
19.6 Need for Further Studies,	326
References,	326
Problems,	327
20 Lead	328
20.1 Solubility of Lead Minerals,	329
20.2 Hydrolysis Species of Lead,	338
20.3 Halide Complexes of Lead,	339
20.4 Other Complexes of Lead,	341
References,	341
Problems,	342
21 Mercury	343
21.1 Stability of Hg(II) Minerals and Complexes,	344
21.2 Stability of Hg(I) Minerals and Complexes,	353
21.3 Stability of Elemental Mercury,	355
21.4 Solubility of Mercury Sulfides in Soils,	358
21.5 Summary Redox Diagram for Mercury,	359
21.6 Organic Mercury Reactions,	362
References,	362
Problems,	362
22 Molybdenum	364
22.1 Molybdenum Species in Solution,	365
22.2 Stability of Molybdenum Minerals in Soils,	367
22.3 The Effect of Redox on Molybdenum Solubility,	369
References,	372
Problems,	372
23 Organic Transformations	373
23.1 Oxidation States of Carbon,	374
23.2 Products of Glucose Metabolism,	375

CONTENTS	xv
23.3 Reactions of Acetic Acid,	380
23.4 Oxidation to $\text{CO}_2(\text{g})$ and Reduction to $\text{CH}_4(\text{g})$,	381
23.5 Stability of Graphite,	382
References,	383
Problems,	383
Appendix Standard Free Energies of Formation	385
Index	423