Contents

1 Introduction 1

2 Aqueous Chemistry 3
2.1 Basic Principles 3
2.1.1 Definitions 3
2.1.2 The First and Second Laws of Thermodynamics 4
2.1.3 Activities, Chemical Potentials and Equilibrium Constants 7
2.2 Pitzer Approach 10
2.2.1 The Osmotic Coefficient and Activity Coefficients 10
2.2.2 Temperature and Pressure Dependencies 15

3 The FREZCHEM Model 19
3.1 Historical Development 19
3.2 Basic Structure 21
3.2.1 Chemical Equilibrium 21
3.2.2 Mass Balances 22
3.2.3 Reaction Pathways 22
3.3 Chemistries and Their Temperature and Pressure Dependence 24
3.3.1 Water Ice/Liquid Water/Water Vapor Equilibria 24
3.3.2 Salt Equilibria 29
3.3.3 Gas/Solution Phase Equilibria 37
3.3.4 Gas Hydrate Equilibria 42
3.4 Mathematical Algorithms 49
3.4.1 The Sequential Approach 49
3.4.2 Gibbs Energy Minimization 50
3.4.3 Other Mathematical Techniques 52
3.5 Validation 56
3.6 Limitations 67
3.6.1 Pitzer-Equation Parameterization Limitations 68
3.6.2 Modeling Limitations 75

4 Limits for Life 79
4.1 Temperature 84
4.2 Salinity 86

4.3 Acidity . . . 88
4.4 Desiccation . . . 89
4.5 Radiation . . . 89
4.6 Pressure . . . 90
4.7 Time . . . 97

5 Biogeochemical Applications to Solar System Bodies . . . 101
5.1 Earth . . . 102
5.1.1 Seawater Freezing . . . 102
5.1.2 Aqueous Saline Environments . . . 110
5.1.3 Snowball Earth-Hothouse Earth . . . 113
5.1.4 Why Are Clouds not Green? . . . 120
5.1.5 Other Earth Applications . . . 123
5.2 Mars . . . 125
5.2.1 Surficial Aqueous Geochemical Evolution . . . 125
5.2.2 Early Mars Oceans . . . 135
5.2.3 A Cold, Intermittently Wet Mars . . . 135
5.2.4 Hydrate Deposits and Thermal Stratification . . . 139
5.3 Europa . . . 141
5.3.1 Ocean Compositions . . . 142
5.3.2 Ice Compositions . . . 148
5.4 Application Limitations . . . 150

6 The Search for and Future of Life in the Universe . . . 155
6.1 A Search Strategy for Life in the Universe . . . 155
6.2 Entropic Death? . . . 158
6.3 Solar System Life . . . 162
6.4 To the Stars or Bust? . . . 169

A FREZCHEM Program Guide . . . 175
A.1 Model Input Limitations . . . 175
A.2 Model Inputs . . . 176
A.3 Model Outputs . . . 177
A.3.1 Seawater Freezing . . . 177
A.3.2 Strong Acid . . . 178
A.3.3 Gas Hydrates . . . 178
A.3.4 Pressure Application . . . 179

B Parameter Tables . . . 193

References . . . 223

Index . . . 247