Contents

Preface — V

1 Introduction — 1

2 Structure and properties of water — 7
  2.1 Structure of water — 7
  2.2 Properties of water — 10
    2.2.1 Density — 10
    2.2.2 Phase diagram – melting point and boiling point — 13
    2.2.3 Energetic quantities — 15
    2.2.4 Viscosity — 17
    2.2.5 Surface tension — 18
  2.3 Water as a solvent — 23
  2.4 Problems — 26

3 Concentrations and activities — 27
  3.1 Introduction — 27
  3.2 Concentrations — 27
    3.3.1 Conversion of concentration units — 31
    3.3.2 Conversion of mass concentration — 31
    3.3.3 Conversion of molar concentration — 32
    3.3.4 Conversion of molality — 33
    3.3.5 Conversion of mole fraction — 33
    3.3.6 Conversion of mass fraction — 34
  3.4 Element-related concentrations — 35
  3.5 Gas phase concentrations — 36
  3.6 Electroneutrality condition and ion balance — 37
  3.7 Hardness as a specific concentration measure — 38
  3.8 Activities and activity coefficients — 42
  3.9 Problems — 46

4 Colligative properties — 47
  4.1 Introduction — 47
  4.2 Vapor pressure lowering — 47
  4.3 Boiling point elevation and freezing point depression — 49
  4.4 Osmotic pressure — 51
  4.5 Colligative properties of real solutions — 53
  4.6 Problems — 53
<table>
<thead>
<tr>
<th>5</th>
<th>The chemical equilibrium: Some general aspects</th>
<th>55</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>55</td>
</tr>
<tr>
<td>5.2</td>
<td>Law of mass action and equilibrium constants</td>
<td>55</td>
</tr>
<tr>
<td>5.3</td>
<td>Conventions on the use of concentration measures in the law of mass action</td>
<td>57</td>
</tr>
<tr>
<td>5.4</td>
<td>Relationships between Gibbs energy of reaction, equilibrium constants, and reaction quotients</td>
<td>58</td>
</tr>
<tr>
<td>5.5</td>
<td>Estimation of equilibrium constants</td>
<td>59</td>
</tr>
<tr>
<td>5.6</td>
<td>Equilibrium constants of reverse and overall reactions</td>
<td>60</td>
</tr>
<tr>
<td>5.7</td>
<td>Problems</td>
<td>61</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>6</th>
<th>Gas–water partitioning</th>
<th>63</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1</td>
<td>Introduction</td>
<td>63</td>
</tr>
<tr>
<td>6.2</td>
<td>Henry’s law</td>
<td>63</td>
</tr>
<tr>
<td>6.3</td>
<td>Alternative formulations of Henry’s law</td>
<td>65</td>
</tr>
<tr>
<td>6.4</td>
<td>Estimation of Henry’s law constants for volatile substances</td>
<td>67</td>
</tr>
<tr>
<td>6.5</td>
<td>Open and closed systems</td>
<td>67</td>
</tr>
<tr>
<td>6.6</td>
<td>Solubilities of atmospheric gases in water</td>
<td>68</td>
</tr>
<tr>
<td>6.7</td>
<td>Calculation of equilibrium concentrations in closed systems</td>
<td>70</td>
</tr>
<tr>
<td>6.8</td>
<td>Problems</td>
<td>72</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>7</th>
<th>Acid/base equilibria</th>
<th>73</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1</td>
<td>Introduction</td>
<td>73</td>
</tr>
<tr>
<td>7.2</td>
<td>Brønsted’s acid/base theory</td>
<td>73</td>
</tr>
<tr>
<td>7.3</td>
<td>Water as an acid/base system</td>
<td>76</td>
</tr>
<tr>
<td>7.4</td>
<td>Protolysis of acids and bases</td>
<td>77</td>
</tr>
<tr>
<td>7.5</td>
<td>pH of aqueous solutions of acids, bases, and salts</td>
<td>81</td>
</tr>
<tr>
<td>7.5.1</td>
<td>pH of acid solutions</td>
<td>81</td>
</tr>
<tr>
<td>7.5.2</td>
<td>pH of base solutions</td>
<td>84</td>
</tr>
<tr>
<td>7.5.3</td>
<td>pH of salt solutions</td>
<td>84</td>
</tr>
<tr>
<td>7.5.4</td>
<td>Buffer systems</td>
<td>89</td>
</tr>
<tr>
<td>7.6</td>
<td>Degree of protolysis and acid/base speciation</td>
<td>91</td>
</tr>
<tr>
<td>7.6.1</td>
<td>Monoprotic acids</td>
<td>91</td>
</tr>
<tr>
<td>7.6.2</td>
<td>Polyprotic acids</td>
<td>93</td>
</tr>
<tr>
<td>7.7</td>
<td>Carbonic acid</td>
<td>95</td>
</tr>
<tr>
<td>7.7.1</td>
<td>Relevance</td>
<td>95</td>
</tr>
<tr>
<td>7.7.2</td>
<td>Speciation of carbonic acid</td>
<td>96</td>
</tr>
<tr>
<td>7.7.3</td>
<td>Determination of the carbonic acid species by acid/base titrations</td>
<td>96</td>
</tr>
<tr>
<td>7.7.4</td>
<td>General definitions of the alkalinitities and acidities on the basis of proton balances</td>
<td>104</td>
</tr>
<tr>
<td>7.7.5</td>
<td>The conservative character of alkalinity</td>
<td>105</td>
</tr>
</tbody>
</table>
7.7.6 Determination of dissolved inorganic carbon (DIC) — 106
7.7.7 pH of pristine rain water — 107
7.8 Problems — 108

8 Precipitation/dissolution equilibria — 110
8.1 Introduction — 110
8.2 The solubility product — 110
8.3 Solubility product and solubility — 111
8.3.1 Relationship between solubility product and solubility — 111
8.3.2 Influence of the ionic strength on the solubility — 113
8.3.3 Influence of side reactions on the solubility — 114
8.4 Assessment of the saturation state of a solution — 116
8.5 Problems — 117

9 Calco–carbonic equilibrium — 119
9.1 Introduction — 119
9.2 Basic equations — 120
9.3 Graphical representation of the calco–carbonic equilibrium:
  Tillmans curve — 122
9.4 Assessment of the calcite saturation state — 126
9.5 Outlook: Assessment of the calcite saturation state under consideration of complex formation — 130
9.6 Special case: Fixed CO₂ partial pressure — 131
9.7 Problems — 132

10 Redox equilibria — 134
10.1 Introduction — 134
10.2 Estimation of oxidation numbers (oxidation states) — 134
10.3 Redox equilibria: Definitions and basic concepts — 137
10.4 Half-reactions — 138
10.4.1 Law of mass action and redox intensity — 138
10.4.2 Redox intensity versus redox potential — 143
10.4.3 Special case: Redox reactions with dissolved gases — 145
10.4.4 Crossover points between predominance areas of reduced and oxidized species — 146
10.4.5 Speciation as a function of pe — 148
10.4.6 Water as a redox system — 149
10.5 Construction of pe–pH diagrams — 152
10.5.1 Introduction — 152
10.5.2 Boundary lines for pure acid/base systems — 153
10.5.3 Boundary lines for complex acid/base systems — 153
10.5.4 Boundary lines for pure redox systems with oxidant and reductant in dissolved form — 154
10.5.5 Boundary lines for pH-dependent redox systems with oxidant and reductant in dissolved form — 155
10.5.6 Boundary lines for pH-dependent redox systems where only one partner occurs in dissolved form — 155
10.5.7 Example: The pe–pH diagram of iron — 156
10.5.8 Example: The pe–pH diagram of sulfur — 162
10.6 Complete redox reactions — 164
10.6.1 Basic relationships — 164
10.6.2 Redox reactions within the global carbon cycle — 170
10.6.3 Further oxidation reactions mediated by microorganisms — 172
10.7 Problems — 173

11 Complex formation — 175
11.1 Introduction — 175
11.2 Ligands in aquatic systems — 177
11.3 Equilibrium relationships and constants — 179
11.4 Strength of complexation: Monodentate versus polydentate ligands — 180
11.5 Complex formation and solubility — 182
11.6 Hydrolysis of hydrated metal ions — 183
11.7 Speciation of metal ions — 185
11.7.1 Introduction — 185
11.7.2 Speciation of dissolved metal ions at constant total metal concentration — 185
11.7.3 Speciation in presence of a solid that determines the liquid-phase concentrations — 190
11.8 Problems — 193

12 Sorption — 196
12.1 Introduction — 196
12.2 Geosorbents — 197
12.3 Sorption isotherms — 198
12.3.1 General considerations — 198
12.3.2 Isotherm equations — 199
12.3.3 Speciation — 203
12.4 Sorption onto charged surfaces — 204
12.4.1 Introduction — 204
12.4.2 Mathematical description of the surface protonation/deprotonation — 205
12.4.3 Modeling of ion sorption — 211