



Chemistry of the Environment

Second Edition

Thomas G. Spiro • William M. Stigliani

CONTENTS

<i>Preface</i>	<i>xi</i>
<i>Introduction</i>	<i>xiii</i>
Part I Energy	1
Chapter 1 Energy Flows and Supplies	3
1.1 Prologue on Energy and Sustainability	3
1.2 Natural Energy Flows	5
1.3 Human Energy Consumption	8
1.4 Human Energy Sources	14
Chapter 2 Fossil Fuels	19
2.1 Carbon Cycle	19
2.2 Origins of Fossil Fuels	21
2.3 Fuel Energy	25
2.4 Petroleum	29
2.4a Composition and Refining	29
2.4b Advantages	31
2.4c Disadvantages	31
2.5 Gas	37
2.5a Advantages	38
2.5b Disadvantages	38
2.6 Coal	38
2.6a Advantages	39
2.6b Disadvantages	39
2.7 Decarbonization	42
2.7a Separation	42
2.7b Storage	42

Chapter 3 Nuclear Energy	44
3.1 Nuclei, Isotopes, and Radioactivity	44
3.2 Naturally Occurring Radioisotopes	47
3.3 Decay Chains: The Radon Problem	49
3.4 Radioactivity: Biological Effects of Ionizing Radiation	50
3.4a Alpha Rays	52
3.4b Beta and Gamma Rays, and Neutrons	52
3.5 Radiation Exposure	53
3.6 Fission	54
3.6a Pressurized Light-Water Reactor	56
3.6b Isotope Separation	57
3.6c Breeder Reactor	58
3.6d Reprocessing	60
3.7 Hazards of Nuclear Power	60
3.7a Reactor Safety: Three Mile Island and Chernobyl	60
3.7b Weapons Proliferation	63
3.7c Nuclear Waste Disposal	65
3.8 Is Nuclear Power Part of the Future?	67
3.9 Fusion	68
3.9a Fusion Reactions	68
3.9b Fusion Power Reactors	70
3.9c Is Fusion the Energy Source of the Future?	73
Chapter 4 Renewable Energy	74
4.1 Solar Heating	77
4.2 Solar Thermal Electricity	79
4.3 Photovoltaic Electricity	80
4.3a Principles of the PV Cell	81
4.3b Photosynthesis and Photoelectrochemistry	85
4.4 Biomass	87
4.4a Ethanol from Biomass	88
4.4b Methane from Biomass	90
4.5 Hydroelectricity	91
4.6 Wind Power	92
4.7 Ocean Energy	95
4.8 Geothermal Energy	96
Chapter 5 Energy Utilization	98
5.1 Heat Engine Efficiencies	100
5.2 Fuel Cells	103
5.3 Space Heating, Cogeneration	109
5.4 Electricity Storage: The Hydrogen Economy	109
5.5 The Materials Connection	112
5.5a Materials Properties: Paper versus Plastics	113
5.5b Recycling	113
5.5c Dematerialization	117

5.6 Systems Efficiency	119
5.6a Transportation	120
5.6b Industrial Ecology	125
5.6c Green Chemistry	128
5.7 Energy and Society	129
<i>Summary</i>	133
<i>Problem Set</i>	134
<i>Suggested Readings</i>	139
Part II Atmosphere	143
Chapter 6 Climate	145
6.1 Radiation Balance	145
6.2 Albedo: Particles and Clouds	150
6.2a Clouds	150
6.2b Aerosol Particles	153
6.2c Sulfur Cycle	156
6.3 Greenhouse Effect	160
6.3a Infrared Absorption and Molecular Vibrations	160
6.3b Greenhouse Gas Trends	165
6.4 Climate Modeling	172
6.5 International Agreements on Greenhouse Gases	178
Chapter 7 Oxygen Chemistry	180
7.1 Nitrogen Oxides: Free Energy	180
7.1a Free Energy and the Equilibrium Constant	181
7.1b Free Energy and Temperature	183
7.2 Nitrogen Oxides: Kinetics	185
7.3 Free Radical Chain Reactions	186
7.3a Oxygen Radicals	187
7.3b Organic Oxygen Radicals	190
7.3c Hydroxyl Radical	191
7.3d Transition Metal Activation of O ₂	192
Chapter 8 Stratospheric Ozone	194
8.1 Atmospheric Structure	196
8.2 Ultraviolet Protection by Ozone	200
8.3 Ozone Chemistry	203
8.3a Formation and Destruction	203
8.3b Calculating the Ozone Steady State	204
8.4 Catalytic Destruction of Ozone	207
8.4a Hydroxyl Radical	207
8.4b Chlorine and Bromine	207
8.4c Nitric Oxide	208
8.5 Polar Ozone Destruction	209

8.6 Ozone Projections	213
8.7 CFC Substitutes	213
Chapter 9 Air Pollution	216
9.1 Pollutants and Their Effects	216
9.1a Carbon Monoxide	216
9.1b Sulfur Dioxide	218
9.1c Toxic Organics	220
9.1d Particles	222
9.1e NO _x and Volatile Organics	223
9.1f Ozone and Other Oxidants	226
9.2 Photochemical Smog	227
9.3 Emission Control	232
9.3a Sulfur Dioxide	232
9.3b Nitrogen Oxides, Carbon Monoxide, and Hydrocarbons	233
9.4 Reformulated Gasoline: Oxygenates	237
9.4a Knocking and Octane	237
9.4b Diesels and Cetane	238
9.4c Lead in Gasoline	238
9.4d Reformulated Gasoline	239
<i>Summary</i>	241
<i>Problem Set</i>	242
<i>Suggested Readings</i>	247
Part III Hydrosphere/Lithosphere	251
Chapter 10 Water Resources	253
10.1 Global Perspective	253
10.2 Irrigation	256
10.3 Groundwater	259
10.4 U.S. Water Resources	260
10.5 The Oceans	262
10.6 Water as Solvent and as a Biological Medium	265
Chapter 11 From Clouds to Runoff: Water as Solvent	266
11.1 Unique Properties of Water	266
11.1a Hydrogen Bonding	266
11.1b Clathrates and Water Miscibility	269
11.2 Acids, Bases, and Salts	272
11.2a Ions, Autoionization, and pH	272
11.2b Weak Acids and Bases	274
11.3 Conjugate Acids and Bases; Buffers	276

11.4 Water in the Atmosphere: Acid Rain	277
Chapter 12 Water and the Lithosphere	282
12.1 Earth as Acid-Base Reactor	282
12.2 Organic and Inorganic Carbon Cycles	284
12.2a The Carbonate Control	286
12.2b Carbonate Sequestration	288
12.3 Weathering and Solubilization Mechanisms	289
12.3a Ionic Solids and the Solubility Product	289
12.3b Solubility and Basicity	290
12.3c Ion Exchange; Clays and Humic Substances	292
12.4 Effects of Acidification	297
12.4a Soil Neutralization	297
12.4b Hardness and Detergents	298
12.4c Acid Deposition and Watershed Buffering	300
12.4d Ecosystem Effects of Acid Rain	303
12.4e Acid Mine Drainage	305
12.4f Global Acidification	305
Chapter 13 Oxygen and Life	307
13.1 Redox Reactions and Energy	307
13.1a Biological Oxygen Demand	309
13.1b Natural Sequence of Biological Reductions	311
13.1c Biological Oxidations	315
13.2 Aerobic Earth	316
13.3 Water as Ecological Medium	319
13.3a The Euphotic Zone and the Biological Pump	319
13.3b Eutrophication in Freshwater Lakes	319
13.3c Nitrogen and Phosphorus: The Limiting Nutrients	323
13.3d Anoxia and its Effects on Coastal Marine Waters	325
13.3e Wetlands as Chemical Sinks	328
13.3f Redox Effects on Metals Pollution	330
13.3g Fertilizing the Ocean with Iron	331
Chapter 14 Water Pollution and Water Treatment	333
14.1 Water Use and Water Quality: Point and Nonpoint Sources of Pollution	333
14.2 Regulation of Water Quality	337
14.3 Water and Sewage Treatment	339
14.4 Health Hazards	341
14.4a Pathogens and Disinfection	341
14.4b Organic and Inorganic Contaminants	344
Summary	346
Problem Set	347
Suggested Readings	351

Part IV Biosphere	355
Chapter 15 Nitrogen and Food Production	357
15.1 Nitrogen Cycle	357
15.2 Agriculture	361
15.2a Fertilizer and the Green Revolution	361
15.2b Environmental Degradation	367
15.3 Nutrition	368
15.3a Energy and Calories	369
15.3b Protein	370
15.3c Minerals and Vitamins	374
15.3d Antioxidants	375
Chapter 16 Pest Control	382
16.1 Insecticides	382
16.1a Persistent Insecticides: Organochlorines	382
16.1b Ecosystem Effects; Bioaccumulation	386
16.1c Nonpersistent Insecticides: Organophosphates and Carbamates	390
16.1d Natural Insecticides	394
16.1e Integrated Pest Management	394
16.2 Herbicides	397
16.3 Genetically Modified Organisms (GMOs)	401
16.3a GM Plants: Actualities and Potential	401
16.3b Resistance to GM Foods	402
Chapter 17 Toxic Chemicals	407
17.1 Acute and Chronic Toxicity	407
17.2 Cancer	410
17.2a Mechanisms	411
17.2b Cancer Incidence and Testing	415
17.3 Hormonal Effects	418
17.4 Persistent Organic Pollutants: Dioxins and PCBs	423
17.4a Dioxins and Furans	423
17.4b Polychlorinated Biphenyls	429
17.4c Global Transport	432
17.5 Toxic Metals	432
<i>Summary</i>	452
<i>Problem Set</i>	454
<i>Suggested Readings</i>	458
Appendix Organic Structures	461
Hydrocarbons; Alkanes	461
Branched Chains; Isomers	462
Rings	463

Contents**ix**

Unsaturated Hydrocarbons	464
Molecular Shape	465
Carbon Framework Representations	465
Aromatic Compounds	466
Hetero-Atoms; Functional Groups	467

471