

Contents

Preface to the first edition — IX

Author's preface to the fourth edition — XI

Author's preface to the third edition — XIII

Author's preface to the second edition — XIX

Prologue — XXI

List of principal symbols — XXXI

1 Introduction — 1

1.1 The human problem: A changing earth system — 2

1.2 The biosphere and evolution — 6

1.3 The climate system and the sciences to study it — 9

2 Physical fundamentals of the climate system — 18

2.1 What is climate? — 18

2.1.1 Climate definition: Historical view — 18

2.1.2 Climate definition: Current view — 30

2.1.3 The climate system — 35

2.2 The atmosphere — 38

2.2.1 Scaling and structure of the atmosphere — 38

2.2.2 Atmosphere as multiphase and multicomponent system — 43

2.2.3 Polluted and clean air — 46

2.2.4 Meteorological elements — 48

2.2.4.1 Air pressure — 48

2.2.4.2 Air temperature — 50

2.3 Water — 51

2.3.1 Clouds — 52

2.3.2 Fog, mist, and haze — 58

2.3.3 Precipitation — 60

2.3.4 Dew, frost, rime, and interception — 62

2.3.5 Air humidity and water vapor — 65

2.3.6 The hydrological cycle and the climate system — 67

2.3.7 Water properties in relation to the climate system — 71

2.3.8 Properties of solutions and droplets — 73

2.3.8.1 Surface tension and surface-active substances — 73

2.3.8.2 Vapor pressure lowering: Raoult's law — 75

2.3.8.3	Freezing point depression — 77
2.3.8.4	Diffusion in solution — 78
2.4	Gases — 79
2.4.1	The gas laws — 79
2.4.2	Mean free path and number of collisions between molecules — 84
2.4.3	Viscosity and diffusion — 87
2.5	Radiation — 90
2.5.1	Solar radiation — 90
2.5.1.1	The Sun and its radiative output — 90
2.5.1.2	Solar radiation transfer through the atmosphere — 91
2.5.2	Absorption and emission of light — 100
2.5.2.1	Absorption (Lambert–Beer law) — 100
2.5.2.2	Emission (Planck’s law and Stefan–Boltzmann law) — 101
2.5.3	Terrestrial radiation and radiation budget — 104
2.6	Dynamics — 106
2.6.1	Effective atmospheric forces — 107
2.6.2	Atmospheric flow: Laminar and turbulent — 109
2.6.3	Fluid characteristics: Wind speed and direction — 112
2.7	Thermodynamics — 114
2.7.1	First law of thermodynamic and its applications — 116
2.7.1.1	Internal energy — 116
2.7.1.2	Molar heat capacity — 117
2.7.1.3	Thermochemistry: Heat of chemical reaction — 118
2.7.2	Second law of thermodynamic and its applications — 120
2.7.2.1	Entropy and reversibility — 121
2.7.2.2	Thermodynamic potential: Gibbs–Helmholtz equation — 122
2.7.2.3	Chemical potential — 124
2.7.2.4	Activity — 126
2.8	Equilibrium — 128
2.8.1	Steady state — 128
2.8.2	Chemical equilibrium: The mass action law — 131
2.8.3	Phase equilibrium — 133
2.8.3.1	Gas–liquid equilibrium: Evaporation and condensation — 134
2.8.3.2	Gas–liquid equilibrium: Special case of droplets (Kelvin equation) — 135
2.8.3.3	Absorption of gases in solution: Henry’s law — 136
2.8.3.4	Solubility equilibrium: Solid–aqueous equilibrium — 140
2.8.3.5	Adsorption and desorption — 141
2.9	Multiphase processes — 143
2.9.1	Aerosols, clouds, and precipitation: The climate multiphase system — 145
2.9.2	Gas-to-particle formation: Homogeneous formation of CCN — 149
2.9.2.1	Classical nucleation theory — 149

2.9.2.2	Formation of secondary organic aerosols —	154
2.9.3	Atmospheric aerosols and properties of aerosol particles —	155
2.9.4	Formation of cloud droplets: Heterogeneous nucleation —	164
2.9.5	Scavenging: Accommodation, adsorption, and reaction (mass transfer) —	166
2.9.5.1	Mass transfer: General remarks —	166
2.9.5.2	Adsorption —	172
2.9.5.3	Surface chemistry: Kinetics of heterogeneous chemical reactions —	172
2.9.5.4	Mass transfer into droplets with chemical reaction —	174
2.10	Removal —	179
2.10.1	Dry deposition —	180
2.10.2	Wet deposition —	187
2.10.3	Characteristic times: Residence time, lifetime, and turnover time —	189
3	Chemical fundamentals of the climate system —	196
3.1	State of matter —	196
3.1.1	Atoms, elements, molecules, compounds, and substances —	197
3.1.2	Pure substances and mixtures —	199
3.1.3	Isotopes —	200
3.1.4	Radicals, groups, and nomenclature —	204
3.1.5	Units for chemical abundance: Concentrations and mixing ratios —	209
3.2	Chemical reactions: Mechanism and kinetics —	215
3.2.1	Chemical bonding —	216
3.2.2	Types of chemical reactions —	222
3.2.3	Reaction rate constant —	224
3.3	Catalysis —	232
3.4	Electrochemical processes —	233
3.4.1	Electrolytic dissociation —	233
3.4.1.1	Acids, bases, and the ionic product of water —	234
3.4.1.2	pH value —	238
3.4.1.3	Hydrolysis of salts and oxides —	241
3.4.1.4	Buffer solutions —	242
3.4.1.5	Complex ions —	243
3.4.2	Acidity —	244
3.4.3	Oxidation–reduction reaction (redox process) —	253
3.4.4	Hydrated electron: A fundamental species —	258
3.5	Photochemical processes —	262
3.5.1	Photoexcitation and photodissociation —	262
3.5.2	Photolysis rate coefficient —	264
3.5.3	Photocatalysis: Photosensitization and autoxidation —	267

4	Substances in the climate system — 272
4.1	Introduction — 273
4.2	Hydrogen — 276
4.2.1	Compounds of hydrogen — 277
4.2.2	Natural sources and occurrence — 278
4.2.3	Chemistry of hydrogen — 281
4.3	Water — 285
4.3.1	Natural occurrence: Water and the hydrosphere — 286
4.3.2	Physical and chemical properties of water — 288
4.3.3	Water structure: Hydrogen bond — 289
4.3.4	Water as solvent — 292
4.3.5	Surface and ground water — 292
4.3.5.1	Soil water and groundwater: Chemical weathering — 293
4.3.5.2	River and lake water — 294
4.3.5.3	Seawater — 295
4.3.5.4	Snow, ice, and glaciers — 297
4.3.6	Cloud water chemistry — 299
4.3.6.1	Understanding cloud chemistry — 300
4.3.6.2	Cloud chemistry at Mt. Brocken — 308
4.3.7	Fog water chemistry — 323
4.3.8	Rainwater chemistry — 325
4.3.8.1	Understanding rain chemistry — 327
4.3.8.2	Precipitation chemistry program Seehausen — 332
4.3.9	Water chemistry: Aqueous-phase and interfacial chemistry — 344
4.4	Oxygen — 348
4.4.1	Natural occurrence of ozone (O_3) — 350
4.4.1.1	Ozone trends in troposphere and stratosphere — 351
4.4.1.2	Ozone changes with altitude — 357
4.4.1.3	Ozone timely variations — 358
4.4.1.4	Ozone budget: Sources versus sinks — 360
4.4.2	Natural occurrence of hydrogen peroxide (H_2O_2) — 361
4.4.3	Natural occurrence of hydroxyl radical (OH) — 375
4.4.4	Chemistry of oxygen (O , O_2 , and O_3) — 377
4.4.5	Chemistry of inorganic oxygen radicals (OH and HO_2) — 381
4.4.5.1	Atmosphere, free of trace species — 382
4.4.5.2	Atmosphere with trace species — 386
4.4.6	Chemistry of organic oxygen radicals and peroxides (RO , RO_2 , $ROOH$) — 391
4.4.7	Aqueous-phase oxygen chemistry — 393
4.4.8	Aqueous-phase chemistry of ozone (O_3) and hydroxyl radical (OH) — 402
4.4.9	Chemistry of hydrogen peroxide (H_2O_2) and hydrogen polyoxides (H_xO_y) — 407

4.4.10	Tropospheric ozone chemistry —	414
4.4.11	Stratospheric oxygen chemistry —	418
4.5	Nitrogen —	423
4.5.1	Sources and natural occurrence —	426
4.5.1.1	Nitrogen monoxide (NO) —	427
4.5.1.2	Ammonia (NH ₃) —	428
4.5.1.3	Dinitrogen monoxide (N ₂ O) —	432
4.5.1.4	Nitrous acid (HNO ₂) and nitrogen dioxide (NO ₂) —	436
4.5.2	Thermal dissociation of dinitrogen (N ₂) —	445
4.5.3	Chemistry of ammonia (NH ₃) —	446
4.5.4	Chemistry of dinitrogen monoxide (N ₂ O) —	449
4.5.5	Inorganic nitrogen oxides (NO _y) and oxoacids (H _x NO _y) —	450
4.5.5.1	Gas-phase chemistry —	451
4.5.5.2	Aqueous-phase and interfacial chemistry —	456
4.5.6	Organic nitrogen compounds —	474
4.5.6.1	Amines, amides, nitriles, and cyanides —	476
4.5.6.2	Organic NO _x compounds —	479
4.6	Sulfur —	481
4.6.1	Sources and natural occurrence of reduced sulfur compounds —	483
4.6.2	Sources and emission of sulfur dioxide (SO ₂) —	488
4.6.3	Chemistry of reduced sulfur (H ₂ S, COS, CS ₂ , and DMS) —	490
4.6.4	Oxides (SO ₂ and SO ₃) and oxoacids (H ₂ SO ₃ and H ₂ SO ₄) of sulfur —	495
4.6.5	Gas-phase SO ₂ oxidation —	496
4.6.6	Aqueous-phase sulfur chemistry —	496
4.6.7	Multiphase sulfur chemistry —	505
4.7	Phosphorus —	508
4.8	Carbon —	511
4.8.1	Organic carbon and chemistry —	513
4.8.2	Elemental carbon and soot —	517
4.8.3	Sources and occurrence of carbon monoxide (CO) —	521
4.8.4	Sources of carbon dioxide (CO ₂) —	524
4.8.4.1	Fossil fuel use —	524
4.8.4.2	Land-use change —	525
4.8.5	Atmospheric concentration of carbon dioxide (CO ₂) —	527
4.8.5.1	The preindustrial CO ₂ level derived from ice core data —	527
4.8.5.2	The increase of atmospheric CO ₂ since 1959 —	530
4.8.5.3	Timely and latitudinal CO ₂ variations —	533
4.8.5.4	The city dome CO ₂ —	535
4.8.6	Sources and occurrence of methane (CH ₄) —	536
4.8.7	Sources of non-methane volatile compounds (NMVOCs) —	541
4.8.7.1	Isoprene and monoterpenes —	544
4.8.7.2	Oxygenated volatile organic compounds (OVOCs) —	546

4.8.8	Inorganic carbon chemistry — 549
4.8.8.1	Gas-phase oxidation of carbon monoxide (CO) — 549
4.8.8.2	Aqueous-phase chemistry of carbon dioxide (CO ₂) — 550
4.8.8.3	The CO ₂ -carbonate system — 553
4.8.9	Organic carbon chemistry — 565
4.8.9.1	Hydrocarbon oxidation and organic radicals — 565
4.8.9.2	Organic C ₁ and C ₂ chemistry — 569
4.8.9.3	Chemistry of alkenes, alkynes, and ketones — 578
4.8.9.4	Chemistry of aromatic compounds — 581
4.8.9.5	Is the atmospheric fate of complex organic compounds predictable? — 584
4.9	Halogens (Cl, Br, F, and I) — 584
4.9.1	Halogens in the environment — 587
4.9.2	Chemistry of sea salt — 598
4.9.2.1	Chemistry of chlorine containing particulate matter — 598
4.9.2.2	Partitioning of hydrochloric acid (HCl) and particulate matter — 602
4.9.3	Gas-phase chemistry of halogens — 605
4.9.4	Aqueous-phase and interfacial chemistry of halogens — 611
4.9.5	Marine halogen and ozone chemistry — 620
4.10	Metals and half-metals — 626
4.10.1	General remarks — 626
4.10.2	Alkali and alkaline earth metals (Na, K, Mg, and Ca) — 629
4.10.3	Iron (Fe) — 630
4.10.4	Mercury (Hg) — 631
4.10.5	Cadmium (Cd) — 634
4.10.6	Lead (Pb) — 635
4.10.7	Arsenic (As) — 636
4.10.8	Silicon (Si) and aluminum (Al) — 636
4.11	Particulate matter (dust) — 637
4.11.1	Sources of dust — 639
4.11.2	Dust in the atmosphere — 640
5	Evolution of the climate system — 646
5.1	The prebiological period — 646
5.1.1	Origin of elements, molecules, and the Earth — 646
5.1.2	Origin of organic bonded carbon — 657
5.1.3	Origin of nitrogen — 662
5.2	Evolution of the atmosphere — 664
5.2.1	Degassing of the Earth: Formation of the atmosphere — 665
5.2.1.1	Volcanic gases — 665
5.2.1.2	Occluded and produced gases from rocks — 666
5.2.1.3	The prebiological primitive atmosphere — 672

5.2.2	Biosphere-atmosphere interaction —	678
5.2.2.1	Origin of life —	678
5.2.2.2	The rise of oxygen and ozone: Biogeochemical evolution —	683
5.2.2.3	What is the role of life in earth's climate system? —	690
5.2.2.4	Abiogenic versus biogenic formation of "fossil fuels" —	694
5.2.2.5	Life limits by catastrophic events: Mass extinction —	695
5.2.3	Climate variation and change —	697
5.3	Biogeochemical cycling —	708
5.3.1	Global cycling: Interactions of cycles —	708
5.3.2	Biological sources —	713
5.3.3	Geogenic sources —	719
5.3.3.1	Volcanism —	719
5.3.3.2	Lightning —	724
5.3.3.3	Soil dust —	726
5.3.3.4	Sea salt —	728
5.3.3.5	Secondary atmospheric processes —	731
5.3.4	Carbon cycling —	733
5.3.4.1	The carbon and oxygen pools and global cycling —	733
5.3.4.2	Primary production of carbon —	742
5.3.4.3	The global carbon budget —	746
5.3.4.4	The CO ₂ residence time —	755
5.3.5	Nitrogen cycling —	759
5.3.6	Sulfur cycling —	764
6	Humans and the climate system —	768
6.1	Air pollution —	768
6.1.1	A short history of air pollution —	769
6.1.2	Emission of air pollutants —	778
6.1.3	Key human activities: Energy and food —	781
6.1.3.1	Fossil fuel use —	785
6.1.3.2	Agriculture and land-use change —	792
6.1.3.3	Biomass burning —	795
6.1.4	Eastern German air pollution decline: A world-wide unique example —	798
6.1.4.1	Change of emissions —	801
6.1.4.2	Change of concentrations —	808
6.1.5	Concentration versus emission change —	824
6.2	Impacts of air pollution on health —	829
6.2.1	The fundamentals —	832
6.2.2	Nitrogen dioxide (NO ₂) —	840
6.3.3	Particulate matter (dust) —	845
6.3	A sustainable climate system —	849

- 6.3.1 Growth and steady-state economy — 852
- 6.3.2 Hydrogen economy — 854
 - 6.3.2.1 Industrial production and use of hydrogen — 855
 - 6.3.2.2 Impacts of hydrogen on the climate system — 857
- 6.3.3 The carbon economy — 858
 - 6.3.3.1 Carbon capture and storage (CCS) — 859
 - 6.3.3.2 Direct air capture (DAC) — 862
 - 6.3.3.3 Carbon dioxide cycling — 865
 - 6.3.3.4 Solar fuels: Carbon as material and energy carrier — 869

- 7 Final remarks — 873

- Appendix A: List of acronyms and abbreviations used in this volume — 875

- Appendix B: Quantities, units, and some useful numerical values — 881

- Appendix C: Earth’s geological timescale — 885

- References — 887

- Name index — 991

- Subject index — 997