

Contents

1. The Description of Physicochemical Systems	1
1. The description of our universe, 1. 2. Physical chemistry, 1. 3. Mechanics: force, 2. 4. Work and energy, 3. 5. Equilibrium, 5. 6. The thermal properties of matter, 6. 7. Definition of temperature, 8. 8. The equation of state, 8. 9. Gas thermometry: the ideal gas, 10. 10. Relationships of pressure, volume, and temperature, 12. 11. Law of corresponding states, 14. 12. Equations of state for gases, 15. 13. The critical region, 16. 14. The van der Waals equation and liquefaction of gases, 18. 15. Other equations of state, 19. 16. Heat, 19. 17. Work in thermodynamic systems, 21. 18. Reversible processes, 22. 19. Maximum work, 23. 20. Thermodynamics and thermostatics, 23.	
2. The First Law of Thermodynamics	27
1. The history of the First Law, 27. 2. Formulation of the First Law, 28. 3. The nature of internal energy, 28. 4. Properties of exact differentials, 29. 5. Adiabatic and isothermal processes, 30. 6. The heat content or enthalpy, 30. 7. Heat capacities, 31. 8. The Joule experiment, 32. 9. The Joule-Thomson experiment, 33. 10. Application of the First Law to ideal gases, 34. 11. Examples of ideal-gas calculations, 36. 12. Thermochemistry—heats of reaction, 38. 13. Heats of formation, 39. 14. Experimental measurements of reaction heats, 40. 15. Heats of solution, 41. 16. Temperature dependence of reaction heats, 43. 17. Chemical affinity, 45.	
3. The Second Law of Thermodynamics	48
1. The efficiency of heat engines, 48. 2. The Carnot cycle, 48. 3. The Second Law of Thermodynamics, 51. 4. The thermodynamic temperature scale, 51. 5. Application to ideal gases, 53. 6. Entropy, 53. 7. The inequality of Clausius, 55. 8. Entropy changes in an ideal gas, 55. 9. Entropy changes in isolated systems, 56. 10. Change of entropy in changes of state of aggregation, 58. 11. Entropy and equilibrium, 58. 12. The free energy and work functions, 59. 13. Free energy and equilibrium, 61. 14. Pressure dependence of the free energy, 61. 15. Temperature dependence of free energy, 62. 16. Variation of entropy with temperature and pressure, 63. 17. The entropy of mixing, 64. 18. The calculation of thermodynamic relations, 64.	
4. Thermodynamics and Chemical Equilibrium	69
1. Chemical affinity, 69. 2. Free energy and chemical affinity, 71. 3. Free-energy and cell reactions, 72. 4. Standard free energies, 74. 5. Free energy and equilibrium constant of ideal gas reactions, 75. 6. The measurement of homogeneous gas equilibria, 77. 7. The principle	

CONTENTS

of Le Chatelier, 79. 8. Pressure dependence of equilibrium constant, 80. 9. Effect of an inert gas on equilibrium, 81. 10. Temperature dependence of the equilibrium constant, 83. 11. Equilibrium constants from thermal data, 85. 12. The approach to absolute zero, 85. 13. The Third Law of Thermodynamics, 87. 14. Third-law entropies, 89. 15. General theory of chemical equilibrium: the chemical potential, 91. 16. The fugacity, 93. 17. Use of fugacity in equilibrium calculations, 95.

5. Changes of State

1. Phase equilibria, 99. 2. Components, 99. 3. Degrees of freedom, 100. 4. Conditions for equilibrium between phases, 101. 5. The phase rule, 102. 6. Systems of one component—water, 104. 7. The Clapeyron-Clausius equation, 105. 8. Vapor pressure and external pressure, 107. 9. Experimental measurement of vapor pressure, 108. 10. Solid-solid transformations—the sulfur system, 109. 11. Enantiotropism and monotropism, 111. 12. Second-order transitions, 112. 13. High-pressure studies, 112.

6. Solutions and Phase Equilibria

1. The description of solutions, 116. 2. Partial molar quantities: partial molar volume, 116. 3. The determination of partial molar quantities, 118. 4. The ideal solution—Raoult's Law, 120. 5. Equilibria in ideal solutions, 122. 6. Henry's Law, 122. 7. Two-component systems, 123. 8. Pressure-composition diagrams, 123. 9. Temperature-composition diagrams, 125. 10. Fractional distillation, 125. 11. Boiling-point elevation, 126. 12. Solid and liquid phases in equilibrium, 128. 13. The Distribution Law, 130. 14. Osmotic pressure, 131. 15. Measurement of osmotic pressure, 133. 16. Osmotic pressure and vapor pressure, 134. 17. Deviations from Raoult's Law, 135. 18. Boiling-point diagrams, 136. 19. Partial miscibility, 137. 20. Condensed-liquid systems, 139. 21. Thermodynamics of nonideal solutions: the activity, 141. 22. Chemical equilibria in nonideal solutions, 143. 23. Gas-solid equilibria, 144. 24. Equilibrium constant in solid-gas reactions, 145. 25. Solid-liquid equilibria: simple eutectic diagrams, 145. 26. Cooling curves, 147. 27. Compound formation, 148. 28. Solid compounds with incongruent melting points, 149. 29. Solid solutions, 150. 30. Limited solid-solid solubility, 151. 31. The iron-carbon diagram, 152. 32. Three-component systems, 153. 33. System with ternary eutectic, 154.

The Kinetic Theory

1. The beginning of the atom, 160. 2. The renaissance of the atom, 161. 3. Atoms and molecules, 162. 4. The kinetic theory of heat, 163. 5. The pressure of a gas, 164. 6. Kinetic energy and temperature, 165. 7. Molecular speeds, 166. 8. Molecular effusion, 166. 9. Imperfect gases—van der Waal's equation, 169. 10. Collisions between molecules, 171. 11. Mean free paths, 172. 12. The viscosity of a gas, 173. 13. Kinetic theory of gas viscosity, 175. 14. Thermal conductivity

and diffusion, 177. 15. Avogadro's Number and molecular dimensions, 178. 16. The softening of the atom, 180. 17. The distribution of molecular velocities, 181. 18. The barometric formula, 182. 19. The distribution of kinetic energies, 183. 20. Consequences of the distribution law, 183. 21. Distribution law in three dimensions, 186. 22. The average speed, 187. 23. The equipartition of energy, 188. 24. Rotation and vibration of diatomic molecules, 189. 26. The equipartition principle and the heat capacity of gases, 192. 27. Brownian motion, 193. 28. Thermodynamics and Brownian motion, 194. 29. Entropy and probability, 195.

8. The Structure of the Atom

1. Electricity, 200. 2. Faraday's Laws and electrochemical equivalents, 201. 3. The development of valence theory, 202. 4. The Periodic Law, 204. 5. The discharge of electricity through gases, 205. 6. The electron, 205. 7. The ratio of charge to mass of the cathode particles, 206. 8. The charge of the electron, 209. 9. Radioactivity, 211. 10. The nuclear atom, 212. 11. X-rays and atomic number, 213. 12. The radioactive disintegration series, 213. 13. Isotopes, 216. 14. Positive-ray analysis, 216. 15. Mass spectra—the Dempster method, 218. 16. Mass spectra—Aston's mass spectrograph, 219. 17. Atomic weights and isotopes, 221. 18. Separation of isotopes, 223. 19. Heavy hydrogen, 225.

9. Nuclear Chemistry and Physics

1. Mass and energy, 228. 2. Artificial disintegration of atomic nuclei, 229. 3. Methods for obtaining nuclear projectiles, 231. 4. The photon, 232. 5. The neutron, 234. 6. Positron, meson, neutrino, 235. 7. The structure of the nucleus, 236. 8. Neutrons and nuclei, 238. 9. Nuclear reactions, 240. 10. Nuclear fission, 241. 11. The transuranium elements, 243. 12. Nuclear chain reactions, 243. 13. Energy production by the stars, 244. 14. Tracers, 245. 15. Nuclear spin, 247.

Particles and Waves

1. The dual nature of light, 251. 2. Periodic and wave motion, 251. 3. Stationary waves, 253. 4. Interference and diffraction, 255. 5. Black-body radiation, 257. 6. Planck's distribution law, 259. 7. Atomic spectra, 261. 8. The Bohr theory, 262. 9. Spectra of the alkali metals, 265. 10. Space quantization, 267. 11. Dissociation as series limit, 268. 12. The origin of X-ray spectra, 268. 13. Particles and waves, 269. 14. Electron diffraction, 271. 15. The uncertainty principle, 272. 16. Waves and the uncertainty principle, 274. 17. Zero-point energy, 275. 18. Wave mechanics—the Schrödinger equation, 275. 19. Interpretation of the ψ functions, 276. 20. Solution of wave equation—the particle in a box, 277. 21. The tunnel effect, 279. 22. The hydrogen atom, 280. 23. The radial wave functions, 282. 24. The spinning electron, 284. 25. The Pauli Exclusion Principle, 285. 26. Structure of the periodic table, 285. 27. Atomic energy levels, 287.

11. The Structure of Molecules	295
1. The development of valence theory, 295. 2. The ionic bond, 296. 3. The covalent bond, 297. 4. Calculation of the energy in H-H molecule, 301. 5. Molecular orbitals, 303. 6. Homonuclear diatomic molecules, 303. 7. Heteronuclear diatomic molecules, 307. 8. Comparison of M.O. and V.B. methods, 307. 9. Directed valence, 308. 10. Non-localized molecular orbitals, 310. 11. Resonance between valence-bond structures, 311. 12. The hydrogen bond, 313. 13. Dipole moments, 314. 14. Polarization of dielectrics, 314. 15. The induced polarization, 316. 16. Determination of the dipole moment, 316. 17. Dipole moments and molecular structure, 319. 18. Polarization and refractivity, 320. 19. Dipole moments by combining dielectric constant and refractive index measurements, 321. 20. Magnetism and molecular structure, 322. 21. Nuclear paramagnetism, 324. 23. Application of Wierl equation to experimental data, 329. 24. Molecular spectra, 331. 25. Rotational levels—far-infrared spectra, 333. 26. Internuclear distances from rotation spectra, 334. 27. Vibrational energy levels, 334. 28. Microwave spectroscopy, 336. 29. Electronic band spectra, 337. 30. Color and resonance, 339. 31. Raman spectra, 340. 32. Molecular data from spectroscopy, 341. 33. Bond energies, 342.	
12. Chemical Statistics	
1. The statistical method, 347. 2. Probability of a distribution, 348. 3. The Boltzmann distribution, 349. 4. Internal energy and heat capacity, 352. 5. Entropy and the Third Law, 352. 6. Free energy and pressure, 354. 7. Evaluation of molar partition functions, 354. 8. Monatomic gases—translational partition function, 356. 9. Diatomic molecules—rotational partition function, 358. 10. Polyatomic molecules—rotational partition function, 359. 11. Vibrational partition function, 359. 12. Equilibrium constant for ideal gas reactions, 361. 13. The heat capacity of gases, 361. 14. The electronic partition function, 363. 15. Internal rotation, 363. 16. The hydrogen molecules, 363. 17. Quantum statistics, 365.	
13. Crystals	369
1. The growth and form of crystals, 369. 2. The crystal systems, 370. 3. Lattices and crystal structures, 371. 4. Symmetry properties, 372. 5. Space groups, 374. 6. X-ray crystallography, 375. 7. The Bragg treatment, 376. 8. The structures of NaCl and KCl, 377. 9. The powder method, 382. 10. Rotating-crystal method, 383. 11. Crystal-structure determinations: the structure factor, 384. 12. Fourier syntheses, 387. 13. Neutron diffraction, 389. 14. Closest packing of spheres, 390. 15. Binding in crystals, 392. 16. The bond model, 392. 17. The band model, 395. 18. Semiconductors, 398. 19. Brillouin zones, 399. 20. Alloy systems—electron compounds, 399. 21. Ionic crystals, 401. 22. Coordination polyhedra and Pauling's Rule, 403. 23. Crystal energy—the Born-Haber cycle, 405. 24. Statistical thermodynamics of crystals: the Einstein model, 406. 25. The Debye model, 408.	

Liquids

1. The liquid state, 413.
2. Approaches to a theory for liquids, 415.
3. X-ray diffraction of liquids, 415.
4. Results of liquid-structure investigations, 417.
5. Liquid crystals, 418.
6. Rubbers, 420.
7. Glasses, 422.
8. Melting, 422.
9. Cohesion of liquids—the internal pressure, 422.
10. Intermolecular forces, 424.
11. Equation of state and intermolecular forces, 426.
12. The free volume and holes in liquids, 428.
13. The flow of liquids, 430.
14. Theory of viscosity, 431.

15. Electrochemistry

1. Electrochemistry: coulometers, 435.
2. Conductivity measurements, 435.
3. Equivalent conductivities, 437.
4. The Arrhenius ionization theory, 439.
5. Transport numbers and mobilities, 442.
6. Measurement of transport numbers—Hittorf method, 442.
7. Transport numbers—moving boundary method, 444.
8. Results of transference experiments, 445.
9. Mobilities of hydrogen and hydroxyl ions, 447.
10. Diffusion and ionic mobility, 447.
11. A solution of the diffusion equation, 448.
12. Failures of the Arrhenius theory, 450.
13. Activities and standard states, 451.
14. Ion activities, 454.
15. Activity coefficients from freezing points, 455.
16. Activity coefficients from solubilities, 456.
17. Results of activity-coefficient measurements, 457.
18. The Debye-Hückel theory, 458.
19. Poisson's equation, 458.
20. The Poisson-Boltzmann equation, 460.
21. The Debye-Hückel limiting law, 462.
22. Advances beyond the Debye-Hückel theory, 465.
23. Theory of conductivity, 466.
24. Acids and bases, 469.
25. Dissociation constants of acids and bases, 471.
26. Electrode processes: reversible cells, 473.
27. Types of half cells, 474.
28. Electrochemical cells, 475.
29. The standard emf of cells, 476.
30. Standard electrode potentials, 478.
31. Standard free energies and entropies of aqueous ions, 481.
32. Measurement of solubility products, 482.
33. Electrolyte-concentration cells, 482.
34. Electrode-concentration cells, 483.

16. Surface Chemistry

1. Surfaces and colloids, 498.
2. Pressure difference across curved surfaces, 500.
3. Maximum bubble pressure, 502.
4. The Du Noüy tensiometer, 502.
5. Surface-tension data, 502.
6. The Kelvin equation, 504.
7. Thermodynamics of surfaces, 506.
8. The Gibbs adsorption isotherm, 507.
9. Insoluble surface films—the surface balance, 508.
10. Equations of state of monolayers, 511.
11. Surface films of soluble substances, 512.
12. Adsorption of gases on solids, 512.
13. The Langmuir adsorption isotherm, 515.
14. Thermodynamics of the adsorption isotherm, 516.
15. Adsorption from solution, 517.
16. Ion exchange, 518.
17. Electrical phenomena at interfaces, 519.
18. Electrokinetic phenomena, 520.
19. The stability of sols, 522.

Chemical Kinetics

1. The rate of chemical change, 528.
2. Experimental methods in kinetics, 529.
3. Order of a reaction, 530.
4. Molecularity of a reac-

CONTENTS

tion, 531. 5. The reaction-rate constant, 532. 6. First-order rate equations, 533. 7. Second-order rate equations, 534. 8. Third-order rate equation, 536. 9. Opposing reactions, 537. 10. Consecutive reactions, 539. 11. Parallel reactions, 541. 12. Determination of the reaction order, 541. 13. Reactions in flow systems, 543. 14. Effect of temperature on reaction rate, 546. 15. Collision theory of gas reactions, 547. 16. Collision theory and activation energy, 551. 17. First-order reactions and collision theory, 551. 18. Activation in many degrees of freedom, 554. 19. Chain reactions: formation of hydrogen bromide, 555. 20. Free-radical chains, 557. 21. Branching chains—explosive reactions, 559. 22. Trimolecular reactions, 562. 23. The path of a reaction, and the activated complex, 563. 24. The transition-state theory, 566. 25. Collision theory and transition-state theory, 568. 26. The entropy of activation, 569. 27. Theory of unimolecular reactions, 570. 28. Reactions in solution, 571. 29. Ionic reactions—salt effects, 572. 30. Ionic reaction mechanisms, 574. 31. Catalysis, 575. 32. Homogeneous catalysis, 576. 33. Acid-base catalysis, 577. 34. General acid-base catalysis, 579. 35. Heterogeneous reactions, 580. 36. Gas reactions at solid surfaces, 582. 37. Inhibition by products, 583. 38. Two reactants on a surface, 583. 39. Effect of temperature on surface reactions, 585. 40. Activated adsorption, 586. 41. Poisoning of catalysts, 587. 42. The nature of the catalytic surface, 588. 43. Enzyme reactions, 589.

18. Photochemistry and Radiation Chemistry

1. Radiation and chemical reactions, 595. 2. Light absorption and quantum yield, 595. 3. Primary processes in photochemistry, 597. 4. Secondary processes in photochemistry: fluorescence, 598. 5. Luminescence in solids, 601. 6. Thermoluminescence, 603. 7. Secondary photochemical processes: initiation of chain reactions, 604. 8. Flash photolysis, 606. 9. Effects of intermittent light, 607. 10. Photosynthesis in green plants, 609. 11. The photographic process, 611. 12. Primary processes with high-energy radiation, 612. 13. Secondary processes in radiation chemistry, 614. 14. Chemical effects of nuclear recoil, 615.

Physical Constants and Conversion Factors

Name Index

Subject Index 623