INDEX

ab initio methods, 190–3
absorption spectra, 226–8
activation energy, 109
active transport, 52, 325
adenosine triphosphatase (ATPase), 14
direct synthesis of, 49–51
adiabatic process, 10
allosterism, 408–11
heterotropic interactions, 408
homotropic interactions, 408
amino acids at neutral pH, structures of, 461–2
anode, 469
anomalous scattering, 210
antioperativity, 400
anti-Stokes lines, 279
antisymmetry principle, 182
Beer–Lambert law, 226–7, 230, 238
biochemical reactions, 43–4
biochemical redox reactions, 373
Bohr radius, 180
Boltzmann distribution, 338–43
Born interpretation, 158
Born–Oppenheimer approximation, 184–6, 357
Bragg equation, 208
Bravais lattices, 206
calorimetry, 13–16
simple batch calorimeter, 14
canonical distribution, 348
catalysis, 122
cathode, 469–70
centrifugation, 421
density centrifugation, 427–8
equilibrium centrifugation, 424–5
preparative centrifugation, 425–7
chemical equilibria, 32–4, 87–9
chemical kinetics, 97–120
first-order kinetics, 102
principles of, 97–120
pseudo-first-order kinetics, 103
radioactive decay, 104–5
rate constants, temperature dependence of, 108–12
rate laws, determination of, 101–4
reaction mechanisms, 105–8
reaction rates, 99–101
reaction rates near equilibrium, 114–16
second-order kinetics, 103
single molecule kinetics, 116–18
thermodynamics and, 112–14
chemical potential, 80–83
classical molecular dynamics, 358
chemical reactions
mechanisms of, See reaction mechanisms
membrane ion gradients establishment by, 51–2
chemical shifts, 293–6
chiral molecules, 253
\( \alpha \)-chymotrypsin, 126–33
steady-state constants for, 127
circular dichroism (CD), 254, 256–7
of nucleic acids, 259–60
of proteins, 257–9
protein secondary structure determined by, 282
circularly polarized light, 253
classical molecular dynamics, 358
closed system, 4
coherent scattering, 210

Physical Chemistry for the Biological Sciences, Second Edition.
Gordon G. Hammes and Sharon Hammes-Schiffer.
© 2015 John Wiley & Sons, Inc. Published 2015 by John Wiley & Sons, Inc.
constructive interference, 170
conversion factors, 459
cooperative process, 62
cooperativity in ligand binding, 397–402
kinetic studies of, 406–8
models for cooperativity, 402–6
COSY (Correlated Spectroscopy), 302
Cotton effects, 256
Cro repressor protein binding to DNA, 395–7
crystal, scattering of X-rays by, 206–8
de Broglie postulate, 157
Debye–Hückel theory, 90–92
degenerate states, 341
degrees Celsius, 4
density centrifugation, 427–8
density functional theory (DFT), 193–4
destructive interference, 170
difference spectroscopy, 233–6
diffusion, 418–21
diffusion constant, 418
dihydrofolate reductase (DHFR), 245–7, 286, 376–9
DNA, 260–263
fingerprinting, 430
interaction with zinc finger proteins, 266–7
melting, 67–72, 142–8
small molecule binding to, 260–263
transcription regulation, 315–18
docking, 364–5
elastic scattering, 207
electrochemistry, 469–73
electron spin resonance (ESR), 306–10
usefulness in biological systems, 307
electronic spectra, 225–51, See also absorption spectra
difference spectroscopy, 233–6
dihydrofolate reductase (DHFR), 245–7
energy transfer application to biological systems, 243–5
fluorescence energy transfer, molecular ruler, 241–3
fluorescence, 236–40
nucleic acid spectra, 230–231
phosphorescence, 236–40
prosthetic groups, 231–3
RecBCD, helicase activity monitored by fluorescence, 240–241
ultraviolet spectra of proteins, 228–30
X-ray absorption spectroscopy, 236
electronic structure, 177–202
atoms and molecules, 177–202
Born–Oppenheimer approximation, 184–6
density functional theory (DFT), 193–4
Hartree–Fock theory, 190–193
hydrogen atoms, 177–80
many-electron atoms, 181–4
molecular orbital theory, 186–90
electrophoresis, 429–32
electrospray ionization (ESI), 446
elementary reactions, 98–9
efficiently polarized light, 253
empirical valence bond (EVB) method, 374
dipeptidase, 126
definition, 9–10
energy transfer application to biological systems, 233–5
ensembles, 346–9
enthalpy, 11–12
reaction enthalpies, 16–18
temperature dependence of, 18–19
entropy, 23–42, See also second law of thermodynamics
calculation of, 26–8
molecular interpretation of, 29–30
statistical interpretation of, 349–50
enzyme catalysis, 121–6, 219–22
Michaelis–Menten mechanism, 121–6
X-ray crystallography, 219–22
enzyme reactions, simulations of, 376–9
enzyme–substrate complexes, structure of, 286–7
equilibrium approximation, 122
equilibrium centrifugation, 424–5
equilibrium dialysis experiment, 393
ergocidal hypothesis, 367
Ewald summation method, 366
exopeptidases, 126
extended chemical potential, 39
extensive properties, 4
facilitated diffusion, 325
fast ion bombardment (FAB), 447
first law of thermodynamics, 9
first-order kinetics, 102
  pseudo-first-order kinetics, 103
first-order saddle point, 196
fluorescence, 225, 236–40
fluorescence energy transfer, molecular ruler, 241–3
fluorescence polarization, 267–9
Förster energy transfer, 241
Fourier transform, 171
Franck–Condon principle, 277
free energy, See Gibbs energy and Helmholtz energy
free induction decay (FID), 293
frictional coefficient, 415–18
galvanic cells, 469
gauze conformations, 360
Gibbs energy, 30–32, See also second law of thermodynamics
  additions to, 39
  calculations, 375–6
  pressure dependence of, 35–6
  temperature dependence of, 35–6
  global minimum, 196
Hartree–Fock theory, 190–193
heat, 5–6
  heat capacity, 5
  heat of formation, 12
helix-coil transition, 350–353
  initiation process, 350–351
  propagation, 350
  α-helix protein structure, 57
Helmholtz energy calculations, 375–6
heme, 231–2
Henry’s law, 82
Heteronuclear Single Quantum Correlation (HSQC), 303
heterotropic interactions, 408
HIV genome integration into host genome, 269–70
homotropic interactions, 408
host genome, HIV genome integration into, 269–70
hybrid quantum/classical methods, 373–5
hydrodynamics of macromolecules, 415–39
  centrifugation, 421
  density centrifugation, 427–8
  diffusion, 418–21
  electrophoresis, 429–32
  equilibrium centrifugation, 424–5
  frictional coefficient, 415–18
  intrinsic viscosity, 428–9
  peptide-induced conformational change of MHC protein, 432–4
  preparative centrifugation, 425–7
  ultracentrifuge analysis of protein–DNA interactions, 434–5
  velocity sedimentation, 422–4
  viscosity, 428–9
hydrogen bond formation, 55
hydrogenic atoms, 177–80
hyperchromicity, 230
hypoachromicity, 230
inelastic scattering, 207
infrared (IR) spectroscopy, 278–9
  protein secondary structure determined by, 282
intensive properties, 4
ion detectors, 445–6
ionic solutions, 89–93
ionization of sample, 446–9
isobestic wavelength, 227
isolated system, 4
isomorphous replacement, 210
isothermal process, 10
α-ketoglutarate dehydrogenase, 270–272
kinetic model of gases, 333–8
kinetic studies of cooperative binding, 406–8
kinetics applications to biological systems, 121–51, See also α-chymotrypsin; enzyme catalysis
DNA melting, 142–8
protein tyrosine phosphatase, 133–7
renaturation, 142–8
ribozymes, 137–42
Koshland, Nemethy, and Filmer (KNF) model, 403–6
lactose permease, 325–8
Larmor frequency, 292
Lennard-Jones 12–6 potential, 363
ligand binding to macromolecules, 385–414
allosterism, 408–11
cooperativity in ligand binding, 397–402
Cro repressor protein binding to DNA, 395–7
experimental determination, 392–5
macroscopic equilibrium constants, 387–9
microscopic equilibrium constants, 387–9
models for cooperativity, 402–6
small molecules binding to multiple identical binding sites, 385–7
statistical effects in, 389–92
linear polarized light, 253
Lineweaver-Burk equation, 125
local minima, 196
London attraction energy, 362–3
macromolecules, ligand binding to, 385–414
macromolecules, vibrations in, 277–88
enzyme–substrate complexes, structure of, 286–7
infrared spectroscopy, 278–9
Raman spectroscopy, 279–81
vibrational spectroscopy, 281–3
macroscopic equilibrium constants, 387–9
macroscopic ionization constants, 388
molecular partition function, 343–6
molecular simulations, 357–81
Gibbs energy calculations, 375–6
Helmholtz energy calculations, 375–6
Hydrogen bonding, 373–5
large-scale simulations, 365–7
molecular mechanics and docking, 364–5
potential energy surfaces, 358–64
molecular orbital theory, 186–90
H₂, 188
He₂, 188
O₂ diatomic molecule, 190
molecular partition function, 343–6
molecular simulations, 357–81
enzyme reactions, simulations of, 376–9
Gibbs energy calculations, 375–6
Helmholtz energy calculations, 375–6
Hydrogen bonding, 373–5
large-scale simulations, 365–7
molecular mechanics and docking, 364–5
potential energy surfaces, 358–64
Monod–Wyman–Changeux model, 403
Monte Carlo approach, 358, 373
multidimensional NMR, 300–306
negative cooperativity, 400
Nernst’s law, 472
neutron diffraction, 212
nodes, 160
NOE walk, 323
normal modes of vibration, 163
nuclear magnetic resonance (NMR), 289–313
chemical shifts, 293–6
magnetic resonance imaging (MRI), 306
multidimensional NMR, 300–306
NMR spectrometers, 292–3
relaxation times, 298–300
spin–spin splitting, 296–7
Nuclear Overhauser Effect Spectroscopy (NOESY), 303–4
nucleation, 145
nuclei, magnetic properties of, 290
nucleic acid components, 463
nucleic acids, 259–60
circular dichroism of, 259–60
optical rotary dispersion of, 259–60
spectra, 230–231
nucleic acid structures, 63–7, 213–15
DNA melting, 67–72
DNA/RNA chain, 63
RNA, 72
open system, 4
optical rotary dispersion (ORD), 254–6
experimental setup, 255
of nucleic acids, 259–60
of proteins, 257–9
optical rotary dispersion, 253–76
optical rotation, 254
osmosis, 85
osmotic pressure, 85–7
overlap density, 187
partial molar quantities, 83–84
particle in a box, 159–62
Pauli principle, 182
peptide-induced conformational change of MHC protein, 432–4
peptides, 450–452
phase changes, 36–9
phase diagrams, 37
phosphorescence, 236–40
photoelectric effect, 155–6
plane polarized light, 253
β-pleated sheets proteins, 58
polarizability, 279
polarization, 268, See also fluorescence polarization
polarized light, 253
potential energy surfaces, 358–64
preparative centrifugation, 425–7
principle of detailed balance, 113
probability density, 158
processive reaction, 241
prosthetic groups, 231–3
heme, 231–2
proteasome structure and function, 328–9
protein–DNA interactions, 318–20
protein folding, 60–63, 263–6, 452–5
dynamics of, 320–322
protein structure, 52–60, 216–19
α-helix, 57
β-pleated sheets proteins, 58
polypeptide chain, 53
primary structure, 216
quaternary structure, 218
secondary structure, 216
tertiary structure, 217
protein tyrosine phosphatase, 133–7
proteins, 257–9, 450–452
circular dichroism of, 257–9
optical rotary dispersion of, 257–9
ultraviolet spectra of, 228–30
P–V isotherm, 8
quadropole mass analyzer, 443
quantum chemistry of biological systems, 194–200
global minimum, 196
local minima, 196
quantum dynamics, 358
quantum mechanical/molecular mechanical (QM/MM) methods, 374
quantum mechanics, 155–75, See also spectroscopy and electronic structure fundamentals of, 155–75
particle in a box, 159–62
rotational motions, 167–8
Schrödinger equation, 158–9
tunneling, 165–7
quantum mechanics (Continued)
  vibrational motions, 162–5
quantum yield, 238

radial distribution function, 180
radioactive decay, 104–5
Raman scattering, 279
Raman spectroscopy, 279–81
  advantages, 280
Raoult’s law, 82
rate constants, 101
rate constants, temperature dependence of,
  108–12
  activation energy, 109
  standard Gibbs energy of activation, 110
  transition state theory, 109
rate laws, determination of, 100–4
  first-order kinetics, 102
  pseudo-first-order kinetics, 103
  second-order kinetics, 103
rates of chemical reactions, See reaction
  rates
reaction enthalpies, 16–18
  temperature dependence of, 18–19
reaction field method, 367
reaction mechanisms, 105–8
  elementary steps, 105
reaction order, 100
reaction rates, 99–101
  near equilibrium, 114–16
RecBCD, helicase activity monitored by
  fluorescence, 240–241
relaxation times, 298–300
renaturation, 142–8
residual dipolar coupling (RDC), 303
resonance Raman spectroscopy, 280, 283–6
reversible path, 8
ribozymes, 137–42
ring currents, 296
RNA, 72
RNA folding, 322–5
root-mean-square deviation (RMSD),
  370–371
root-mean-square fluctuation (RMSF), 371
rotational motions, 167–8
scattering phenomenon, 279
Schrödinger equation, 158–9
second law of thermodynamics, 24
  statement of, 24–6
second-order kinetics, 103
sedimentation coefficient, 421
selection rules, 225
self-consistent-field (SCF) method, 192
simple batch calorimeter, 14
single molecule kinetics, 116–18
  singlet, 239
small molecules binding to multiple
  identical binding sites, 385–7
sodium dodecyl sulfate–polyacrylamide gel
  electrophoresis (SDS-PAGE), 431
spectroscopy, 169–73
  basics of, 169–73
  constructive interference, 170
  destructive interference, 170
  spin–lattice relaxation time, 298
  spin–spin relaxation time, 298
  spin–spin splitting, 296–7
  standard electrochemical potentials,
    471–2
  concentration dependence of, 472–3
  standard enthalpy changes, 465, 467
  standard Gibbs energy, 465, 467
  of activation, 110
  standard states, 12–13, 32
  state function, 10
statistical effects in ligand binding to
  macromolecules, 389–92
statistical entropy, 349–50
statistical mechanics, 333–55
  Boltzmann distribution, 338–43
  canonical distribution, 348
  ensembles, 346–9
  fundamentals of, 333–55
  helix-coil transition, 350–353
  kinetic model of gases, 333–8
  molecular partition function, 343–6
  statistical entropy, 349–50
steady-state approximation, 123
structure determination with vibrational
  spectroscopy, 281–3
system, 4
  closed system, 4
  extensive properties, 4
  intensive properties, 4
  isolated system, 4
  open system, 4
  properties, 4
INDEX 481

tandem mass spectrometry (MS/MS), 445
temperature, 4
  Celsius temperature scale, 4
  Kelvin temperature scale, 4
temperature dependence of Gibbs energy,
  35–6
temperature dependence of the reaction
  enthalpy, 18–19
thermal equilibrium, 4
thermodynamics, 28–9, 77–94
  applications to biological systems,
  43–75
  biochemical reactions, 43–4
  chemical equilibria, 87–9
  chemical potential, 80–83
  first law of thermodynamics, 9
  and kinetics, 112–14
  ionic solutions, 89–93
  mathematical tools, 77–8
  Maxwell relations, 78–80
  osmotic pressure, 85–7
  partial molar quantities, 83–4
  second law of thermodynamics, 24–6
  third law of thermodynamics, 28–9
  third law of thermodynamics, 28–9
trans conformations, 360
transient kinetics, 127
transition state (TS), 196
transition state theory, 109, 112
translin, 434
transverse relaxation optimized spectroscopy
  (TROSY), 305
tunneling, 165–7
ultracentrifuge analysis of protein–DNA
  interactions, 434–5
ultraviolet spectra of proteins, 228–30
umbrella sampling, 375
van der Waals repulsion energy, 362–3
velocity sedimentation, 422–4
velocity Verlet algorithm, 368–9
vibrational motions, 162–5
  normal modes, 163
vibrational spectroscopy, structure
determination with, 281–3
viscosity, 428–9
  intrinsic viscosity, 428–9
work, 6–9
work function, 155
X-ray absorption spectroscopy, 236
X-ray crystallography, 205–24, 282
  anomalous scattering, 210
  coherent scattering, 210
  elastic scattering, 207
  enzyme catalysis, 219–22
  ‘hammerhead’ ribozyme, 215
  inelastic scattering, 207
  neutron diffraction, 212
  nucleic acid structure, 213–15
  protein secondary structure determined
  by, 282
  protein structure, 216–19
  scattering of X-rays by a crystal, 206–8
  structure determination, 208–12
zinc finger proteins, DNA interaction with,
  266–7