activated complex, 264
activation, Gibbs energy of, 264
  volume of, 266
activity coefficient see electrolytes; ionic;
  solvents, mixed aqueous
amphiphiles, 239
anions, extraction of, 261
Antoine expression, 70
batteries, 248–50
  energy storage density in, 248, 249
biomolecules, 269–74, 277–9
catalysis, phase transfer, 266, 267
chromatography, liquid, 262
colloids, 269, 270, 274
compressibility see ions, aqueous; solvents
computer simulations see hydration
  numbers; solvent dynamics
conductivity see ions, aqueous, solvents
consolute temperature, lower, 276
crown ethers, as solvating ligands, 259, 260, 268
dielectric relaxation spectroscopy, 233, 234
  see also ions, dielectric
  dielectric saturation, 37, 49, 111, 165 see
  also hydration of ions; ions,
  aqueous
drugs, ionizable, solvation of, 262–3
electrode potential scale, 251, 254–7
electrolyte dissolution, enthalpy of, 199
electrolytes, activity coefficients of,
  219–24, 227, 229–31, 233, 238
  average ion distance in, 225
  BET expression for, 225–7
  colligative properties of, 224, 225
  ionic atmosphere, 219, 223, 230
  osmotic coefficients of, 219, 220, 223
  solubility of, 247, 250, 262
  water activity, 225, 226
electron affinity, 11, 14–16
electron capture, 11
electrospray, 26
electrostriction, 37, 38, 44–9, 202, 236,
  272, 278
Subject Index

enthalpy see hydration of ions; ions, aqueous; ions, formation; ion solvation; ion transfer; pair interactions; solvents
enthalpy-entropy compensation, 194, 264
entropy see hydration of ions; ion clusters; ion solvation; ion transfer; ions; ions, bare; ions, structural; water, structural
expansibility see ions, aqueous; solvents
extrathermodynamic assumption, 38, 39, 43, 255, 256
TATB/TPTB, 39, 43, 194, 215, 247, 255, 256

Gibbs energy see activation; hydration of ions; ion clusters; ion solvation; ion transfer; ions, aqueous; ions, formation
Grotthus mechanism, 204

heat capacity see ions, aqueous; ions, bare; ions, formation; ion transfer; solvents; water, structural
heat capacity of interaction, 200, 201
heat conductivity see solvents
Hofmeister series of ions, 269–75
hydration (solvation) number, 223–7
concentration dependence of, 225–7
hydration numbers, from bulk properties, 141, 143–6
from computer simulations, 139, 141, 142
from diffraction of x-rays, neutrons, 138–40
hydration of ions, absolute values of, 109, 119
Born equation for, 111
cavity formation for, 110, 112, 200, 274
conventional values of, 109, 119
dielectric saturation, 111
electrostatic interactions, 110–112
enthalpy of, 113–17
entropy of, 113–16
Gibbs energy of, 109, 110, 113–15, 118, 261
hydrometallurgical processes, 257–9
hydrophilic/hydrophobic balance, 262, 274, 275

ion association, Bjerrum electrostatic theory, 230, 232, 234
Eigen–Tamms mechanism of, 227, 229, 234
ion aggregates, 237–9
methodology for, 232–4
solvent release on, 234–7
triple ion formation, 237, 238
volume change of, 234, 236
water structure enforced, 229
ion clusters, 134, 135
formation, entropy of, 26
solvation, Gibbs energy of, 26, 28
ion effects on solvent dynamics, 171–4
ion exchange equilibria, 261
ion pairing, 227, 233–6, 261
ion pairs, contact (CIP), 227, 233, 234, 236
neutral, activity coefficients of, 230, 231
solvent separated (2SIP), 227, 233, 234, 236
solvent shared (SIP), 227, 233, 234, 236
ion solvation, enthalpy of, 29
ion transfer, enthalpy of, 126–9, 194, 196–8
entropy of, 130–131, 194, 196–8
extrathermodynamic assumption, 117–21, 126, 127, 130
Gibbs energy of, 118, 121–6, 194–6, 206, 210–213, 253–5, 259, 261, 264
heat capacity of, 130, 132, 133
thermodynamics of, 117, 121–7
volume of, 133–5
ionic activity coefficient, conventional, 252, 253
ion-ion interactions, 219–39
ionization, 11
ionization potential, 11–16
ions, absolute properties of, 36–39, 43, 45
acid/base properties of, 151, 152
aqueous, compressibility of, 46–9
cconductivity of, 49–54
dielectric decrements of, 55–7
dielectric saturation of, 111
electrostatic interactions of, 110–112
enthalpy of, 113–17
entropy of, 113–16
Gibbs energy of, 109, 110, 113–15, 118, 261
hydrometallurgical processes, 257–9
hydrophilic/hydrophobic balance, 262, 274, 275
ions, absolute properties of (cont’d)
  NMR relaxation of, 52–5
  self-diffusion of, 50–54
  surface potentials of, 56–8
  surface tension of, 50, 57
  water rotation times of, 55
ions, association of, 227–39
ions, bare, 10–25
  entropy of, 17–20
  heat capacity of, 17–20
ions, chaotropic/cosmotropic, 156, 163,
  269, 270, 275
clusters of, 10, 26-29
conduction of, 49–54, 181, 182,
  203, 204
conventional properties of, 36, 43,
  45, 55
coordination number of, 30, 136, 139
correlation volume near, 213
derhydration of, 273
dielectric relaxation of, 158, 159, 162,
  171, 176–8
diffusion of, 147, 150
dispersion forces, 274
electric self-energy of, 21, 111
field strength of, 37, 38, 44, 49
formation, enthalpy of, 11, 17–20
  Gibbs energy of, 11, 17–20, 26
globular, 20, 30
homo-/hetero-solvation, 193, 214
hydrodynamic radius of, 181
isolated, 10–25
iso-solvation point of, 207, 208
local solvent composition, 205–16, 263
lyotropic numbers of, 269
magnetic susceptibility of, 21–5
molar mass of, 11–13
molar refractivity of, 271
NMR relaxation of, 158, 159, 171, 178
orientation correlation times of, 186
pair correlation function of, 136, 137
polarizability of, 21–5, 58, 274
preferential solvation of, 193, 202,
  205–16, 247, 262, 263
  constant, 206, 207
  IKBI method, 213–15, 263
  QLQC method, 211–13, 263
  parameter, 206, 213, 216
  radius of, 30, 32–4, 58
salting-in by, 239, 240, 242, 244, 270, 276
salting-out by, 231, 239–44, 258,
  270–272, 276
selective solvation of, 193, 203, 208, 259
size of, 30–35
softness/hardness of, 21–5, 58
solvation number of, 35, 136–8, 147–9
solvent exchange near, 150, 265
specific effects of, 269, 270, 275
spectroscopic properties of, 205–10
stepwise solvent replacement near, 206,
  213, 215
structural entropy, 273
viscosity B-coefficients of, 45, 51–4,
  157–9, 168, 181, 183, 184, 203, 275
volume of, 30–34, 201, 202
volume, intrinsic, 31–5, 48, 49, 227,
  231, 242
water release rate from, 150
water residence times near, 150
water structure breaking/making, 54, 55,
  58, 156–74, 177, 179, 180, 229,
  269, 270, 275
linear solvation energy relationship
  (LSER), 81, 82, 121, 264
liquid junction potential, negligible, 251–6
molten hydrated salt, 31
nuclear fuel reprocessing, 257, 258
nucleophilic substitution, bimolecular, 264
octanol/water partition coefficient, 243, 262
osmotic coefficients see electrolytes; water
pair interaction enthalpy, 199, 200
permittivity see solvents; solvents, mixed
  aqueous
pH scale, 251–4
pH, ion effects on, 274
polyions, 10, 239
protein hydration, 277–9
proton affinity, 11, 14–16
PUREX process, 257
reaction rate, ion effects on, 264–9
reference redox couple, 255, 256
restricted primitive model, 35, 206
Setchenow constant, 239, 240, 276
solute, chemical potential of, 107, 108
solvation, standard quantities of, 108, 109
the process of, 107–9
solvatochromic index, $AN$, 82
$DN$, 82, 83, 208, 262
$E$, 81–3, 101–3, 262, 265
Kamlet-Taft $\alpha$, 82, 101–3
Kamlet-Taft $\beta$, 82, 101–3
Kamlet-Taft $\pi^*$, 82, 83, 101–3, 243
$Z$, 83
solvatochromic probes, 80, 81
solvatochromic scales, 81–3, 101–3
solvent accessible surface, 277
solvent criteria for use in batteries, 249
solvent dynamics, computer simulations of, 170–174, 180
solvents, acceptor properties of, 77, 260, 268, 269
acidity/basicity of, 86–8, 103, 104
anion affinity for, 213
autoprotolysis of, 86–8
boiling points of, 64, 66
cohesive energy density of, 77
compressibility of, 64, 67, 68, 77, 79
conductivity of, 75, 76
Debye-Hückel slope of, 73–5
density of, 64, 67
dipole moment of, 71, 72, 80, 83
dipole orientation correlation of, 78–80
donor properties of, 77, 208, 262
electrochemical window of, 90
electron pair acceptance of, 82, 84, 85
electron pair donicity of, 82–4, 101
enthalpy of vaporization of, 69, 70, 75
temperature of vaporization of, 79
expansibility of, 64, 66, 67
fluidity of, 75, 76
free volume of, 68, 75, 78, 79
freezing points of, 64, 66
heat capacity of, 69, 77–9
heat conductance of, 77
hydrogen bond acceptance of, 82–4
hydrogen bond donicity of, 82, 84, 85
hydrogen bonded, 80
internal pressure of, 77, 168, 169
intrinsic volume of, 67, 68
ion conductivities in, 181, 182
ionic dielectric decrements in, 184, 185
ionic surface tension de-/increments in, 185, 273
lipophilicity/hydrophobicity of, 88, 89
liquid range of, 64
magnetic susceptibility of, 73–5
miscibility with water, 88, 89
solvents, mixed aqueous, 90–104
acid/base properties of, 103, 104
activity coefficients of, 93
excess thermodynamic functions of, 92–5
internal pressure of, 99
microheterogeneity, 100, 101, 103
molar electrostriction of, 73–5
molar volume of, 66, 67
openness of, 78
order of, 78, 79
partial molar quantities of, 92, 93
permittivity of, 70–5, 96–8, 268, 269
polarity of, 81–3, 101
polarizability of, 71, 72
preferential solvation in, 99–101
protogenic, 80, 84, 86
proton affinity of, 86, 87
refractive index of, 71, 72, 98
self-association of, 77
self-diffusion of, 75, 76
softness/hardness of, 77, 82, 85, 86
softness index $\mu$ of, 82
solubility parameter of, 69, 70, 77, 81, 243
source for ion transfer, 194
stiffness of, 77, 78
structuredness of, 77–9, 98–100
surface potential of, 72, 73, 75, 273
surface tension of, 69, 70, 94–8
transparency window of, 90, 91
UV cutoff of, 90
van der Waals volume of, 68
vapor pressure of, 69, 70, 93
viscosity of, 75, 76, 96–8
water structure enhancement, 99, 100
solvolytic, unimolecular, 264
structure see ion association; ions; solvents, mixed aqueous; water
supercapacitors, 248, 250, 259
power delivery of, 248, 250
surface tension see ions, aqueous; ionic; solvents, mixed aqueous; solvents; surfactants, 239

Tait expression, 67

viscosity see ions; solvents, mixed aqueous
volume see activation; ion association; ions; ion transfer; ions, aqueous; ions, correlation; ions, intrinsic; solvents; solvents, free; solvents, intrinsic; solvents, van der Waals

Walden product, 203, 204
Walden’s rule, 181
water structure enhancement by co-solvent, 199

water
  activity of see electrolytes
  hydrogen bond lifetime in, 278
  hydrogen bonding in, 276
  internal pressure of, 168, 169
  mean residence times near ions, 171–4
  osmotic coefficients, 170
  rate of release from ions, 174
  reorientation times, 158, 160
  self-diffusion of, 156–8
  “slow”, 159, 175–8
  structural entropy of, 163–8
  structural heat capacity of, 165–7
  structural temperature of, 169, 170
  vibrational spectroscopy of, 160–162, 170, 171, 186
  x-ray absorption/scattering by, 162, 163
  x-ray, neutron scattering, 277
  x-rays see also hydration numbers; water
  zwitterions, 231