Index

A
Abel-Ruffini theorem 291
Acrivos, perturbation theory 393
activation energy
– apparent 150, 275
– catalytic oscillators 250
– changes 296–297
– definition 147, 409
– single-route linear mechanisms 157–158
active center, definition 409
active site
– definition 409
– kinetic monitoring 355
– types 73
active zone
– concentration 364–366
– uniformity 327
adsorbed-layer models
– critical phenomena 217
– non-ideal 403
adsorbed species, lateral interaction 262
adsorption, irreversible 342–343
adsorption mechanisms 411, see also Langmuir mechanism
– catalytic oscillators 246
– parallel 237–244
– parallel and consecutive 217–218
– slow relaxation 240
– steady states 223
adsorption steps, reversibility 235
affinity forces 385
algebraic equations
– analysis of steady states 236
– quasi-steady-state approximation 278
alteration-degree scale 354
alternating oxidation-reduction, catalytic oscillations 250
ammonia synthesis, complex reaction routes 87
Amundson, mathematical chemical kinetics 392
apparent kinetic parameters 147–158
– activation energy 147, 150, 157–158
– partial reaction order 148–149, 151–156
apparent reaction order, definition 147
apparent time delays 357
applied kinetics, goal of 3
Aris, mathematical chemical kinetics 392
Arrhenius, classical chemical kinetics 386
Arrhenius parameters 139
astronomic time, definition 1, 409
asymptotic stability, definition 189
asymptotology 394
atomic composition, and linear algebra 72–76
autocatalytic reactions 212–213, 244–245
– definition 409
– models 245
autonomous rate oscillations 256
B
“bad-neighbors” problem 93–94
batch reactor
– consecutive reactions 41–46
– formal analysis of 38–46
– ideal 32–33
– irreversible reactions 38–39
– material balance 38–39, 42
– parallel reactions 41–46
– reversible reactions 39–41
– schematic representation 31
– with solid catalyst 35
Belousov-Zhabotinsky reaction 212
Bendixon see Poincare-Bendixon criterion
Berthelot, rate of reaction 385
Berzelius, catalysis 384

Published 2011 by WILEY-VCH Verlag GmbH & Co. KGaA
chemical time and intermediates, early history 383
chemical transformation rates 320
chemico-mathematical period 390
citric acid, nonlinear mechanisms 211
Clarke, application of graph theory to stability analysis 393
Clément, chemical time 383
clock time, definition 1, 409
closed reactors. see also batch reactor
– definition 29
closed systems
– definition 410
– relaxation in 183–186
"combinatorial catalysis" procedures, definition 3
common intermediates
– multi-route mechanisms 131–132
– single-route mechanisms 98
– two-route mechanisms 129–130
common steps
– multi-route mechanisms 132–134
– single-route mechanisms 98
– two-route mechanisms 129–130
complex balancing 260–261, 392
complex mechanisms, representation as graphs 94–103
complex reactions
– derivation of reaction rate 104–117
– detailed mechanism 79–88
– Horiuti numbers 79–85
– Horiuti rule for routes 86–88
– matrices and independent routes 86–88
– rate equation 284
– steady-state chemical kinetics 93–135
– two-step mechanism 86
complexity
– and chemical reactions 17–27
– decoding of 2
– definition 1
– killing of 4–6
– and linear algebra 71–88
– new paradigm 402–403
component segregation, principle of 170–171
computational fluid dynamics (CFD) 327
concentration
– definition 73
– parameter for reaction rate 146
– zone models 367
concentration gradients
– active zone 327
– in catalytic reactors 52–54
concentration polynomials, critical simplification 302
consecutive reactions
– distinguishing from parallel reactions 41–46
– ideal simple models 217–218
– material balance 42
continuous-flow reactors, schematic representation 31
continuous stirred-tank reactor (CSTR) 327. see also non-steady-state continuous stirred-tank reactor
– consumption rate 330
– ideal 33–34
– kinetic-model-free analysis 49–52
– material balance 33, 35
– nonisothermal 211
– schematic representation 31
– with solid catalyst 35–36
convectional pulse reactor, schematic representation 31
coupling reactions
– kinetic resistance 169
– three-step mechanism 123–124
– two-step mechanisms 151–155
Cramer’s rule, kinetic 104–111
critical phenomena 216–217, 256–262
– definition 410
– diversity 216–217
– heterogeneous catalysis 213–217
– heuristic interpretation 257
– multiplicity of steady states 217
– nonlinear mechanisms 211–213
– relationships 256–262
critical points, slow relaxation 254
critical simplification
– general understanding and application 309–310
– kinetic polynomials 301–310
– limitations 308–309
critical slowing down phenomenon, relaxation characteristics 268
critical stoichiometry 303
CSTR see continuous stirred-tank reactor
Cuvier, Georges 6
cycle characteristic
– definition 410
– kinetic polynomials 285
– vicinity of thermodynamic equilibrium 290
cycles
– with common intermediate 131–132
– with common step 132–134
cycles (Continued)
– with two common steps 134
– types of coupling 134–135
cyclohexane, dehydrogenation 276

D
Damköhler number
– first 34, 46
– second 57–58
Davy, catalysis 383
de Groot, irreversible thermodynamics 392
de Saint-Gilles, rate of reaction 385
dead volume 328
decoding of complexity 2
– future 401
– new paradigm 402–403
– past 383–401
Desormes, chemical time 383
desorption rate coefficient 343
detailed equilibrium 261
– definition 410
– principle of 183–186
detailed kinetics, goal of 3
detailed mechanism, definition 410
determinant, definition 70
diagnostics, of kinetic experiments 52–64
differential equations, qualitative theory of 187–189
differential plug-flow reactor, schematic representation 31
diffusion. see also Knudsen diffusion
– molecular 63–64
diffusional-geometrical parameter, multiple zone reactors 345
diffusional pulse reactor, schematic representation 31
diffusivity 63–64, 325
dimension, of kinetic parameters 25–26
Dirac delta function 339
direct problems, of kinetic modeling 160
Döbereiner, catalysis 383
dynamic-equilibrium mass-action-law 385
dynamics, nonlinear 211–272

E
edges, definition 93, 410
elementary reactions 258
– definition 19, 26, 410
– heterogeneous 21–22
– homogeneous 19–21
– and linear algebra 79–88
– and mass-action law 19–23
– rate expressions 22–23
elementary steps
– of chemical reactions 17–18
– definition 410
Eley-Rideal mechanism 84–85, 218, 257, 285–286
– complex balancing 261
– definition 410
– kinetic polynomials 285
– stoichiometric matrix 279
energy balance, external heat transfer 59
enzyme-catalyzed reaction, King-Altman equilibrium
– detailed 183–186
– thermodynamic 290–291
equilibrium cycles, kinetic polynomials 294–301
equilibrium point, definition 183–184
equilibrium subsystems 277
Ertl model 253, 258, 263
ethylene, catalytic oxidation 269
ethylene oxidation, pump-probe TAP experiments 333
Euler, graph theory 93
exchange reaction, catalytic oscillations 252
experimental diagnostics, of kinetic experiments 54–56
experimental tools, of kinetic experiments 403–405
external heat transfer, theoretical diagnostics 59–60
external mass transfer
– experimental test for 54–55
– theoretical diagnostics 57–58
external recirculation, thin-zone TAP reactor 346
external time, definition 1

F
fast catalytic processes 346
fast steps
– critical simplification 309
– equilibrium approximation 198
– parameter for reaction rate 142–143
Feinberg, optimization problems 392
first-order reaction. see also unimolecular reaction
– definition 19
five-step mechanisms 126–127, 163
flux, three-zone TAP-reactor 361
four-color theorem 93
four-factor overall reaction rate equation 291
four-step mechanisms 163
  – single-route 124–126
Fourier transform, Y procedure 364
Frank-Kamenetskii, mathematical chemical kinetics 392
free active site concentration 248
Fulhame, chemical time 383
furan oxidation, state-by-state kinetic monitoring 350–358

G
“gas-catalyst” coefficient 349
gas-solid interactions 321
global dynamics, analysis of 195–197
global stability, concept of 187
global transfer matrix equation 358
goals, of this book 6–7
Gol’dshein, model reduction 394
Gorban, decoding complex kinetic behavior 393
gradients
  – in catalytic reactors 52–54
  – guidelines for minimizing 56
graph, definition 410
graph recipe, steady-state kinetic equations for single-route mechanism 118
graph theory. see also chemical graphs
  – history 393
  – introduction to 93–94
  – number of independent cycles and Horiiuti’s rule 100–103
  – representation of complex mechanisms 94–103
  – single-route mechanisms 95–98
  – two-route mechanisms 98–100
“gray-box” approach, of killing complexity 4–5
guidelines, for minimizing temperature and concentration gradients 56
Guldberg, mass-action law 385

H
heat, generation and removal 211
heat transfer, theoretical diagnostics 59–60
heat transport, theoretical diagnostics 64
Heineken, Michaelis-Menten model 393
heterogeneous catalysis 328
  – active center 409
  – decoding of 2, 11
  – diagnostics of kinetic experiments 52–64
  – isothermal critical effects 213–217
  – kinetics 389
  – and mass-action law 21–22
  – reaction rate 23, 215–216
  – self-sustained oscillations 215
heuristic interpretation, critical kinetic phenomena 257
n-hexane, catalytic reforming 101–103
hidden reversible steps 263
Higgins, chemical time 383
high vacuum 319
Hinshelwood, theory of chain reactions 389
homogeneous reactions
  – kinetic parameters 25–26
  – and mass-action law 19–21
Horiuti
  – complexity and simplicity 388–389
  – mathematical chemical kinetics 392
Horiuti-Boreskov problem 114–115
Horiuti matrix 278
  – Eley-Rideal mechanism 280
Horiuti numbers
  – and complex reactions 79–85
  – definition 410
Horiuti rules
  – for complex reaction routes 86–88
  – determination of number of reaction routes 88
  – and graph theory 100–103
  – single-route mechanism 82
Horn, optimization problems 392
Horn-Jackson-Feinberg mechanism 258–262
  – complex balancing 261
Hougen-Watson (HW) equation 276
HW see Hougen-Watson
hydrogen oxidation 98, 126, 257
  – detailed mechanism 80
  – elementary steps 18
  – kinetic resistance 168–169
  – reaction rate 255
  – single-route mechanisms 97
hydrogenation, liquid-phase 97
hypergeometric functions, thermodynamic branch 291
hysteresis
  – autocatalytic models 249
  – critical phenomena 216
  – multiplicity of steady states 214
  – simple models 227
hysteresis thermodynamics 304

I
ideal models, assumptions 403
ideal reactors 32–49
  – batch reactor (see batch reactor)
  – continuous stirred-tank reactor 33–36
ideal reactors (Continued)
– formal analysis of 38–49
– gradients on reactor scale 52–54
– plug-flow reactor 34–36
– pulse reactor 37
– with solid catalyst 35–37
– steady-state plug-flow reactor 46
– thin-zone TAP reactor 48–49
ideal simple models
– dynamics 237–256
– steady state 217–237
impact mechanism. see also Eley-Rideal mechanism
– consumption rate 228–229
– definition 411
– formation rate 228–229
– ideal simple models 218–221
– reaction reversibility 227
– steady-state kinetic dependence 221
– steady-state values 228
independent cycles, and graph theory 100–103
intermediates. see also common intermediates
– competition 233–237
– definition 73
– early history 383
– interaction mechanisms 256–258
– reaction acceleration 275
internal heat transport, theoretical
diagnostics 64
internal mass transport
– experimental test for 55
– theoretical diagnostics 60–64
internal steady states
– parallel adsorption mechanism 221–222
– uniqueness 233
internal time, definition 410
interphase gradients, in catalytic reactors 52–54
interrogative cycle 322
interrogative kinetics 329, 357–358
– definition 411
– strategy 350–358
intrapellet gradients, in catalytic reactors 52–54
intrinsic chemical kinetics, definition 56
intrinsic time, definition 1, 410
inverse problems, of kinetic modeling 160
irreversibility, definition 411
irreversible adsorption/reaction, quantitative
TAP data description 342
irreversible adsorption steps, reaction orders 234
irreversible isomerization reaction, relaxation 182–183
irreversible reactions 342–343
– two-step mechanisms 148–150
irreversible steps, parameter for reaction rate 145–146
isomerization reaction
– graph 96
– kinetic resistance 170
– linear relaxation 177–179
– mechanism 81
– model 116
– number of identifiable parameters 139–142
– relaxation 182–183
– temperature dependence 139–142
isothermal critical effects 213–217
isothermal TAP reactor 342
isothermicity, as experimental requirement 29–30
isotopic step-response experiments 329
IUPAC Gold Book, definition of elementary reaction 19, 26
Ivanova, relationship between stability and reaction mechanisms 393

J
Jackson, complex balancing 392

K
Kaganovich, chemico-geometric approach 394
Karlin, model reduction 394
key components
– linear algebra 74–76
– number of 74–76, 79
key overall reactions, number of 78
key reactions, number of 79
Khudyayev, stability for a subsystem of intermediates 393
kinetic characteristics, observed 328–329
kinetic characterization 320
kinetic coefficients
– overview 351–353
– TAP pulse-response data 349
kinetic complexity 388
– kinetic coupling, definition 410
– derivation of steady-state kinetic equations 129–135
– types 134–135
kinetic Cramer’s rule, and trees of chemical graphs 104–111
Index

kinetic dependences
– fine structure 254–256
– multiplicity of steady states 214
– three-dimensional 225
– water-gas shift reaction 295

kinetic experiments
– classification of reactors 31
– concepts and realizations 29–64
– diagnostics of 52–64
– experimental requirements 29–30
– formal analysis of reactors 38–49
– kinetic-model-free analysis 49–52
– material balances 30–31

kinetic fingerprints, analysis of 5–6
kinetic information, obtaining relevant 328–329
kinetic mass-conservation law 79
kinetic-model-free analysis 49–52
– non-steady state 51–52
– steady state 49–51
kinetic modeling, direct and inverse problems of 160
kinetic models
– complex balancing 261
– definition 3
kinetic monitoring 350–358
– exact mathematical solution 363–364
– numerical experiments 366–369
– oxidation of furan 350–358
– solution principles 360–363
– strategy 350–358
kinetic multiplicity 117
– critical simplification 305
kinetic parameters
– dimension of 25–26
– fast catalytic processes 346
– order of magnitude 25–26
kinetic phenomena, heuristic interpretation 257
kinetic polynomials 273
– classical approximations and simplifications 287–294
– consistency 284
– critical simplification 301–310
– cycles across an equilibrium 294–301
– definition 411
– derivation 281–287
– linear introduction 273–276
– mathematical basis 281–283
– order 285
– physically meaningful solutions 284
– properties 281–287
– rate-limiting step 288–290
– results of theory 294–301
– simplification 301–310
– steady-state approximation 278–281
– testing 295–301
– thermodynamic branch 291–294
– vicinity of thermodynamic equilibrium 290–291

kinetic regimes 302
kinetic resistance 113–114, 164–170, 275, 290, 294, 300
– coupling reaction 169
– definition 411
– hydrogen oxidation 168–169
– identifying and decoding mechanisms 165–166
– isomerization reaction 170
– and relaxation times 179–181
– SO2 oxidation 166–168
kinetic screening, non-steady-state 6
kinetic testing 295–301
kinetic tools, advanced experimental 403–405

kinetics. see also chemical kinetics
– applied 3
– intrinsic 56
– mathematical chemical 389–395
King-Altman graph, single-route enzyme-catalyzed reaction 95
King-Altman relationship 106–107
Knudsen diffusion 63, 319, 325
– definition 411
– irreversible adsorption/reaction 342
– one-zone reactor 338
– three-zone reactor 344–345
Königsberg, seven bridges of 93–94
Korzukhin, decoding of kinetic oscillations 392

L
Langmuir, paradigm of mechanism 388–389
Langmuir adsorption mechanism 84–85, 261, 276, 286–287
– critical simplification 301
– definition 409, 411
– kinetic parameters 273, 286
– quasi-steady-state approximation 280
Langmuir denominators 284
Langmuir-Hinshelwood (LH) rate equation 276
Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate equation 142, 164, 276
law of conservation, catalytic mechanisms 257
limitation principle see rate-limiting step
linear algebra
– and atomic composition of components 72–76
– basic elements 69–71
– in chemical kinetics 69–89
– and complexity of chemical reactions 71–88
– and elementary reactions 79–88
– key components 74–76
– and mass conservation laws 72–74
– and stoichiometry 76–79
linear and nonlinear relaxation 175–206
linear equations, definition 71
linear mechanisms 95, 257
– definition 411
linear relaxation, catalytic isomerization reaction 177–179
linearly independent reactions, number of 78
liquid-phase hydrogenation
– graph 96
– single-route mechanisms 97, 121–122
local stability
– concept of 187
– rigorous definition 190–191
– system with two variables 191–195
logic, of this book 7–8
Lomonosov, mathematical chemistry 391
Lorenz attractor 189
Lotka-Volterra equations, catalytic oscillators 244
Lyapunov function 196, 261, 394
– definition 411
Lyapunov stability, definition 189

M
Macaulay resultant 283
malonic acid (MA), nonlinear mechanisms 212
Marcelin-de Donder formalism 403
Mason’s rule 106–107
mass-action law 244, 385
– critical simplification 309
– definition 411
– and elementary reactions 19–23
– heterogeneous reactions 21–22
– homogeneous reactions 19–21
– quasi-steady-state approximation 278
– rate expressions 22–23
mass balances, reversible adsorption 343
mass-conservation laws
– kinetic 79
– and linear algebra 72–74
mass spectrometer, TAP 324
mass transfer
– catalytic oscillations 252
– experimental test for 54–55
– theoretical diagnostics 57–58
mass transport, theoretical diagnostics 60–64
material balance equation, conceptual 37
material balances
– batch reactor 38–39, 42
– consecutive and parallel reactions 42
– continuous stirred-tank reactor 33, 35
– kinetic experiments 30–31
– non-steady-state CSTR 46–47
– plug-flow reactor 34
mathematical chemical kinetics 389–395
mathematical chemistry 391
mathematical kinetics, goal of 4
matrices, and independent routes 86–88
matrix, definition 69–70
matrix determinant, definition 70
matrix rank, definition 71
Mazur, irreversible thermodynamics 392
MBS see molecular beam scattering
mechanism complexity, kinetic polynomials 274
mechanisms. see also specific types
– definition 2, 411
– as fundamental concept of chemical kinetics 18
– ideal simple models 218–221
– interpretation of multiplicity of steady states 221–227
– reaction reversibility 227
– from steady-state kinetic data 158–171
– structures 256–262
methane, steam reforming 100
methane-steam interaction, elementary steps 18
methanol conversion, single-pulse TAP experiments 332
Michaelis-Menten mechanism
– definition 411
– graph 96, 98, 119
microreactor 371
– experiments 320
microscopic reversibility, definition 411
minimal mechanisms 160–164
– definition 412
model-free kinetic data interpretation 329–330
model validity 367
modeling. see also kinetic modeling
– nonlinear mechanics 237
models
  – dynamics 237–256
  – relaxation of self-sustained oscillations 250
  – simple in nonlinear mechanics 217–237
molecular beam scattering (MBS) 319
molecular matrix, and linear algebra 72
molecularity
  – definition 412
  – rate-limiting step 289
moment-based quantitative description, TAP experiments 347–350
multi-route mechanisms
  – coupling types 134–135
  – cycles with common intermediate 131–132
  – cycles with common step 132–134
  – cycles with two common steps 134
  – derivation of steady-state kinetic equations 129–135
multi-zone TAP reactor 359
multiplicity, kinetic 117
multiplicity of steady states 213–215, 221–227
  – boundaries 229
  – definition 412
  – hysteresis 214
  – kinetic dependences 214
  – kinetic description 219
  – parallel adsorption mechanism 221
multipart TAP experiments 336–338
  – carbon monoxide oxidation 336
null clines 241–243
O
  one-zone reactor, quantitative TAP data description 338
  Onsager reciprocal relationships, discovery of 9–10
  open reactors, see also continuous-flow reactors
  – definition 29
  – open system, definition 412
  Oppenheim, perturbation theory 393
  Oregonator model 213
  – catalytic oscillators 245
  oscillators
    – catalytic 244
    – other catalytic 250–254
    – self-sustained 215–216
    – simplest catalytic 244–250
  Ostwald, catalysis 388
  overall reaction rates 275
  – nonlinear 284
  – rate-limiting step 289
  overall reactions
    – distinction to reaction routes 85
    – “natural” 116–118
    – reaction triangle 184
  oxidation-reduction, alternating 250–251
P
  packed-bed reactor 338
  parallel adsorption mechanisms 217–218
    – dynamic model 233
    – ideal simple models 217–218
    – multiplicity of steady states 221
    – pressure dependence 230–231
parallel adsorption mechanisms (Continued)
  – relaxation characteristics 237–244
  – steady states 234
  – temperature dependences 230–232
parallel reactions
  – distinguishing from consecutive reactions 41–46
  – material balance 42
parameter domain, autocatalytic models 247
parameters, kinetic 25–26
partial reaction order
  – definition 412
  – irreversible reactions 148–149
  – two-step mechanisms 151–156
particle diameter, reaction rate and 55
perturbation theory 393
PFR see plug-flow reactor
phase patterns, relaxation characteristics 268
phase portrait 237–240
  – definition 412
phase space 187, 237, 240–243, 249
  – definition 175, 412
phase trajectory 237, 240
  – definition 187, 412
physicochemical understanding, confusion ending 389
plug-flow reactor (PFR)
  – ideal 34–35
  – kinetic-model-free analysis 52
  – material balance 34
  – schematic representation 31
  – with solid catalyst 36
Poincaré-Bendixon criterion 196, 245
polynomials, kinetic 273. see also kinetic polynomials
Prater, first-order mass-action law systems 392
predator-prey equations 244
pressure gap 329, 403
Prigogine, autocatalytic reactions 213
principle of detailed equilibrium 183–186
probabilistic theory
  – experiments 371–372
  – single-particle TAP experiments 371–372
pseudo steady-state approximation
  (PSSA) see quasi steady-state approximation
pseudo-thermodynamic relationships 305
pulse-by-pulse experiments, interrogative kinetics 357–358
pulse reactor
  – schematic representation 31
  – with solid catalyst 37
pump-probe TAP experiments 321, 333–336
Q
QSSA see quasi steady-state approximation qualitative TAP data analysis 332–338
quantitative description, moment-based 347–350
quantitative TAP data description, theoretical analysis 338–350
quasi-equilibrated steps, parameter for reaction rate 144–145
quasi steady-state 389
quasi steady-state approximation (QSSA) 278
  – definition 412
  – kinetic polynomials 277
  – mathematical basis 278–281
  – non-steady-state models 200–206
R
radical, mathematical 413
radiophysics 244
rate see reaction rate
rate coefficient 217, 384–385
  – definition 20, 412
  – dimension of 25
  – rate-determining step (RDS) 308. see also rate-limiting step
rate equations 275
  – analysis 139–146
  – complex reaction 284
  – kinetic polynomials 274
  – semi-empirical 276
rate expressions, and mass-action law 22–23
rate-limiting step 308
  – definition 412
  – kinetic polynomials 288–290
  – non-steady-state models 199
  – parameter for reaction rate 143–144
rate oscillations, heterogeneous catalytic reactions 215
RDS see Rate-determining step reaction acceleration 275
reaction-diffusion parameter, multiple zone reactors 345
reaction enthalpy, definition 20
reaction mechanisms see mechanisms reaction order 234
  – definition 147
reaction rate 222, 226
  – bursts 255
  – catalytic mechanisms 256
  – concentration dependence 262
Index

- definition 19
- dependence on concentrations 146
- dependence on particle diameter 55
- derivation for complex reactions 104–117
- fast steps 142–143
- forward and reverse 111–112
- heterogeneous catalysis 23
- irreversible step(s) 145–146
- kinetic Cramer’s rule and trees of chemical graph 104–111
- kinetic equation for reverse reaction 114–115
- kinetic polynomials 281–283
- and net rate of production 23–24
- oscillations 249
- overall reaction 116–118
- parameters 139–142
- quasi-equilibrated steps 144–145
- rate-limiting steps 143–144
- reconstruction 364
- resultant 281–283
- self-sustained oscillations 215–216
- single polynomial 277
- thermodynamic oscillations 291–292
reaction rate approximation, rate-limiting step 288
reaction rate coefficients 337
reaction rate equation, thermodynamic branch 291
reaction reversibility, simple models 227–233
reaction routes. see also single-route mechanisms, two-route mechanisms
- complex reactions 86–88
- determination of number according to Horiuti rules 88
- distinction to overall reactions 85
- and matrices 86–88
- nonlinear and multiple 84
- number of 278
- rates along 279
reaction triangle, overall reactions 184
reaction weight 105
- definition 413
reactors. see also ideal reactors
- classification of 29, 31
- TAP configuration 345–347
- TAP data description 344–345
- transport in 32
relaxation
- in closed system 183–186
- linear 177–179
- linear and nonlinear 175–206
- models of self-sustained oscillations 250
- self-sustained oscillations 250
- types of 175–176
relaxation characteristics, parallel adsorption mechanism 237–244
relaxation oscillation 250
relaxation time, definition 413
residence time
- average 348
- definition 1, 413
- and steady-state reaction rate 179–183
resistance, kinetic. see kinetic resistance
rest points
- definition 188, 190
- types of 193
reversibility
- adsorption steps 235
- definition 413
- Horn-Jackson-Feinberg mechanism 260
- impact mechanism 227
- microscopic 411
- simple models 227–233
reversible adsorption, quantitative TAP data description 343
reversible steps, hidden 263
reversible surface phase transitions, catalytic oscillations 251
Richter, mathematical chemistry 391
S
Sayasov, stability for the subsystem of intermediates 393
SDC. see standard diffusion curve
second-order reaction. see also bimolecular reaction
- definition 19
secondary reactions, van’t Hoff 386
self-organization, catalytic oscillations 251
self-sustained oscillations 249
- chemistry 211
- nonlinear mechanisms 215–216
- relaxation 250
Semenov
- mathematical chemical kinetics 392
- theory of chain reactions 389
semi-empirical rate equation, kinetic polynomials 276
separatrices 237
seven bridges of Koenigsberg, graph theory 93–94
simple models
- competition 233–237
- dynamics 237–256
- steady state 217–237
simplest catalytic oscillator 244–250
simplest mechanism, interpretation of multiplicity of steady states 221–227
simplification, kinetic polynomials 287–294, 301–310
single-particle microreactor configuration, time analysis of products 324
single-particle TAP experiments, probabilistic theory 371–372
single-pulse TAP experiments 332–333
single-route irreversible mechanisms, apparent partial reaction order 156
single-route linear mechanisms
  – activation energy 157–158
  – general case 113–114
single-route mechanisms 82, 95–97. see also reaction routes
  – apparent partial reaction order 156
  – with buffer step 97–98
  – derivation of steady-state kinetic equations 118–128
  – five-step 126–127
  – four-step 124–126
  – graph recipe 118
  – kinetic polynomials 277
  – quasi-steady-state approximation 280
  – three-step 122–124
  – two-step 119–122
singular point see rest points
slow relaxation 240, 269
  – kinetic dependence fine structure 254
slowing down phenomenon, relaxation characteristics 268
small parameter, definition 413
SO2 oxidation
  – kinetic resistance 166–168
  – three-step mechanism 122–123
  – two-step mechanism 115
solid catalysts, in ideal reactors 35–37
space time, definition 413
spanning tree weight 108
  – definition 413
spanning trees 107–109
  – definition 413
sparse resultant 283
spatial self-organization, catalytic oscillations 251
SSITKA see steady-state isotopic transient kinetic analysis
stability, concept of 187–197
standard diffusion curve (SDC) 340
state-altering experiment
  – definition 413
  – time analysis of products 322
state-by-state kinetic monitoring, oxidation of furan 350–358
state-defining experiments
  – definition 413
  – multi-zone TAP reactor 359
  – time analysis of products 321
stationary point see rest points
steady-state approximation, kinetic polynomials 278–281
steady-state chemical kinetics 93–135
  – activation energy 147–158
  – analysis of rate equations 139–146
  – apparent kinetic parameters 147–158
  – graph theory 93–94
  – impact mechanism 221
  – machinery 139–171
  – parallel adsorption mechanism 230–232
  – reaction order 147–158
  – revealing mechanisms from 158–171 steady-state isotopic transient kinetic analysis (SSITKA) method 180, 322
steady-state kinetic equations
  – derivation for multi-route mechanisms 129–135
  – derivation for single-route mechanisms 118–128
  – graph recipe 118
steady-state model, physically meaningful solution 220
steady-state plug-flow reactor, formal analysis of see plug-flow reactor
steady-state points, autocatalytic models 247
steady-state rate equations, recipe for writing 110
steady-state reaction rates 225
  – kinetic polynomials 277
  – partial pressure dependency 226
  – pressure dependence 230–231
  – and relaxation times 179–183
steady-state reactors, definition 31
steady states
  – complex balancing 261
  – ideal simple models 217–237
  – impact mechanism 228
  – kinetic dependences 254
  – multiplicity 213–215, 221–227
  – nonlinear mechanics 211–272
  – stability 225
  – surface transformation 220
steam reforming of methane, graph 125
steps. see also common steps
  – fast 142–143
  – irreversible 145–146
– quasi-equilibrated 144–145
– rate-limiting 143–144
sticking coefficient 221
stoichiometric matrix 76–79, 259
– Eley-Rideal mechanism 279
– quasi-steady-state approximation 278
stoichiometric number. see also Horiuti numbers
– definition 410
stoichiometric matrix, rate-limiting step 289
stoichiometry, of chemical reactions 76–79
super-equilibrium 307
surface concentrations
– normalized 321
– steady states 223
surface coverage, definition 73–74, 414
surface intermediates
– adsorbed-layer models 218
– definition 73
– interaction 256
– kinetic polynomials 275
surface phase transitions, reversible 251
surface structure rearrangement 252–253
surface transformation dynamics 236

T
TAP. see also temporal analysis of products
TAP data analysis, qualitative 332–338
TAP data description, quantitative 338–350
TAP experiments 321–322
– dead volume 328
– moment-based quantitative description 347–350
– multipulse 336–338
– pump-probe 333–336
– single-particle 371–372
– single-pulse 332–333
TAP pulse-response data 349
TAP reactor 327
– description and operation 322–324
– schematic representation 31
– thin-zone 345–347
– three-zone 344–345, 360
– two-zone 344–345
– Y procedure 361
Taylor, concept of the active site 390
Temkin, theory of steady-state catalytic reactions 389–390
Temkin-Boudart mechanism 82, 273
– two-step 155, 157
Temkin’s rule, relaxation times 181–183
temperature gradients, in catalytic reactors 52–54
temperature-programmed desorption (TPD) 322
temperature-programmed reduction (TPR) 322
temporal analysis of products 327–328, 403, see also TAP
– basic principles 324–326
– definition 6
– domain of conditions 327–328
– position among other kinetic methods 326–332
– principles, applications and theory 319–383
temporal self-organization, catalytic oscillations 251
termolecular reaction. see also third-order reaction
– definition 19
theoretical diagnostics, of kinetic experiments 56–64
theoretical frontiers, TAP 358–372
thermodynamic branch, kinetic polynomials 291–294
thermodynamic equilibrium 275
– kinetic polynomials 287, 290–291
Thiele modulus 60–61
thin-zone activity parameter 366
thin-zone configuration, temporal analysis of products 323
thin-zone TAP reactor (TZTR) 345
– configuration 345–347
– formal analysis of 48–49
– net rate of production 37
– numerical experiments 366
– schematic representation 31
third-order reaction. see also termolecular reaction
– definition 19
three-step adsorption mechanism
– catalytic oscillators 244
– kinetic polynomials 273
three-step irreversible isomerization reaction, relaxation 183
three-step mechanisms 161–162
– single-route 122–124
three-zone TAP reactors
– configuration 323
– solution principles 360
– TAP data description 344–345
Tikhonov, perturbation theory 393
time
– in chemistry 383
– meanings of 1
time-of-flight mass spectrometer 323