Instrumental Methods of Analysis

Sixth Edition

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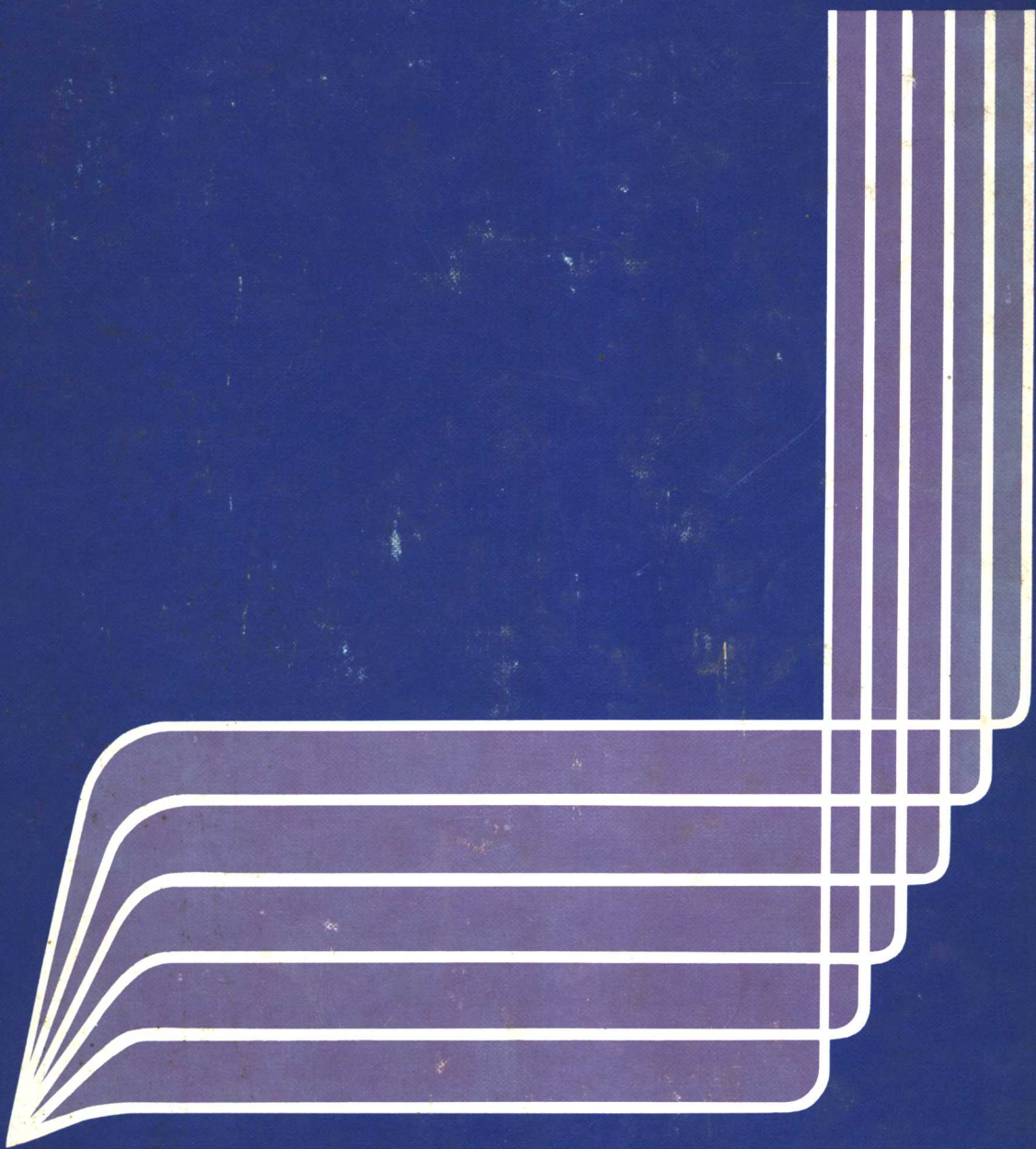

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Preface

Shortly after the publication of the Fifth Edition, our senior author, Dr. Hobart H. Willard, died. Dr. Willard was one of the pioneers in the establishment of courses in instrumental methods of analysis and was the instigator of this textbook. We sorely miss his wise counsel and guidance.

The Sixth Edition welcomes a new, younger co-author, Frank Settle. Dr. Settle is qualified by teaching and research experience in instrumental analysis, especially the electronic and instrumental design aspects, and he has completely rewritten these sections. The Sixth Edition contains five new or completely rewritten chapters entitled "Electronics: Fundamentals of Solid State Design," "Electronics: Commonly Used Signal Modifying Circuits," "Data Handling," "Computer-Aided Analysis," and "Process Instruments and Automatic Analysis."

The use of chromatographic methods of analysis has burgeoned since the last edition was published. Accordingly, the chapter on gas chromatography has been expanded from a single chapter to four chapters covering the general principles of chromatography, gas chromatography, liquid column chromatography instrumentation and methods, and high-performance liquid chromatography methods.

An entirely new chapter on the chemical analysis of surfaces is included in the Sixth Edition. The chapter departs somewhat from the approach of other chapters in that most other chapters describe specific methods and their application to many substances or their use in many situations. This new chapter describes the application of various methods, such as surface spectroscopy, sputter-etching, ion-scattering spectrometry, secondary ion mass spectrometry, ion microprobe mass analysis, Auger emission spectroscopy, and electron spectroscopy for chemical analysis to the specific task of characterization and analysis of surfaces.

An introduction to absorption and emission spectroscopy has been added. This chapter describes some relationships among representative optical phenomena that produce signals with chemical information. It gathers together many of the fundamental laws and principles that were previously dispersed in several chapters.

Some materials were consolidated or eliminated in order to accommodate the new content. Detectors for X rays and radioactivity are now gathered together in the chapter on X-ray methods. The discussion of refractometry and interferometry, methods that are not so widely used now, are shortened and combined into one chapter with polarimetry, circular dichroism, and optical rotatory dispersion. Separations by electrolysis and coulometric methods are combined into a single chapter since these methods have much in common. Voltammetry and amperometric titrations are also combined.

The sequence of the chapters in the Sixth Edition is somewhat changed to achieve a more logical order. Individual chapters are designed, in general, to stand alone, so that the order of presentation is not critical. Instructors may select materials for several levels of

achievement and to suit their preferences for order of presentation. References to the literature and collateral readings are included in each chapter. The book should also be suitable as a reference.

Numerous examples are incorporated into the text, including those illustrating mathematical operations. These examples introduce the student to the units of measurement and reduce or eliminate dependence upon additional problem books. There are, in addition, a large number of problems at the end of most chapters. Selected answers are given separately at the end of the text. Many of these problems contain data that would be obtained in laboratory experiments and are thus of particular value for those unable to furnish equipment for specific areas of instrumentation, for supplementing experiments when laboratory periods are limited, or for self-study. An Instructor's Solutions Manual that provides solved problems is available from the publisher.

The experiments formerly included at the ends of the chapters have been collected together at the back of this edition. Some of the experiments are described in considerable detail for use by less experienced undergraduate students. Others are merely sketched outlines or suggestions for work to give instructors in advanced courses flexibility in eliciting from students a degree of independence and originality in the outline and execution of experimental work.

The Sixth Edition presents, as did the previous editions, a comprehensive overview of the field of instrumental analysis as commonly practiced today. We remain convinced that all chemistry students and, indeed, students in many of the other physical and biological sciences, will benefit from a comprehensive course reviewing the major methods available with a discussion of the basic principles, advantages and disadvantages, limitations, and applicability of each method. In their later work, the students should then be able to select the best method or a limited number of methods that will solve their immediate problem. The references contained herein will then lead them to more detailed and advanced discussions of the method or methods selected.

Separate listings of abbreviations and symbols are included in the front of the book. Whenever available, recommendations of concerned nomenclature commissions have been followed. In addition, the Appendixes provide a comprehensive tabulation of oxidation-reduction potentials in aqueous solution, polarographic half-wave potentials and diffusion-current constants, acid dissociation constants, formation constants of some metal complexes, flame emission and atomic absorption spectra, a conversion table involving values of absorbance for percent absorption, and a wavenumber-wavelength conversion table. A four-place table of common logarithms, a table of 1971 atomic weights, and a periodic chart of the elements facilitate computations and provide ready reference data.

The authors remain greatly indebted to the manufacturers who have generously furnished schematic diagrams, photographs, and technical information of their instruments. We would like to thank the following reviewers for their helpful comments: Arno Heyn, Boston University; George Morrison, Cornell University; Stanford Tackett, Indiana University of Pennsylvania; and Thomas Copeland, Northeastern University. Thanks are expressed also to many colleagues who have kindly helped with suggestions and improvements.

Lynne L. Merritt, Jr.
John A. Dean
Frank A. Settle, Jr.

Abbreviations

absorption	Abs
alpha particle	α
alternating current	ac
American Society for Testing Materials	A.S.T.M.
American standard code for information interchange	ASCII
ampere	A
analog-to-digital converter	ADC, A/D
angstrom	Å
anodic	anod, a (subscript)
aqueous	*aq*
Association of Official Analytical Chemists	A.O.A.C.
atmosphere	atm
atomic absorption spectrometry	AAS
atomic emission spectroscopy	AES
atomic fluorescence spectrometry	AFS
atomic weight	at. wt.
attenuated total reflectance	ATR
Auger electron spectroscopy	AES
back scatter	BS
barn (10^{-24} cm^2)	b
beta particle	β
binary coded decimal	BCD
boiling point	bp
calorie	cal
capacitance	C
cathode ray tube	CRT
cathodic	cath, c (subscript)
centi- (prefix) (10^{-2})	c-
centimeter	cm
centipoise	cP
central processing unit	CPU
circa	*ca.*
citrate	Cit
complementary metal oxide semiconductor	CMOS

Compton edge	CE
conductance	$1/R$
coulomb	C
counts per minute (second)	cpm (cps)
cubic centimeter	cm^3
curie	Ci
cycles per second (hertz)	Hz
cylindrical mirror analyzer	CMA
decibel	dB
degree Celsius	$^\circ C$
degree Kelvin	$^\circ K$
deuteron	d
diameter	diam
differential scanning calorimeter	DSC
differential thermal analysis	DTA
digital-to-analog converter	DAC, D/A
digital voltmeter	DVM
dilution value of pH buffer	$\Delta pH_{1/2}$
diode transistor logic	DTL
direct current	dc
direct digital control	DDC
direct memory access	DMA
disintegrations per minute (second)	dpm (dps)
dropping mercury electrode	dme, de (subscript)
dual-in-line package	DIP
dyne	dyn
effective aperture ratio	*f*/number
electromotive force	emf
electron	e, e^-
electron capture detector	ECD
electron spectroscopy for chemical analysis	ESCA
electron spin resonance	ESR
electron volt	eV
equivalent weight	equiv wt
erasable programmable read-only memory	EPROM
et alii (and others)	*et al.*
ethyl	Et
ethylenediamine-*N,N,N',N'*-tetraacetate	EDTA, Y^{4-}
exclusion chromatography	EC
exempli gratia (for example)	e.g.
exponential	exp
external	ext
farad	f
fast Fourier transformation	FFT
field-effect transistor	FET

flame emission spectroscopy	FES
flame ionization detector	FID
flame photometric detector	FPD
formal (concentration)	*F*
Fourier transformation	FT
frequency	f
full width at half maximum	FWHM
gamma radiation	γ
gas (physical state)	*g*
gas chromatography	GC
gas chromatography/mass spectrometry	GC/MS
gas–liquid chromatography	GLC
gas–solid chromatography	GSC
gauss	G
Geiger–Müller	GM
geminal	*gem*
gram	g
hertz	Hz
hierarchial distributed control	HDC
high-performance liquid chromatography	HPLC
hour	hr
id est (that is)	i.e.
inch	in.
indicator	ind
inductance	L
induction coupled (argon) plasma	ICAP, ICP
infrared	ir
input/output	I/O
inside diameter	i.d.
integrated circuit	IC
integrated injection logic	IIL
internal	int
International Union of Pure and Applied Chemistry	IUPAC
ion-exchange chromatography	IEC
ion microprobe mass analyzer	IMMA
ion scattering spectroscopy	ISS
joule	J
kilo- (prefix) (10^3)	k-
kilocalorie	kcal
Kovats retention index	R.I.
large-scale integration	LSI
least significant bit	LSB
light emitting diode	LED
limiting	lim
liquid (physical state)	liq, l

liquid chromatography	LC
liquid chromatography/mass spectrometry	LC/MS
liquid–liquid (partition) chromatography	LLC
liquid–solid (adsorption) chromatography	LSC
liter	liter (alone), l (with prefixes)
logarithm (common or Briggsian or decadic)	log
logarithm (natural or Naperian)	ln
logical AND operation in Boolean algebra	• (center dot)
logical OR operation in Boolean algebra	+
lumen	lm
mass spectrometer	MS
maximum	max
medium-scale integration	MSI
mega- (prefix) (10^6)	M-
meta-	*m*-
metal oxide semiconductor	MOS
metastable (state)	m,m^*
meter	m
methyl	Me
micro- (prefix) (10^{-6})	μ-
micrometer (micron)	μm
microsecond	μsec
milli- (prefix) (10^{-3})	m-
milliampere	mA
milliequivalent	mequiv
milliliter	ml
millimole	mM
million electron volts	MeV
minimum	min
minute	min
molar (concentration)	*M*
mole	mol
molecular weight	mol wt
monolayer	ML
most significant bit	MSB
multiple internal reflectance	MIR
nano- (prefix) (10^{-9})	n-
nanometer (millimicron)	nm
Naperian base	*e*
negative	neg
nephelometric turbidity unit	NTU
neutron	*n*
normal (concentration)	*N*
normal (alkyl chain)	*n*-
not AND (results of AND operation negated)	NAND

not OR (results of OR operation negated)	NOR
nuclear magnetic resonance	NMR
numerical aperture	NA
ohm	Ω
operational amplifier	op amp
optical speed	*f*/number
optimum	opt
ortho-	*o*-
outside diameter	o.d.
oxidant	ox
oxide semiconductor field-effect transistor (MOSFET without metal gate)	OSFET
page(s)	p. (pp.)
para-	*p*-
parent ion	M
particle-induced X-ray emission	PIXE
parts per billion, volume	ppb, ng/ml
parts per billion, weight	ppb, ng/g
parts per million, volume	ppm, μg/ml
parts per million, weight	ppm, μg/g
pascal	Pa
percent	%
phenyl	ϕ
photoionization detector	PID
pico- (prefix) (10^{-12})	p-
positive	pos
positron	β^+
potential	*E*
programmable read-only memory	PROM
propyl	Pr
proton	*p*
proton magnetic resonance	PMR
quantum (energy)	$h\nu$
quantum efficiency	QE
radian	rad
radio frequency	rf
random access memory	RAM
read-only memory	ROM
reciprocal ohm	mho, Ω^{-1}
reductant	red
reference	ref
reset–set	R–S
resistance	*R*
reverse phase–ion pair partition	RP–IPP
revolutions per minute	rpm
sample and hold	*S/H*
saturated	satd

saturated calomel electrode	SCE
scanning Auger microprobe	SAM
scanning electron microscopy	SEM
second	sec
secondary ion mass spectrometry	SIMS
sigma	σ
small-scale integration	SSI
solid (physical state)	*s*
solvent (general)	S
specific gravity	sp gr
standard hydrogen electrode	SHE, NHE
standard temperature and pressure	STP
surface coated open tubular (column)	SCOT
Système International	SI
tesla	T
temperature	*T*, temp
tertiary	*tert-*, *t-*
tetramethylsilane	TMS
thermal conductivity detector	TCD
thermal gravimetry	TG
thermionic emission detector	TED
thermomechanical analysis	TMA
thousand electron volts	keV
torr (mm of mercury)	torr
transistor–resistor logic	TRL
transistor–transistor logic	TTL
tritium	t, ^{3}H
ultraviolet	uv
universal asynchronous receiver transmitter	UART
vacuum	vac
vacuum-tube voltmeter	VTVM
versus	vs.
very large-scale integration	VLSI
volt	V
volume	vol, *V*
volume per volume	v/v
volume per weight	v/w
wall coated open tubular (column)	WCOT
watt	W
wave number	cm^{-1}
X-ray absorption edge	*K* edge, L_I edge
X-ray absorption level	*K*, L_I
X-ray emission lines	$K\alpha$, $K\beta$, $L\alpha$
X-ray energy spectrometry	XES
year	yr

Symbols

A	absorbance; activity (radiochemistry); area; atomic weight
A_o	amplifier gain
a	specific absorptivity
a_i	hyperfine coupling constant (ESR)
a_x	activity of species x
AF	asymmetry factor
B	source brightness
b	distance; grating constant; optical path length; thickness
C	concentration
C_M	concentration of solute in mobile phase
C_S	concentration of solute in stationary phase
c	velocity of light in a vacuum
D	dielectric constant; diffusion coefficient
D_M	diffusion coefficient in mobile phase
D_S	diffusion coefficient in stationary phase
D^{-1}	linear reciprocal dispersion
D_c	concentration distribution ratio
d	diameter; distance; spacing
d_c	diameter of collimating mirror; cross section or column bore
d_f	effective thickness of stationary phase
d_p	particle diameter
E	electrode potential; energy of a photon; potential of half-reaction
E°	standard electrode potential
$E_{1/2}$	half-wave potential
E_b	core-electron binding energy
E_i	ionization energy
E_{ind}	indicator electrode potential
E_j	liquid-junction potential
E_k	kinetic energy
E_{ref}	reference electrode potential
e, e^-	electronic charge; Naperian base; base of natural logarithms (2.718. . .)
e°	solvent strength parameter
F	faraday; fluorescence
F_c	volume flowrate of mobile phase

f	focal length; fractional abundance; oscillator strength, frequency
f_x	activity coefficient of species x
$f(\theta)$	geometrical factor (fluorometers)
ΔG°	Gibbs free energy
g	spectroscopic splitting factor; statistical weights of particular species
$g(\lambda)$	detector efficiency
H	magnetic-field strength; plate height (chromatography)
ΔH	enthalpy change; peak-to-peak separation (ESR)
ΔH_s	molal heat of solution
ΔH_v	molal heat of vaporization
h	height; Planck's constant [$6.626\ 176(36) \times 10^{-34}$ J · sec]; reduced plate height
I	radiant intensity; spin quantum number of nuclei
I_d	diffusion-current constant
I_o	incident radiant energy; output intensity
I_v	emission line intensity
i	angle of incidence; current
i-	(prefix) iso-
i_d	diffusion current
i_{lim}	limiting current
i_r	residual current
J	spin–spin coupling constant (nuclei)
j	compressibility factor (gas chromatography)
K_a	acid dissociation constant
K_{auto}	autoprotolysis constant
K_d, K	partition coefficient
K_f	formation constant
K_i	ionization constant (gaseous state)
K_{sp}	solubility product
K_w	ion product of water
k	Boltzmann constant [$1.380\ 662(44) \times 10^{-23}$ J · K^{-1}]; force constant (infrared); general constant
k'	partition ratio or capacity factor (chromatography)
$k_{M/N}$	selectivity coefficient for solutes M and N
k_o	column permeability
k_v	absorption coefficient (optical)
L	inductance; length or distance; lightness (color)
l	reduced column length (chromatography)
M	mass
M_I	spin quantum number (nucleus)
M_n	number–average molecular weight
M_s	angular momentum quantum number (electron)
M_w	weight–average molecular weight
m	mass; mass of mercury (polarography); order number (optical); metastable state (superscript)

m^*	metastable state
m^+	ionized mass fragment
m/e	mass-to-charge ratio
N	noise; plate number (chromatography); total number of something
N_A	Avogadro constant ($6.022\ 045 \times 10^{23}\ mol^{-1}$)
N_{eff}	effective plate number
N_j, N_m, N^*	number of species in excited energy state
N_n, N_o	number of species in ground energy state
N_{req}	plates required
$N(E)$	energy distribution (Auger spectroscopy)
n	number of electrons transferred (electrochemistry); principal quantum number; unshared p-electrons
n-	semiconducting material containing a majority of negative charge carriers
n_{theor}	theoretical plate number
P	phosphorescence; pressure; radiant power
P_i	inlet gas pressure
P_M	parent mass peak
P_o	incident radiant power; outlet gas pressure
ΔP	pressure drop across a column
p	partial pressure of some gaseous material; depolarization ratio (Raman); type of electron
p-	semiconducting material containing a majority of positive charge carriers
p°	solute vapor pressure
Q	flowrate; heat capacity; number of coulombs
R	gas constant (molar) [8.314 41(26)J·mol^{-1}·K^{-1}; 1.987 19(6)cal·mol^{-1}·K^{-1}]; resolution (chromatography); resolving power (optical)
R	retardation factor
R_L	load resistance
r	angle of diffraction; counting rate; radius; resolution (radiochemistry detectors)
r°	programmed rate of temperature increase (chromatography)
r_D	specific refraction
S	electron spin; saturation factor (radiochemistry)
S_1	first excited (singlet) electronic state
S_o	ground electronic state
ΔS	entropy change
S/N	signal-to-noise ratio
T	temperature; transmittance (optical)
T_1	first excited triplet (electronic) state; spin–lattice (or longitudinal) relaxation time (NMR)
T_2	spin–spin (or transverse) relaxation time (NMR)
T_b	boiling point
T_c	column temperature (chromatography)
t	time; prism base length
$t_{1/2}$	half-life
t_M	transit time of nonretained solute (chromatography)

t_p	time of solute passage through one plate
t_R	retention time
t'_R	adjusted retention time
u	reduced mass
$\bar{u}$	average linear velocity
V	volume
V_g°	specific retention volume (at 0°C)
V_g	volume of column occupied by gel matrix (exclusion chromatography)
V_i	internal volume within porous particles
V_M	volume of mobile phase
V_N	net retention volume
V_R	retention volume
V'_R	adjusted retention volume
V_S	cumulative internal volume within porous particles; volume stationary phase
V_t	total bed volume
v	velocity; volume
W	physical slitwidth (optical); weight; zone width at base line, 4σ (in chromatography)
$W_{1/2}$	zone width at 1/2 peak height
W_b	peak width at base line
w	effective aperture width
w_L	weight of stationary liquid phase
w_S	weight of adsorbent phase
X_C	capacitive reactance
X_L	inductive reactance
x	distance; general designation of species
Z	atomic number of an element; impedance
z	valence
z_+, z_-	ionic charge
α	degree of ionization; relative retention ratio
$[\alpha]$	specific rotation
α_i	degree of ionization
β	blaze angle; buffer value (pH); volumetric phase ratio (chromatography)
β_N	Bohr magneton
γ	activity coefficient; emulsion characteristic (photography); surface tension; obstructive (or tortuosity) factor (chromatography)
Δ	(prefix) symbol for finite change; spectral width (NMR)
δ	chemical shift (NMR); thickness of diffusion layer
ϵ	molar absorptivity
ϵ_{tot}	total porosity of column
η	index of refraction; viscosity
η_D	index of refraction (D line of sodium)
Θ	cell constant (conductance)
θ	angle; angle of diffraction

2θ	angular setting of diffraction angle (X ray)
$[\theta]$	molecular ellipticity
κ	specific conductance
Λ	equivalent conductance
Λ_∞	equivalent conductance at infinite dilution
λ	column packing uniformity (chromatography); decay constant (radiochemistry); wavelength
λ_+, λ_-	limiting equivalent ionic conductance
$\Delta\lambda$	base spectral width
λ_{max}	wavelength of an absorption maximum
μ	ionic strength; linear absorption coefficient; magnetic moment
μ_B	Bohr magneton [$9.274\,078(36) \times 10^{-24}$ J · T^{-1}]
μ_e	electron magnetic moment [$9.284\,832(36) \times 10^{-24}$ J · T^{-1}]
μ_m	mass absorption coefficient
μ_N	nuclear magneton [$5.050\,824(20) \times 10^{-27}$ J · T^{-1}]
μ/ρ	mass absorption coefficient
ν	frequency; reduced velocity (chromatography); designation of vibrational levels
$\bar{\nu}$	wave number
π	pi (3.1416. . .); type of electron or bond
ρ	density; resistivity
Σ	summation symbol
σ	reaction cross section; shielding constant (NMR, X ray); standard deviation
σ_{hkl}	reciprocal lattice vectors
τ	chemical shift (NMR); mean emission lifetime, resolving time; time constant
ν	designation of vibrational level; velocity
Φ	number of bombarding particles or flux
ϕ	column flow resistance parameter; photoluminescence efficiency; work function
ω	angular frequency; chopping frequency; overpotential
ω_c	angular velocity
[ ]	molar concentration of species within brackets
*	(asterisk) metastable state

Contents