

ADVANCED INORGANIC CHEMISTRY

A Comprehensive Text

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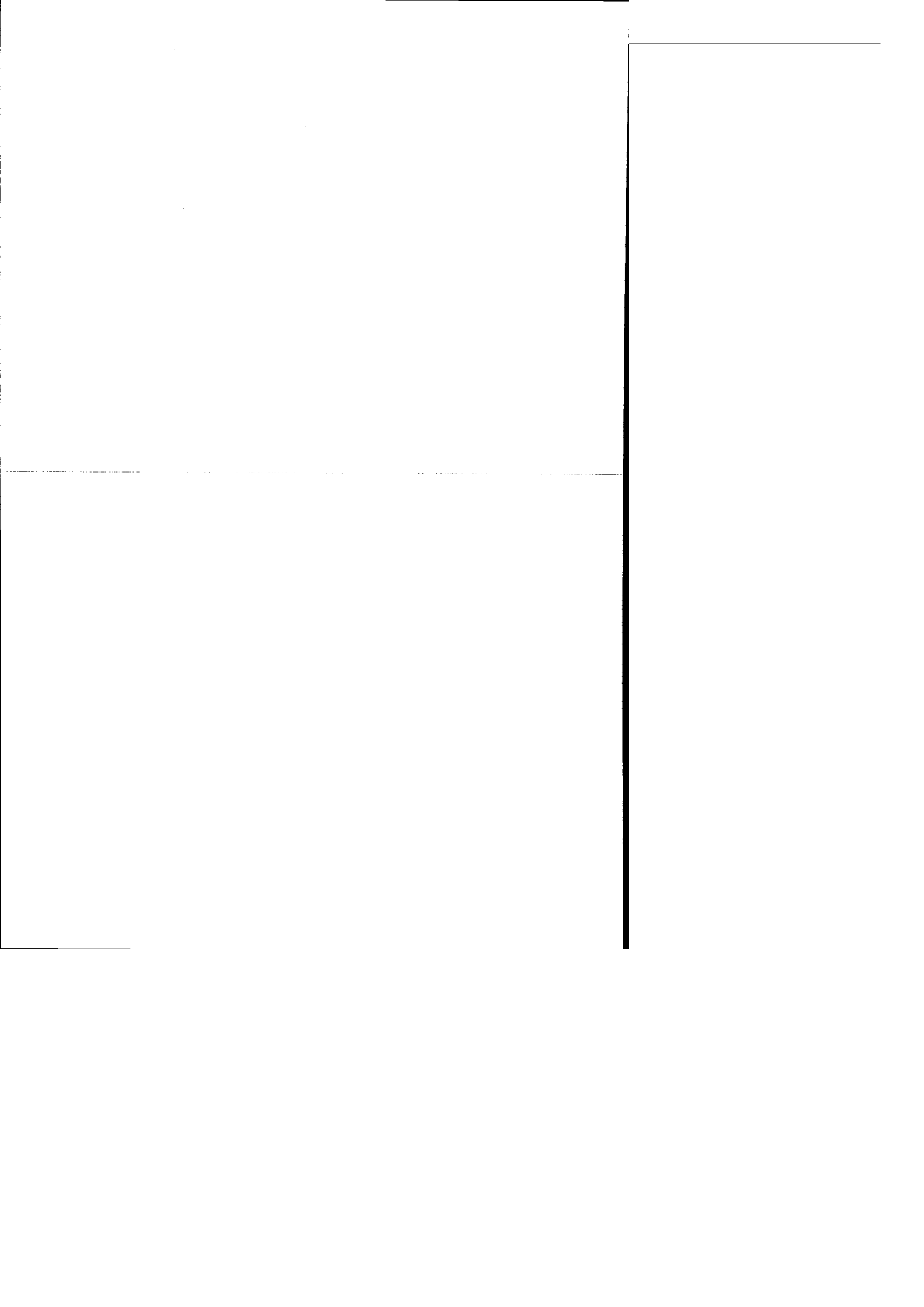
In Memoriam

to

Ronald Sydney Nyholm, F.R.S.

29.1.17–4.12.71

**whose teaching and research have contributed
much to the Renaissance of Inorganic Chemistry**



Preface to the Third Edition

Since the second edition of this text, the literature in inorganic chemistry has continued to grow at an extremely rapid rate. The work has been characterised by increasing sophistication in the use of physical methods as well as in concepts and insights. Although these developments have posed serious problems, we have maintained the same basic approach with the object of providing the student with a background sufficient for the comprehension of current research literature in the field.

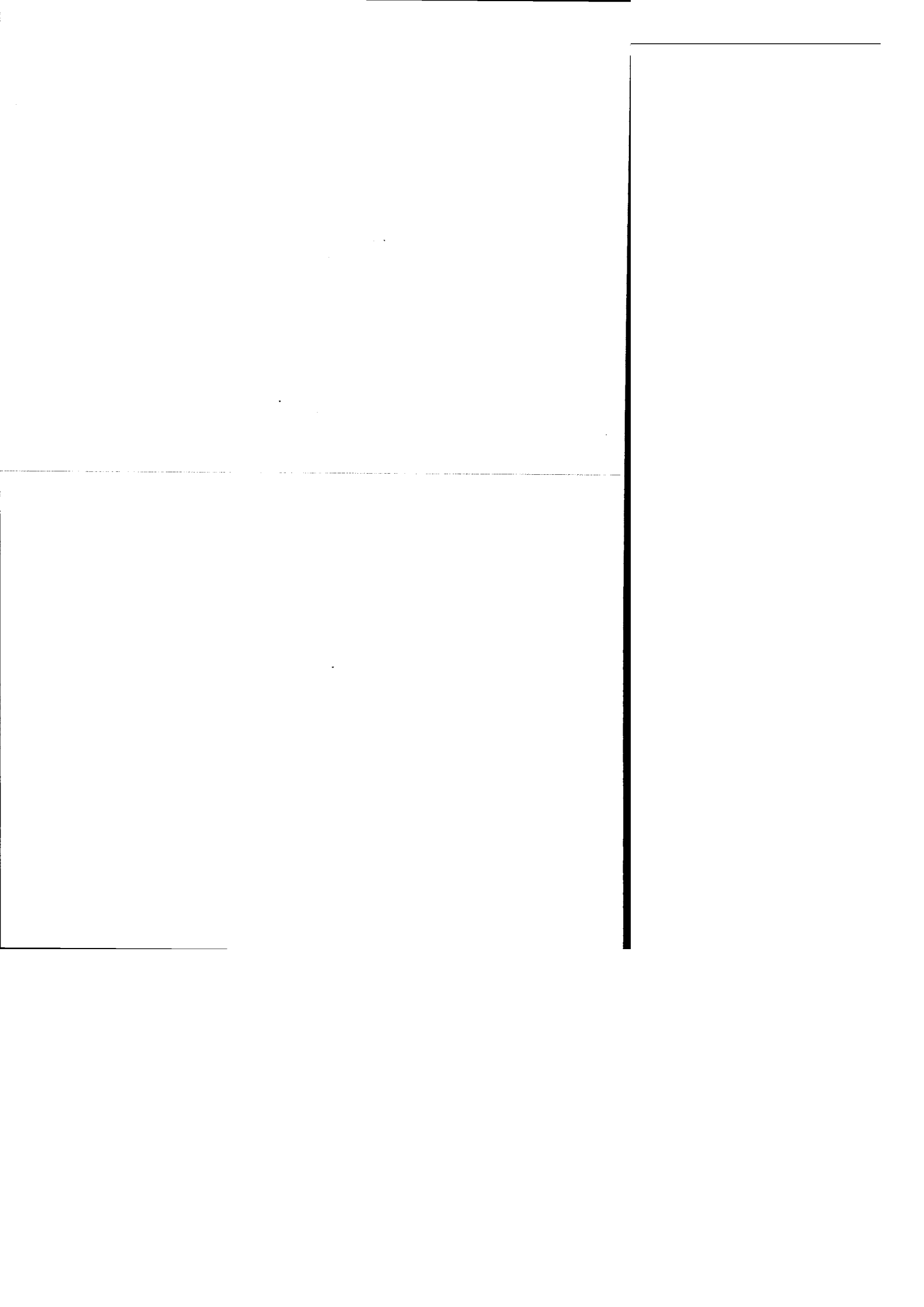
We have attempted to include factual material appearing up to around mid-1971 and a new set of references covers progress since the second edition. Since this book is intended primarily as a student textbook, the citations are not exhaustive and do not impute priority or originality being intended solely as a guide to the literature.

In order to accommodate new material, several changes have been made. The first four chapters have been modified so as to eliminate the more elementary aspects of atomic structure and give more coverage of symmetry and molecular structure. Various rearrangements of chapters and of material within sections have been made. One new chapter, on selected aspects of homogeneous catalysis by transition metal organometallic compounds has been added while some information on the biochemistry of iron, copper, cobalt, zinc and molybdenum is now provided.

We thank all those who have offered comments on the previous editions and suggestions for corrections or improvements to this edition would be welcome.

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Preface to the Second Edition

Although the basic structure of the text is unaltered, we have rearranged several sections and have brought up to date essentially all of the factual material. The vast amount of recent literature has meant an increase in the size of the book, but it is intended to be a *teaching* text and not a reference book and it is our view that it is better to have too much material on hand rather than too little, since sections can always be omitted.

In response to numerous requests, we have improved on the handling of documentation of which there are three levels. First, for the great majority of long known and well established facts and theories, no explicit reference is given since such material can be readily located through standard reference texts and treatises, listed at the end of the text.

Secondly, some material not so available appears in review articles and monographs; a pertinent list is provided at the end of each chapter.

Finally, we have introduced as footnotes in each chapter, some original research references. These cover broadly the period from January 1962 to August 1965 and are intended primarily for teachers and research workers as guide references to recent work.

We take this opportunity to thank all those who gave us their comments on the first edition.

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Preface to the First Edition

It is now a truism that, in recent years, inorganic chemistry has experienced an impressive renaissance. Academic and industrial research in inorganic chemistry is flourishing, and the output of research papers and reviews is growing exponentially.

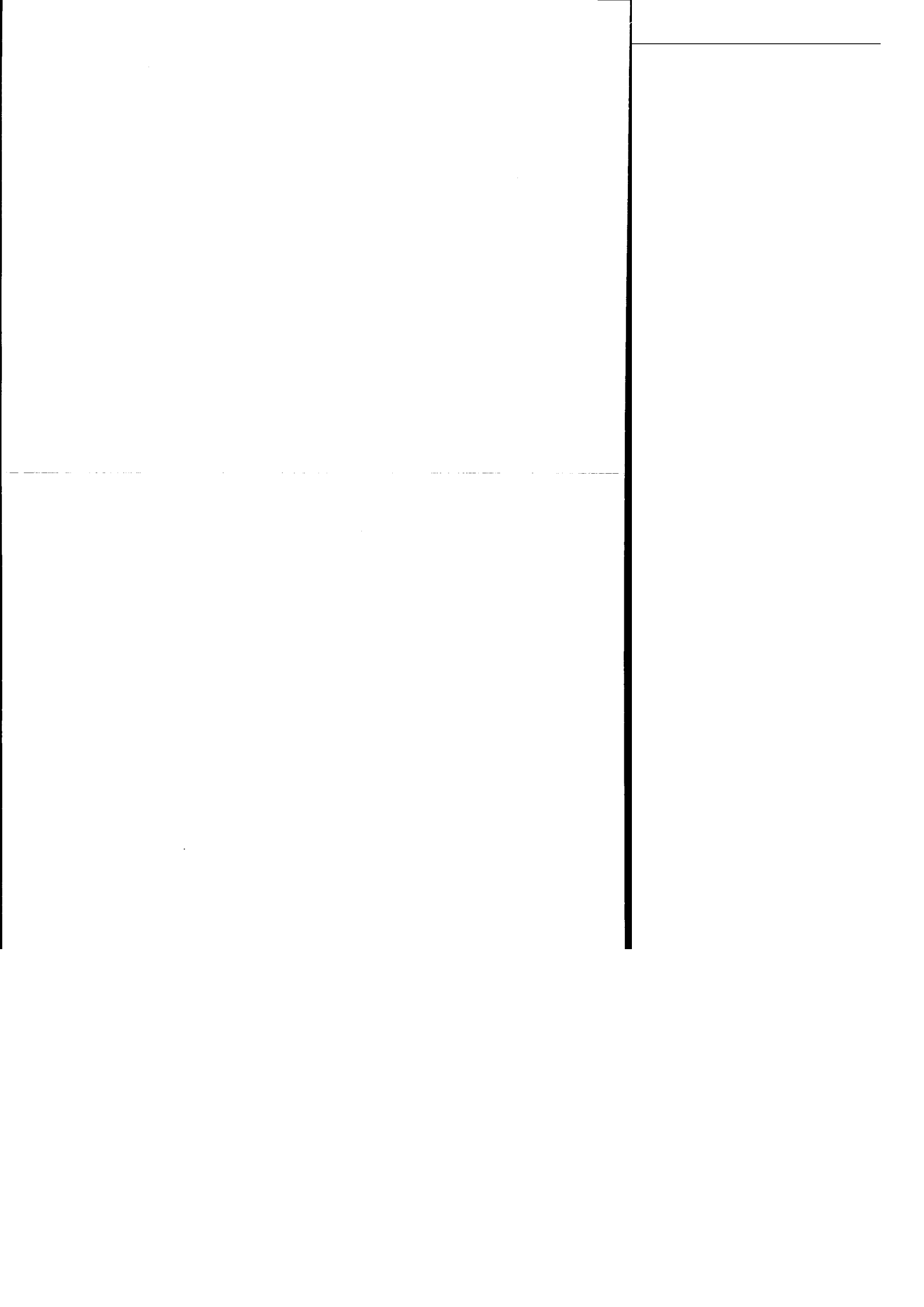
In spite of this interest, however, there has been no comprehensive textbook on inorganic chemistry at an advanced level incorporating the many new chemical developments, particularly the more recent theoretical advances in the interpretation of bonding and reactivity in inorganic compounds. It is the aim of this book, which is based on courses given by the authors over the past five to ten years, to fill this need. It is our hope that it will provide a sound basis in contemporary inorganic chemistry for the new generation of students and will stimulate their interest in a field in which trained personnel are still exceedingly scarce in both academic and industrial laboratories.

The content of this book, which encompasses the chemistry of all of the chemical elements and their compounds, including interpretative discussion in the light of the latest advances in structural chemistry, general valence theory, and, particularly, ligand field theory, provides a reasonable achievement for students at the B.Sc. honors level in British universities and at the senior year or first year graduate level in American universities. Our experience is that a course of about eighty lectures is desirable as a guide to the study of this material.

We are indebted to several of our colleagues, who have read sections of the manuscript, for their suggestions and criticism. It is, of course, the authors alone who are responsible for any errors or omissions in the final draft. We also thank the various authors and editors who have so kindly given us permission to reproduce diagrams from their papers: specific acknowledgements are made in the text. We sincerely appreciate the secretarial assistance of Miss C. M. Ross and Mrs. A. B. Blake in the preparation of the manuscript.

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Abbreviations

1. Chemicals, Ligands, Radicals, etc.

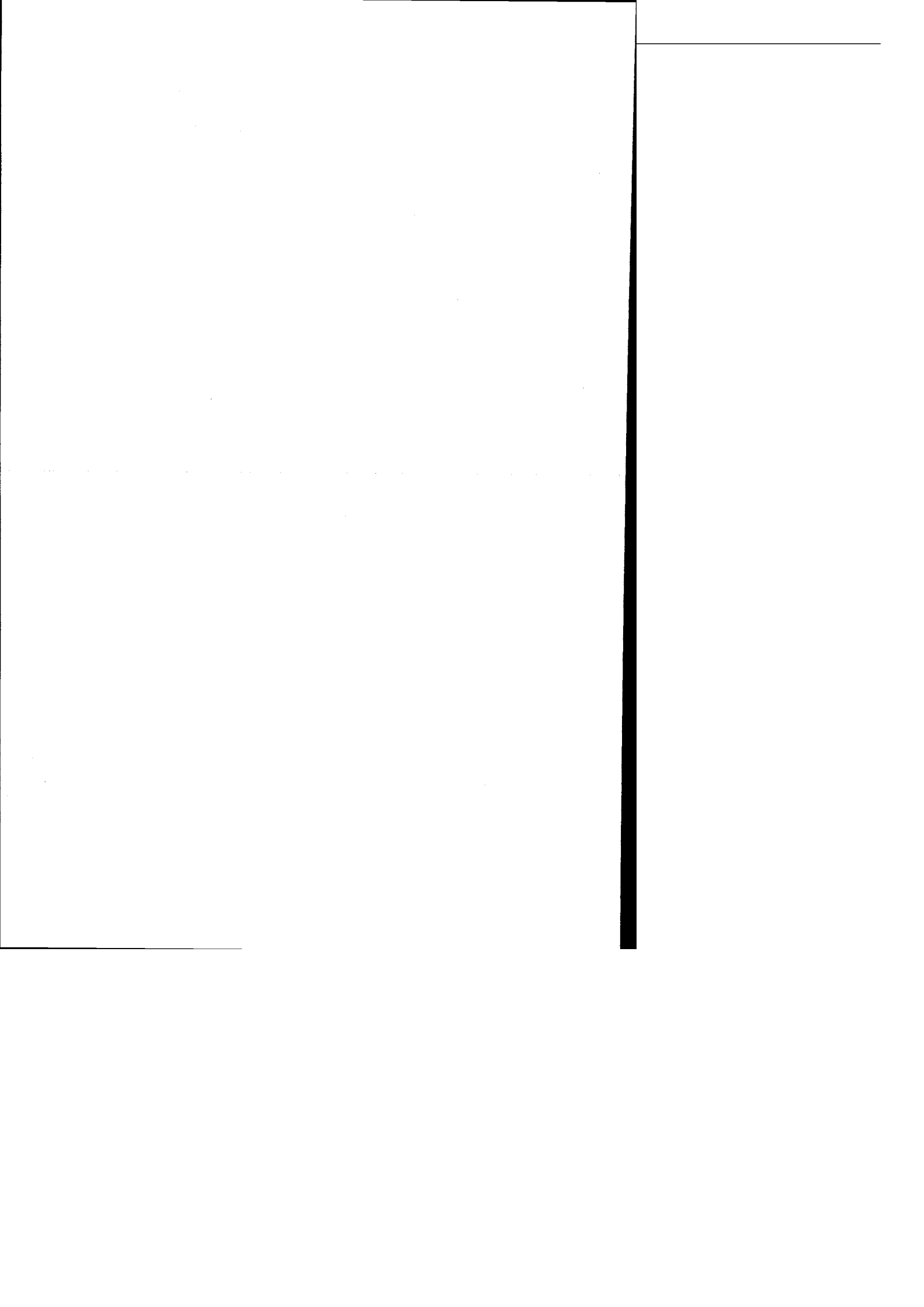
acacH	acetylacetone
am	ammonia (or occasionally an amine)
Ar	aryl or arene (ArH)
aq	aquated, H ₂ O
<i>bcc</i>	body centered cubic
bu	butyl (prefix <i>n</i> , <i>i</i> or <i>t</i> , normal, iso or tertiary butyl)
bz	benzene
<i>ccp</i>	cubic close packed
Cp	cyclopentadienyl, C ₅ H ₅
diars	<i>o</i> -phenylenebisdimethylarsine, <i>o</i> -C ₆ H ₄ (AsMe ₂) ₂
diglyme	diethyleneglycoldimethylether, CH ₃ O(CH ₂ CH ₂ O) ₂ CH ₃
dipy	2,2'-dipyridine
DMF	<i>N,N'</i> -dimethylformamide, HCONMe ₂
DMGH ₂	dimethylglyoxime
DMSO	dimethylsulfoxide, Me ₂ SO
EDTAH ₄	ethylenediaminetetraacetic acid
EDTAH ₄ ⁿ⁻	anions of EDTAH ₄
en	ethylenediamine, H ₂ NCH ₂ CH ₂ NH ₂
Et	ethyl
glyme	ethyleneglycoldimethylether, CH ₃ OCH ₂ CH ₂ OCH ₃
<i>hcp</i>	hexagonal close packed
L	ligand
M	central (usually metal) atom in compound
Me	methyl
Me ₆ tren	tris-(2-dimethylaminoethyl)amine, N(CH ₂ CH ₂ NMe ₂) ₃
NTAH ₃	nitrilotriacetic acid, N(CH ₂ COOH) ₃
ox	oxalate ion, C ₂ O ₄ ²⁻

Ph	phenyl, C ₆ H ₅
phen	1,10-phenanthroline
PNP	Bis-(2-diphenylphosphinoethyl)amine, HN(CH ₂ CH ₂ PPh ₂) ₂
pn	propylenediamine (1,2-diaminopropane)
Pr	propyl (prefix <i>i</i> for isopropyl)
QAS	Tris-(2-diphenylarsinophenyl)arsine, As(<i>o</i> -C ₆ H ₄ AsPh ₂) ₃
QP	Tris-(2-diphenylphosphinophenyl)phosphine, P(<i>o</i> -C ₆ H ₄ PPh ₂) ₃
R	alkyl or aryl group
Salen	bis-salicylaldehydeethylenediimine
TAN	Tris-(2-diphenylarsinoethyl)amine, N(CH ₂ CH ₂ AsPh ₂) ₃
TAP	Tris-(3-dimethylarsinopropyl)phosphine, P(CH ₂ CH ₂ CH ₂ AsMe ₂) ₃
TAS	Bis-(3-dimethylarsinopropyl)methylarsine, MeAs(CH ₂ CH ₂ CH ₂ AsMe ₂) ₂
THF	tetrahydrofuran
TMED	<i>N,N,N',N'</i> -tetramethylethylenediamine
tn	1,3-diaminopropane (trimethylenediamine)
TPN	Tris-(2-diphenylphosphinoethyl)amine, N(CH ₂ CH ₂ PPh ₂) ₃
trien	Triethylenetetraamine, (CH ₂ NHCH ₂ CH ₂ NH ₂) ₂
tren	Tris-(2-aminoethyl)amine, N(CH ₂ CH ₂ NH ₂) ₃
TSN	Tris-(2-methylthiomethyl)amine, N(CH ₂ CH ₂ SMe) ₃
TSP	Tris-(2-methylthiophenyl)phosphine, P(<i>o</i> -C ₆ H ₄ SMe) ₃
TSeP	Tris-(2-methylselenophenyl)phosphine, P(<i>o</i> -C ₆ H ₄ SeMe) ₃
TTA	thenoyltrifluoroacetone, C ₄ H ₃ SCOCH ₂ COCF ₃
X	halogen or pseudohalogen

2. Miscellaneous

Å	Angstrom unit, 10 ⁻¹⁰ m
asym	asymmetric or antisymmetric
B.M.	Bohr magneton
b.p.	boiling point
cm ⁻¹	wave number
CFSE	crystal field stabilization energy
CFT	crystal field theory
d	decomposes
<i>d</i> -	dextrorotatory

esr	electron spin resonance
eV	electron volt
(g)	gaseous state
<i>h</i>	Planck's constant
Hz	herz, sec ⁻¹
ICCC	International Coordination Chemistry Conference
ir	infrared
IUPAC	International Union of Pure and Applied Chemistry
(l)	liquid state
<i>l</i> -	levorotatory
LCAO	linear combination of atomic orbitals
LFT	ligand field theory
m.p.	melting point
MO	molecular orbital
nmr	nuclear magnetic resonance
<i>R</i>	gas constant
(s)	solid state
<i>spy</i>	square pyramid(al)
str	vibrational stretching mode
sub	sublimes
sym.	symmetrical
<i>tbp</i>	trigonal bipyramid(al)
<i>U</i>	lattice energy
uv	ultraviolet
VB	valence bond
<i>Z</i>	atomic number
ϵ	molar extinction coefficient
ν	frequency (cm ⁻¹ or Hz)
μ	magnetic moment in Bohr magnetons
χ	magnetic susceptibility
θ	Weiss constant



Units and Conversion Factors

1. The SI Units

In recent years many scientific and engineering groups have recommended or adopted a set of units called the *Système International d'Unités*, the SI units. While these have not yet been universally accepted, even in pure science, there is a growing trend toward general acceptance. In this book some SI units have been adopted, while others have not. We summarize here the SI units and comment on choices made for use in this book.

The SI system is based on the following set of defined units:

<i>Physical Quantity</i>	<i>Name of Unit</i>	<i>Symbol for Unit</i>
length	meter	m
mass	kilogram	kg
time	second	s
electric current	ampere	A
temperature	kelvin	K
luminous intensity	candela	cd

Multiples and fractions of these are specified using the following prefixes:

<i>Multiplier</i>	<i>Prefix</i>	<i>Symbol</i>
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	μ
10^{-9}	nano	n
10^{-12}	pico	p
10	deka	da
10^2	hecto	h
10^3	kilo	k
10^6	mega	M
10^9	giga	G
10^{12}	tera	T

In addition to the defined units, the system includes a number of derived units, of which the following are the main ones

<i>Physical quantity</i>	<i>SI unit</i>	<i>Unit symbol</i>
Force	newton	$N = \text{kg m s}^{-2}$
Work, energy, quantity of heat	joule	$J = \text{Nm}$
Power	watt	$W = \text{J s}^{-1}$
Electric charge	coulomb	$C = \text{As}$
Electric potential	volt	$V = \text{WA}^{-1}$
Electric capacitance	farad	$F = \text{A s V}^{-1}$
Electric resistance	ohm	$\Omega = \text{V A}^{-1}$
Frequency	hertz	$\text{Hz} = \text{s}^{-1}$
Magnetic flux	weber	$\text{Wb} = \text{Vs}$
Magnetic flux density	tesla	$T = \text{Wb m}^{-2}$
Inductance	henry	$H = \text{V s A}^{-1}$

The *energy unit* immediately derived from the basis units is the *joule*, J, $\text{kg m}^2 \text{sec}^{-2}$. We have adopted this unit, which is equal to $(4.184)^{-1}$ calories, as the unit of energy. In most places it is more convenient to use the kilojoule, kJ. In a few places, e.g., for ionization energies, the *electron volt*, eV, has been used, as before. One $\text{eV} = 96.5 \text{ kJ mol}^{-1}$. The eV is the energy acquired by an electron accelerated by a potential difference of one volt.

In common with many chemists and crystallographers, we have continued to use the Angstrom, Å, defined as 10^{-8} cm, as a unit of length on the atomic and molecular scale, although SI units are the nanometer, nm (10^{-9} m) or picometer, pm (10^{-12} m). The C—C bond length in diamond is $1.54 \text{ Å} = 0.154 \text{ nm} = 154 \text{ pm}$.

We have also retained other familiar units, such as dyne and atmosphere (pressure). This is in line with the objective of preparing the student to read the contemporary literature, which is still written almost exclusively in such units.

Signs. When energy is absorbed in a process, the energy of that process will be defined as positive.

For electrochemical processes we shall use the conventions recommended by the International Union of Pure and Applied Chemistry (IUPAC). Because these differ, often confusingly, from the Latimer or American convention still found in many publications in the USA, a detailed explanation of the International system is provided on pages 164–165.

2. Conversion Factors

Some useful relationships between different units are given below. The symbols N and J stand for Newton and Joule, the SI units of force and energy, respectively.

1 atm = 760 mm Hg (= torr) = 1.01325×10^6 dyne cm^{-2} = 101.325 Nm^{-2}
 1 bar = 10^6 dyne cm^{-2} = 0.987 atm = 105 Nm^{-2}
 1 Bohr Magneton = 9.273×10^{-24} Am² molecule⁻¹ = 9.273×10^{-21} erg
 gauss⁻¹
 1 calorie (thermochemical) = 4.184 J
 1 coulomb = 0.10000 emu = 2.9979×10^9 esu = 1 amp sec
 1 dyne = 10^{-5} N
 1 erg = 2.3901×10^{-8} cal = 10^{-7} J
 1 eV = 8066 cm^{-1} = 23.06 kcal/mole = 1.602×10^{-12} erg = 1.602×10^{-19} J
 1 gauss = 10^{-4} T
 1 kJ mole⁻¹ = 83.54 cm^{-1}
 1 mass unit, mu, = 931.5 Mev = 1.660×10^{-24} erg
 Molar Magnetic Susceptibility (SI) = Molar Susceptibility (cgs) $\times 4\pi \times 10^{-6}$
 $RT(T = 300 \text{ K}) = 0.1425 \text{ kJ mol}^{-1} = 208.4 \text{ cm}^{-1}$

3. Fundamental Constants, etc.

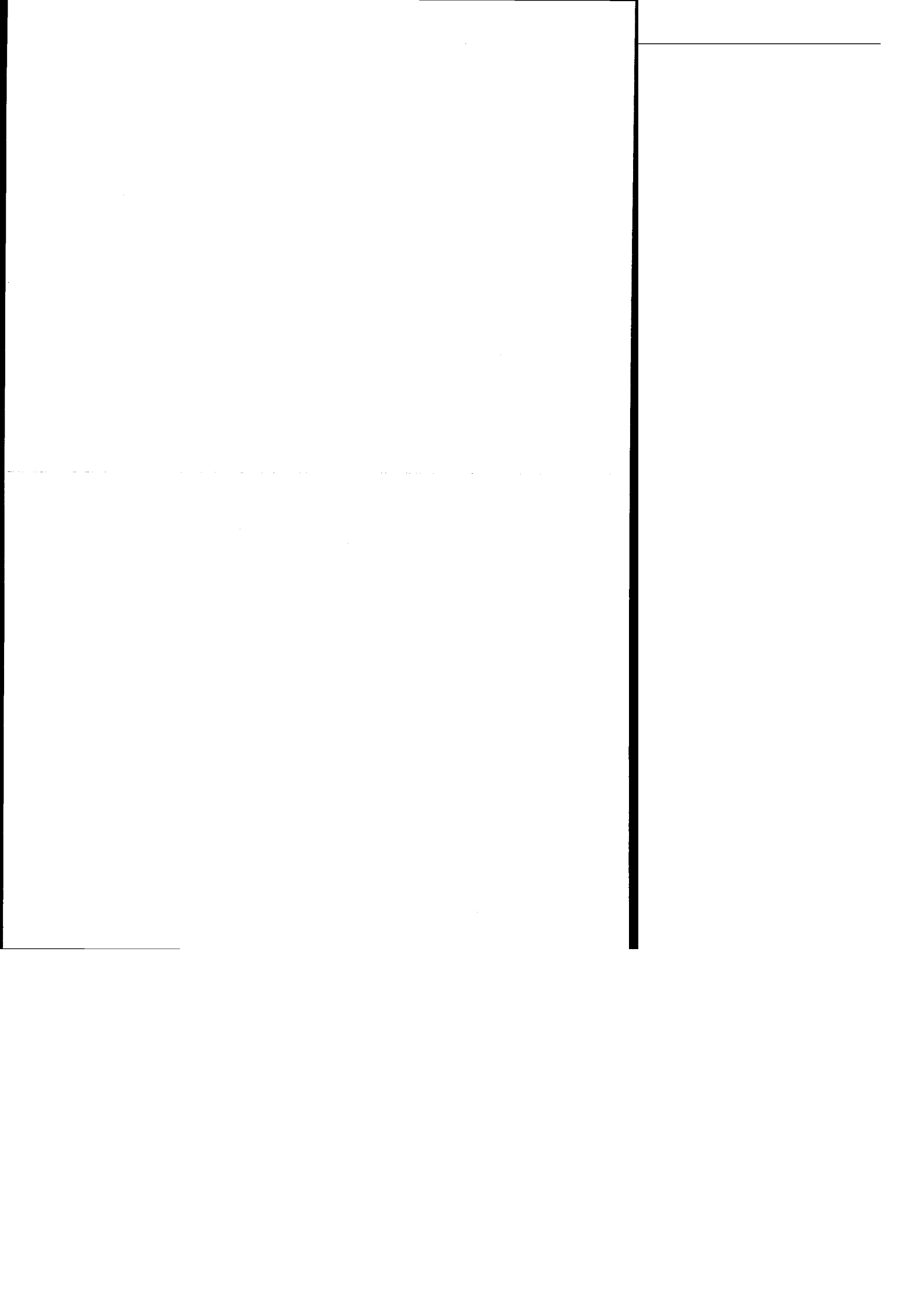
Avogadro's number ($C^{12} = 12.0000\dots$), $N_A = 6.02252 \times 10^{23} \text{ mol}^{-1}$
 Boltzmann's constant $k = 1.3805 \times 10^{-16}$ erg deg⁻¹ = $1.3805 \times 10^{-23} \text{ JK}^{-1}$
 Bohr radius, $a_0 = 0.52917 \times 10^{-10}$ m
 Curie-Weiss Law: $\mu = 2.84 [\chi_M(T-\theta)]^{1/2} = 797.5 [\chi_M(T-\theta)]^{1/2}$ (SI)
 Electron charge, $e = (4.8030 \pm 0.0001) \times 10^{-10}$ abs. esu = 1.602×10^{-19} C
 Electron mass, $m = 9.1091 \times 10^{-31}$ kg = 0.00054860 mu = 0.5110 Mev
 Faraday constant, $F = 96,487$, coulomb. g. equiv⁻¹ = $9.6487 \times 10^4 \text{ C mol}^{-1}$
 Gas constant, $R = 1.9872$ defined cal deg⁻¹ mol⁻¹ = $8.3143 \text{ JK}^{-1} \text{ mol}^{-1} =$
 $0.082057 \text{ liter atm deg}^{-1} \text{ mol}^{-1}$
 Ice point: $273.150 \pm 0.01 \text{ K}$
 Molar volume (ideal gas, 0°C, 1 atm) = $22.414 \times 10^3 \text{ cm}^3 \text{ mol}^{-1} =$
 $2.241436 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$
 Planck's constant, $h = 6.6256 \times 10^{-27}$ erg. sec = 6.6256×10^{-34} Js
 Proton mass, $M_p = 1.6725 \times 10^{-24}$ g
 Velocity of light in vacuum = $2.99795 \times 10^8 \text{ m sec}^{-1}$
 $\pi = 3.14159$; $e = 2.7183$; $\ln 10 = 2.3026$
 S.T.P. = $1.013 \times 10^5 \text{ Nm}^{-2}$ and 273.15°K



ADVANCED INORGANIC CHEMISTRY

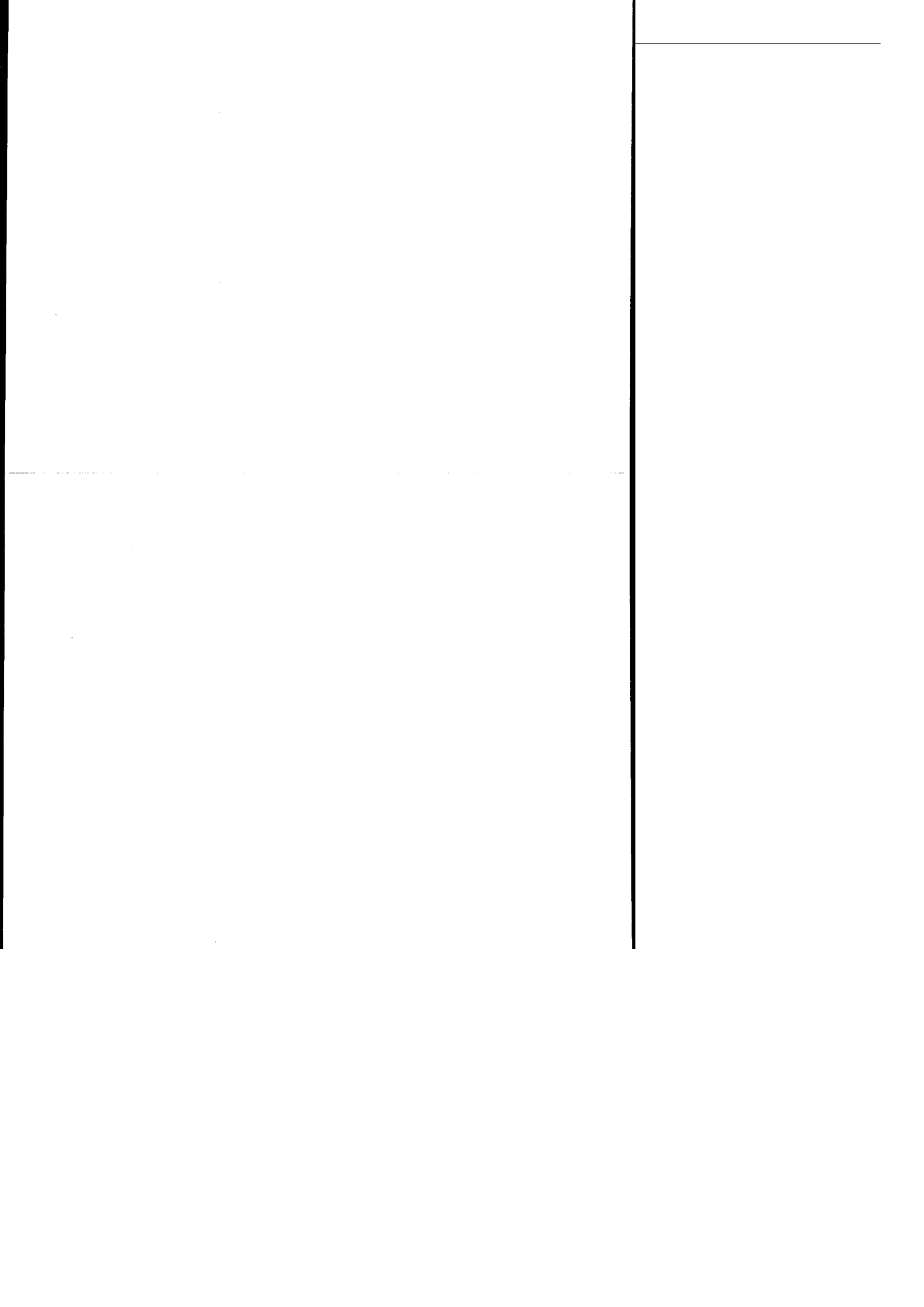
A Comprehensive Text

THIRD EDITION



PART ONE

General Theory



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