

Contents

Chapter 1	Chemically Induced Dynamic Electron Polarization (CIDEP)	1
	<i>By P. J. Hore, C. G. Joslin, and K. A. McLauchlan</i>	
1	Introduction	1
2	The Triplet Mechanism	2
	Theory	2
	Interpretation	6
3	The Radical-pair Mechanism	10
	A Vector Model	13
	Theory	14
	S-T _{±1} Mixing	17
4	Observation and Experiment	18
	Experimental Methods	18
	The Bloch Equations	19
	Pulse Experiments	22
	Time-resolved Continuous Generation Experiments	25
	Steady-state Experiments	28
	Modulation Experiments	28
	Spectrometer Response	28
	Kinetic Models	28
5	Experimental Tests of the Theories	29
	Tests of TM Theory	29
	Tests of ST ₀ RPM Theory	32
	Tests of ST _{±1} RPM Theory	36
6	Secondary Polarization	37
7	Systems Investigated	39
8	Biological Applications	39
9	Further Polarization Mechanisms and Relaxation Effects	44

Chapter 2	Theoretical Aspects of ESR <i>By A. Hudson</i>	46
1	Introduction	46
2	The Calculation of Spin Hamiltonian Parameters	46
3	Miscellany	50
Chapter 3	ENDOR and ELDOR <i>By K. Möbius</i>	52
1	Introduction	52
2	ENDOR in Solids	53
	Free Radicals	53
	Defect Centres	54
	Metal Ions	56
	Triplets	58
3	Biological Systems	58
4	ENDOR in Solution	60
5	ELDOR	63
6	Instrumentation	64
Chapter 4	Triplets and Biradicals <i>By A. Hudson</i>	66
1	Introduction	66
2	Ground State Triplets	66
3	Biradicals	69
4	Photoexcited Triplets	71
Chapter 5	Transition-Metal Ions <i>By A. L. Porte</i>	76
1	Introduction	76
2	General	77
	Experimental Techniques	77
	Spin-Hamiltonians, Analysis of Spectra and Computing	84
	Bonding	87
	Jahn–Teller Effects	93

3	$S = \frac{1}{2}$	97
	d^1 Configuration	97
	Tervalent Titanium	97
	Quadrivalent Vanadium, Niobium, and Tantalum	99
	Quinquevalent Chromium, Molybdenum, and Tungsten	102
	Sexivalent Manganese and Rhenium	107
	d^5 Configuration	108
	Bivalent Manganese and Rhenium, Tervalent Iron, Ruthenium, and Osmium	108
	d^7 Configuration	111
	Zerovalent Manganese, Univalent Iron, Bivalent Cobalt, Tervalent Nickel	111
	Bivalent Rhodium, Tervalent Palladium, and Tervalent Platinum	115
	d^9 Configuration	116
	Bivalent Copper: Tetrahedral, Pseudotetrahedral, Trigonal Bipyramidal, and Square Pyramidal	116
	Bivalent Copper: Square and Octahedral	120
	Univalent Nickel, Palladium and Platinum, and Bivalent Silver	122
	Zerovalent Cobalt and Rhodium, and Iron(-1)	123
4	$S = 1$	124
	Dimeric, Trimeric, Tetrameric and Higher Polymeric Bivalent Copper, Dimeric Bivalent Silver	124
	Dimeric Bivalent Manganese	124
	d^8 Configuration	124
	Bivalent Nickel	124
5	$S = \frac{3}{2}$	125
	d^3 Configuration	125
	Bivalent Vanadium	125
	Tervalent Chromium and Molybdenum	126
	Quadrivalent Manganese and Quinquevalent Iron	127
	d^5 Configuration	128
	Tervalent Iron	128
	d^7 Configuration	128
	Bivalent Cobalt	128
6	$S = 2$	129
	Bivalent Chromium and Iron, and Tervalent Manganese	129
7	$S = \frac{5}{2}$	129
	Univalent Chromium	130
	Bivalent Manganese	130
	Tervalent Iron	132

Chapter 6	Inorganic and Organometallic Radicals	134
	<i>By M. C. R. Symons</i>	
1	Introduction	134
2	Trapped and Solvated Electrons	134
3	Monatomic Radicals	140
4	Diatomic Radicals	143
5	Triatomic Radicals (AB_2) and Related Species	146
6	Tetra-atomic Radicals (AB_3) and Related Species	148
7	Penta-atomic Radicals (AB_4) and Related Species	151
8	AB_5 and AB_6 Radicals	154
9	Environmental Factors	156
10	Mechanistic Aspects	157
11	Spin Trapping and Metal-nitroxides	160
12	Radical Pair Trapping	163
13	Gas-phase Studies	163
14	Transition-metal Alkyls, Aryls, Carbonyls, and Related Species	164
Chapter 7	Organic Radicals: Structure	167
	<i>By B. C. Gilbert</i>	
1	Introduction	167
2	Carbon-centred Radicals	167
	The Geometry of Simple Radicals	167
	Splittings in Delocalized Species	172
	β -Splittings and Conformational Studies	181
	Long-range Splittings	184
3	Nitrogen-centred Radicals	186
	Aluminium Cation-radicals, Aminyls, and Iminyls	186
	Nitroxides	190
	Aromatic Radicals and Radical-ions	192
4	Sulphur-centred Radicals	193
5	Other Radicals	198

Chapter 8	Organic Radicals: Kinetics and Mechanisms of their Reactions	201
	<i>By R. C. Sealy</i>	
1	Introduction	201
2	Radical Initiation	201
3	Carbon-centred Radicals	203
4	Oxygen-centred Radicals	214
5	Nitrogen-centred Radicals	223
6	Sulphur-centred Radicals	225
7	Miscellaneous Reactions	226
Chapter 9	Organic Radicals in Solids	228
	<i>By T. J. Kemp</i>	
1	Introduction	228
2	Spectroscopic Studies	229
	Alkyl Radicals	229
	Substituted Alkyl Radicals	230
	Conjugated Radicals	230
	Benzyl Radicals	231
	Aliphatic Anion Radicals	231
	Aromatic Anion Radicals	233
	Nitrogen-centred Radicals	233
	Oxygen-centred Radicals	234
	Sulphur-centred Radicals	234
3	Mechanistic Studies	235
	Alkane Radiolysis	235
	Acetonitrile	236
	Alkanol Radiolysis	237
	Disaccharides	238
	Alkyl Halides	238
	Tetrafluoroethylene	238
	Carboxylic Acid Derivatives	239
	Nitrogen-containing Systems	239
	Sulphur-centred Radicals	239
4	Amino-acids and Peptides	241
	Amino-acids	241
	Peptides	244
5	Pyrimidines and Purines	246

6 Polymer Radicals	251
Natural Polymers	254
7 Adsorbed Radicals	254
Chapter 10 Spin Label Studies	256
<i>By B. M. Peake</i>	
1 Introduction	256
2 Lipids and Membranes	258
Nature and Location of Spin labels	260
Lipid Organisation and Order	262
Membrane and Lipid Mobility	263
Phase, Phase Transitions, and Temperature Effects	268
Lipid-Protein Interactions	271
Effects of Drugs and Other Substances on Membrane Properties	274
Immunology	278
Virology	280
Other Studies	282
3 Proteins	285
Muscle	285
Haemoglobin	286
Serum Albumin	288
ATPases	289
Acetylcholine Esterase	292
Dehydrogenases	293
Other Studies	294
4 Nucleotides	300
5 Polymers	302
6 Liquid Crystals	305
7 Detergent and Micelle Formation	306
8 Assay Procedures	307
9 Miscellaneous	309
10 Synthesis of Spin Labels	313
Chapter 11 Biological and Medical Studies	318
<i>By P. F. Knowles and B. M. Peake</i>	
1 Introduction	318

2 Metalloproteins	318
Proteins Containing Copper	318
Type I	318
Type II	318
Type III	320
Mixed Types I, II, and III	320
Proteins Containing Molybdenum	323
Proteins Containing Iron	324
Iron–Sulphur Proteins	324
Group I : Ferredoxins	324
Group II : High Potential Iron–Sulphur Proteins	325
Group III: Rubredoxins	325
Group IV: ‘Conjugated’ Iron–Sulphur Proteins	325
(i) Mitochondrial Systems	325
(ii) Photosynthetic Systems	327
Other Proteins Containing Non-haem Iron	328
Haem Proteins: Model Systems	328
Haemoglobin and Myoglobin	329
Cytochrome P450	331
Other Haem Proteins	333
Other Proteins Where Metal Ions Are Required for Function	335
3 ESR Studies in Biology and Medicine	337
Photosynthetic Electron Transfer	337
Electron Transfer in Mitochondria and in Bacterial Membranes	342
Applications of ESR in Medicine	343
Cancer	344
Other Studies	346
4 Other Studies	349

Author Index	357
--------------	-----

