

Contents

Prefaces	v
--------------------	---

CHAPTER 1

Resonance and the Chemical Bond

1-1. The Development of the Theory of Valence	3
1-2. Types of Chemical Bonds	5
The Chemical Bond Defined	6
The Ionic Bond and Other Electrostatic Bonds	6
The Covalent Bond	7
The Metallic Bond; Fractional Bonds	10
1-3. The Concept of Resonance	10
1-4. The Hydrogen Molecule-Ion and the One-Electron Bond	14
The Normal Hydrogen Atom	14
The Hydrogen Molecule-Ion	15
The Virial Theorem	19
The Hellmann-Feynman Theorem	21
The Conditions for the Formation of a One-Electron Bond	21
1-5. The Hydrogen Molecule and the Electron-Pair Bond	23
Condon's Treatment of the Hydrogen Molecule	23
The Heitler-London Treatment of the Hydrogen Molecule	24
Partial Ionic Character and Deformation	25
The Conditions for the Formation of an Electron-Pair Bond	27

CHAPTER 2

The Electronic Structure of Atoms and the Formal Rules for the Formation of Covalent Bonds

2-1. The Interpretation of Line Spectra	28
2-2. Stationary States; The Bohr Frequency Principle	31
2-3. Stationary States of the Hydrogen Atom	32

2-4. The Electronic Structure of Alkali Atoms	37
The Selection Rule for l	40
2-5. The Spinning Electron and the Fine Structure of Spectral Lines	41
2-6. The Electronic Structure of Atoms with Two or More Valence Electrons	44
2-7. The Pauli Exclusion Principle and the Periodic System of the Elements	47
2-8. The Zeeman Effect and the Magnetic Properties of Atoms and Monatomic Ions	58
Hybrid Atomic States	59
2-9. The Formal Rules for the Formation of Covalent Bonds	61

CHAPTER 3

*The Partial Ionic Character of Covalent Bonds and the
Relative Electronegativity of Atoms*

3-1. The Transition from One Extreme Bond Type to Another	65
Continuous Change in Bond Type	66
Discontinuous Change in Bond Type	68
3-2. Bond Type and Atomic Arrangement	69
3-3. The Nature of the Bonds in Diatomic Halogenide Molecules	73
3-4. Bond Energies of Halogenide Molecules; The Energies of Normal Covalent Bonds	79
The Postulate of the Geometric Mean	82
3-5. Empirical Values of Single-Bond Energies	83
3-6. The Electronegativity Scale of the Elements	88
The Formulation of the Electronegativity Scale	88
3-7. Heats of Formation of Compounds in Their Standard States; The Complete Electronegativity Scale	91
3-8. Relation to Other Properties	95
3-9. The Electronegativity of Atoms and the Partial Ionic Character of Bonds	97
3-10. The Enthalpy Change in Organic Rearrangements and the Electronegativity Scale	103
3-11. The Correlation of Color and Bond Character	105

CHAPTER 4

The Directed Covalent Bond; Bond Strengths and Bond Angles

4-1. The Nature and Bond-forming Power of Atomic Orbitals	108
4-2. Hybrid Bond Orbitals; The Tetrahedral Carbon Atom	111
Derivation of Results about Tetrahedral Orbitals	116
Quantum-mechanical Description of the Quadrivalent Carbon Atom	118
4-3. The Effect of an Unshared Pair on Hybridization	120

Contribution of Unshared Electron Pairs to the Electric Dipole Moments of Molecules	123
4-4. Orbitals for Incomplete <i>s-p</i> Shells	124
4-5. Concentration of Bond Orbitals	126
4-6. Electron Distribution in Completed Shells	128
4-7. Restricted Rotation about Single Bonds	130
Restricted Rotation about Single Bonds between Atoms with Unshared Electron Pairs	134
4-8. Orbitals and Bond Angles for Multiple Bonds	136
4-9. Partial Ionic Character of Multiple Bonds	142
4-10. The Effect of Unshared Pairs on Bond Energies and Bond Lengths	142

CHAPTER 5

Complex Bond Orbitals; The Magnetic Criterion for Bond Type

5-1. Bonds Involving <i>d</i> Orbitals	145
5-2. Octahedral Bond Orbitals	147
5-3. Square Bond Orbitals	153
5-4. The Magnetic Criterion for Bond Type	161
5-5. The Magnetic Moments of Octahedral Complexes	162
5-6. The Magnetic Moments of Tetrahedral and Square Coordinated Complexes.	168
5-7. The Electroneutrality Principle and the Stability of Octahedral Complexes.	172
5-8. Ligand Field Theory	174
5-9. Other Configurations Involving <i>d</i> Orbitals	175
5-10. Configurations for Atoms with Unshared Electron Pairs	180

CHAPTER 6

The Resonance of Molecules among Several Valence-Bond Structures

6-1. Resonance in Nitrous Oxide and Benzene.	183
6-2. Resonance Energy	188
Values of Bond Energies for Multiple Bonds	189
Ionic Resonance Energy and Partial Ionic Character of Multiple Bonds.	190
The Nitrogen-Nitrogen Triple Bond	191
Empirical Values of Resonance Energies	191
6-3. The Structure of Aromatic Molecules	198
The Quantitative Treatment of Resonance in Aromatic Molecules	203
The Orientation of Substituents in Aromatic Molecules	205
The Effect of Resonance on the Electric Dipole Moments of Molecules	209

- 6-4. The Structure and Stability of the Hydrocarbon Free Radicals 211
 6-5. The Nature of the Theory of Resonance 215

CHAPTER 7

*Interatomic Distances and Their Relation to the Structure
 of Molecules and Crystals*

- 7-1. Interatomic Distances in Normal Covalent Molecules: Covalent Radii 221
 7-2. The Correction for Electronegativity Difference 228
 7-3. Double-Bond and Triple-Bond Radii 230
 7-4. Interatomic Distances and Force Constants of Bonds 231
 7-5. Interatomic Distances and Resonance 232
 Bond Lengths in Aromatic Hydrocarbons 236
 7-6. Bond Order and Bond Length; Change in Bond Length Caused by Resonance between Two Equivalent Structures 239
 7-7. Single-Bond:Triple-Bond Resonance 240
 7-8. The Conditions for Equivalence or Nonequivalence of Bonds 241
 7-9. Tetrahedral and Octahedral Covalent Radii 244
 Tetrahedral Radii 244
 Octahedral Radii 248
 Other Covalent Radii 252
 The Anomalous Manganese Radius 254
 7-10. Interatomic Distances for Fractional Bonds 255
 7-11. Values of Single-Bond Metallic Radii 256
 7-12. Van der Waals and Nonbonded Radii of Atoms 257

CHAPTER 8

Types of Resonance in Molecules

- 8-1. The Structure of Simple Resonating Molecules 265
 Carbon Monoxide and Carbon Monosulfide 265
 Carbon Dioxide and Related Molecules. 267
 The Cyanides and Isocyanides 269
 8-2. The Adjacent-Charge Rule and the Electroneutrality Rule. 270
 Cyanates and Thiocyanates 273
 8-3. The Nitro and Carboxyl Groups; Acid and Base Strengths. 274
 8-4. The Structure of Amides and Peptides 281
 8-5. The Carbonate, Nitrate, and Borate Ions and Related Molecules 282
 8-6. The Structure and Properties of the Chloroethylenes and Chlorobenzenes 288
 8-7. Resonance in Conjugated Systems 290
 Overcrowded Molecules 298
 Conjugated Systems Involving Triple Bonds 299
 8-8. Resonance in Heterocyclic Molecules 300
 8-9. Hyperconjugation 308

CHAPTER 9

*The Structure of Molecules and Complex Ions Involving
Bonds with Partial Double-Bond Character*

9-1. The Structure of Silicon Tetrachloride and Related Molecules	310
9-2. Silicon Tetrafluoride and Related Molecules	313
9-3. The Fluorochloromethanes and Related Molecules; The Effect of Bond Type on Chemical Reactivity	314
9-4. Partial Double-Bond Character of Bonds between the Heavier Non- metal Atoms	316
9-5. The Boron Halogenides	317
9-6. The Oxides and Oxygen Acids of the Heavier Elements.	320
The Chlorate Ion and Related Ions	323
The Strengths of the Oxygen Acids	324
Sulfuryl Fluoride and Related Molecules	328
Oxides of the Heavier Elements	329
9-7. The Structure and Stability of Carbonyls and Other Covalent Com- plexes of the Transition Metals.	331
The Cyanide and Nitro Complexes of the Transition Elements	336

CHAPTER 10

*The One-Electron Bond and the Three-Electron Bond;
Electron-deficient Substances*

10-1. The One-Electron Bond	340
10-2. The Three-Electron Bond	341
The Conditions for Formation of a Stable Three-Electron Bond	342
The Helium Molecule-Ion	343
10-3. The Oxides of Nitrogen and Their Derivatives	343
Nitric Oxide	343
Dinitrogen Dioxide	344
The Nitrosyl Halogenides.	345
Nitrosyl-Metal Complexes	347
Nitrogen Dioxide	348
Dinitrogen Tetroxide	349
10-4. The Superoxide Ion and the Oxygen Molecule	351
The Ozonide Ion	354
10-5. Other Molecules Containing the Three-Electron Bond	355
The Structure of the Semiquinones and Related Substances	357
10-6. Electron-deficient Substances	363
10-7. The Structure of the Boranes	367
10-8. Substances Related to the Boranes.	379
10-9. Substances Containing Bridging Methyl Groups	381
Carbonium Ions as Reaction Intermediates	383
Complexes of Olefines and Silver Ion	384

10-10. Ferrocene and Related Substances	385
A Resonating-Bond Treatment of Ferrocene	386

CHAPTER 11

The Metallic Bond

11-1. The Properties of Metals	393
11-2. Metallic Valence	394
11-3. The Metallic Orbital	398
11-4. Interatomic Distances and Bond Numbers in Metals	400
11-5. The Closest Packing of Spheres	404
Cubic and Hexagonal Closest Packing of Equivalent Spheres	404
Closest-packed Structures Containing Nonequivalent Spheres	407
11-6. The Atomic Arrangements in Crystals of Metallic Elements	409
Closest-packed Structures	409
Metal Structures Related to Closest-packed Structures	412
The Cubic Body-centered Arrangement	414
11-7. The Electronic Structure of the Transition Metals	414
11-8. Metallic Radii and Hybrid Bond Orbitals	417
11-9. Bond Lengths in Intermetallic Compounds	421
1-10. Structures of Intermetallic Compounds Based on the Simple Elementary Structures	424
11-11. Icosahedral Structures	425
11-12. The γ -Alloys; Brillouin Polyhedra	429
11-13. Electron Transfer in Intermetallic Compounds	431
11-14. Compounds of Metals with Boron, Carbon, and Nitrogen	435
11-15. Molecules and Crystals Containing Metal-Metal Bonds	436
11-16. The Structures of Sulfide Minerals	442

CHAPTER 12

The Hydrogen Bond

12-1. The Nature of the Hydrogen Bond	449
12-2. The Effect of the Hydrogen Bond on the Physical Properties of Substances	454
12-3. Hydrogen Bonds Involving Fluorine Atoms	460
12-4. Ice and Water; Clathrate Compounds	464
Clathrate Compounds	469
Water	472
12-5. Alcohols and Related Substances	473
12-6. Carboxylic Acids	477
Symmetrical Hydrogen Bonds between Oxygen Atoms	484
12-7. The Spectroscopic Study of the Hydrogen Bond	485
Compounds Showing Strong Hydrogen-Bond Formation	486
The Formation of Weak Intramolecular Hydrogen Bonds	490
Factors Affecting Hydrogen-Bond Formation	495

12-8. Hydrogen Bonds in Proteins	498
12-9. Hydrogen Bonds in Nucleic Acids	503

CHAPTER 13

The Sizes of Ions and the Structure of Ionic Crystals

13-1. Interionic Forces and Crystal Energy	505
The Born-Haber Thermochemical Cycle	510
13-2. The Sizes of Ions: Univalent Radii and Crystal Radii	511
13-3. The Alkali Halogenide Crystals	519
Anion Contact and Double Repulsion	520
The Cesium Chloride Arrangement	522
A Detailed Discussion of the Effect of Relative Ionic Sizes on the Properties of the Alkali Halogenides	523
Alkali Halogenide Gas Molecules	530
13-4. The Structure of Other Simple Ionic Crystals	533
The Alkaline-Earth Oxides, Sulfides, Selenides, and Tellurides	533
Crystals with the Rutile and the Fluorite Structures; Interionic Distances for Substances of Unsymmetrical Valence Type	533
The Effect of Ligancy on Interionic Distance	537
The Effect of Radius Ratio in Determining the Relative Stability of Different Structures	540
13-5. The Closest Packing of Large Ions in Ionic Crystals	541
13-6. The Principles Determining the Structure of Complex Ionic Crystals	543
The Nature of the Coordinated Polyhedra	544
The Number of Polyhedra with a Common Corner: The Electro- static Valence Rule	547
The Sharing of Polyhedron Corners, Edges, and Faces	559

CHAPTER 14

*A Summarizing Discussion of Resonance and
Its Significance for Chemistry*

14-1. The Nature of Resonance	563
14-2. The Relation between Resonance and Tautomerism.	564
14-3. The Reality of the Constituent Structures of a Resonating System	567
14-4. The Future Development and Application of the Concept of Resonance	569

Appendices and Indices

I. Values of Physical Constants	573
II. The Bohr Atom	574
III. Hydrogenlike Orbitals	576
IV. Russell-Saunders States of Atoms Allowed by the Pauli Exclusion Principle	580

The Zeeman Effect	581
The Paschen-Back Effect	583
The Extreme Paschen-Back Effect	584
Two Equivalent p Electrons	584
The Landé g -Factor	586
V. Resonance Energy	589
VI. Wave Functions for Valence-Bond Structures	592
VII. Molecular Spectroscopy	594
Electronic Energy Curves; The Morse Function	595
The Vibration and Rotation of Molecules	596
Microwave Spectroscopy	599
Electronic Molecular Spectra	600
Raman Spectra	601
VIII. The Boltzmann Distribution Law	602
The Boltzmann Distribution Law in Classical Mechanics	603
IX. Electric Polarizabilities and Electric Dipole Moments of Atoms, Ions, and Molecules	605
Electric Polarization and Dielectric Constant	605
Electronic Polarizability	608
The Debye Equation for Dielectric Constant	608
X. The Magnetic Properties of Substances	611
Diamagnetism	611
Paramagnetism	612
Ferromagnetism	614
Antiferromagnetism	615
Ferrimagnetism	617
XI. The Strengths of the Hydrohalogenic Acids	618
XII. Bond Energy and Bond-Dissociation Energy	622
Author Index	625
Subject Index	636