

# UNIVERSITY *Chemistry*

DONATION-HILL NOT FOR RESALE  
ONLY 12 ASAD

**Brian B. Laird**

# University Chemistry

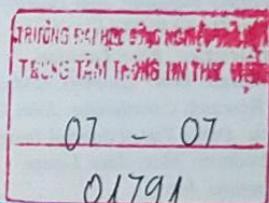
Brian B. Laird

*University of Kansas*

With significant contributions by

Raymond Chang

*Williams College*



GIFT OF THE ASIA FOUNDATION  
NOT FOR RE-SALE

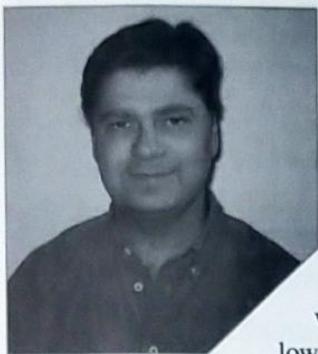
QUÀ TẶNG CỦA QUỸ CHÂU Á  
KHÔNG ĐƯỢC BÁN LẠI



**McGraw-Hill  
Higher Education**

Boston Burr Ridge, IL Dubuque, IA New York San Francisco St. Louis  
Bangkok Bogotá Caracas Kuala Lumpur Lisbon London Madrid Mexico City  
Milan Montreal New Delhi Santiago Seoul Singapore Sydney Taipei Toronto

# About the Author



**Brian B. Laird**, a native of Port Arthur, Texas, is currently a Professor of Chemistry at the University of Kansas in Lawrence, Kansas. He received Bachelor of Science degrees in Chemistry and Mathematics from the University of Texas, Austin, in 1982, and a Ph.D. in Theoretical Chemistry from the University of California, Berkeley, in 1987. Prior to his current position, he held postdoctoral and lecturer appointments at Columbia University, Forschungszentrum Jülich, Germany (NATO Fellowship), University of Utah, University of Sydney, and the University of Wisconsin. His research interests involve the application of statistical mechanics and computer simulation to the determination of properties of liquid and solids. In addition to honors general chemistry, he regularly teaches undergraduate physical chemistry and graduate courses in quantum and statistical mechanics. In his spare time, he enjoys golfing, bicycling, playing the piano, and traveling.

# Brief Contents

0	The Language of Chemistry .....	1
1	The Quantum Theory of the Submicroscopic World .....	71
2	Many-Electron Atoms and the Periodic Table .....	126
3	The Chemical Bond .....	170
4	Molecular Structure and Interaction .....	222
5	The States of Matter I: Phase Diagrams and Gases .....	281
6	The States of Matter II: Liquids and Solids .....	333
7	Thermochemistry: Energy in Chemical Reactions .....	364
8	Entropy, Free Energy, and the Second Law of Thermodynamics ....	423
9	Physical Equilibrium .....	466
10	Chemical Equilibrium .....	511
11	Acids and Bases .....	556
12	Acid-Base Equilibria and Solubility .....	611
13	Electrochemistry .....	663
14	Chemical Kinetics .....	712
15	The Chemistry of Transition Metals .....	772
16	Organic and Polymer Chemistry .....	800
17	Nuclear Chemistry .....	855
<b>Appendix 1</b>	Measurement and Mathematical Background .....	A-1
<b>Appendix 2</b>	Thermodynamic Data at 1 Bar and 25°C .....	A-14
<b>Appendix 3</b>	Derivation of the Names of Elements .....	A-20
<b>Appendix 4</b>	Isotopes of the First Ten Elements .....	A-26

# Expanded **Contents**

*List of Applications* *xiv*

*Preface* *xv*



## 0 The Language of Chemistry

0.1	Chemistry Is the Study of Matter and Change .....	2
0.2	Matter Consists of Atoms and Molecules .....	11
0.3	Compounds Are Represented by Chemical Formulas .....	20
0.4	Reactions Are Represented by Balanced Chemical Equations .....	31
0.5	Quantities of Atoms or Molecules Can Be Described by Mass or Number .....	34
0.6	Stoichiometry Is the Quantitative Study of Mass and Mole Relationships in Chemical Reactions .....	52



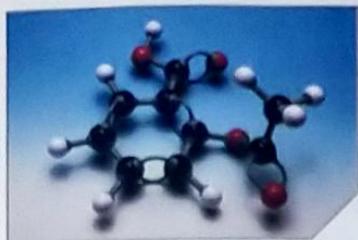
## 1 The Quantum Theory of the Submicroscopic World

1.1	Classical Physics Does Not Adequately Describe the Interaction of Light with Matter .....	72
1.2	The Bohr Model Was an Early Attempt to Formulate a Quantum Theory of Matter .....	83
1.3	Matter Has Wavelike Properties .....	94
1.4	The Hydrogen Atom Is an Exactly Solvable Quantum-Mechanical System .....	109

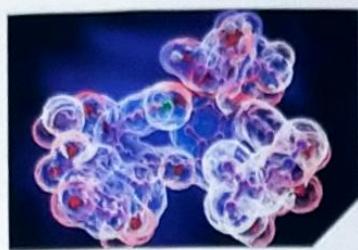


## 2 Many-Electron Atoms and the Periodic Table

2.1	The Wavefunctions of Many-Electron Atoms Can Be Described to a Good Approximation Using Atomic Orbitals .....	127
2.2	Electron Configurations of Many-Electron Atoms Are Constructed Using the <i>Aufbau</i> (or “Building-up”) Principle .....	134
2.3	The Periodic Table Predates Quantum Mechanics .....	143
2.4	Elements Can Be Classified by Their Position in the Periodic Table .....	146
2.5	The Properties of the Elements Vary Periodically Across the Periodic Table .....	149



<b>3 The Chemical Bond</b>	<b>170</b>
3.1 Atoms in a Molecule Are Held Together by Chemical Bonds	171
3.2 A Covalent Bond Involves the Sharing of Electrons Between Atoms in a Molecule	173
3.3 Electronegativity Differences Determine the Polarity of Chemical Bonds	182
3.4 Drawing Correct Lewis Structures Is an Invaluable Skill for a Chemist	189
3.5 Molecular Orbital Theory Provides a Detailed Description of Chemical Bonding	202



<b>4 Molecular Structure and Interaction</b>	<b>222</b>
4.1 The Basic Three-Dimensional Structure of a Molecule Can Be Predicted Using the VSEPR Model	223
4.2 The Polarity of a Molecule Can Be Described Quantitatively by Its Dipole Moment	234
4.3 Valence Bond Theory for Polyatomic Molecules Requires the Use of Hybrid Orbitals	240
4.4 Isomers Are Compounds That Have the Same Molecular Formula but Different Atomic Arrangements	252
4.5 Bonding in Polyatomic Molecules Can Be Explained Using Molecular Orbitals	257
4.6 The Interactions Between Molecules Greatly Affect the Bulk Properties of Materials	262



<b>5 The States of Matter I: Phase Diagrams and Gases</b>	<b>281</b>
5.1 Pressure and Temperature Are Two Important Macroscopic Properties of Chemical Systems	282
5.2 Substances and Mixtures Can Exist as Solid, Liquid, or Gas, Depending upon the External Conditions	286
5.3 The Ideal-Gas Equation Describes the Behavior of All Gases in the Limit of Low Pressure	292
5.4 The Kinetic Theory of Gases Provides a Molecular Explanation for the Behavior of Gases	308
5.5 Real Gases Exhibit Deviations from Ideal Behavior at High Pressures	317



<b>6 The States of Matter II: Liquids and Solids</b>	<b>333</b>
6.1 The Structure and Properties of Liquids Are Governed by Intermolecular Interactions	334
6.2 Crystalline Solids Can Be Classified in Terms of Their Structure and Intermolecular Interactions	341
6.3 The Properties of Crystalline Solids Are Determined Largely by Intermolecular Interactions	351
6.4 Band Theory Accurately Explains the Conductivity of Metals, Semiconductors, and Insulators	356



<b>7 Thermochemistry: Energy in Chemical Reactions</b>	<b>364</b>
7.1 Thermodynamics Is the Study of Energy and Its Transformations in Macroscopic Systems .....	365
7.2 The Energy Absorbed by a System as Heat in a Constant-Pressure Process Is Equal to the Change in Enthalpy .....	375
7.3 The Temperature Change of a System upon Heating Is Governed by Its Heat Capacity .....	381
7.4 The Enthalpy Changes for any Reaction Can Be Calculated Using Standard Enthalpies of Formation .....	395
7.5 The Reaction Enthalpies Can Be Estimated from Bond Enthalpies .....	401
7.6 Enthalpy Changes Also Accompany Physical Transformations .....	405
7.7 The Temperature Dependence of Reaction Enthalpies Can Be Determined from Heat Capacity Data .....	412



<b>8 Entropy, Free Energy, and the Second Law of Thermodynamics</b>	<b>423</b>
8.1 The Entropy of an Isolated System Always Increases in Any Spontaneous Process .....	424
8.2 The Entropy Change for a Process Can Be Calculated Using the Thermodynamic Definition of Entropy .....	432
8.3 The Third Law of Thermodynamics Allows Us to Determine Absolute Entropies .....	440
8.4 The Spontaneity of a Process at Constant Temperature and Pressure Is Governed by the Gibbs Free Energy .....	446
8.5 The Mixing of Pure Substances Leads to an Increase in the Entropy and a Decrease in the Gibbs Free Energy .....	456
8.6 In Living Systems, Spontaneous Reactions Are Used to Drive Other Nonspontaneous, but Essential, Biochemical Processes .....	459



<b>9 Physical Equilibrium</b>	<b>466</b>
9.1 The Phase Boundaries in Pure Substances Can Be Predicted Using Thermodynamics .....	467
9.2 The Solubility of a Substance Is Determined by Temperature, Pressure, and Intermolecular Forces .....	473
9.3 The Liquid-Vapor Phase Equilibrium of a Solution Can Be Understood in Terms of the Entropy of Mixing and the Intermolecular Forces .....	483
9.4 Colligative Properties Are Properties of Solution Phase Equilibria That Depend Only upon the Number of Solute Molecules, Not Their Type .....	491

## **10 Chemical Equilibrium** ..... **511**

10.1 The Equilibrium Constant Governs the Concentration of Reactants and Products at Equilibrium .....	512
10.2 The Equilibrium Constant Can Be Used to Predict the Direction and Equilibrium Concentrations of a Chemical Reaction .....	524
10.3 The Equilibrium Constant for a Reaction Can Be Determined from the Standard Gibbs Energy Change .....	531
10.4 The Response of an Equilibrium System to a Change in Conditions Can Be Determined Using Le Châtelier's Principle .....	536



## 11 Acids and Bases ..... 556

11.1	Many Processes in Chemistry Are Acid-Base Reactions .....	557
11.2	The Acid-Base Properties of Aqueous Solutions Are Governed by the Autoionization Equilibrium of Water .....	564
11.3	The Strengths of Acids and Bases Are Measured by Their Ionization Constants .....	570
11.4	The pH of an Acid or Base Can Be Calculated If Its Ionization Constant Is Known .....	579
11.5	The Strength of an Acid Is Determined in Part by Molecular Structure .....	590
11.6	Many Salts Have Acid-Base Properties in Aqueous Solution .....	594
11.7	Oxide and Hydroxide Compounds Can Be Acidic or Basic in Aqueous Solution Depending on Their Composition .....	600



## 12 Acid-Base Equilibria and Solubility ..... 611

12.1	Ionization of Weak Acids and Bases Is Suppressed by the Addition of a Common Ion .....	612
12.2	The pH of a Buffer Solution Is Resistant to Large Changes in pH .....	615
12.3	The Concentration of an Unknown Acid or Base Can Be Determined by Titration .....	622
12.4	An Acid-Base Indicator Is a Substance That Changes Color at a Specific pH .....	631
12.5	A Precipitation Reaction Occurs when a Reaction in Solution Leads to an Insoluble Product .....	633
12.6	The Solubility Product Is the Equilibrium Constant for the Dissolution Process .....	635
12.7	The Solubility of a Substance Is Affected by a Number of Factors .....	644
12.8	The Solubility Product Principle Can Be Applied to Qualitative Analysis .....	653

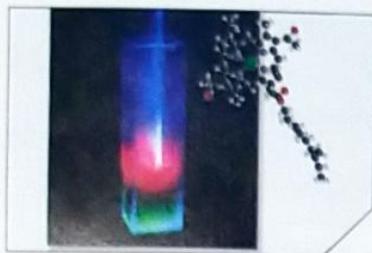


## 13 Electrochemistry ..... 663

13.1	Oxidation-Reduction (Redox) Reactions Involve a Transfer of Electrons from One Species to Another .....	664
13.2	Redox Reactions Can Be Used to Generate Electric Current in a Galvanic Cell .....	671
13.3	The Standard Emf of Any Electrochemical Cell Can Be Determined If the Standard Reduction Potentials for the Half-Reactions Are Known .....	674
13.4	The Emf of an Electrochemical Cell Is Directly Related to the Gibbs Free-Energy Change of the Redox Reaction .....	681
13.5	The Concentration Dependence of the Emf Can Be Determined Using the Nernst Equation .....	686
13.6	Batteries Use Electrochemical Reactions to Produce a Ready Supply of Electric Current .....	692
13.7	In Electrolysis, an Electric Current Is Used to Drive a Nonspontaneous Reaction .....	697



<b>14</b>	<b>Chemical Kinetics</b>	<b>712</b>
14.1	Chemical Kinetics Is the Study of the Rates at Which Chemical Reactions Occur .....	713
14.2	The Rate Law Gives the Dependence of the Reaction Rate on the Reactant Concentration .....	720
14.3	Integrated Rate Laws Specify the Relationship Between Reactant Concentration and Time .....	723
14.4	The Arrhenius Equation Gives the Temperature Dependence of Rate Constants .....	736
14.5	The Reaction Mechanism Is the Sequence of Elementary Steps That Lead to Product Formation .....	744
14.6	Reaction Rates Can Often Be Increased by the Addition of a Catalyst .....	754



<b>15</b>	<b>The Chemistry of Transition Metals</b>	<b>772</b>
15.1	Transition Metals Have Electron Configurations with Incomplete d or f Shells .....	773
15.2	Transition Metals Can Form a Variety of Coordination Compounds .....	777
15.3	Bonding in Coordination Compounds Can Be Described by Crystal Field Theory .....	786
15.4	The Reactions of Coordination Compounds Have a Wide Number of Useful Applications .....	793



<b>16</b>	<b>Organic and Polymer Chemistry</b>	<b>800</b>
16.1	Hydrocarbons Are Organic Compounds Containing Only Hydrogen and Carbon .....	801
16.2	Hydrocarbons Undergo a Number of Important Chemical Reactions .....	811
16.3	The Structure and Properties of Organic Compounds Are Greatly Influenced by the Presence of Functional Groups .....	815
16.4	Polymers Are Large Molecular Weight Compounds Formed from the Joining Together of Many Subunits Called Monomers .....	826
16.5	Proteins Are Polymer Chains Composed of Amino Acid Monomers .....	833
16.6	DNA and RNA Are Polymers Composed of Nucleic Acids .....	841



<b>17</b>	<b>Nuclear Chemistry</b>	<b>855</b>
17.1	Nuclear Chemistry Is the Study of Changes Involving Atomic Nuclei .....	856
17.2	The Stability of a Nucleus Is Determined Primarily by Its Neutron-to-Proton Ratio .....	860
17.3	Radioactive Decay Is a First-Order Kinetic Process .....	867
17.4	New Isotopes Can Be Produced Through the Process of Nuclear Transmutation .....	873
17.5	In Nuclear Fission, a Large Nucleus Is Split into Smaller Nuclei .....	876
17.6	In Nuclear Fusion, Energy Is Produced When Light Nuclei Combine to Form Heavier Ones .....	882
17.7	Radioactive and Stable Isotopes Alike Have Many Applications in Science and Medicine .....	884
17.8	The Biological Effects of Radiation Can Be Quite Dramatic .....	886

<b>Appendix 1 Measurement and Mathematical Background .....</b>	<b>A-1</b>
A1.1    Measurement .....	A-1
A1.2    Mathematical Background .....	A-7
<b>Appendix 2 Thermodynamic Data at 1 Bar and 25°C .....</b>	<b>A-14</b>
<b>Appendix 3 Derivation of the Names of the Elements .....</b>	<b>A-20</b>
<b>Appendix 4 Isotopes of the First Ten Elements .....</b>	<b>A-26</b>
<i>Glossary .....</i>	<i>G-1</i>
<i>Answers to Even-Numbered Problems .....</i>	<i>AP-1</i>
<i>Credits .....</i>	<i>C-1</i>
<i>Index .....</i>	<i>I-1</i>