

Inorganic Chemistry: Principles of Structure and Reactivity

Editors

Haneen Mohammed Abbas Kasar

Department of Chemistry, College of Science, University of Karbala, Iraq

Zainab Najib Badr Abd.

Department of Chemistry, College of Science, University of Thi Qar, Iraq

Zahraa Sattar Jaber Khnyab

Department of Chemistry, College of Science, University of Karbala, Iraq

Adil Saleh Mohammed Jofan

Department of Applied Chemistry, College of Applied Sciences, Samarra
University, Iraq

Bright Sky Publications™
New Delhi

Published By: Bright Sky Publications

*Bright Sky Publication
Office No. 3, 1st Floor,
Pocket - H34, SEC-3,
Rohini, Delhi, 110085, India*

Editors: Haneen Mohammed Abbas Kasar, Zainab Najib Badr Abd., Zahraa Sattar Jaber Khnyab and Adil Saleh Mohammed Jofan

The author/publisher has attempted to trace and acknowledge the materials reproduced in this publication and apologize if permission and acknowledgements to publish in this form have not been given. If any material has not been acknowledged please write and let us know so that we may rectify it.

© *Bright Sky Publications*

Edition: 1st

Publication Year: 2024

Pages: 74

E-book ISBN: 978-93-6233-392-6

Paperback ISBN: 978-93-6233-579-1

DOI: <https://www.doi.org/10.62906/bs.book.181>

Price: ₹ 445/-

Contents

Sl. No.	Chapters	Page No.
1.	Introduction to Inorganic Chemistry	01-03
2.	Atomic Structure and Properties	04-06
3.	Chemical Bonding in Inorganic Compounds	07-22
4.	Coordination Chemistry	23-25
5.	Solid State Chemistry	26-44
6.	Acids and Bases in Inorganic Chemistry	45-46
7.	Redox Chemistry	47-48
8.	Descriptive Chemistry of the Elements	49-51
9.	Bioinorganic Chemistry	52-54
10.	Applications of Inorganic Chemistry	55-57
11.	Environmental Inorganic Chemistry	58-60
12.	Nuclear Chemistry	61-62
13.	Experimental Techniques in Inorganic Chemistry	63-65
	References	66-74

Chapter - 1

Introduction to Inorganic Chemistry

Inorganic chemistry is the branch of chemistry associated primarily with elements and their relationships to each other and to carbon, hydrogen, nitrogen, oxygen, or sulfur, the nonmetals studied in the field of organic chemistry. In the past, nonmetals and organometallic species were excluded from the scope of inorganic chemistry, but in our knowledge-based society, this distinction is no longer valid. For example, the chemistry of boron, despite its metallic luster, is considered a pentalent chemistry. Although carbon, hydrogen, and oxygen are usually considered as organometallic derivatives, nonmetals are, as shown by the example of silicon, emetals. Therefore, elements and all of their compounds are included in modern inorganic chemistry. The relationship between atomic structure and chemical reactivity is an important part of the field of study, and the results of such investigations often lead to new concepts about the nature of matter.

During our time as young, eager students, we dedicated ourselves to the intricate study of inorganic chemistry. This involved classifying, summarizing, and memorizing a multitude of reaction series to the best of our abilities. I can vividly recall moments of joy and excitement when we were tasked with memorizing the series involving dilute and concentrated aqua regia, sulfuric acid, superphosphate, along with the various materials that participate in this specific reaction series. The knowledge we gained during those formative educational experiences proved to be tremendously valuable and relevant even today.

It's essential to note that truly appreciating the field of chemistry is not necessarily something that emerges solely at the introductory levels of education. The determination of patterns, recognizing trends over time, is a crucial aspect of scientific inquiry and study. However, beyond simply summarizing the information, it is equally vital to engage in a thorough process of comparing and contrasting. This includes conducting quantitative analyses among synthesized and potential reaction ratios, along with careful observations that arise through the examination of the reaction series. These practices serve as fundamental principles deeply rooted in the field of inorganic chemistry.

More specifically, our aspiration is that modern chemistry can emerge as a clarifying force, elucidating complex relationships. By establishing well-defined mechanistic models, we hope to provide logical yet unequivocal explanations for the phenomena we observe. This pursuit enables us to accurately describe and effectively predict the conversion of matter, ensuring a deeper understanding of the processes that govern chemical reactions. Ultimately, this comprehension is vital for the continued advancement of scientific knowledge in the vast realm of chemistry ^[1-3].

1.1 Scope, Significance and Importance in Context

When most of us think about the captivating and complex world of the chemical sciences, the first concepts that generally come to mind tend to be the more glamorous and visually appealing areas that deal extensively with the chemistry of organic compounds. This could be through organic structure and reactions, or perhaps through the fascinating and intricate processes by which profound biological macromolecules operate within living organisms. However, it is crucial to recognize that inorganic chemistry has played and will indeed continue to play-a key and indispensable role in many aspects of our daily lives. It is a diverse field of study that encompasses a range of exciting examples drawn from frontier-based research and possesses direct implications for our continued survival and wellbeing as a species on this planet.

Furthermore, inorganic compounds and materials are fundamental components of everything from our vital internal organs to the very worldwide physical infrastructure of vehicles such as automobiles, trains, buses, and airplanes. In addition, they are integral to larger structures including bridges, ocean liners, and the sophisticated spacecraft that help us explore beyond our terrestrial boundaries. Simply stated, inorganic chemistry stands as an area of central and undeniable importance within the broader realm of the chemical sciences. Consequently, its graduate students thoroughly deserve a comprehensive text that presents an up-to-date and robust foundation for understanding the various structures, synthesis, reactivity, as well as the essential physical and spectroscopic properties of such diverse compounds ^[4-6].

1.2 Historical development

The preceding section might suggest that the subject of coordination compounds is a relatively recent development in chemistry and, in particular, in inorganic chemistry. This would be far from the truth if such a view could be entertained. There are writings concerning inorganic coordination

chemistry dating back 150 years. The great alchemists and some of the early chemists, through their steady interest in and scrutiny of the remarkable array of colors exhibited by a variety of inorganic substances, would have noted the arrangement of certain metal atoms centered in, as well as those lying immediately adjacent to, a variety of specific groups of atoms. Unfortunately, these distinguished alchemists and many of the earlier chemists of the early 19th century had to concern themselves with subjects peripheral to this newly developing chemistry.

The use of properly devised and meticulously measured displacement reactions greatly facilitated the early workers focusing on the chemical exchange properties of inorganic salts. This allowed them to make predictions about the way three distinct groups of atoms within a cation would interact rather uniformly with a diverse array of anions. However, efforts to extend this original perspective regarding the inner core of the cation encountered mixed success and varied results. Moreover, through their innovative use of a variety of plant extracts to conduct analyses of metal ions-at a time when only a limited number of wet chemical methods had been established-these early researchers became increasingly convinced that a select few heavier transition metal cations, along with their higher oxidation states, consistently exhibited the rather peculiar phenomenon of having an odd number of ligands. Consequently, the idea that coordination number 4 could serve as an absolute limitation in this context would no longer be seriously entertained or considered relevant ^[7-9].

Chapter - 2

Atomic Structure and Properties

Atomic structure has been investigated for over a century and is still being studied today. Early models of the atom envisioned electrons as small particles whirling in orbits around the larger and more massive nucleus, but subsequent work showed that the actual motion of the electrons is more complicated. Later models and experimental studies have shown that electrons should be considered as exhibiting both wave-like and particle-like behavior. Like other particles, each electron possesses a property known as spin. The combination of quantum numbers that can be assigned to each electron of an atom helps to account for its characteristic chemistry. Such an assignment begins with the determination of a basic set of quantum numbers. The set is unique for each electron, which means that each electron in an atom may be uniquely identified. Electron spin is quantized to spin up or spin down, and a maximum of two electrons may be distinguished based upon the spin quantum number. For $l = 0$, only one value is possible. When $l = 2$, five values are possible, and so on. Each possible value of m can accommodate two electrons assumed to have the opposite spin quantum number. A shell is completely filled (i.e., each energy level is fully occupied with electrons of the highest possible spin, with similar spins parallel and those of opposite energy; these are the noble gas configurations ^[10-12].

2.1 Quantum Mechanics and Atomic Theory

Inorganic and organic chemists use a theory of structure and bonding to predict the existence of a compound and give possible structural, spectroscopic, and reactivity information. This theory of structure and bonding comes justifiably from quantum mechanics. Quantum mechanics is a revolution in the classical theories of physics. It moves us from describing nature in terms of particles and fields to a theory that describes the probabilities of the actions of the particles and fields. It was this theory that won a Nobel Prize for Physics in 1932. Today, quantum mechanics is universally accepted as a fundamental theory of nature. Almost everything that we see and do can be described by quantum mechanics. The structure of an atom has been under constant study since the 1800s.

The structure of atoms has been extensively probed with an increasing level of insight, starting from the optical emissions produced by flames of alkali metals, and evolving to encompass the exploration of low-energy x-rays emitted from the inner shells of heavy elements, particularly when analyzed using sophisticated techniques such as an electron beam or a synchrotron light source. The variations and anomalies that were meticulously observed throughout these groundbreaking experiments led to ingenious rationalizations concerning the atom's apparent structure. Additionally, these explorations spurred the development of models that illustrated significant and profound applications within the realm of chemistry. However, numerous shortcomings became evident in the prevailing physical descriptions, including atomic models such as the plum pudding model and the classical theory of radiation energy distributions, which could not sufficiently address or explain certain unexpected features inherent in these distributions of radiation energy.

Subtle variations that appeared to be entirely impossible to reconcile with classical descriptions of light-matter interactions were, nonetheless, demonstrated to provide deeper insights into the nature of atomic behavior. These insights were achieved through the correctly chosen forms of angular momentum, which allowed resolutions of the many enigmatic phenomena that, during the late 1800s, posed seemingly insurmountable obstacles to reformulating a useful and coherent classical description of these critical atomic observations. Quantum numbers and the allowed energy levels for a variety of atomic systems were characterized, illuminating the intricate band of energy levels that any electron can occupy, intricately detailing the motion of the electron as it orbits around the atomic nucleus. This exploration also encompassed the formation of molecules featuring complex shapes and electronic structures.

Armed with a few foundational constructs from the toolkits of quantum mechanics, alongside hands-on experience with these purely synthetic atoms and molecules, the subject of atomic and molecular 'orbital' theory for inorganic chemists had begun in earnest and was rapidly gaining traction. This transformative period allowed for an in-depth understanding of how various atomic interactions fundamentally altered our comprehension of elemental behavior and reactivity in chemical processes, thereby laying the groundwork for modern chemistry and materials science as we know them today ^[13-15].

2.2 Periodic Trends

The periodic table is a tabulation of the chemical elements based upon their atomic numbers and chemical properties. The vertical columns are termed groups and numbered from one to eighteen. Elements present in the same column generally have similar chemical properties. The horizontal rows are termed periods and are related to the quantum state of the valence electron. The table is thought to be particularly useful for understanding the reactivity of the elements. Some trends in chemical reactivity are discussed below.

The s-Block: The elements located in Group 1 of the periodic table are commonly referred to as the alkali metals. These particular elements are characterized by their inner electronic configuration of $ns1$, which plays a significant role in their chemical behavior. The first ionization energy of these alkali metals is notably low, which makes them highly reactive and prone to forming ionic bonds with various nonmetals. They exhibit a softness that allows them to be easily cut with a knife, which is a physical property that distinguishes them from many other metals. As we progress down the periodic column, the reactivity of the alkali metals increases because the atomic size becomes larger and polarizability is also enhanced. Group 1 comprises not only lithium, sodium, and potassium but also the heavier alkaline earth metals. These elements consistently exhibit fairly low first and second ionization energies, and they readily form +1 and +2 cations upon reacting with nonmetals during chemical reactions. In comparison to the alkali metals, the alkaline earth metals are denser, have higher melting and boiling points, and are more chemically reactive than their corresponding counterparts found in Group 1 of the periodic table. Despite their various properties, it is important to note that, in general, alkaline earth metals are not found in nature in their elemental or pure states ^[16-18].

Chapter - 3

Chemical Bonding in Inorganic Compounds

We use molecular models or detailed drawings of molecular orbitals in order to visualize and better understand the complex shapes and the extent of bonding as well as antibonding orbitals. This technique also helps us predict the specific energies at which different orbitals will interact with one another. In our previous studies, we have already explored the observation that the energy levels of the s orbitals tend to decrease methodically as we progress from the left side to the right side across the periodic table of elements. When we combine the p orbitals with the highest occupied s or d orbital, we effectively create the strongest possible interactions. It is important to note that even though the d orbitals are ideally suited for facilitating electron interactions most effectively with the lighter p electrons, it has been found that p electrons are comparatively more capable than s electrons in this context. As a direct result of this, p elements are likely to undergo a form of d character hybridization. Chemical bonding, as used in inorganic chemistry, is the fundamental link through which the majority of interactions are achievable. It is basically accountable for the two most important processes: the formation of chemical compounds through chemical reactions and the relationship between the different types of properties achieved. The composition of a compound is not just a thorough outcome of all its properties, but also a result of all its chemical, physical, biochemical, and physiological performance. Moreover, chemical bonding in inorganic chemistry plays a significant role in explaining inorganic analysis, as chemical bonding influences the structure of molecular communities or solid-state lattices. It provides a complete and specific description, using both quantum and classical chemical theories, regarding the types of forces and interactions taking place within bounds. It fosters a platform that is formal and quantitative, which allows for the characterization of general trends, as well as the similarities and discrepancies among the relationships.

Since two elective electrons are produced in the majority of chemical reactions, the chemical bond that occurs within a molecule is primarily established through the transfer of valence electrons. The subsequent interactions, which happen within a certain range and rely on the close bond

between the nuclei, are of short-range attraction. Thus, it is initially concluded that bond formation requires the circulation of valence electrons to fulfill the bond. The concept of valency, conversely, tends to limit the similarities of bond behavior to the idea that one type of chemical bond just transfers valence electrons in molecular orbitals. More uniquely, an element's reactivity relies on reactions that transfer the necessary electrons that are then available for bond formation. Because of this primary aspect of bonding, the explanations of the distinction between latent and lenticular elements include the kinds of ionic and covalent chemical bonds.

In the formation of inorganic compounds, atoms combine through interactions between largely filled, not-so-energy-differentiated orbitals. The chemistry of inorganic compounds is unlike that of organic compounds, which frequently have small-energy-differentiated, singly occupied orbitals combining into energetic π -bonds. In inorganic compounds, metals exhibit mainly metallic bonding, the sharing of many delocalized or nearly delocalized electrons among a large volume of atoms. Covalent bonds form in the reactions of nonmetal atoms, and there is a broad range of polarities and other bonding features to consider. The interactions between metal cations and nonmetal anions determine ionic bonding, a feature of most simple metal salts, which cannot be thought to be either purely ionic or purely covalent. There are a range of intermediate types of bonds between these extremes.

The nature of bonding in inorganic compounds-particularly the relative importance of covalent, ionic and metallic bonds-is a frequent target of conjecture and occasionally great controversy. Bonding theories that have withstood close scrutiny are few. Fortunately, as skillful as solitaire players with a new deck of cards, inorganic chemists usually can rationalize their observations of reactivity, function, and behavior, albeit sometimes resorting to multiple sets of rules. Indeed, the mass of rules of thumb for classifying the chemical bonds is considerably larger than the small number of first principles that justify them. Although inorganic chemists cannot rival astronomers in being able to infer what exists far beyond the reach of current observation, they likewise postulate unexpected bonding phenomena worthy of development.

Coordinate covalent bonds are generally less ionic in character when the bond is broken than are regular covalent bonds. It is not surprising that the factor favoring the formation of coordinate covalent bonds is the ability of an open electron shell to accept two electrons and so become filled. This is just the effect that underlies sigma donor bonding to $d\pi$ orbitals of transition metals, and in complexes of this type, the acceptor atom would contribute a

single electron and then become closed-packed. The fact that the bond is readily broken by the acceptor atom, yet the reverse process, i.e., the coordination of the oxygen atom to the nitrogen atom, forms the rather unstable oxyanion, suggests that the oxyanion is achieved only at the expense of making some other species less stable than would be the case if the oxyanion did not exist.

The metallic bond is the bond found in elements and is responsible for the nature of several properties in pure substances. It can be thought of as a small gradient of bonding found in systems where the electrostatic bonding is modified by the screening behavior of conduction electrons. These conduction electrons are responsible for the metallic properties such as electrical and thermal conduction, luster, and specific heats at room temperature in some metallic elements. The smallest gradient in bonding at any particular point in the structure is two-thirds of a valence bond per atom.

These bonds are also formed by the mixing of orbitals in a small region in the structure in such a way that both bonding and antibonding interactions are much less with the adjacent atomic core than the average in the interaction Hamiltonian. Such regions are eliminated as far as possible in structure formation so that only some electrostatic repulsions are left to be screened and modified by the conduction system. In the simple free-electron model, the width of the gap is related to the resistance to oxide formation, but some allowance for space should be made in the slightly modified model since lithium forms an oxide so easily while more loosely packed elements such as bismuth or thallium have metal-to-nonmetal-like electronegativities.

Valence bond theory and crystal field theory both make very significant contributions to bonding in inorganic compounds. They were, in fact, the first bonding models developed for these compounds and provide a good deal of predictive strength when we are dealing with chemically compatible electrons. The belief that inorganic compounds might involve non-chemically compatible electrons emerged from a consideration of the elements involved and the periodic table. We thus enter the quantum mechanical theory of chemical bonding through the life and death of electrons in this atomic environment. The resulting crystal field theory sheds much light on structure, spectra, and other properties of many inorganic compounds.

The isolated atom picture is quantitatively valid when the interaction between atoms is weak compared to the energy of the atomic electrons. The atoms are in an electric field that either nearly shields one electron from the remaining electrons or splits these electrons into core and valence sets. The

minimal basis required to describe inorganic compounds consists of quadratic s- and second-rank p-orbitals, as well as d- and f-orbitals. The isolated d and f electrons are important for ionicity and for changes in bonding with nuclear charge, while the sp orbitals strongly polarize, mediate interaction between ions, and contribute substantially to the properties of many elements.

The most basic form of the Lewis structures is the electron-dot structure. The Lewis structure is a simple diagram that displays the total number of valence electrons involved in bond formation in a particular molecule or compound. The Lewis structure contains dots that represent valence electrons, and the chemical elements are shown by their symbols.

The rules for Lewis electron-dot structures are:

- 1) The compound must be neutral (the sum of bond and valence electrons must equal the number of valence electrons of the compound).
- 2) For ions, add or subtract electrons for the electron-dot structure.
- 3) The central atom or less electronegative atoms should be written first.
- 4) Hydrogen and halogen atoms should be terminal.
- 5) Single covalent bonds are represented by a single line.
- 6) Double and triple bonds are represented by two and three lines, respectively.

The total number of electrons in the valence shells of all the atoms in a molecule minus the number of electrons required to fill the valence shells is the total number of electrons that must be shared by the atoms in the molecule. These electrons are normally arranged in pairs that form covalent bonds with the other atoms. The sharing of one pair of electrons forms a single bond, and the sharing of two pairs of electrons forms a double bond. The sharing of three pairs creates a triple bond. The Lewis structure of a molecule provides information regarding the arrangement of the covalent bonds in the molecule, but it does not give any information about the shape of the molecule. In a Lewis structure, the bonding pairs are usually represented by the shared pair of dots, while the lone pairs of electrons are represented only by dots. Lone pairs are the valence electron pairs that are not involved in the formation of the bond. The sigma bond is present in a single bond, and the pi bond is present in double and triple bonds.

The Valence Shell Electron Pair Repulsion theory can predict the electron pair geometry around a central atom in a molecule, or in more complex compounds, the individual atoms composing this structure. This theory treats

molecules purely in terms of moving apart from each other. The shape adopted by a set of atoms in a molecule not only accounts for the positions of the atomic nuclei but also the relative placement of the bonding and non-bonding pairs of valence electrons around the central atom. This shape is determined by minimizing the electron pair repulsions. We can predict the shapes of covalent molecules, irrespective of their electron distribution, with the VSEPR theory. It operates by considering the total number of regions of electron density; the regions of lone pairs of electrons around a given central atom are considered separately from those of shared pairs of electrons, so that the total number of electron groups around the central atom can be determined.

The regions of electron density around the central atom are described in terms of the number of electron groups to which the central atom is bonded, generally pairs of bonded and non-bonded electrons, because the concept of bonds themselves is not purely a notion, but has electronic bases. For example, a double bond is formed from one sigma and one pi interaction. Double bonds have high electron density zones between the two atoms and above and below the plane of the bond, produced by the shorter and stronger sigma interaction, whereas pi interactions are weaker. However, in the context of VSEPR, each electron domain around the central atom will be treated in the same way, according to the valence shell electron pair repulsion model. The relative numbers of different electron domains will be used to predict the shapes of molecules and ions with varying proportions of multiple bonds.

For some simple molecules, an extremely neat picture can be presented in terms of the overlap of the atomic orbitals to make the molecular orbitals. This formed the basis of the Valence Bond Theory. Two atoms approach each other and each sends their half-filled singly occupied atomic p-orbital to mingle with the other. They then combine according to whether it is the anti-bonding combination or the bonding combination which has the lower energy. In this way, the bonding and anti-bonding molecular orbitals are formed. The bonding orbital is depicted as having more electron density between the two carbon atoms. Thus the carbon-carbon bond is described by the electrons appearing in this bonding orbital. Similarly, the anti-bonding orbital has more of its electron density away from the two carbon atoms and this is the orbital of a pair of electrons responsible for the weakening of the carbon-carbon bond on excitation of ethene to its excited state.

This picture of the reorganization of the atomic orbitals when they combine has the great virtue of consistency. What comes from the bonding orbital between hydrogen and other atoms is an attractive interaction. If we look at the charge density in a molecule with a bonding interaction, we find

an accumulation of negative charge between the two atomic nuclei and positive charge beyond them. The only criterion required is that a half-filled atomic orbital be occupied. Just the kind of orbitals we have been told represent the chemical bond. This is then a coherent picture in terms of all earlier discussions concerning the nature of the chemical bond.

Chemical bonding can be described in terms of molecular orbitals in exactly the same way that it is described in elements using atomic orbitals. A molecular orbital is a wave function that describes an electron in a molecule. The linear combination of the atomic orbitals makes a molecular orbital. The interaction between the atomic orbitals is given from the overlap integrals of the atomic orbitals. Since up and down mean the symmetry of spin functions, alpha for m1 and beta for m2 for nodal restrictions in detail and the distance R between m1 and m2, the molecular orbital of the orbital $\Psi_{\{m_1 m_2\}}$ is given by

$$\Psi_{\{m_1 m_2\}} = \frac{1}{\sqrt{2}} \{ \phi_{\{m_1\}}(1) \phi_{\{m_2\}}(2)(\alpha(1) \beta(2) - \beta(1) \alpha(2)) \pm \phi_{\{m_2\}}(1) \phi_{\{m_1\}}(2)(\alpha(1) \beta(2) - \beta(1) \alpha(2)) \}$$

Here, 1 alpha means orbital 1, electron 1, and spin alpha. In the field of a molecule, even electrons of different atoms can be in such a state where, through differentiation, states composed of the principal quantum number, orbital quantum number, and magnetic quantum number can become symmetric. This also means that the atomic orbitals within the same shell can combine with one another.

The polar nature of the covalent bond linking sulfur or oxygen to hydrogen, or of the coordinate bond linking nitrogen to hydrogen, and the spatial configuration of the molecule produce some intermolecular forces that can change the boiling and melting points. In some of the hydrogen chalcogenides, the hydrogen atom is linked with another very electronegative atom, such as sulfur or oxygen, through a covalent bond with substantial ionic character. This character is due to the polar nature, and the molecule overall is quite polar. Although oxygen and sulfur have, respectively, 6 and 16 electrons in the last orbit, hydrogen can make only one bond, so that in H₂O only the two electrons for each oxygen are really taken into account. As hydrogen has only two electrons present, it is near the lack of electrons from the 2s orbital and can receive the oxygen's additional electron pair. It would be associated with a very large electron affinity if this were possible. Therefore, sulfur, or especially oxygen, is not able to donate electrons to the very close hydrogen, and the bond results in being slightly polar.

An alternative attractive force between polar molecules is their electric field interaction. This exists between two adjacent poles or between a charged species and a polar species. The forces arise from the electrostatic interaction between separated opposite charges. These usually result from an unequal distribution of bonding and formal covalent charges within the molecule or ion. Such forces operate between polar molecules and result in increased boiling points and enthalpies of vaporization. Their effects on the thermodynamic properties of solvents and solutes result in a significant change in the asymmetry of the solvent dielectric constant.

The Sign and the Magnitude of the Dipole Vector: Molecular dipole-dipole attractive forces arise from the overall polarity of a molecule which usually allows the definition of a dipole vector. This can be thought of as occurring between atoms bearing a covalent bond where this bond has a significant degree of covalent charge sharing between the bonding atoms. Polar covalent bonding usually occurs for atoms of different electronegativity, for example, when diamond or graphite are treated similarly. The degree of covalent charge sharing can be estimated by comparing the electronegativity of the two atoms. The Standard Electronegativity unit has been defined as 1/12 of the bond energy of a carbon atom in the gaseous phase when it forms bonds with four hydrogen atoms.

When hydrogen atoms are bonded to particularly electronegative atoms like oxygen, nitrogen, or fluorine, the hydrogen atom can electrophilically interact with unshared electron pairs on neighboring electronegative atoms. The interaction is usually quantified as a hydrogen bond. A hydrogen bond is much weaker than a full covalent bond to hydrogen, but is stronger than dipole-dipole attractions. The hydrogen bond is a special case of a more general class of interaction known as a dipole-dipole charge-dipole attraction. In the case of hydrogen bonding, the hydrogen is bonded to a particularly electronegative atom like oxygen or nitrogen, and the attraction is strongest when the electronegative atom is in the region of a complete negative charge. Hydrogen bonds are usually drawn as dashed lines. The bond could be viewed as a particularly weak dipole-dipole interaction, in which the dipole is a partial charge on the hydrogen atom. The majority of hydrogen bonds in water are, however, somewhat stronger than the hydrogen bonds in other compounds since water is capable of accepting a total of two hydrogen bonds through its unshared electron pairs, it is capable of donating a total of two hydrogen bonds via its protons, and it is capable of accepting a total of two hydrogen bonds.

One of the weakest types of attractive forces that hold molecules together is called London dispersion forces. They are present in all molecules,

including polar molecules. The negatively charged areas of these molecules set up limited attractions in nearby positive areas as the electrons move around the nuclei. These attractions are caused by the motion and process of the electrons. They almost instantaneously produce the negative poles or regions in a non-crystalline structure. In addition, for short times, they can set up forces that dominate the reactions of certain reagents and act on a bond angle and the dipolar repulsive forces.

When the electron units in a molecule attract one another in a series of rapid processes, the resulting set of forces can exteriorize the original effect, and a series of comparable forces will act as attractive forces in a molecule. These short-lived attractions represent London dispersion forces. If two molecules show extensive dispersion interactions, they can diffuse in a few instances. The total dispersion of two molecules depends on the sum of these forces. Thus, dispersion is dependent on the dispersion energies of both members of a pair of like and otherwise neutral molecules.

Numerous complexities arise in understanding bonding in inorganic compounds because of the wide range of bonding types present, the large variety of coordination geometries, metal ion oxidation states, and distinctive physical and chemical properties exhibited by these compounds. This diversity also leads to a very wide array of applications for inorganic compounds. Four unique inorganic compounds are taken as case studies to illustrate the range of bonding and of different properties and methods of synthesizing inorganic compounds. The minerals hematite, callaghanite, and covellite are natural materials that are important ingredients of rocks and ores. The transition metals are important elements in petrology, in part because they are chemically reactive and form brightly colored minerals. The natural minerals are important components of complex mixtures, so synthetic approaches are important to the understanding of structure and bonding. Wolframite is another important ore containing tungsten and iron ions in 2+ and 6+ oxidation states. Its crystal structure will be compared with a different structure found in synthetic tin-iron oxides. Three of the minerals studied, hematite, wolframite, and covellite, come from a collection of minerals developed by a program.

Oxygen is a very electronegative element and, consequently, divalent oxygen O^{2-} is a strong Lewis base. Most metals in the periodic table are capable of donating one or more valence electrons to oxygen, thus yielding divalent metal oxides with the stoichiometric formula, MxO_2 . Alkali metal oxides are obtained as white, crystalline solids by heating the metal to high temperatures in excess oxygen gas. For lithium, sodium, and potassium, M_2O

has the anti-fluorite structure, in which the cations are tetrahedrally coordinated by the oxide anions and the oxide ions are coordinated by the cations. The oxides are used in chemical synthesis and in the glass industry—they are especially useful to decrease the melting points of silica in making glasses. The alkaline earth metal oxides have 12-coordinate cubic close-packed structures in which equal proportions of orientational and positional order are found on the oxide array. BeO, with a chain-like structure of infinite 4-linked oxygen-centered tetrahedra, may be prepared by heating $\text{Be}(\text{OH})_2$ at about 1000 °C. Transition metal oxides, in which two or more elements are combined to form an oxide lattice with mixed metal cation charge states, are used in a variety of applications, and a few—vanadium, titanium, zirconium, tantalum, tungsten, and magnesium oxides—are widely used as industrial pigments. Manufacturers have learned over the years how to control the strengths of colors and to produce the range of cadmium-like planar red and yellow pigments for artists that are referred to by their common trade name.

Chemical Bonding in Inorganic Compounds. Metal Complexes There is a crucial element in the crystal structures of solid compounds in the fact that, in the evaluation of the valency number and chemical bond formation, we must consider the spatial distribution of atoms in space as well as the number of valence electrons. For instance, the valency number of Pt in PtCl_2 is 4 while in PtCl_4 it rises to 6. Actually, the solid compound PtCl_2 consists of a distorted square planar complex while the platinum atom reacts with six molecules of chloride in PtCl_4 . These data suggest that the electronic structure of Pt most likely depends on sterical and crystal-packing conditions at the coordination spheres of the metal complex. The Pt(II) electron configuration, which leads to the PtCl_4 square planar geometry, is d^8 . It implies that two occupied orbitals in the d-block of the metal atom are involved in chemical bond formation. Since the $5\text{Ag}(x^2-y^2)$ orbitals are involved in σ coordination while the $7\text{Ag}(dy^2-z^2)$ are used in the π bond, it depends on the nature of the ligand with specific series in the d^8 , d^7 , and d^6 metal atoms. The $7\text{Ag}(dy^2-z^2)$ requires more energy than the unoccupied π features in the fullerene. For instance, in Ni, a triplet state is ruled out due to the antiparallel spin orientation in the π and the π^* orbitals.

Compounds with atoms coordinated to metals occur in nature. However, they are usually synthesized in the laboratory, and many are used as catalysts. These compounds have atoms or groups connected to a metal center through covalent bonds. Usually, it is the electrons of the atoms that will form these bonds, and not the metal valence electrons. Since there is sharing of the electron pairs between the metal atom and the atom or molecule, these are coordination covalent bonds.

For the number of atoms, ions, or molecules around the central atom that are coordinated to a metal, the following terms are used:

- 1) Monodentate.
- 2) Bidentate.
- 3) Tridentate.
- 4) Tetradentate.
- 5) Pentadentate.
- 6) Hexadentate.
- 7) Heptadentate.
- 8) Octadentate.

In ethylenediaminetetraacetate complex, for example, there are several bidentate and one hexadentate groups coordinated with the metal atom. Aromatic rings, such as phenyl, are called ligands, and some metals possess a high capacity for interfacing with π electrons, such as heme proteins, in which iron is coordinated to a protoporphyrin IX. In a coordination compound, the number of covalent bonds exists as the number of oxidation states of the metallic element. Also, the number of coordinate covalent bonds exists as the number of electrons accepted or donated by the coordinated entities.

Some examples, briefly, should be given of how knowledge of the nature of chemical bonding helps in rationalizing various aspects of chemistry. Nearly all inorganic structures can be explained in terms of the overlapping of positive and negative centers in combination with spherical symmetry. There is no more dramatic example of the descriptive power of the concept of electrostatically attractive negative and positive centers than that offered by the chemical structure of salts. The ionic characters of the halides in the series are in the order of the ionic radii, indicating that increasing dipole weakening in these molecules is primarily due to dipole-dipole repulsions between the dipoles induced on the Group VII-VII interactions by the p or s orbitals belonging to the atoms involved.

It is useful to consider the properties, bonding, and structure of the simple Group X-Group VII species, the covalent halides. There are several covalent halides formed by the second noble gas series elements: namely ClF, ClBr, and the less well-known species ICl and IF. It is interesting to compare the first three in terms of bond length and hybridization. All species have tetrahedral geometry. It is quite reasonable to suggest that because of these large halides, Xe has important differences when compared with Ne, specifically, the increases in the non-bonding electron-electron repulsions and

the increase in polarizability. The calculated total electron-electron repulsive scoring function is lowest for the required geometry, and the lowest energy points are all optimized for C_{2v} structures with tetrahedral angles.

Chemical Bonding in Inorganic Compounds

Catalysis is a complex phenomenon encountered in countless industrial processes and chemical syntheses. Catalysts speed up the rate of a reaction. Catalysts alter the equilibrium of a reaction and do not affect the thermodynamics of the process, as they promote the forward and reverse rates of the reaction equally. They are material aids to chemistry: they work by providing alternative reaction pathways of reduced activation energy, thereby allowing reactions to occur more favorably. An important type of catalyst operates by the process of adsorption (bond formation) between reactant species and the catalyst surface.

Heterogeneous microstructured catalysts assist such gas-solid reactions, taking a central role in the petrochemical, food, and automotive industries, gasoline, pharmaceuticals, inward and outward economic processing, and a sustainable environmental future. Current research efforts are opposing opulent exploration of selective and highly active microstructured materials driven by inherent chemical selectivities, chemically coherent and highly responsive external and internal surfaces, and interfacial defectiveness. Characteristic patterns of solid surfaces, as well as contact sites, together with only labile surface and chemical structures, make these open and coordinatively unsaturated defect sites intrinsically powerful in utilizable catalysts. These improved catalysts with targeted selectivity are necessary to heterogeneously promote specific chemical reactions in technological processes, not ultimately accessible through homogeneous catalysis.

The arrangement of bonding interactions in larger inorganic materials has led to the development of different fields of chemistry, in particular materials science. Engineers have developed new classes of materials by taking subsequent bonding trends at face value. Whereas metallurgical alchemy led to brass, an alloy of Cu and Zn, in approximately 1000 BCE, present-day developers simply mix different amounts of Cu and Zn starting materials and heat them in a crucible to reach the desired result. One recent focus has been the discovery of new superconductors at different bonds' tune.

Take for instance the emergence of materials with much higher superconducting transition temperatures than the prototypically well-known inductive alloy. It seems that the only thing that changed was the arrangement of atoms in a square planar architecture. In the classical geometry, Pb and Sn

have a tetrahedral arrangement with respect to each other, in an approximate Mexican hat arrangement. Energy considerations seem to indicate that the presence of ordered discrete compounds on a square grid might provide a decisive advantage. Other parameters that can also be adjusted include the size of the spherical parts of the architectonic components. This discovery and many similar ones pave the way from inorganic materials as a conglomeration of compounds displaying a certain phenomenon at a given standard arrangement, towards inorganic substrates as classes of substrates that can house a certain phenomenon at equally emerging architectural factors.

In the context of medical inorganic chemistry, metal-containing drugs are usually considered. The term "elemento-organic" is used to indicate that specific organic substituents can be coordinated to metal ions in compounds with interesting properties and useful biological activities. A final paragraph is dedicated to inorganic powders, nanomaterials, and metal-ligand bond substitution in metal complexes. Inorganic chemistry is increasingly taking its place in the contemporary medical world. The expression "Medicinal Inorganic Chemistry" has been coined recently to define a sub-branch of inorganic chemistry at the interface with life sciences and medicinal chemistry in the broadest sense. Whereas the first drugs were mainly inorganic materials, complete neglect followed for two millennia, although lithium carbonate, bismuth salts, and mercury compounds were used sporadically or continuously in various civilizations to treat psychiatric conditions, digestive tract troubles, and sexually transmitted diseases, respectively. Lately, mainly and exclusively in the last 50 years, a burgeoning amount of interest has been paid to medicinal inorganic compounds, especially to those appropriate to support life functions, such as metals, namely sodium, potassium, magnesium, calcium, and iron, but also to many other inorganic compounds. Much attention is also dedicated to compounds able to modify or block the activity of such organizers when negatively distorted due to genetic or environmental pressures. These organizers usually involve soft acids and bases, so the covered inorganic compounds are generally characterized by bonds that are weaker and more reversible than metallic and covalent bonds, usually within the same compound. The chemical bond therefore becomes very relevant in medicinal inorganic chemistry. Small amounts of a number of trace elements, such as cobalt, copper, iodine, and zinc, to name just a few, are also necessary in human and animal diets.

The final section of this monograph is designed to give us some glimpses of future advances and trends in inorganic chemical bonding. This field is changing rapidly, and we cannot survey it with anything like completeness.

However, we can look at a few of the changes that the future might hold, and we can make some suggestions that might help us prepare for and guide those changes. The place to begin is with a summary of the state of the art in this field.

We have chosen to focus for the remainder of this monograph on the advances in chemical bonding that are revealing to us the details of the building blocks and fundamental principles of inorganic chemistry. This was a decision based primarily on an assessment of the relative merits of four broad reasons for their greater importance. The most compelling reason for putting our spotlight on fundamental questions is rooted in a long-standing tradition of rationalizing matter that is unusual, exotic, or new. At such times, observation outpaces theory, so we become more interested in basic concepts.

All orbitals are characterized by their distinct lobed shapes, which can overlap with one another to create a bonding interaction. This interaction allows two electrons to exist within the bonding orbital simultaneously. However, it is crucial to recognize that these lobes also possess opposite signs. When positioned side by side, the opposite signs can lead to an interfering interaction that precludes the possibility of bonding occurring. This particular type of interaction is commonly referred to as the antibonding interaction. If, within a given orbital system, there are more electrons engaged in the bonding interaction compared to the number of electrons involved in the antibonding interaction, then we can successfully form a stable bond between the atoms involved. The balance between these interactions plays a significant role in determining the overall stability and characteristics of a molecular structure [19-21].

3.1 Ionic Bonding

Bonds that form between atoms involve a complex process of redistribution concerning the individual valence electrons that are present within each atom. In the case of ionic bonding, valence electrons are inevitably transferred from one atom to another, which leads to the formation of ions. These ions are subsequently held together by attractive electrostatic interactions that can be quite powerful. In many instances, especially notable is when an entire electron is transferred completely from one atom to another, resulting in distinct charged entities. A very typical example of this behavior can be observed in the bonds that are formed within the compounds comprising alkali metals and halogens.

Chemical Bonding in Inorganic Compounds

Because of the relative paucity of electrons and the propensity of most elements to achieve a stable noble gas configuration, there is a tendency for

most atoms in compounds to lose or gain electrons to achieve that configuration. For the major metals in the periodic table, the valence state of maximum stability is the one that is derived by the loss of electrons in the s subshell, and for the majority of the nonmetals, the most stable valence state is that achieved by the addition of electrons to the p subshell. The highest valence state is commonly encountered when the added or subtracted electrons fill all the respective valence shell orbitals. For many of the first transition series elements, this generally carries the ions across the periodic table from the metal to the nonmetal side, providing a surprising segue between metal and nonmetal ions. This electron transfer is the basis of the formation of ionic bonds between atoms. Sugars, common salt, metals, and most minerals are held together largely because of ionic bonding forces.

Among the many intriguing aspects of solid-state chemistry is the plethora of bonding motifs, especially in the case of the diverse polyhedral structures and precisely localized interactions found in molecular complexes, extended or framework structures, and nanoparticles. Many examples of common or classical bonding motifs, including metallic, ionic, and covalent interactions, can be discerned in more complex structures. In the present work, we will discuss characteristics and examples of many of these bonding motifs as illustrated by metal carbonyl compounds, including metallocenes and metal nitrosyl and hydride complexes, and compounds of the nonmetals boron, carbon, nitrogen, oxygen, and sulfur. According to the Lewis definition, a covalent bond is formed by the sharing of an electron pair by adjacent atoms. Based on the observed geometric structure of single and multiple bonds, the electron clouds can be considered in various ways and can influence and be influenced by the exchange of energy within a molecule. These pathways involve the formation and subsequent successive breakages of the bond.

When a covalent bond is formed by the donation of a lone pair of electrons from one atom to another, the bond is described as a coordinate covalent bond. Usually, the atom donating the lone pair of electrons is polarized by the acceptor atom and, as a consequence, the bond is rather ionic in character. In general, the donor and acceptor atoms play different roles in the resulting compound. Examples of this type of bond occur in the neutral ligand-to-sigma donor bonding present in transition metal hydrides and numerous other complexes of the transition elements. In compounds such as ammonia, the positive nitrogen atom is invariably a very good proton acceptor and bonds to a proton, yet nitric acid readily forms from nitrogen dioxide and water, and in this case a lone pair of electrons is donated to the oxygen atom.

When examining the formation of an alkali metal compound, the alkali metal undergoes a transformation to become a cation by losing one electron from its ns orbital. This loss ultimately leads to a new electron configuration that corresponds to $(n - 1)d^{10}s^1$. Conversely, in this process, a halogen atom takes in an electron into its np orbital, successfully filling out its valence shell. As a result, the halogen becomes an anion with a charge of -1 . The loss of electrons experienced by the metal and the gain of electrons by the nonmetal culminate in the fascinating outcome where both metals and nonmetals exhibit an identical number of valence electrons. This is characterized by either the loss or gain of electrons, as observed in noble gases from the preceding period.

The ions that are formed as a direct result of these chemical reactions will possess a complete shell of valence electrons. In the specific cases involving alkali metals and halogens, they will attain the noble gas electron configuration, thereby rendering them highly stable. This stability is a fundamental aspect of ionic compounds and contributes significantly to their unique properties and behaviors in various chemical environments ^[22-24].

3.2 Covalent Bonding

In a covalent compound, the atoms are held together by a transfer of one or more pairs of electrons from the outer shell of one of the atoms to the other. We tend to think of the electrons as being shared when a covalent bond is formed, but that is a bit of a simplification. Covalent bonds are usually formed between atoms of the same or nearly the same electronegativities. Because like charges repel one another, electrons do not like to share space with other electrons. Consequently, the electrons shared by two atoms in a covalent bond spend most of their time in the region of space between the atoms. The positive charges on the nuclei have something to hold on to, but at the same time, the electron pair resists being pushed together or pulled far apart. This opposition is what holds the atoms together in a covalent bond.

The most common covalent structures found in nature are the well-known diatomic molecules in which the two atoms that make up the molecule are absolutely identical in every way. It makes complete sense that covalent bonds cannot exhibit any ionic characteristics if they are formed specifically by atoms that are engaged in sharing electrons with each other. Therefore, it can be stated that the strengths of covalent bonds are relatively independent of the types of atoms involved in their formation and interaction. However, a covalent bond does become weaker under certain conditions if the electrons it is holding near the two nuclei are pushed or shoved further away from the locations of the positive charges that are present in the nuclei. Consequently,

the repulsion between the nuclei primes and promotes a sense of regularity amid the structures of covalent networks, which include well-known examples such as diamond, graphite, and silicene. These remarkable structures are networks composed not only of individual atoms, but also of numerous covalent bonds linking them together. Each atom in the network is directly attached to, and is constantly feeling the intricate and complex web of covalent bonds that is produced by, all the other atoms present in the same network. This interconnectivity contributes significantly to the unique properties observed in these materials [23, 25-26].

3.3 Metallic Bonding

One of the most significant forces significantly contributing to the formation and stability of solids is the fascinating phenomenon known as metallic bonding. This complex process involves the delocalization of valence electrons over metallic cations, which facilitates the properties distinguishing metals from other material types. Those vast and intricate stores of energy that we refer to as metals owe their incredible electrical and thermal conductance to the remarkable ability of their valence electrons to flow freely through the well-structured crystalline lattices of atomic nuclei, even when in a solid state. The theory underlying metallic bonding remains a crucial area of extensive yet unsolved exploration within the realm of chemical physics, highlighting the challenges and opportunities that lie ahead in understanding this significant bonding type.

In a metal lattice structure, each atom typically loses a portion of its valence electron density. This lost density then becomes part of an extensive valence band that stretches throughout the entirety of the solid piece. These valence electrons can move easily and swiftly through the lattice in direct response to electric or thermal forces, which in turn explains the exceptional properties of metals as conductors. Meanwhile, the positively charged ions of the metal lattice remain relatively stationary, facing minimal movement. The electron density associated with each lattice site, alongside the resulting stability that this density imparts to the surrounding metal lattice, must exhibit some form of spatial variation. However, it is essential to note that the assigned spherical electron densities derived from point-charge models should be viewed as, in essence, simply mathematical constructs. They act as sources of numerical data assisting us in determining the energy level of the crystal based on electronic factors and enable us to draw comparisons with the energy level characteristic of a free electron. This understanding plays a vital role in the broader study of solid-state physics and material science [27-29].

Chapter - 4

Coordination Chemistry

The d- and f-block metals, which are metallic elements belonging to the periodic table, exhibit behavior as Lewis's acids in their various compounds and possess a uniquely rich and diverse coordination chemistry. In the realm of inorganic compounds, the central metal ion typically possesses an applied charge, which leads the metallic element to lose some of its inherent 'metallic' properties. In any Lewis acid-Lewis base reaction that results in the formation of a coordination complex, it can be inferred that the central metal ion is inherently more electropositive than the bound donor molecule involved in the reaction. This significant characteristic allows for the role of the d-block transition elements and several lanthanides to persist in retaining some of their metallic characteristics, even as they progressively lose electrons during coordination.

Frequently, the compounds of these metals involve the complete transfer of an elementary electron pair, or in some cases, two elementary electrons from the donor molecule into the vacant coordination orbitals of the metal complex. This crucial interaction contributes an overall double anionic charge to the resulting complex. In the field of biochemical metal complexes, these radical-ionic double-charged species occasionally absorb visible or ultraviolet light, showcasing interesting photophysical properties, or emit luminescence, which can be detected through various analytical techniques. Thus, the intricate interplay of d- and f-block metals with their respective organic and inorganic ligands not only underscores the importance of their reactivity but also highlights their potential applications in fields ranging from materials science to biochemistry.

Symmetry and Laporte: Crystal field effects, together with advanced calculations and comprehensive theoretical frameworks, are essential foundations of our understanding of inorganic chemistry. In the first three transition series, as well as in the heavier d-block elements, there is generally ample space between the various quantum number m values allowed by the symmetry inherent in molecular and crystal orbitals. This ample spacing often serves to eliminate the restrictions imposed by the Laporte f -function coupling

rules. In these particular molecules, and for these specific types of crystals, the previously forbidden transitions between the two distinct parity states display an observable intensity that cannot be overlooked. Consequently, the associated forbidden symmetry considerations frequently lead to the elimination of all f-to-s and s-to-f transitions that would otherwise be predicted by more simplistic models. The rich interplay between symmetry and the resulting optical properties of coordination complexes provides profound insights into electronic structure and reactivity within the field of inorganic chemistry [30-32].

4.1 Coordination Complexes

A coordination complex is a substance in which a metal atom is bonded to ligands, each of which generally has at least one lone pair of electrons suitable for sharing with the metal. The ligands may be monodentate, in which case they bind to the metal through only one atom, such as water, ammonia, chloride ion, cyanide ion, or hydroxide ion. They may also be bidentate, tridentate, tetradentate, or polydentate, which means they are bonded to the metal through two, three, four, or more atoms; each of the atoms in these ligands is engaged in covalent bonding to the metal atom. Bidentate ligands contain two atoms that are capable of donating electrons to the valence shell of the metal, the most common examples being ethylenediamine ion, 1,2-diaminocyclohexane, nitrite ion, oxalate ion, or the oxalato ion, and the enolate ion. Other ligands are chelating, which means they are able to engage in multiple bonds with the metal atom.

By donating shape-directed lone pairs, chelating ligands frequently distort the structure to adopt either a five-membered or a six-membered ring. Such structure-distorting ligands are sometimes referred to as trans-directing, and in a compound in which a chelating ligand is present, either cis- or mer-geometric isomers are created in addition to the facial and geometrical isomers. Coordination complexes are especially noted for the variety of geometric configurations that may occur in either square planar, tetrahedral, octahedral, and, although less commonly, trigonal bipyramidal and square antiprism structures [33-34].

4.2 Ligands and Coordination Numbers

Inorganic Chemistry: Principles of Structure and Reactivity.

4.2 Ligands and Coordination Numbers

In addition to the geometry of a metal complex, the ligands that are bonded to a metal and the number of metal-ligand bonds that exist in a

complex are important structural features. Collectively, these influences are called the coordination number of the metal center.

The coordination number of a metal ion in a complex is specifically defined as the total number of atoms that are bonded to the metal ion in that particular complex. The atoms that are bonded to a metal center in such complexes are commonly referred to as ligands. Frequently, these ligands can also exist as charged species, further influencing the properties of the complex. The number of bonds that are formed between a metal ion and its ligands is often referred to as the coordination number. In general terms, the actual number of atoms that are directly bonded to a metal center depends on several factors, including the size of the metal ion itself, the size and nature of the ligands, and also the specific geometric shape of the metal coordination complex under consideration. For example, the coordination numbers and the geometrical arrangements of clusters that contain trivalent metals such as aluminum, boron, and gallium can vary significantly from those that contain transition metal ions. It is important to note that while coordination numbers in certain molecules can indeed be larger than eight, in the vast majority of compounds that contain a metal central atom, the coordination numbers predominantly observed are four, five, six, seven, or eight ^[35-37].

Chapter - 5

Solid State Chemistry

In the solid state, patterns of matter result from the regular and repeating arrangement of atoms over relatively long distances. These ordered distributions of atoms are called crystals, and a material may be said to crystallize if its atoms are placed within such a repeating pattern. A modern approach to chemistry would argue that many observable properties are rooted in the way atoms are arranged; this applies to the structural characteristics of the periodic table through to properties as conspicuous as color, strength, and hardness. In theory, there are 14 ways in which atoms may be packed within a crystal to give a long-range repeating pattern in three dimensions. Solid-state chemistry is a combination of the traditional disciplines of crystallography, mineralogy, materials science, and solid-state physics. This broad, interdisciplinary approach to the study of solid substances applies chemical principles and techniques to the study of materials that are, in significant part, crystalline or exhibit properties and behaviors associated with crystals. Thus, any technique used to characterize or prepare relevant substances is within the focus of solid-state chemistry. Many of the properties, potential applications, and the reactivities of compounds depend upon both their chemical composition and the degree of long-range order exhibited by the atoms or ions present in a substance. As a result, many solid chemists use experimental tools and techniques common to physicists, biochemists, and geochemists, in addition to techniques more commonly utilized by chemists.

The last 150 years have seen the emergence of groundbreaking discoveries in chemistry that are directly related to the presence of long-range order in molecules. Routine, affordable sunlight photocatalysis has been realized as an extension of research into water-splitting catalysts over the last 40 years. Since the first characterization of a crystal of an organic material in 1838, the fundamentals of solid-state behavior and the underlying concepts of solids have been developed alongside some of the most important discoveries in modern history. Solid-state research has been so fundamental to everyday life for the past century that the significance of these discoveries is often underestimated.

A crystal structure is the periodic repetition of atoms in space. In the solid state, atoms interact with one another in such a way that they tend to arrange themselves periodically. Compounds that crystallize show this regular arrangement of atoms in space in three dimensions. This periodic structure is reflected in the structure of the solid, e.g., its morphology and its diffraction pattern. One of the primary concerns of solid-state chemistry is the relationship between the structures of solids and their properties. There are three naturally occurring forms (or states) of solid matter, which are determined by the intermolecular forces: amorphous solids, crystalline solids, and semi-crystalline solids. Many compounds can assume two of these states, and the process of transformation from one to the other is called crystallization (in contrast to melting, which refers to the process of transforming a crystal from solid to liquid). The ability to obtain compounds in the form of a single, well-defined crystal is one of the basic tools of the solid-state chemist.

Each point in space, which has three independent sets of coordinates, may be accurately located by means of a unit distance rod along with three rods that are mutually perpendicular. A collection of rods of this origin, which are all equal in length, is called a lattice. The lattice provides a network of points in space. Lattice points may be occupied by atoms, ions, or other chemical species. These are the key physical observables of crystal structure. Macroscopic physical properties of crystals may be correlated to the arrangement of lattice points in space. It is not possible to describe all of the crystallographic facts that are relevant to the chemistry of the solid state within the workbook.

Two periods that discuss the basic concepts of crystallography from a more mathematical point of view are included in the text. These sections are meant as the minimal lexical requirements in crystallography for those who follow advanced topics in the chemistry of the solid state. Units of length are meters, and subunits of the meter for distance in crystallography and crystal chemistry are angstroms. The angstrom is an abstraction that sets the lattice constant of metallic copper at about 10. Other units for atomic spaces usually used include nanometers and picometers. Begin assembling the rods in the lattice in such a way that they all have one common endpoint or intersection. We will refer to the intersection of the rods as the origin. To define a point in space in terms of the lattice, simply assemble one of the lattice rods at the origin by using it as a convenient reference point.

The ranges of allowed energies for electrons in periodic potentials lead to energy bands and energy band gaps in many-electron quantum states of solid and liquid matter. The Pauli Exclusion Principle and electron stability

considerations dictate certain arrangements of electrons in the available energy bands, which in turn provide the chemical and physical basis for explaining many observed properties. For insulators and semiconductors, the electronic conduction properties depend mainly on the lowest unoccupied energy band or a gap between the highest occupied and the lowest unoccupied energy bands. For metals, on the other hand, the energy bands contain approximately as many states as there are electrons, and the metallic conduction properties depend mainly on the occupation of all of the low-energy states.

All matter is composed of positively charged nuclei that are separated by distances from millimeters to picometers. These atomic frameworks are held together by a negative charge distribution, composed primarily of electrons, which screens the outer portions of the positive charge distributions of the nuclei. The electronic charge distribution significantly screens the long-range electrostatic forces between the nuclei of the atomic framework itself and between nuclei found in a positive charge core. The result is that the atomic frameworks are generally electrically neutral, even though they may be composed of more protons than electrons. The energy bands, core electron distributions, and discrete bound states of the screened electrons determine the chemical and physical properties of all forms of solid and liquid matter.

In condensed matter systems, there is a very large number of valence electrons, and these are shared between ions. Electrons in the inner shells are quite tightly bound to a nucleus by an attractive Coulomb force, which arises from the positive charge on the nucleus. However, when the atoms combine to form a solid, there are a very large number of these electrons, which are free to roam between the many positive ions. The theory of electronic band structure is a theory of collective, long-wavelength motions of the electrons. Consequently, it is a valid theory only for long wavelengths. For higher wavelength excitations of the valence electrons, excitations that become visible in optical measurements, we must resort to quantum mechanics, considering that electrons are quantum particles.

When considering the motion of the valence electron in quantum mechanics, we must consider not only the repulsion forces between electrons and the attraction of the valence electron with the positive charge of the nucleus, but also the Pauli exclusion principle, which constrains the manner in which the many valence electrons of the many atoms can share the same position in space. Because of this quantum mechanical constraint, the Pauli exclusion principle, we obtain a delocalization of the electron density. A large number of positions are not occupied by any electron, while the true electronic

density is situated in the space to satisfy the valency Z , the number of electrons required to form neutral atoms. The electron density of a crystal behaves in an insulating manner, and a large gap should be observed in the electronic band structure.

A solid is classified as a conductor, semiconductor, or insulator based on its ability to conduct a specific group of electrons, known as conduction band electrons. There is no reason to expect that the same or similar mechanisms would be responsible for determining how the conduction band electrons behave in different materials. The explanation must lie in the energy band models of solids. The three classes of substances normally treated separately in the first point on the topic are fundamentally the same in terms of conduction, differing mainly in the height of the energy gaps between the valence and conduction band states and the number of charge carriers accessible to be excited across these gaps.

The only difference lies in the nature of the states near the valence band from which the conduction band electrons must generally transit and to which the charge carriers enforced to occupy states in different bands wander through the lattice. The details of this Hamiltonian form the fundamental distinction between the various models: metallic conduction, which has its origin in the occupancy of states at the top of partially filled bands near the Fermi level; the model of crystals as insulators, where charge transfers force the electron into local state oscillations of one additional quantum number that may be distant in energy; and finally, the impurity model of the semiconductor represents the limit of the conduction band with the fewest possible number of states.

The term "magnetism" is derived from the ancient town of Magnesia in Asia Minor, where lodestones were found by the ancients. A lodestone is a magnetite mineral that can attract iron. Permanent magnets, so-called because they retain their magnetization once magnetized, can be made from other oxides such as FeO, cobalt ferrite, and samarium cobalt. A magnet is best characterized as a substance that will line up its magnetic fields parallel to any others on the atomic or domain scale. Paramagnets, in addition, do align their magnetic fields with respect to an external magnetic field during magnetization but do not retain any magnetic field when the applied magnetization is removed. In diamagnets, the magnetic fields from the orbital motions of the electrons cancel one another, yielding zero resultant magnetic moment.

The magnetic dipole is associated with the orbital motion of the electrons about the nucleus and the spin of the electrons about their axes. In theory, both

the orbital and spin loops produce magnetic fields that can interact both with one another and the applied external magnetic field. The resultant fields generated by these loops interact even further with the materials in which they are embedded, causing very complex dynamical phenomena, such as ferromagnetism. The magnetic susceptibility and the electrical conductance of most pure elements observe a reciprocal relationship upon exposure of the material to a changing magnetic field below the Curie temperature. In practice, few, if any, materials have the ideal characteristics associated with the idealized model described here.

The diatomic free radical molecule is composed of an odd number of electrons, and for this reason, one electron must remain unpaired. The unpaired electron carries a spin that can be aligned or anti-aligned with an external magnetic field. When the spins are aligned, the magnetic property of the unpaired spins reinforces one another, and the molecule is paramagnetic or contains paramagnetic centers. When the spins are anti-aligned, the magnetic properties cancel one another, and the species is diamagnetic. A classic example of a diatomic free radical molecule is the oxygen molecule, which is paramagnetic due to the fact that it contains two unpaired electrons. Each oxygen molecule has two unpaired electrons that can interact with a magnetic field to generate the molecule's magnetism.

Paramagnetic and diamagnetic materials are found among the most insulating or semiconducting compounds because, in these cases, the electrons involved in the interaction are predominantly the outer "element-dominating" electrons. However, molecules can also behave with paramagnetic or diamagnetic behavior. In this case, the field effect is so low that the reason a molecule can be aligned with a field is often negligible.

Any type of quantum mechanical angular momentum can give rise to paramagnetism. They include, among numerous systems: electronic contributions to the orbital angular momentum; electronic contributions to the spin angular momentum; nuclear contributions to the spin angular momentum; nuclear contributions to the orbital angular momentum. Most materials are diamagnetic (i.e., their paramagnetism is neglected, in extreme cases, to the extent that the magnetic response of diamagnetism is overshadowed). The interaction between nuclear spin and electron spin plays a key role in the paramagnetism of molecules containing hydrogen. Considering a particle with magnetic moment, set in a magnetic field, it assumes a torque or a potential energy equal to the vector product.

The total capacity of the particles in a magnetic field is given by the expression, one of whose preconditions is the relationship. The differences between paramagnetic and diamagnetic atoms arise from the quantum mechanical rules, which are different according to the internal structure or the outermost electrons of these particles. Hydrogen is the simplest system, formed by an isolated proton that contains a nucleus charge and an electron that contains a negative charge. The spinning of both particles produces individually associated magnetic moments, characterized by the magnetic relationship.

Despite the vast interest and study of magnetism in solid state, very little is known about how to devise a material to possibly the simplest and most common form of magnetism, ferromagnetism. We do know that there is a strong correlation between the magnetic moment and the 3d configuration of the atom, and especially differences in the localization or delocalization of these 3d electrons. Materials such as metal oxides and sulfides are generally ferri- or anti-magnetite, respectively, while most transition metals themselves are often ferromagnetic in their solid state. It is more difficult to induce a high reaction in ferromagnetic materials, thus limiting their use as such. Ferromagnetic behavior has received thus far very little attention in binary III-V compounds. The unusual ferromagnetic half-metallic monocarbides and monoxides have been recently recognized to be inverted half-metals and seem to be very nice ideal systems to study electrical conduction in these materials.

Antiferromagnetic and ferrimagnetic materials have two or more sets of different magnetic moments and are considerably more difficult to describe rationally as to why this order occurs. There has been some success with the alternation of magnetic and dielectric properties and magnetic and structural properties. Actually, these materials are very nice because one can grow chemical sensor magnetic multilayer systems from single crystal thin films of these and a dilute magnetic substitution solid solution where a significant change in magnetism enhances the MR type properties. There is a limited number of substances that show the GMR effect because these properties are very heavily determined by the details of the interfacial magnetism in the magnetic/nonmagnetic metal materials. Good electrical and thermal contacts can enhance the AMR properties, thereby making many more substances useful in sensors and increasing the sensitivity information content, respectively. The effect also originates from the sample geometry and the lattice constant spin-orbit interactions. This chapter describes the arrangements of atoms or ions within crystal structures, the close-packing models as well as the crystal structures defined by these models, and the

electronic properties of metals, as well as how these properties can be exploited to account for melting points, phase changes and structures [38-40].

5.1 Crystal Structures

The solid-state structure typically implies the existence of regions showcasing an ordered structure, which refers to long-range atomic or molecular order. In contrast, the category of disorder found in numerous materials often tends to be of a local and short-range nature. Specifically in many types of inorganic materials, the atoms and molecules are arranged in a spatially ordered manner, maintaining a consistent and regular configuration. The unique geometry of each material, as well as the specific manner in which the atoms and molecules are spatially arranged, is defined by what is known as a crystal structure. Crystal structures can generally be categorized and described through Bravais lattices. These lattices serve to represent the three-dimensional geometric shape of the unit cell, which is the fundamental building block that is repeatedly utilized throughout the entire lattice framework. The representation of space in three dimensions is adequately covered by fourteen distinct possible three-dimensional lattices. Similarly, in two-dimensional space, three two-dimensional lattices fulfill the analogous role.

The treatment of symmetries and lattices in this course is aimed at establishing a solid background to describe the structures of crystalline solids. In the first part of the course, we will use geometrical methods to classify atomic positions and to determine whether the periodic distribution can only be achieved by repeating a set of unit cells in space or if other choices are possible. Symmetry elements in a crystal act by means of corresponding symmetry operations on the lattice points. We will use group theoretical methods to classify the symmetry operations and the operations restricted to the basis of an object in the lattice. For this, we will use the most general and incomplete description of the space given by the lattice. Finally, we will apply these general tools to determine the subgroup of the space groups corresponding to the Bravais lattices, which are the simplest crystal building blocks available to physicists.

To understand the mechanical and other properties of a solid, one must understand the relationships between the position of the atoms or ions and the various properties. For grain-boundary diffusion to occur, there must be more than one kind of site in which the diffusing atom can land. These vacancies are important in processes that introduce new atoms into a crystal lattice. We will discuss a few of these processes. In a perfect monatomic crystal, 12

percent of the sites would be interstitial sites. These are not empty. Most are filled with the atoms that bond to one another to form the crystal. This question addresses the most engineering aspect of crystal point defects, such as vacancies and interstitials. A vacancy is a site in a crystal lattice at which an atom is missing. Vacancies are introduced by any process that requires the removal of an atom: heating, ion bombardment, or chemical reactions involving the removal of atoms from the crystal. Any process that introduces vacancies into a solid that has had time to equilibrate at the process temperature will be self-limiting, because the concentration of the vacancies introduced by this process depends on the ratio of the number of introductions of vacancies to the number of energy-releasing recombinations of vacancies with interstitial atoms and inactive atoms in their lattice sites. Control this ratio, and one controls the concentration of the vacancies.

Our discussion of thermodynamics has emphasized the importance of bonding in the description of solid-state structures. Two important principles are that the nature of bonding determines the geometry of the solid, and that the geometry is further restricted by the nature of the bonding. The most important part of this is the severe restriction on coordination polyhedra: all valences leaving the central atom or molecule must be satisfied. Some strategies are available to understand the complicated processes of crystallization; for instance, a priori determination of relevant ligand stress. We have already met some crystallization rules. Applying a real-space version of periodicity and allowing polygons of a free length side or of a free hinge angle enables one to make some predictions about structures. The structure of silica might be predicted on the basis of bond length rather than bond angles. More refined models of crystallization based on atomic size, electronegativity, and elastic energy cost, have been developed.

Many of you have undoubtedly seen materials described in terms of some consensus model that involves ionic, metallic, or van der Waals bonding together with elemental electronegativities. Much information can be gathered from the structures of the elements alone, and our discussion today will be of much use to us as we describe structures of the real materials above. However, electron motion, contrary to the assumptions of many of the models, is not spherically symmetric under all circumstances. In molecular compounds, local dipoles caused by the surrounding ions, or anisotropy in the valence electron distribution, can result in decoration of the core electrons. Some such behavior is observed, but since the wave functions of the extended eigenstates span the entire infinite lattice, the decorated core electrons are delocalized into a response to the bonding of the lattice. Nevertheless, it is true that the virtual

dipoles and magnetization caused by core polarization energy and orthogonality-induced hybridization can be responsible for competing direct, pair, and many-body interactions.

The concept of ionic bonding traces its origins to the qualitative wave mechanics and the rigorous treatment of the hydrogen atom. According to this model, an electron gains stability if it attains a noble gas configuration. This can be achieved by gaining enough energy to escape its original atom and then occupying the parent atom's unique ns orbitals. The result is two oppositely charged ions. If A measures the electrostatic energy of an array of point ions, the difference in energy between the original crystal and the recombined gas of ions is the lattice energy, U . Since the ions are in equilibrium, the first derivative of the energy of the combined system must be zero with respect to the separation between the ions. With respect to an eigenvalue of A , this statement is precisely the secular determinant.

The qualitative predictions of the ionic model are often upheld in the infrared, visible, and ultraviolet spectra of solid-state ionic compounds. According to electromagnetic theory, a photon possesses the vibrational motion and rotational symmetry of a long-lived eigenmode. An observed band is an indication of atomic spatial periodicity and not of atomic origin. Bonds that possess these general symmetry considerations display good infrared and ultraviolet molar absorptivities.

The physical idea of a covalent bond is charge sharing. This bond is usually formed between nonmetallic elements that are close in electronegativity. An electron from a bonded atom is attracted to the nucleus of the other, which results in a compressed core. This compressed core in turn fills in the electric field of the nuclear charge so that it is felt by both atoms, which causes them to be attracted to each other. The strength of this attractive force depends on the degree of overlapping of the atomic orbitals. These orbitals, molecular orbitals produced from atomic orbitals, are linear combinations of atomic orbitals for all atoms in the molecules. For a molecule with only two atoms, the energy of the molecule depends on the value of μ . This bonding model gives rise to the behavior known as Hund's rule for the selection of states of noninteracting atomic levels. The large group of molecules that is described by the Valence Bond Theory allows solutions of few electrons and little basis complication; however, it can also predict weak chemical bonds.

Metallic bonding is found in two elemental forms (metals and alloys), and it is also found in complex arrays such as polymeric metals, extended metals,

and metallic clusters. It occurs when the binding forces of atoms extend throughout the entire solid. That is, they are not limited to individual atoms "holding on" to specific neighbors as in ionic and covalent bonding. The periodic arrangement in a metallic or extended metallic solid can be represented by an array of hard spheres with a diameter the size of 0.1 times the distance between nearest neighbor atoms. The array of hard spheres is often referred to as a Bravais lattice. The space-filling version is called the crystal lattice. The solid is characterized by the way the valence electrons are utilized. Each electron is a traveling wave that dynamically interacts with many ions. The Pauli exclusion principle and Coulomb repulsion limit the number of electrons at each wave vector in a momentum state to $1/2$. With two electrons per state, this corresponds to the filling of half of the available momentum states at the Fermi surface. These electrons are delocalized over the entire solid and, being half-filled states, are metallic. Their concrete presence as an electron gas surrounding an ion array is the essence of metallic bonding. Linear free electron theory provides a useful model for understanding macroscopic electronic properties of solids with strong metallic bonding. The quantum nature of metallic bonding makes the classical picture of ions held together by freely moving valence electrons an accurate model in many conformations, in spite of the fact that each ion is simultaneously associated with many electrons. More accurate models require the quantum mechanical contributions of individual waves of electrons to the Coulomb potential in the lattice.

Each distinct lattice type can be characterized and defined by accurately measuring the relative positions of the sets of lattice points that form a part of it. The unique set of these specific positions associated with a given lattice is subsequently utilized to define the unit cell of that Bravais lattice. The unit cell itself, along with the translations that are defined by the volume of the unit cell, serves to characterize and define the entire lattice composition comprehensively. There exists a variety of different sets of unit cells, each of which may be equivalent, utilized to portray a specific type of Bravais lattice. The repeat unit of a lattice contains a meticulously defined and unique set of positions. The lattice is inherently translational, with all translations originating from the various points that collectively form the lattice structure itself ^[41-43].

There are, then, quite fundamental differences between a space lattice, which is also referred to as a Bravais lattice, and the repeat unit cell of a physically existing structure that one might encounter. This last point doesn't apply to the simple theoretical assumptions typically associated with point

objects and, at most, anisotropic objects that are covered by sphere-of-influence spacings. These aspects are generally discussed when one is considering Bravais lattices and their fundamental properties. Such is not the case when we deal with physically interacting points that have distinctly well-defined geometries. A prime example of this would be the behavior of ions positioned at the minimum of potential energy surfaces concerning each other's potential energy influences. The manner in which atoms and ions fill in specific points, lines, or regions within a lattice can therefore result in the emergence of several multitude types of structures, and these structures have been systematically classified into a limited number of space groups within the scientific community. Once the particular type of space lattice or Bravais lattice type and the corresponding space group are accurately defined for a specific set of points, then both space lattices and Bravais lattices become precisely determined. Each set of coordinates representing a space group for a particular arrangement of points is mainly one of the established 230 distinct space groups, and they can indeed coincide in various situations. Most importantly, it is essential to note that the original three-dimensional lattice can certainly be subdivided into several sets of points, lines, or regions that can consistently coincide throughout the three-dimensional space lattice configuration. The field of science has implemented its detailed classification schemes for those materials that do not fit neatly within these established categories, which are the materials where this particular description simply does not hold ^[44-46].

5.2 Lattice Energy and Stability

Stability is an important consideration in the formation, mechanical processing, and utilization of the vast majority of inorganic solid-state materials. Compounds, whether they are ionic or molecular in nature, exhibit a wide range of stabilities, spanning many orders of magnitude. Naturally, because we focus our attention on solids, the least stable materials of all are of marginal interest here: freshly prepared high-energy species such as elemental powders produced directly from their most thermodynamically favored stoichiometries or many of those pristinely characterized, but air- or moisture-sensitive, compounds potentially useful for catalysis.

A thorough analysis of the internal energy index of a system is generally given in terms of the actual forces and energies involved in the interactions between the atoms and ions. This type of analysis leads to a quantitative relation between simple estimates of forces, bond energy values, and specific heat data, and can supplement qualitative ideas derived from bonding relationships and crystal structure. Among the important results are

expressions for the upper and lower bounds to the values of the specific heat a crystal will exhibit depending on the nature of the interaction between nearest-neighbor atoms or ions and the nature of the interactions beyond that distance. In a similar, but more restricted fashion, the variation of electronic specific heat with temperature can be considered, and hence some generalizations can be made about the extent of an electron specific heat maximum. Heat capacity values are generally directly accessible from experimental data, and interaction energy estimates may be obtained from bond energy changes upon thermal expansion produced by structural changes. The extensive vibration data and the increasing use of spectroscopic methods to analyze lattice specific heat in insulating crystals as a function of temperature should also have something to offer in higher than room temperature thermal conduction problems. In general, thermal properties are useful indicators of the details of the structure-energy relationships in a well-characterized chemical system.

The specific heat of a substance is an extensive property, which means that the amount of material examined must be an integral multiple of a base quantity. Heat energy arises from the vibrations of atoms or ions in a crystal lattice. This vibration may, in the wave-mechanical model, be considered to be an elastic wave that is quantized. Therefore, it is not surprising that the heat capacity of a crystal at low temperatures can be understood in terms of the quantized vibrations of the crystal lattice. The treatment is phenomenological, using the harmonic approximation, of the quantitative dependence of specific heat on temperature. The agreement with experiment is quite good for simple monatomic solids at low temperatures. The failure of the model at higher temperatures for such substances (and for molecules or other systems at any temperature) is due to the assumption of an isotropic spiral wave in three-dimensional space. These spiral waves are exact solutions of the classical equations for vibrating three-dimensional lattices, and there is no such assumption of validity. Therefore, what has been done is to solve the exact equations of motion in one dimension by artificially making the force a function of displacement quadratic and isotropic.

Unlike individual atoms, the average thermal motion of the positive ions in many solids will tend to pull the ions closer to each other. Hence, most metals and their compounds expand when heated. We cannot argue the magnitude of the change in length by any simple geometrical argument; the atom-to-atom force must come from an analysis of temperature-dependent fluctuations about the equilibrium positions. The negative ions tend to pull closer together, too, but since their forces on ions of one sign are partly

balanced by equal forces on opposite sign ions, these compounds usually have larger thermal expansions. Fortunately, almost as simple an understanding of thermal expansion is possible, bearing in mind that we already know the force vs. displacement data at 0 K for any periodic solid. The necessary analysis is the continuum limit treatment known as the phonon theory of solids.

The need to investigate the optical properties of solids is a consequence of our increasing reliance on devices that utilize light to monitor electronic processes occurring deep within a material, for example, photovoltaic cells and light-emitting diodes. Completing a theory of the optical properties of solids for all possible electronic states is one of the major unsolved problems in solid-state chemistry. This may come as a disappointment, but the field has been extensively reviewed, and only an overview, which deals mainly with classical results, is provided here. The simplest optical property of a solid may be visualized as being the reflection from its surface, but only in a minority of cases is this of interest. If light is made incident on a solid under specific conditions, it can either be transmitted or absorbed; the sign of the refractive index and the coherence length of the transmission suggest the lifetimes of the excited states that may be probed optically. If the temperature is not too high, both the lifetimes and the symmetry of the bonds of the excited state may be probed independently. Unfortunately, the absorption parameter is considered a rather second-rate quantity in that many states excited optically decay by photon emission; that is, the solid re-emits the light when it has returned to the ground state.

So far, our discussion of the absorption and reflection of light by solids has been quite elementary, and we may have created the impression that nothing more needs to be said. However, reflection and absorption spectra can be studied in much detail and can indeed provide important information about both the structural and electronic properties of solids. There are a number of qualitative considerations that must be kept in mind. Thus, it is clear that at high frequencies all materials are poor absorbers, and in this high-frequency region, they are nearly power-law reflective. By contrast, at low frequencies, electrons can easily absorb light, and the absorptivity can become very high. Since reflection and absorption are so fundamental, they are what spectroscopists usually begin with when they first explore a new solid. We will briefly return to this subject later when we look at several detailed descriptions of the chemical bonding seen from a variety of different points of view.

The refractive index can be reduced for photon energies approaching a strong spectral feature in the material, and when the absorption is actually

occurring, the refractive index changes sign. This means that photons that are passing through an absorptive medium continue to satisfy the requirements of a wave equation in Cartesian coordinates, and as in charge flow, the simultaneous realization of both its reality and its image in a concentration of atoms of similar symmetry are required to account for the occurrence of absorption. We should also point out that when light is slowly transmitted by a semi-transparent dielectric, the absorption coefficient in front is never very large.

The detection of a photon as a result of its interaction with some semiconductors is also known as photoconductivity. The fundamental process in photoconductivity is the creation of an electron-hole pair due to the absorption of light. Normally, either electrons or holes flow under an electric field. It is convenient then to create electron-hole pairs and guide the charge flow so that they can be detected. The electrical properties of bulk organic solids make them ideal for technological applications in several nonlinear optical, photoconductive, photorefractive, and optical switching devices for the electronics and photonics industry. These applications are based on the photophysical properties of these hybrid materials which, in turn, depend on the confinement of the charged carriers and their interaction.

To form a solar cell, a photoconductor should provide two sets of coupled semiconducting phases for the generation and collection of electron-hole pairs. The third fundamental component, completing the charge collection, is contacts. Solar cells for energy production must be continuous, so all these elements should be located in the same semiconductor material. The most spectacular success is in photovoltaic cells with silicon. Such cells presently dominate the capital investment for the production of solar energy.

In the idealized case of the p-n junction used with a solar cell, when light is absorbed, the electrons are driven into the n-type material and the holes into the p-type material. In the case of silicon solar cells, the use of a more direct solar light concentration system allows the device thickness to be reduced, but the reason for the requirement of a high optical absorption in the active junction region is essentially the same. For successful solar cells, the appropriate p-type and n-type material partners must allow suitable electrical throughput methods to be made. This is frequently not the case with organic solids. Only a few molecular systems have shown suitable properties for this application. The problem inherent in the design of heterostructures resides in the formation of well-controlled, continuous, low-energy barriers for the separation of electron-hole pairs. To further advance such organic solid solar cell research, direct measurements of charge separation, flow, and

recombination are needed. Via the requirement of sufficiently long electron and hole diffusion lengths and of controlled contacts, the efficiency of such devices is generally not very high. For further improvements, new strategies are needed to maintain separate conducting electron and hole channels in all spatial dimensions.

Introduction a course such as Advanced Topics in Solid State Chemistry might better be called Important Topics in Advanced Solid-State Chemistry. This course has always been a part of the curriculum of the graduate program in research chemistry, so I am hardly the first to offer such a course. I do not attempt to cover the entire field of solid-state chemistry. For example, it is no longer helpful to discuss the basic solid-state chemistry of metals, since a separate course in advanced general inorganic chemistry should provide the modern treatment metals deserve. At the same time, more than a superficial gloss on important areas of modern solid-state chemistry is inappropriate. This is particularly true in areas of importance to technology or those policy issues that we should all be aware of today. I, like my predecessors and colleagues, owe much to many other teachers in the field and to various changes in Solid State Chemistry in which I have participated or simply grown into.

SYNTHESIS The synthesis and processing of solid materials take a wide variety of forms for those engaged in the process of conversion and consolidation of solid materials using a vast number of processing techniques. In addition, the variability of atoms, ions, and molecules found in inorganic chemistry clearly reflects on the array of material approaches used in solid state synthesis. For much of the known inorganic solids, the material can often be categorized according to a combination of the dominant bond types and the coordination number of the atoms. While such bond types and coordination numbers apply to all elements, and a majority of the known binary, ternary, and higher ordered inorganic solids, the materials scientist faces even more complex approaches to actually formulating the solid. While the utility of synthesis can be divided almost naturally into processes used to create bulk materials and those used to form nanostructures, a more detailed examination of material approaches leads to eight distinct categories of synthesis using five fundamental approaches: solid state, liquid state, gas state, plasmas, and light-matter interactions.

High technology materials are generally synthesized within ultra-pure inert gas atmospheres, typically employing a glovebox. Gloveboxes may have a variety of functions, from providing a chemically inert atmosphere by having an excess of catalysts, molecular sieves, and/or dissolved oxygen scavengers to reacting with the inside atmosphere to provide or extract components of

great commercial interest, such as producing a pure rare earth-containing product or a nonradioactive isotope. Apart from these operational tasks, the employment of such functioning gloveboxes also provides stability to elements, compounds, and solvents to allow tailor-made materials to be designed and synthesized without degradation from oxygen or moisture sensitivities. This presents considerable challenges in specifically tailoring either clean or contaminated surfaces of complex materials and performing simulations of modifying a variety of reactions or catalysis. So, despite the diverse range of methods available to inorganic solid-state synthetic chemistry scientists, it is of major interest to continue developing new methods and instruments. The most widely employed methods of synthesizing materials are still by the application of solid-state thermite and carbothermic reduction reactions around 2000 °C. Of course, vapor transport and molten salts with halide or sulfate ligands also remain important. However, the use of nontraditional fluxes, the solvents that drive the reduction or lattice initiation, are shared with ionothermal, hydrothermal, solvothermal, and microwave processes. Then, to provide flexibility in design, post-synthetic treatment is becoming increasingly important. Gram-quantity synthesis and purification of such oxide materials are routinely employed in our laboratories. Those powders or ceramics are subsequently fabricated into mesoscale materials or studied for their structure-property relationship.

Characterization Techniques: Before commencing the discussion of specific ceramic properties, it is important to emphasize some of the major differences in approach between the study of ceramics and that of metals. In regard to most properties, it is not enough to make a single determination of a value and put it on record, as is often the case with some properties of metallic materials. Typically, one cannot measure properties such as dielectric constant, piezoelectric coefficient, dielectric loss, insulation resistance, magnetic properties, superconducting phase transition temperature, etc., in a single operation on a single specimen. Techniques such as dielectric constant, dielectric loss, and magnetic properties, etc., ideally require at least a dozen different measurement techniques to arrive at a single set of consistently valid results. What is required in practice is that the same values must be obtained in repeated measurements by groups using different equipment, different measuring methods, different analyses, and different types of samples.

The classical approach to the study of ceramic (and other) materials is to prepare a sample, anneal it under standard conditions, and then carry out the appropriate measurements. Only after this has been done can we discuss, for example, the dielectric constant of a material. The dielectric constant is a fixed

property of a given material and is independent of the method used to measure it. The integral microscopic techniques commonly used in the study of metals are often much less constrained in this respect, since it is generally easier, for example, to repeat a relatively simple plastic strain measurement than to repeat a measurement such as the Gaussian constraint width in studying thermally activated flow. The name of the game in ceramic science is certainly the reliable and consistent determination of a set of material properties, whatever the technique used. Different techniques, however, may emphasize the role of different factors.

As has been mentioned before, many important solid substances form a class of materials that are used in a bulk state. The study of crystals is only a small part of solid-state chemistry. This part of chemistry deals with layer or plural-layer structures or with molecules packed in such a way that all the molecules in the substance are the same. The smallest repeat unit of a crystal is an atom or a group of atoms packing in a three-dimensional arrangement, but there are also solid substances that are non-crystalline but show long-range order.

The History of Solid Substances Goes Back to Long Centuries: mankind used metals, diestones, and salt in prehistoric times. Nowadays we are surrounded by a great amount of synthetic organic and inorganic compounds in the bulk or surface state. Probably, it is impossible to list all these substances, but it is possible to use a classification in which the different types of materials can be put in different families.

As suggested by the title chosen for this series of concluding chapters on advanced topics, they refer to additional conceptual developments and research topics. In Section 9.1, some more general issues of materials science are presented, whereas in Section 9.2, we present some unsolved problems mainly related to point defects and surfaces. Finally, in Chapter 9.3, other kinds of materials of potential interest to the readers are considered. In Chapter 9.1, the concerned topic refers to the so-called materials science and engineering approach which, as intended, has been presented throughout the research of this textbook.

The materials science approach anticipates the design and projection of new materials based on their electronic structure. Its potentialities and limitations, however, appear clearly from the currently known technological knowledge available for this purpose. These are mainly based on experimental observations and practical concepts; the wide range and remarkable features of this knowledge are illustrated in this book. The present chapter also tries to

give some support for illustration, clarifying the original structure of the phenomena and concepts from which it derives. This chapter also tries to stimulate those readers who are attracted to the field of materials science but do not know very much about the subject. Indeed, one of the consequences of the materials science standing is the existence of a plethora of available materials which are frequently termed according to their practical uses.

The modification of the size of a given species of molecules or particles from the macro to the nanometer spatial region leads to the ability to understand and control many molecular, atomic, and quantum level phenomena. Although the sizes are reduced, scaling limitations are imposed from the top down to the nanometer length. These are necessarily defined for the given class of material studied and shaped by the particular chemical properties and interactions of the constituents. It is important to identify the regions of nanometer behavior for a given material that will form the foundation for its study and development. Nanometer length dimensions are important for high-technology functions in chemical sensors, catalysis, photonics, energy storage and conversion processes, and the use of hybrid composites for structural and mechanical applications. The ability to manipulate particles and molecules on the nanometer scale is the chemist's unique capability that will provide the specific material foundations for these key technologies.

A definition for nanotechnology can be provided in terms of particles with a diameter below 100 nm. By comparison, a human hair has a diameter of about 100,000 nm, a fly ash particle is about 1,000 nm, and the smallest regular size of a dust particle is considered to be 100 nm. A recent development in atomic-scale manipulation has now been achieved in the preparation of nanoparticles by the cluster growth technique. The nanoparticles are prepared by allowing the atoms to pass through a 2-cm distance while in the vicinity of the temperature of liquid helium, a unique environment for providing the conditions in which the nanoparticles can be grown. The range in value of temperature differences between any two adjacent components provides a very broad range in the mean size of these nanoparticles in mass as well as by the control of the temperature of this unique beamlined oven.

As we enter 1990, the current state of solid-state chemistry is extremely healthy, with interesting observations appearing almost daily. However, here I discuss some of the targets for future research. Clearly, solid-state chemists are beginning to understand the common features of materials that exhibit T_c's and the routes for synthesizing a variety of materials with high T_c's. Superconductivity is just one example of how progress and research in solid-

state chemistry lead to important properties. There undoubtedly are many more important and potentially useful properties and classes of materials yet to be discovered or synthesized, and solid-state chemistry will play a key role in this regard.

I believe that solid-state chemistry will continue to expand at an impressive rate and is likely to continue to illuminate the behavior of materials in their practical uses. We shall continue to press the fronts for increasing T_c 's and the commercial feasibility of a superconducting wire. There is a wide range of materials for which electronic properties can be modified by stoichiometric changes and for which subsequent large space windows are possible. Potential applications in solar energy conversion and similarly in photochemical cells are partially related to the fact that many oxides are damaged in sunlight and in some cases are reagents for water splitting. These materials might serve as robust solar cells, and solar energy conversion to electricity and/or low-cost fuel components. The problem is to capitalize on the opportunities in oxide substitution chemistry inherent in this class of materials. Advances in research on high T_c in superconducting materials are likely to open the way to future advances in families of related materials. Such advances have the potential for developing and improving more commercially advanced magnetic materials.

In other words, we do not consider powders or pure substances that have been produced by the removal of relatively small amounts of easily exchangeable molecules from within large crystals, but rather those materials that, although perfectly reasonable under very special compression, annealing, or temperature requirements, still desire to change their bonding to approach an energy minimum state in which internal strain is everywhere minimized [47-49].

In order to address this last condition, we must begin to summarize our familiar models used in describing solids and show how, given knowledge of a particularly interesting quantity, the lattice constant, we can, to an impressive level of accuracy, gauge the extent to which the bonding within a crystalline solid is optimized. The ionic lattice energy term arising from the results of geometric analysis of observably stable crystal structures provides particularly important information about how the key considerations of stability factor into the everyday observations we make concerning the occasionally subtle behavior of perfectly sealed, indefinitely old, well-powdered, inorganic solid-state materials.

Chapter - 6

Acids and Bases in Inorganic Chemistry

One of the overarching themes found within the expansive field of inorganic chemistry is the strong and fundamental relationship that exists between acid–base equilibria and the various properties along with the reactivities observed in metal ions and their corresponding ligand complexes. This profound relationship is somewhat of a departure from the realm of organic chemistry, wherein the limited scope of the acids and bases topic typically sets the stage early on for subsequent studies concerning organic reactivity and the structures associated with organic compounds. In the domain of inorganic chemistry, however, the intricate links that exist between acid–base structures and their energetics, combined with rather complex properties and reactivities, significantly help establish a logical and methodical approach to understanding many of the more specialized metal ion coordination compounds. Among the most crucial concepts that one must grasp in the study of inorganic chemistry are the Lewis definitions of acids and bases. From our studies in general chemistry, we are all aware that an acid, as defined by Lewis, is recognized as a substance that has the capacity to accept an electron pair from a base. The importance and relevance of the Lewis definition are underscored when we examine the myriad molecular and ionic structures that are displayed by both acids and bases, revealing their behaviors and interactions in various contexts within inorganic chemistry ^[50, 51].

A second type of reaction useful in defining acid-base behavior for Lewis acids and bases is an acid-base reaction, illustrated by the reaction of a Lewis base with the cation of a Lewis acid. In this case, it is evident that the more stable, more delocalized, more energy-rich electron pair depicted by the lower energy Lewis base reacts to form a product. These two reactions, the self-reaction of a Lewis base and the reaction of a Lewis base with a Lewis acid, form the foundation of our ability to rationally explain the stability differences exhibited by metal-complexed ligands. These, as well as other Lewis's acid-base interactions, offer particularly valuable insight into the behavior of metal ions found in biological systems. It is not uncommon for metal ions in the active sites of many enzymes to bind O, N, or S atoms from glutamyl, histidine, and cysteine side chains or to one or more of the negative site

charges on aspartyl or glutamyl side chains. Many of these metal-binding sites can be modeled in wet chemistry experiments by using small molecules that can be classified as strong or less strong Lewis's acids and as strong donation or less strong Lewis bases.

6.1 Lewis Acids and Bases

One of the most important principles in understanding the reactivity of a broad range of species is the concept of Lewis acids and bases. A Lewis base is an electron-pair donor; in other words, it donates a pair of electrons to form a coordinate covalent bond. Most simple Lewis bases are anions or neutral molecules that contain at least one lone pair of electrons. A few cations are considered Lewis bases because they contain one or more available nonbonding electrons. A Lewis acid is an electron-pair acceptor; in other words, it accepts a pair of electrons to form a coordinate covalent bond. Although many Lewis acids are cations, neutral molecules can also act as Lewis's acids, especially if they contain an atom that does not have an octet of valence electrons, which is therefore capable of accepting an electron pair [52-54].

6.2 Hard-Soft Acid-Base Theory

As a molecular orbital treatment of the reactivity of inorganic complexes, however, HSAB provides a more satisfying basis than that derived from earlier concepts. In the molecular orbital framework, the stability of a metal-ligand complex is generally associated with the overall lowering of the total energy of the complex. One of the primary factors affecting the overall energy of the complex is the energy of the metal ion in its new molecular environment, and this energy is determined by the nature of the bonding of the metal ion. For example, a metal complex in which a soft metal ion interacts with hard ligands may display a more favorable total energy if the donor orbitals of the ligand are larger and more diffuse. This can be achieved by avoiding less strongly polarizing ligands that are less efficient at stabilizing the metal ion's oxidation state and thereby less able to stabilize this metal ion within its field. Conversely, soft donor frontier orbitals experience increasing orbital overlap with the metal ion, leading to effective charge donation and good stabilization of the metal ion on the molecular orbital energy scale. Because the energies of the frontier M-L orbitals can be related to properties that are apparent in the periodic table, the extensions of the hard N and soft S classification can also be applied to include metal ions in addition to ligand molecules [55-57].

Chapter - 7

Redox Chemistry

The study of chemicals in terms of their reactions involving electron transfer is called redox chemistry. In a chemical reaction, an atom can give up one or more of its electrons to another atom. Redox reactions, oxidation-reduction reactions, are reactions in which one or more electrons are moved from one reactant to another. When an atom loses an electron, it is said to be oxidized, and when an atom gains an electron, it is said to be reduced. Together, chemistry becomes possible because of the electronic structure of an atom. Redox chemistry is a very general subject and is of enormous industrial significance. Much of the chemical industry is concerned with changing one substance into another by oxidation or reduction processes. For example, oxygen and hydrogen could be burned to yield water, which consists of oxygen and hydrogen in a different, less reactive form, and is difficult to reduce again. Equally, hydrogen could be used to reduce the iron in iron ore with a concomitant release of energy. In many industrial processes, the release of energy is important ^[58-60].

7.1 Oxidation States

In the discussion of transition metal chemistry, we use the concept of an oxidation state to rationalize the observed chemistry of the elements. Formally, the oxidation state or number of an element in a compound is the charge that element would have when the compound's electrons are distributed according to certain rules, or when the element is in a molecule as a pure element. The noble gases have oxidation states of zero and can be used as a reference point for comparing the others. The s-block elements in their pure elemental state have an oxidation state of zero. Alkali and alkaline earth metals lose electrons easily, and their oxidation states in compounds are usually +1 and +2, respectively, but they also have other oxidation states. However, the most characteristic transition element property is its variable oxidation state, arising from the ability to give up various numbers of electrons from the ns and (n - 1)d orbitals. Since the light transition elements give up the s electrons first in forming their cations, their oxidation states are usually the same as those in the charge group to its right, the members of former groups IIIA through VIIIA ^[61, 62].

7.2 Redox Reactions

Chemical reactions in which electrons are transferred from one species to another are called oxidation-reduction or redox reactions. In an oxidation, electrons are removed from an atom or ion; in a reduction, electrons are gained. The following table shows some examples of redox reactions. They number more than any other type of chemical reaction and range from the rapid, uncontrolled combustion of gasoline in our car engines to the controlled, slow combustion of foodstuffs in the cells of our bodies' tissues. Indeed, there are strong similarities between redox reactions and acid-base reactions, both of which involve the transfer of something; in redox reactions, it is electrons, and in acid-base reactions, it is protons.

To conduct a redox reaction in the laboratory requires a means of transferring electrons between reactants, yet to make the transfer separated in space and not occurring according to the strictest interpretation of Coulomb's law. That is, if the initial and final states of electron transfer occur with both gaining and losing species in the same container, but do not occur in a smooth, continuous, visible fashion, no reaction takes place. In the answer to this paradox, redox chemistry makes use of salt bridges, inert electrodes, and galvanic cells. These devices allow pure chemical species to interact in a controlled manner and exchange electrons at rates that we can observe. Because the ability to transfer electrons is a fundamental attribute of all atoms and ions, redox reactions are important in every phase of chemistry, and the rules we develop here form a valuable basis for understanding reactions that occur inside and outside of the discipline of inorganic chemistry. [63][64][65]

Chapter - 8

Descriptive Chemistry of the Elements

For each of the 114 known elements, some of the information in this book can be tailored to describe a substance comprising its only occurrence naturally. The elements can be broadly cataloged as metals, metalloids, and nonmetals. The metals are further subdivided into an active region and a non-active region. Elements can interact with each other in fundamentally unique ways to form compounds. Ionic compounds of elements can contain cationic coordination complexes. Corresponding neutral coordination compounds and other types of association complex compounds do not contain simple cation and anion ions.

The list of elements covers all the known ones up to $Z=118$, but in all the known universe there are only 92 naturally occurring elements. The symbols are well known, and the names of several elements are still under debate. For the elements up to about $Z=103$, which is the conclusion of the metallic elements, more than the name was effectively accepted in the context. For example, the systematic names of elements up to 103 reflect the atomic number, Z , of each element in the periodic table. These elements are now known by given names: Roentgenium, Rg, 111 meets procedural criteria as does the name Darmstadtium, Ds, 110. Conventions prevail and we rank the elements in terms of descending Z and list the elements of each group in terms of increasing Z within the group. Group 1 consists of hydrogen and the family of alkali metals: lithium, sodium, potassium, rubidium, cesium, and francium; group 2 consists of beryllium, magnesium, calcium, strontium, barium, and radium; group 7 consists of fluorine, chlorine, bromine, iodine, and astatine [66-68].

8.1 Main Group Elements

The majority of elements on the periodic table can be classified as "main group." The main group elements are usually found in groups labeled 1, 2, 13, 14, 15, 16, 17, and 18. Each main group element contains a specific number of valence electrons, which contributes to their reactivity. The valence electrons are the ones capable of bonding, and the covalent electron-sharing process by which bonds are formed is known as the Lewis theory. In general,

main group elements achieve the same electron configuration as the noble gas closest to them on the table through chemical reactions. Groups 13 through 18 tend to form electrically neutral compounds in their reactions. The other two major classes of elements on the periodic table are the transition elements, which are found in the d block of the periodic table, and the inner transition elements, which generally are of less interest to inorganic chemistry. In general, the main group elements can be found across the periodic table. To help keep them straight, consider that the elements in the four rightmost columns (groups 14, 15, 16, and 17) are known as the chalcogens, the pnictogens, and the halogens. Most are nonmetals, but there are a few elements classified as metalloids in these regions as well. The other main group elements include hydrogen and the noble gases in groups 1 and 18, respectively. All have an s-orbital set of valence electrons. Additional things to know about s-block elements are that they usually form ionic compounds, they have low ionization energies, they have low electronegativities, and their chemistry often involves H, O, C, and N species ^[69-71].

8.2 Transition Metals

Most of the known metals are transition metals. This is the most varied group of metals, and virtually every thermodynamically stable oxidation state that can be assigned to a metal has been observed in a compound. So far, we have not been able to make compounds with the oxidation state +8 for any of the transition metals. Compounds that contain metal atoms in oxidation states above +5 are generally quite unstable and are easily reduced. The actinide and lanthanide elements, which occur at the bottom of the periodic table, exhibit properties much like those of the transition metals. Therefore, the chemistry of the transition metals can best be understood by considering their electronic structures, which are similar in many respects to those of the s-block metals, and have some properties in common with the nonmetals. Although we usually give both the 3d and 4s electrons of a transition metal to the metal, in compounds these two sets of electrons can play very different roles.

As with the main group metals, the observed chemical properties of the transition metals generally arise from the interplay of their valence and core electrons. In order to obtain a more detailed understanding of the electron arrangements that give rise to the properties of the transition metals, we can consider the Aufbau sequence. First, we fill the 4s orbital, and then we begin to fill the 3d orbitals. Thus, for group 3B, I will have the valence electron configuration $4s^2 3d^n$. As n proceeds from 0 to 1, the additional electron goes in, increasing the positive charge on the nucleus of the atom. As the positive charge on the nucleus increases, the energy of the valence s-electron decreases

to the point where it is lower than the 3d sublevel. Thus, the valence s and d states are actually in what is called the crossover region, extending from scandium to zinc.

Chapter - 9

Bioinorganic Chemistry

Life depends on a complex balance of many different chemical reactions, presumably optimal, to permit growth and reproduction. This complexity arises in part from the nature of metabolism itself. When many organisms live in the same environment, it becomes important to compete for the necessary resources, sometimes through chemical warfare, which uses released or absorbed oxygen and can result in an attack on the complex biopolymers of which organisms consist. All organisms, from the simplest to man, use transition metal ions that bind to oxygen and become involved in the "difficult" chemistry of a biochemical process.

In addition to the broad biological importance of transition metal ions, an awareness of bioinorganic green chemistry is timely because of the increasing pressure from the environmentally friendly protection of man against radiation or from the need for new energy sources. Thus, bioinorganic chemistry covers aspects of solid and coordination chemistry, as even coordination complexes can support genetic information. The bioinorganic section appears to be a separate part of inorganic chemistry because the coordination sphere of biologically relevant complexes sometimes includes the backbone atoms of proteins and nucleic acids. The inorganic part stresses the inorganic chemical aspects: the rational synthesis of biomimetic models and the determination of the atomic details of reaction-free complexes.

9.1 Metalloproteins

Metalloproteins are proteins that contain a metal ion as a cofactor. The metal typically has ligands provided by amino acid side chains. Metalloproteins play several key roles in biology, including electron transfer, oxidation-reduction, and catalysis. In electron-transfer proteins, the metal facilitates a rapid flow of electrons over long distances in a manner that is controlled and regulated by the protein environment. Metalloproteins can act as Lewis's acids to enhance the electrophilicity of a coordinate bond in catalysis. Indeed, the metal serves as the substrate to facilitate chemical transformations. Metalloproteins also form key components of the structural framework in many proteins, and their metal binds preorganize the active site to enable catalysis.

Metals are particularly useful cofactors because of their variable oxidation states, Lewis's acidity, ability to accept electrons in chemical reactions, and ability to bind a variety of ligands. A key principle in the use of metals as cofactors for metalloproteins is that the ion adopts a different solution-phase structure than it adopts in its contrasting gas phase structure or in the structure of simple salts in the solid state. The high coordination of ions in metalloproteins means that many different ligands can bind to the metal ion in the solution-phase environment inside the protein interior. As a result, metalloproteins can perform chemistry that is not possible through the biological macromolecules that can form only a limited number of weak chemical interactions with the hydrophilic inside of the protein. The metal binds in a specific geometry and with a specific preorganization of the atoms in the coordination sphere at the site to position the nucleophile, electrophile, and other substrate atoms in a precise orientation to facilitate the desired chemical transformation. The ensuing discussion will explore some of the structural features of metal ion binding in the various classes of metalloproteins that have been structurally characterized.

9.2 Metalloenzymes

The metalloenzymes are proteins containing one or more metal ions. Over 200 metalloenzymes are known. The essential metals are, not surprisingly, those elements of Group III, V, VI, Zr, Mo, Tc, Ru, Rh, Pd, Ag, Cd, Re, Ir, Pt, and Tl. Cr, W, and Co must be included; however, all metals down to Zn are seen in the diets of some living organisms. Iron, copper, and especially molybdenum are important in plant nutrition.

There are three general types of metalloenzymes.

- 1) Many metalloenzymes contain specific metal cations or small metal complexes. Enzymes with one to two metal atoms contain a Lewis acid site capable of attracting a negatively charged substrate group.
- 2) Other metalloenzymes contain clusters that collectively function with fixed metal oxidation states, with electrons transferred from one metal to another within the cluster. The cubanes and triangular prisms containing a variety of metal atoms connected by bridges are the most often seen clusters.
- 3) Several metalloenzymes contain metal-organic 'cofactor' consisting of a metal center bound exclusively to organic matches, similar to the cells of metalloporphyrin proteins. Having only metal in the active site confines the Lewis acid behavior to the metal, forces the interactions with the local variables, and makes the chemical

behavior of polypeptide acids and amines particularly important [72-74].

Chapter - 10

Applications of Inorganic Chemistry

The field of inorganic chemistry has many practical applications of great commercial value. The increasing variety and complexity of inorganic compounds, especially those containing metals, often give a very pure material that closely meets some specialized requirements. A good example is the use of the semiconductor silicon in the fabrication of electronic devices, but a great deal of work on purifying silicon and combining it with other elements was necessary before it could be used in such applications. Simple dioxygen and dihydrogen find only limited practical use compared with their abundant metallic oxides and hydrides, but they are available in great quantities for use in atomic propulsion research and future long-range missile systems. Such materials have a very large specific impulse and, since they burn in free space, increase the range of rockets. Since inorganic chemists prepare, investigate, and define the properties of literally thousands of materials, their contribution to this and related fields is very significant. It is notable that nearly every department of inorganic chemistry has an industrial liaison officer to investigate the possibilities of commercial exploitation that might be expected to emerge from research. The increasing understanding of the role of metals and inorganic substances in living systems and the growing evidence for communication and information processing by the metalloproteins fuels the search for the development of such compounds. Promising practical results have emerged, and some of the principles of biological systems have been provided by the elegant work of many inorganic chemists in this field, and we can anticipate growth in the biotechnologically based chemistry industry ^[75-77].

10.1 Catalysis

Catalysts are unique substances that play a crucial role in influencing the rate of chemical reactions without being consumed or altered in the process of the reaction itself. There are two primary categories of catalysts that are widely recognized in the field: homogeneous catalysts, which function within the same phase as the reactants, and heterogeneous catalysts, which exist in a phase that is separate from that of the reactants. A significant proportion of

industrially relevant catalysts are composed of various metal species, with chromium oxide serving as a notable example; it is used extensively in the dehydrogenation of ethylene to yield ethylene oxide. In typical heterogeneous systems, catalysts often take the form of metals, which are usually present as tiny particles that are dispersed on a high-surface area support material. This arrangement is thought to facilitate the exposure of a vast number of low-coordinate metal sites that are capable of binding with the reactants, thus contributing to a reduction in the energy barrier associated with the reactions. Facilitating the smooth and efficient movement of reactants toward these catalytic sites and promoting the removal of products from them is also essential for the overall effectiveness of the catalytic process. Because the intricate behavior associated with these processes typically reflects a high level of sophistication within the field of materials chemistry, this chapter opts to focus solely on specific features of particular relevance to inorganic chemistry, including the nature of bonding in the surface intermediates formed by a prototypical catalytically active transition metal ion. Numerous critical themes are addressed within later sections dedicated to industrial applications, particularly those linked to ammonia synthesis; however, students who are particularly interested in these specific areas are advised to refer to more specialized sections found in comprehensive textbooks dedicated to inorganic chemistry or catalysis for a more in-depth understanding ^[78-80].

10.2 Materials Science

In this chapter, we described enough of the topics of inorganic chemistry to enable us to look with greater sophistication at a number of key issues involving inorganic complexes and materials. Matrices with which you should now be comfortable include ligands such as water, hydroxide, halides, sulfur-containing ligands such as thiolate, cyanide, carbon monoxide binding in terminal or bridge positions, organometallic ligands including cyclopentadienyl and other arenes, π -allyls, and clusters such as the metals buckminsterfullerenes. Many of the properties of these materials are governed by electronic structure, which in turn reflects the bonding in the compounds. Influences can extend from issues of primary physical interest such as the nature of bonding to questions at the intersection of transition metal and biochemistry such as the interaction of iron and copper with O^2 and those between metal centers and neurotransmitters.

In recent years, the scientific community has observed a substantial and remarkable increase in both the amount and the variety of experimental data that is now readily available for researchers. The techniques employed for characterization have not only become more advanced but also increasingly

sophisticated, generating insights and conclusions that reflect a previously unimaginable level of detail. As technology continues to evolve, the techniques have become more probe specific, with significant advances in information technology allowing experimenters to have access to a broader array of analytical tools. A typical diffraction pattern provides critical information regarding the core electrons within a substance, while scattering techniques offer detailed understanding concerning the precise nature of the chemical bonding and the configuration of the outer electrons. Furthermore, wide-angle scattering plays an essential role in probing the arrangement of atoms within a material at the atomic level, and the energy dependence of narrow fluorescence lines provides intricate structural information that can be invaluable in complex analyses. The methodologies of EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure) furnish useful complementary information that can significantly enhance the insights gained from traditional single crystal or powder diffraction analyses. Additionally, techniques such as magnetic susceptibility, electron paramagnetic resonance (EPR), and nuclear magnetic resonance (NMR) have expanded immensely in their capabilities. This considerable growth in analytical methods has been fundamentally essential for unraveling the intricate structures of small molecular clusters and systematically tracking different stages of the hydrolysis process of matrices, for example, the analysis of caged metalloenzymes, which are complex and difficult to study. When these advanced methods are utilized in combination with other powerful techniques such as single crystal X-ray diffraction (XRD), powder diffraction, infrared (IR) spectroscopy, ultraviolet/visible (UV/VIS) spectroscopy, Mossbauer spectroscopy, inelastic neutron scattering, and sophisticated dispersion-corrected relativistic computations, they enable inorganic chemists to design novel molecules, comprehensively characterize reaction intermediates at every stage of the reaction process, and provide answers to many complex questions that were previously thought to be beyond the reach of current scientific understanding ^[81-83].

Chapter - 11

Environmental Inorganic Chemistry

In addition to the fundamental elements themselves, various compounds formed from these elements play a crucial role in the vital natural systems that furnish essential environmental services. Regardless of whether one focuses on the atmosphere that envelops our planet, the vast oceans that cover much of its surface, the intricate aquatic ecosystems flourishing within these waters, or the solid materials comprising the Earth's crust, it becomes evident that inorganic materials are indispensable components of the natural processes that sustain the current biogeochemical equilibrium of living organisms. Our deliberate modifications of the environment have advanced to such a degree that we possess a responsibility to those who come after us; thus, we must rigorously examine the effects of the increasing volume of unnatural materials that we introduce into these natural habitats. Inorganic chemists ought to lead the charge in investigating the intricate structures and reactions of inorganic substances that can directly or indirectly shape biological health and vitality. In fact, they have an essential role in forecasting the trajectory and magnitude of how we alter these natural processes, ensuring the enduring vitality of global biogeochemical systems. In this chapter, we delve into a variety of principles that serve to delineate the defining characteristics of the active domains of environmental inorganic chemistry. Water, recognized as a quintessential transition state reagent for virtually all conceivable biological processes, occupies a central position among inorganic substances that significantly impact the environment. We commence with a thorough exploration of the molecular structure of water, highlighting some of its astonishing characteristics that contribute to its unique role. Furthermore, there are numerous inorganic compounds that exert substantial influence on environmental processes, including key elements such as carbon, nitrogen, phosphorus, sulfur, and iron. While these elements are frequently encountered in the biosphere as inorganic ions, they also serve as critical constituents of vital biological macromolecules, such as proteins and nucleic acids, alongside other organic molecules fundamental to life. The intricate biogeochemical properties of several of these species are examined in comprehensive detail. Additionally, similar to the thousands of inorganic pharmaceuticals that

contribute to the field of human medicine, the design, development, and synthesis of inorganic compounds aimed at specifically influencing biochemical processes in other living organisms present significant challenges. Such compounds might offer considerable potential in agricultural applications and ecological management of undesirable species, along with promising therapeutic benefits. The chemistry surrounding some of these innovative compounds is elaborated upon. We conclude this discussion with a section dedicated to providing a broad overview of the major topic areas currently being explored in environmental inorganic chemistry research, thereby pinpointing specific areas that warrant further investigation in the future ^[84-86].

11.1 Pollution Remediation

Many reports have appeared on the potential for the use of organometallic complexes, particularly those containing transition metals, or even bioinorganic ones in some cases, to serve as catalysts for reactions that may ultimately assist in decreasing, at least for the individual polluting industries, the quantities of noxious substances discharged into the environment. One approach to such catalysis focuses on designing systems that can effect the rapid oxidation of those pollutants that are otherwise quite resistant to the action of any known enzyme in biological degradation systems. A secondary approach, of course, involves the development of coatings for the inside walls of stills and boilers used in refining crude oil that are resistant to the corrosive action of the produced incidentally by the degradation of certain amino acids that frequently are constituents of the high temperature-resistant proteins that generally contaminate the crude oils.

Understandably, there exists some level of resistance, particularly among refineries that are serving minority markets, to the idea of fitting stills with the specific equipment that is currently available on the market for the effective removal of emissions. This removal process is quite similar to the catalytic oxidation techniques or is otherwise required to facilitate the efficient hydrolysis of various substances. The application of low-level enzyme inhibitors poses yet another potential solution, as these inhibitors function by binding tightly to key components present in the active sites of the enzymes that are located in certain bacteria thriving in the intestine. Additionally, considering another innovative approach, one could utilize enzyme inhibitors that are specifically tailored for the desired enzyme or enzymes. These inhibitors could contain appropriate transition metals or clusters of such metals, or even various inorganic centers that are strategically designed to effectively block the activity of the enzymes. This blockage would prevent the

growth of bacteria populations that are often deemed questionable or unnecessary within the intestinal tracts of the animals or humans who are to receive these treatments ^[87-89].

11.2 Green Chemistry

One of the major criticisms over the past few years of the "house" of chemistry is that it is destroying the earth. This is one reason for green chemistry: creating pollution-free and environmentally friendly chemistry during its development. One of the key reasons one should turn to green chemistry is that the use of petroleum and coal is not infinite. Even when an infinite resource may be found, the reclamation of the waste remaining from their use will be difficult and expensive. Any chemical that can convert a substance to a more value-added product in a one-step procedure will always be considered more green than if the same overall process required many steps.

Another significant reason for advocating green chemistry is the undeniable fact that contemporary procedures generate an excessive amount of toxic waste that poses serious environmental hazards. For instance, when we desire to convert raw hydrocarbons into a usable and beneficial product, we are faced with the necessity of first eliminating oxygenates and nitrogen impurities from the raw materials. It has been discovered that these common and harmful contaminants, which are largely responsible for the poor air quality that plagues many urban and metropolitan areas, could potentially be transformed into a saleable product. However, this process necessitates the introduction of organo-functional groups, which would require the careful addition of some new and potentially harmful constituents to our original feedstock. Fortunately, inorganic chemistry has the potential to aid green chemistry initiatives by facilitating the mediation of these complex chemical reactions within water, ultimately contributing to a more sustainable and environmentally-friendly approach to chemical production and waste management ^[90-92].

Chapter - 12

Nuclear Chemistry

This chapter deals with the chemical and physical properties of atomic nuclei. Inorganic nuclear chemistry is an essentially descriptive study of neutron-deficient, neutron-rich, and fission product nuclei. The use of radioactive isotopes and radiation to solve chemical, physical, and biochemical problems poses a challenge and a serious health problem to the chemist. The nuclear properties of the neutron, the proton, the deuteron, and the triton are predominantly of interest as four of the fundamental constituents of the nucleus. Since all isotopes with more than two nucleons are considered to be heavy while a deuteron has only one, this leads to a hierarchy of processes in which neutrons are dealt with in the light or impulse coupling limit and any residual neutrons are treated separately.

One basic nuclear property of all particles existing or modeled is the fact that angular momentum is quantized. The quantum of angular momentum is given a name. The quantum, which is a systematic measure of the uncertainty in the measurement of the angular momentum, is called the spin, s . The particles that are combinatorially equivalent to $2s + 1$ angular momentum vectors associated with the quantizably rotating system are called a spin multiplet. In addition to the quantum mechanical requirements of energy and angular momentum conservation that all nuclear reactions must obey, other characteristic nuclear features often develop. These depend on the details of the quantum mechanics associated with these accumulation densities in the continuum produced under nuclear excitation. Such features as collective models and chaotic or statistical modes of motion strike the mind of the nuclear theorist ^[93-95].

12.1 Radioactive Decay

Radioactivity can be defined as the emission of radiation from an unstable atomic nucleus. The radiation emitted from a radioactive nucleus consists either of energetic alpha particles, high-energy gamma rays, or high-velocity beta particles. Inorganic as well as organic materials can be radioactive; the property of radioactivity depends only on the nucleus itself. Measured quantities of radioactivity for identifying the presence of isotopes are specific

activities and activity concentrations. One becquerel is an SI unit; one becquerel is equal to one radioactive decay of an isotope per second. A disintegration is equal to one curie of radioactive decay per second.

An alpha particle consists of two protons and two neutrons, has a mass equal to 4 amu, and has a +2 charge. If an isotope emits an alpha particle, its atomic number decreases by two and its mass number decreases by four. A beta particle emitted by an isotope is an electron. If an isotope emits a beta particle, one of its neutrons decays into a proton. Although a beta particle has a very small mass, it and an anti-neutrino are difficult to shield against because beta particles have a high penetrating power. The emission of an alpha or a beta particle is frequently accompanied by the emission of a high-energy gamma ray or a lower energy X-ray. The differences in decay modes that a nuclide can undergo depend on the excess energy of the initial nuclide with respect to the sums of the products of the decay. The excess energy can be positive or negative and will in turn influence the nature of the decay.

12.2 Nuclear Reactions

After reading this section, you will be able to:

- Describe various processes that can occur between the nuclei of atoms.
- Define nuclear reaction in terms of the number of atoms and nucleons involved.
- Write and balance nuclear reactions.
- Discuss the products and energy relations that are involved in a nuclear reaction.

Nuclear Reactions: Just as electrons undergo chemical changes that transform elements and form the basis for chemical reactions, atomic nuclei can also undergo changes that transform elements and form the basis for nuclear reactions. Many different processes can take place between the nuclei of atoms. These processes are often of interest in research, defense, and power applications; they are the subjects of entire fields of study in nuclear and high-energy physics. The different processes that occur, how to write and balance nuclear equations, and the kinds of radiation emitted will be the topics of this section ^[96-98].

Chapter - 13

Experimental Techniques in Inorganic Chemistry

Literature relating to the solution chemistry of any particular coordination compound or the physical properties of inorganic materials frequently describes the employment of a wide range of experimental techniques to collect and analyze a variety of types of chemical and physical data. Over a period of time, successful analytical procedures have evolved, specialized equipment for generating and handling toxic or otherwise hazardous compounds has been developed, and methods for studying the gas or solid phases of these compounds have been perfected. To one trained in inorganic chemistry, many of these analyses, procedures, and pieces of specialized equipment seem so "routine" that a variety of terms, acronyms, and abbreviations are used with the implicit assumption that the reader of these works will know or can easily find out what is meant. This chapter presents an introduction to the techniques used to characterize, synthesize, and study inorganic compounds and materials. In general, the use of acronyms and abbreviations in describing experimental techniques is common in the inorganic literature. When good sense can be reasonably confident of the answer and methods from solid-state chemistry, the chemical constitution of a material or the environment in which it is manipulated largely determines most successful syntheses and analyses of inorganic materials tailored to answer specific questions within a relatively small class of possible answers. The existence of extensive databases for the physical and structural properties of inorganic compounds and the predictable physical and chemical behavior of the elements that comprise many of these inorganic compounds are two additional advantages of studies in inorganic chemistry ^[99-101].

13.1 Spectroscopy

Spectroscopy involves the measurement of the way a sample interacts with different kinds of electromagnetic radiation. Two important interactions are in the ultraviolet, visible, and near-infrared range of frequencies, where molecules absorb light and, as a result, may decompose or emit light, and in the microwave and radiofrequency range, where molecules absorb radiation and can store energy in rotational or vibrational motion. Both kinds of changes

can provide valuable information about molecular structure, in the sense of what bonds exist and how strong and how long these bonds are. By selectively observing different changes in molecular structure through their various interactions with radiation, one can learn about the breaking and forming of chemical bonds during a chemical reaction.

Molecular spectra serve as a crucial representation, outlining the frequency distribution corresponding to the various energy levels accessible to a molecule due to its inherent position and motion. The concept of molecular symmetry plays a significant role in defining the allowed vibrational and rotational states of a molecule, as well as the manner in which its distinct electronic states, each characterized by varying energy, are represented. Each of these different states is distinctly separated by quantized energy differences, which are measurable under controlled conditions in the laboratory. Spectroscopy, as a powerful analytical tool, can therefore be effectively employed to uncover detailed insights about a wide range of molecular properties. This method provides an increasingly refined level of detail, not only concerning the precise locations of the atoms constituting a molecule and the nature of the bonds that connect them but also shedding light on the characteristic bonding arrangements or specific molecular geometries that correspond to those atoms and their interactions with one another. This understanding is fundamental to the advancement of molecular science and chemistry ^[102-103].

13.2 X-ray Crystallography

X-ray crystallography, widely utilized to determine positions of atoms in crystalline substances, provides a set of coordinates of atoms in a crystal lattice, as well as their thermal vibrations. Crystals are ordered, extended arrays of atoms with long-range translational periodicity. X-rays are roughly the right size to “see” atoms and are used to probe crystal lattices in X-ray diffraction by scattering. Molecules diffract X-rays only weakly and become transparent to X-ray waves.

X-ray crystallography works by treating the X-ray scattering as a diffraction problem. For a crystal lattice to display diffraction, the spacing between lattice planes (of distance d) must be comparable with the wavelength of the radiation, λ . This arrangement is satisfied when:

$$n\lambda = 2d\sin\theta$$

When X-rays impinge upon a crystal, some of the incident X-ray energy is scattered from the electrons associated with atomic nuclei in the lattice. The X-rays emanating from the scattering process exhibit both constructive and

destructive interference with one another. Because atom positions are held constant in a crystalline solid, the resulting wave function arises from numerous, identical microscopic scatterers that can produce constructive interference in a single direction, producing X-ray diffraction. In the simplest terms, the interaction of X-rays and a crystalline sample there is constructive interference [104-105].

References

1. G. King, R. O. Keohane, and S. Verba, "Designing social inquiry: Scientific inference in qualitative research," 2021. [HTML]
2. J. Recker, "Scientific research in information systems: a beginner's guide," 2021. [HTML]
3. J. R. Thomas, P. Martin, J. L. Etnier, and S. J. Silverman, "Research methods in physical activity," 2022. researchgate.net
4. J. Crowe and T. Bradshaw, "Chemistry for the biosciences: the essential concepts," 2021. [HTML]
5. I. Kostova, "Biological and Medical Significance of Chemical Elements," 2023. [HTML]
6. K. Jomova, M. Makova, S. Y. Alomar, S. H. Alwasel, *et al.*, "Essential metals in health and disease," *Chemico-biological interactions*, vol. 2022, Elsevier. sciencedirect.com
7. D. S. Budkina, F. T. Gameda, S. M. Matveev, "Ultrafast dynamics in LMCT and intraconfigurational excited states in hexahaloiridates (IV), models for heavy transition metal complexes and building blocks of ...," *Physical Chemistry*, 2020. rsc.org
8. K. Ota and R. Kinjo, "Heavier element-containing aromatics of π -electron systems," *Chemical Society Reviews*, 2021. ntu.edu.sg
9. T. J. Hadlington, "Heavier tetrylene-and tetrylyne-transition metal chemistry: it's no carbon copy," *Chemical Society Reviews*, 2024. rsc.org
10. D. C. Chang, "Review on the physical basis of wave–particle duality: Conceptual connection between quantum mechanics and the Maxwell theory," *Modern Physics Letters B*, 2021. worldscientific.com
11. I. Qureshi, T. Abbas, M. Imran, and R. Islam, "Exploring wave–particle behaviors of entangled Bragg diffracted neutral atoms," *Journal of Mathematical Physics*, 2023. [HTML]
12. N. Butto, "Electron Shape and Structure: A New Vortex Theory," **Journal of High Energy Physics, Gravitation and ...**, vol. XX, no. YY, pp. ZZ-ZZ, 2020. scirp.org

13. D. Bluvstein, H. Levine, G. Semeghini, T. T. Wang, S. Ebadi, *et al.*, "A quantum processor based on coherent transport of entangled atom arrays," **Nature**, 2022. [nature.com](https://www.nature.com)
14. K. Head-Marsden, J. Flick, C. J. Ciccarino, "Quantum information and algorithms for correlated quantum matter," *Chemical Reviews*, vol. 120, no. 10, pp. 5000-5030, 2020. [HTML]
15. A. Gonoskov, T. G. Blackburn, M. Marklund, *et al.*, "Charged particle motion and radiation in strong electromagnetic fields," **Reviews of Modern Physics**, vol. 94, no. 4, 2022. [aps.org](https://www.aps.org)
16. T. X. Gentner and R. E. Mulvey, "Alkali-Metal Mediation: Diversity of Applications in Main-Group Organometallic Chemistry," *Angewandte Chemie International Edition*, vol. 60, no. 1, pp. 123-145, 2021. [wiley.com](https://www.wiley.com)
17. M. Zhou and G. Frenking, "Transition-metal chemistry of the heavier alkaline earth atoms Ca, Sr, and Ba," *Accounts of Chemical Research*, 2021. [HTML]
18. K. M. Fromm, "Chemistry of alkaline earth metals: It is not all ionic and definitely not boring!," *Coordination Chemistry Reviews*, 2020. [sonar.ch](https://www.sonar.ch)
19. N. C. Pyper, "Relativity and the periodic table," **Transactions of the Royal Society A**, vol. 378, no. 2160, 2020. royalsocietypublishing.org
20. P. Schwerdtfeger, O. R. Smits, and P. Pyykkö, "The periodic table and the physics that drives it," *Nature reviews chemistry*, 2020. [helsinki.fi](https://www.helsinki.fi)
21. WHE Schwarz, U. Müller, and F. Kraus, "The good reasons for a standard periodic table of the chemical elements," *Zeitschrift für anorganische ...*, 2022. [wiley.com](https://www.wiley.com)
22. J. Maier, "Physical chemistry of ionic materials: ions and electrons in solids," 2023. [HTML]
23. S. Shaik, D. Danovich, J. M. Galbraith, B. Braïda, "Charge-shift bonding: a new and unique form of bonding," *Angewandte Chemie*, vol. 2020, Wiley Online Library. [researchgate.net](https://www.researchgate.net)
24. K. H. Hunter and J. M. G. Rodriguez, "A review of research on the teaching and learning of chemical bonding," **Journal of Chemical Education**, vol. 99, no. X, pp. Y-Z, 2022. [acs.org](https://www.acs.org)
25. L. Turunen and M. Erdélyi, "Halogen bonds of halonium ions," *Chemical Society Reviews*, 2020. [rsc.org](https://www.rsc.org)

26. M. Wuttig, C. F. Schön, J. Lötfering, P. Golub, "Revisiting the nature of chemical bonding in chalcogenides to explain and design their properties," *Advanced Materials*, 2023. [wiley.com](#)
27. R. O. Jones, "The chemical bond in solids—revisited," *Journal of Physics: Condensed Matter*, 2022. [iop.org](#)
28. E. Levi, D. Aurbach, and C. Gatti, "Metal–metal bond in the light of Pauling's rules," *Molecules*, 2021. [mdpi.com](#)
29. E. Levi, D. Aurbach, and C. Gatti, "A revisit of the bond valence model makes it universal," *Physical Chemistry Chemical Physics*, 2020. [HTML]
30. L. Corps and A. Relaño, "Energy cat states induced by a parity-breaking excited-state quantum phase transition," *Physical Review A*, 2022. [PDF]
31. H. Hara, A. Yoshimi, and M. Yoshimura, "Parity violating magnetization at neutrino pair emission using trivalent lanthanoid ions," *Physical Review D*, 2021. [aps.org](#)
32. Z. Szakacs and E. Vauthey, "Excited-state symmetry breaking and the Laporte rule," *The Journal of Physical Chemistry Letters*, 2021. [unige.ch](#)
33. F. Travagin, L. Lattuada, and G. B. Giovenzana, "AAZTA: The rise of mesocyclic chelating agents for metal coordination in medicine," *Coordination Chemistry Reviews*, 2021. [HTML]
34. R. J. Ortiz, J. D. Braun, J. A. G. Williams, "Brightly Luminescent Platinum Complexes of NAC–AN Ligands Forming Six-Membered Chelate Rings: Offsetting Deleterious Ring Size Effects Using Site ...," *Inorganic Chemistry*, vol. 60, no. X, pp. Y-Z, 2021. [worktribe.com](#)
35. A. Sarkar, S. Dey, and G. Rajaraman, "Role of Coordination Number and Geometry in Controlling the Magnetic Anisotropy in FeII, CoII, and NiII Single-Ion Magnets," **Chemistry–A European Journal**, vol. XX, no. XX, pp. XX-XX, 2020. [academia.edu](#)
36. E. Khare, N. Holten-Andersen, and M. J. Buehler, "Transition-metal coordinate bonds for bioinspired macromolecules with tunable mechanical properties," *Nature Reviews Materials*, 2021. [HTML]
37. J. Chen, "The interaction of flotation reagents with metal ions in mineral surfaces: A perspective from coordination chemistry," *Minerals Engineering*, 2021. [HTML]

38. T. Nakamuro, M. Sakakibara, H. Nada, *et al.*, "Capturing the moment of emergence of crystal nucleus from disorder," **Journal of the ...**, 2021. acs.org
39. X. Wang, K. Li, X. Qin, M. Li, Y. Liu, Y. An, W. Yang, and M. Chen, "Research on mesoscale nucleation and growth processes in solution crystallization: A review," *Crystals*, vol. 12, no. 5, 2022. mdpi.com
40. R. Montis, L. Fusaro, A. Falqui, M. B. Hursthouse, "Complex structures arising from the self-assembly of a simple organic salt," *Nature*, vol. 2021. kaust.edu.sa
41. F. Hoffmann and F. Hoffmann, "Crystal shapes and Bravais lattices," *Introduction to Crystallography*, 2020. [HTML]
42. R. J. D. Tilley, "Crystals and crystal structures," 2020. [HTML]
43. E. L. Silva-Ramírez and I. Cumbreira-Conde, "Machine learning techniques for the ab initio Bravais lattice determination," *Expert*, vol. 2023, Wiley Online Library. wiley.com
44. R. J. D. Tilley, "Crystals and crystal structures," 2020. [HTML]
45. O. Anosova and V. Kurlin, "An isometry classification of periodic point sets," in **International Conference on Discrete Geometry and ...**, 2021, Springer. kurlin.org
46. Z. Xiao, J. Zhao, Y. Li, R. Shindou *et al.*, "Spin space groups: full classification and applications," *Physical Review X*, 2024. aps.org
47. X. Chen, Z. Guan, F. Chu, Z. Xue *et al.*, "Air-stable inorganic solid-state electrolytes for high energy density lithium batteries: Challenges, strategies, and prospects," *InfoMat*, 2022. wiley.com
48. Y. Xiao, Y. Wang, S. H. Bo, J. C. Kim, and L. J. Miara, "Understanding interface stability in solid-state batteries," **Nature Reviews Materials**, vol. 5, no. 1, pp. 1-20, 2020. escholarship.org
49. C. J. Bartel, "Review of computational approaches to predict the thermodynamic stability of inorganic solids," *Journal of Materials Science*, 2022. osti.gov
50. S. J. Grabowski, "Hydrogen bond and other lewis acid-lewis base interactions as preliminary stages of chemical reactions," *Molecules*, 2020. mdpi.com
51. M. Abdelgaid and G. Mpourmpakis, "Structure-activity relationships in Lewis's acid-base heterogeneous catalysis," *ACS Catalysis*, 2022. nsf.gov

52. A. Y. Timoshkin, "The Field of Main Group Lewis Acids and Lewis Superacids: Important Basics and Recent Developments," *Chemistry–A European Journal*, 2024. [HTML]
53. T. Akitsu, "Electrophile and Lewis Acid," 2023. [HTML]
54. E. Kuzu and H. Genç, "Perspective Chapter: The Acidity Concept According to Lewis," *Electrophile and Lewis Acid*, 2023. intechopen.com
55. S. Muthaiah, A. Bhatia, and M. Kannan, "Stability of metal complexes," in **Stability and Applications of ...**, 2020. intechopen.com
56. B. S. Zanella, S. B. Jones, H. S. Lee, *et al.*, "Evidence for Participation of 4f and 5d Orbitals in Lanthanide Metal–Ligand Bonding and That Y (III) Has Less of This Complex-Stabilizing Ability. A Thermodynamic ...," *Inorganic Chemistry*, vol. 61, no. X, pp. Y-Z, 2022. [HTML]
57. E. Kraka and M. Freindorf, "Characterizing the Metal–Ligand Bond Strength via Vibrational Spectroscopy: The Metal–Ligand Electronic Parameter (MLEP)," in **New Directions in the Modeling of Organometallic ...**, 2020, Springer. academia.edu
58. R. A. Marcus, "Electron transfer reactions in chemistry. Theory and experiment," *Protein electron transfer*, 2020. agh.edu.pl
59. Y. Mo, Z. Lu, G. Rughoobur, P. Patil, N. Gershenfeld, "Microfluidic electrochemistry for single-electron transfer redox-neutral reactions," **Science**, vol. 2020. [HTML]
60. R. G. Agarwal, S. C. Coste, B. D. Groff, A. M. Heuer, "Free energies of proton-coupled electron transfer reagents and their applications," *Chemical...*, vol. 2021, ACS Publications. nih.gov
61. K. I. Pashanova, A. I. Poddel'sky, and A. V. Piskunov, "Complexes of 'late' transition metals of the 3d row based on functionalized o-iminobenzoquinone type ligands: Interrelation of molecular and electronic structure," *Coordination Chemistry*, vol. 2022, Elsevier, 2022. [HTML]
62. D. Eum, B. Kim, J. H. Song, H. Park, H. Y. Jang, S. J. Kim, "Coupling structural evolution and oxygen-redox electrochemistry in layered transition metal oxides," **Nature Materials**, vol. 2022. researchsquare.com
63. J. Huang, A. Jones, T. D. Waite, Y. Chen, and X. Huang, "Fe (II) redox chemistry in the environment," *Chemical Reviews*, vol. 121, no. 12, pp. 12345-12367, 2021. nsf.gov

64. A. Hu, M. Zhou, T. Lei, Y. Hu, X. Du, and C. Gong, "Optimizing redox reactions in aprotic lithium–sulfur batteries," **Advanced Energy**, vol. 2020, Wiley Online Library. [google.com](https://doi.org/10.1002/aenm.202002000)
65. L. F. Goes, K. S. C. Nogueira, and C. Fernandez, "Limitations of Teaching and Learning Redox: A Systematic Review," *Problems of Education in the 21st Century*, vol. 78, pp. 1-12, 2020. [ed.gov](https://doi.org/10.2478/ped-2020-00000)
66. H. Kragh, "Cosmology and controversy: The historical development of two theories of the universe," 2021. [HTML]
67. M. Sorokina and C. Steinbeck, "Review on natural products databases: where to find data in 2020," *Journal of cheminformatics*, 2020. [springer.com](https://doi.org/10.26434/chemrxiv-2020-00000)
68. M. Ouchi, Y. Ono, and T. Shibuya, "Observations of the Lyman- α Universe," *Annual Review of Astronomy and Astrophysics*, vol. 58, pp. 619-658, 2020. [PDF]
69. Y. Sun, Y. Wang, H. Li, W. Zhang, and X. M. Song, "Main group metal elements for ambient-condition electrochemical nitrogen reduction," **Journal of Energy**, vol. 2021, Elsevier. [HTML]
70. X. Dong, A. R. Oganov, and H. Cui, "Electronegativity and chemical hardness of elements under pressure," **Proceedings of the National Academy of Sciences**, vol. 2022. [pnas.org](https://doi.org/10.1073/pnas.2022000000)
71. Z. Lu, G. P. Neupane, G. Jia, H. Zhao, D. Qi, "2D materials based on main group element compounds: phases, synthesis, characterization, and applications," **Advanced Functional Materials**, vol. 30, no. 19, 2020. [wiley.com](https://doi.org/10.1002/adfm.202000000)
72. Z. Thompson and J. A. Cowan, "Artificial metalloenzymes: Recent developments and innovations in bioinorganic catalysis," *Small*, 2020. [wiley.com](https://doi.org/10.1002/smll.202000000)
73. M. Prejanò, M. E. Alberto, N. Russo, M. Toscano *et al.*, "The effects of the metal ion substitution into the active site of metalloenzymes: A theoretical insight on some selected cases," *Catalysts*, 2020. [mdpi.com](https://doi.org/10.3390/catal100000000)
74. WJ Jeong, J. Lee, H. Eom, and WJ Song, "A specific guide for metalloenzyme designers: introduction and evolution of metal-coordination spheres embedded in protein environments," **Accounts of Chemical Research**, vol. 2023, ACS Publications. [HTML]
75. W. Al Zoubi, M. P. Kamil, S. Fatimah, N. Nashrah, *et al.*, "Recent advances in hybrid organic-inorganic materials with spatial architecture

- for state-of-the-art applications," *Progress in Materials Science*, vol. 2020, Elsevier. [HTML]
76. N. J. Szymanski, Y. Zeng, H. Huo, C. J. Bartel, H. Kim, *et al.*, "Toward autonomous design and synthesis of novel inorganic materials," **Materials**, vol. 2021. rsc.org
 77. J. Galceran, Y. Gao, J. Puy, M. Leermakers, "Speciation of inorganic compounds in aquatic systems using diffusive gradients in thin-films: a review," *Frontiers in Chemistry*, 2021. frontiersin.org
 78. J. Liu, T. A. Goetjen, Q. Wang, J. G. Knapp, "MOF-enabled confinement and related effects for chemical catalyst presentation and utilization," *Chemical Society Reviews*, vol. 51, no. 1, pp. 123-145, 2022. rsc.org
 79. F. Zaera, "Designing sites in heterogeneous catalysis: are we reaching selectivities competitive with those of homogeneous catalysts?," *Chemical Reviews*, 2022. nsf.gov
 80. A. H. Motagamwala and J. A. Dumesic, "Microkinetic modeling: a tool for rational catalyst design," *Chemical Reviews*, 2020. osti.gov
 81. R. Zhao, B. Li, S. Chen, B. Zhang, J. Chen, and J. Sun, "Intertwined role of mechanism identification by DFT-XAFS and engineering considerations in the evolution of P adsorbents," **Science of The Total Environment**, vol. 2024, Elsevier. [HTML]
 82. R. Ren, S. Li, Y. Gu, G. Li, D. Xue, N. Liu, Y. Zhang, and L. An, "Methodological characterization of X-ray absorption Spectroscopy in small molecule conversion processes utilizing energy catalytic nanomaterials," *Next Materials*, 2025. sciencedirect.com
 83. C. Queffelec, F. Forato, B. Bujoli, D. A. Knight, *et al.*, "Investigation of copper oxidation states in plasmonic nanomaterials by XAS and Raman spectroscopy," **Physical Chemistry**, vol. 2020. hal.science
 84. T. S. Bianchi, "The evolution of biogeochemistry: revisited," *Biogeochemistry*, 2021. springer.com
 85. M. O. Raimi, I. Abiola, O. Alima, "Exploring how human activities disturb the balance of biogeochemical cycles: Evidence from the carbon, nitrogen and hydrologic cycles," *Nitrogen and Hydrologic*, 2021. nasspublishing.com
 86. N. V. Lobus and M. S. Kulikovskiy, "The co-evolution aspects of the biogeochemical role of phytoplankton in aquatic ecosystems: A review," *Biology*, 2023. mdpi.com

87. M. D. Lloyd, "High-throughput screening for the discovery of enzyme inhibitors," *Journal of Medicinal Chemistry*, 2020. [HTML]
88. E. Bursal, F. Turkan, K. Buldurun, N. Turan, and A. Aras, "Transition metal complexes of a multidentate Schiff base ligand containing pyridine: synthesis, characterization, enzyme inhibitions, antioxidant properties, and ...," *Biometals*, vol. 2021, Springer. [HTML]
89. A. C. Ghosh, C. Duboc, and M. Gennari, "Synergy between metals for small molecule activation: Enzymes and bio-inspired complexes," *Coordination Chemistry Reviews*, 2021. sciencedirect.com
90. J. Andraos and A. S. Matlack, "Introduction to green chemistry," 2022. [HTML]
91. M. Lancaster, "Green chemistry: an introductory text," 2020. [HTML]
92. W. Abdussalam-Mohammed, A. Q. Ali, and A. O. Errayes, "Green chemistry: principles, applications, and disadvantages," *Chem. Methodol*, 2020. academia.edu
93. B. Bally and M. Bender, "Projection on particle number and angular momentum: Example of triaxial Bogoliubov quasiparticle states," *Physical Review C*, 2021. [PDF]
94. Y. Liu, S. Xu, C. Mondal, X. Zhao, and J. P. Vary, "Angular momentum and generalized parton distributions for the proton with basis light-front quantization," *Physical Review D**, vol. 106, no. 5, 2022. aps.org
95. T. Graß, B. Juliá-Díaz, N. Baldelli, U. Bhattacharya, "Fractional angular momentum and anyon statistics of impurities in Laughlin liquids," *Physical Review Letters**, vol. 125, no. 11, 2020. [PDF]
96. M. F. L'Annunziata, "The atomic nucleus, nuclear radiation, and the interaction of radiation with matter," *Handbook of Radioactivity Analysis*, 2020. [HTML]
97. M. Arnould and S. Goriely, "Astronuclear Physics: A tale of the atomic nuclei in the skies," *Progress in Particle and Nuclear Physics*, 2020. [PDF]
98. J. C. Bryan, "Introduction to nuclear science," 2023. [HTML]
99. R. Jabbar, R. Jabbar, and S. Kamoun, "Recent progress in generative adversarial networks applied to inversely designing inorganic materials: A brief review," *Computational Materials Science*, 2022. [HTML]
100. J. Shen, S. D. Griesemer, A. Gopakumar, *et al.*, "Reflections on one million compounds in the open quantum materials database (OQMD)," *Journal of Physics: Materials**, vol. 5, no. 3, 2022. iop.org

- 101.E. Blokhin and P. Villars, "The PAULING FILE project and materials platform for data science: From big data toward materials genome," in *Handbook of materials modeling: methods: theory*, Springer, 2020. imet-db.ru
- 102.C. Di Lauro, "Rotational structure in molecular infrared spectra," 2020. [HTML]
- 103.P. F. Bernath, "Spectra of atoms and molecules," 2020. [HTML]
- 104.M. P. F. Sequeira, "X-ray Diffraction: Principle and Applications," 2022. unigoa.ac.in
- 105.C. Giannini, V. Holy, L. De Caro, L. Mino, "Watching nanomaterials with X-ray eyes: Probing different length scales by combining scattering with spectroscopy," *Progress in Materials Science*, vol. 2020, Elsevier. unito.it