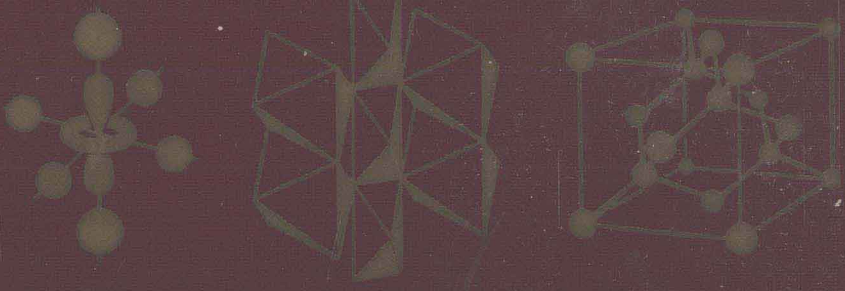

INTRODUCTION TO PHYSICAL INORGANIC CHEMISTRY

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Physical Chemistry

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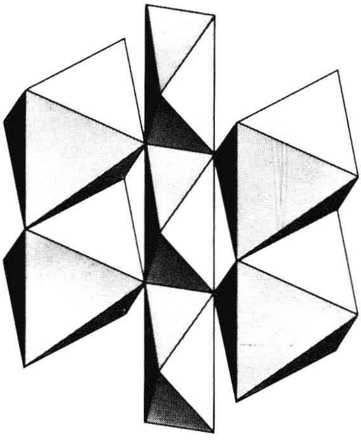

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Preface

The rapid advancement of modern science makes a constant reappraisal of teaching methods an inevitable necessity. Nowhere is this truer than in the field of inorganic chemistry, where prolific research is producing an accumulation of data which is staggering in both volume and diversity. One result has been the raising of doubts in the minds of scientists as to the advisability or even the practicability of the teaching of descriptive inorganic chemistry in its classic form. A ramification of this line of thought, in progressive institutions, is the decreasing emphasis on qualitative inorganic analysis. Fortunately, the problem itself provides the solution, for the theoretical aspect of science has progressed with the experimental, so that it is no longer necessary to treat introductory inorganic chemistry from a phenomenological point of view. On the contrary, advances in the theories of structure and reaction mechanism make it possible to correlate the bulk of chemical phenomena with fundamental atomic and molecular properties.

Therefore, our objective in this book is to emphasize the principles underlying chemical behavior rather than the phenomena themselves. On the other hand, we try to make the approach an experimental one by including sufficient data so that the student himself can make an objective evaluation of the explanation he has been given. Indeed, to foster the student's ability to make such judgments must always be one of the principal aims of the teaching of science.

Because this book attempts to describe the chemical behavior of 103 elements in different states of aggregation, its scope is pretentiously broad. There is certainly more material than can be accommodated in the average one-year course of study. (We, personally, cover little of the material in Chapters 6 and 10. Depending on the level at which the course is given and the prerequisites for it, a different choice of chapters may be preferable.) At the same time, the book has some omissions, a few of which might appear serious. For example, there is no systematic treatment of the descriptive chemistry of the elements and their compounds. However, a surprising amount of this material actually is covered in the text, although from a different point of view. Any such deficiency may, we feel, be adequately compensated for by an accompanying laboratory course. A more serious, but unavoidable, omission is that there is no detailed mathematical treatment of many subjects. But since this course is intended to follow the first university course in general chemistry, more mathematics, at this level, would serve only to confound the majority of students. On the other hand, it is to the credit of mathematics teachers that the mathematical capabilities of students at this level are rapidly improving, so that in a few years such a conclusion may no longer be valid.

Detailed acknowledgment of all our sources of material is virtually impossible. Let us simply say that we have made extensive use of existing literature in the field, which is inevitable in writing an introductory textbook. We must also acknowledge a debt of gratitude to our colleagues at the University of British Columbia, for innumerable helpful discussions. Many will no doubt be sursurprised at how efficiently their brains have been picked. We are grateful, too, for the helpful suggestions of reviewers, including our students, who used the preliminary edition. Finally, we must express our appreciation for the assistance we have received from our wives and from the staff at Addison-Wesley in the preparation of the manuscript.

Vancouver, British Columbia K.B.H.
November 1962 G.B.P.

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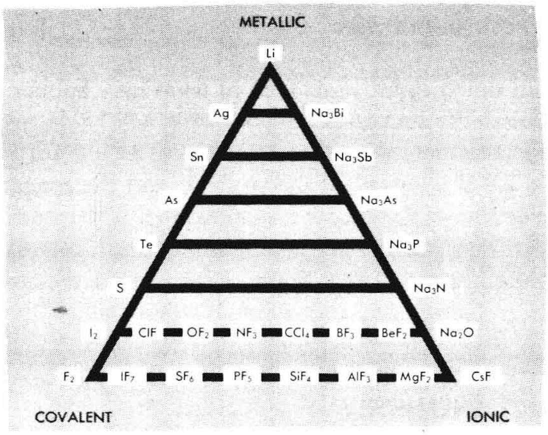

CHAPTER ONE

Introduction

The study of the chemistry of 103 elements is a major undertaking, and an intelligent approach to the vast amount of information to be assimilated requires that we do more than catalog this data; we must seek the principles underlying the phenomena being studied. If successful, we will then have a theoretical and/or empirical background which will allow us to correlate known chemical behavior with fundamental quantities and enable us to predict the behavior in unfamiliar situations. At the same time, it is necessary that the reader become conversant with the language and methods of chemistry and learn to recognize the physical and chemical parameters relevant to the problem at hand.

1–1. THEORY AND EXPERIMENT

Learning should, in fact, proceed through the same objective evaluation of experimental facts that is common to a well-executed research program. The correlation between theory and experiment must be examined critically to bring out the shortcomings and limitations of the relationship. Inherent in such an examination is an awareness of the approximations and assumptions involved in the development of the theory. A student who leaves the study of a subject querying the validity of the explanation he has been given, or concerned about how the theory might be improved to eliminate a shortcoming, can usually be satisfied that he has gained the necessary familiarity with the material.

The manner in which a principle is discovered or a theory evolves from experimental data is rarely a straightforward one in practice. Some knowledge of the theoretical background of a phenomenon is necessary for the intelligent planning of an experiment so that the results will be relevant to the problem. The data obtained may then suggest an explanation or provide an empirical relationship which, in turn, leads to further experimentation.

Experiments are rarely carried out without some idea of what may happen, but there is always the delightful possibility that something exciting will be discovered accidentally. Much the same element enters into the selection of results for inclusion in a textbook. One hopes for the benefit of the student, and the reputation of the authors, that such a selection is as objective as possible. Unfortunately, this aspect is out of the hands of the student. The evaluation of the results is not, however, and it is one of the major aims of this book to develop in the student the habit of scientific criticism.

1–2. PHYSICAL INORGANIC CHEMISTRY

For the purposes of introduction, a convenient primary breakdown of the phenomena to be studied can be made in terms of structure and the process of reaction. The reader will quickly realize that such a division is not definitive. Certain chapters, such as those on atomic and molecular structure and crystal chemistry, are largely devoted to problems of structure, and others, such as that on thermochemistry, rest more or less on the dividing line. The partition is nevertheless a meaningful and very useful one.

(a) Structure

The description of the structure of a chemical species, from an experimental point of view, has several facets. One must, first of all, establish the stoichiometry of the compound. If, for example, we are concerned with boron chloride, this would mean determining that there are three chlorine atoms and one boron atom combined to give a formula BCl_3. As a second step, we would be likely to investigate the symmetry of the molecule or the spatial configuration of the nuclei. If this were done, with one or more of the methods described in Section 5–1(b), we should find that the four nuclei are coplanar, with the chlorine nuclei situated symmetrically about the boron nucleus. In the more sophisticated terminology of Chapter 5, the molecule would be described as trigonal planar.

Carrying the process one step further, we would use the same methods of investigation to make the description quantitative and to establish that the separation of the nuclei is 1.76 A and that the $\angle$ClBCl is 120°. Finally, to complete the description, it is necessary to make some statement regarding the energetics of the molecule. This is most conveniently done by stating that the energy released in the formation of one mole of gaseous BCl_3 from atomic boron and chlorine is 317.7 kcal, i.e.,

$$\mathrm{B(g) + 3Cl(g) = BCl_3(g) + 317.7\ kcal.}$$

It is apparent from our description in terms of the position of the atoms or nuclei that the atoms retain at least some of their individuality when combined in a molecule. It is logical, therefore, to introduce the concept of the chemical bond between atoms as the medium through which combination occurs. The

TABLE 1-1

PHYSICAL PROPERTIES ASSOCIATED WITH THE FOUR BOND TYPES

Property	Ionic	Covalent	Metallic	van der Waals
Mechanical	Strong, giving hard crystals	Strong, giving hard crystals	Strength varies, malleability common	Weak, giving soft crystals
Thermal	Fairly high mp; low coefficient of expansion	High mp; low coefficient of expansion	Variable mp; coefficient of expansion large	Low mp; large coefficient of expansion
Electrical	Solids are moderate insulators; ion conductors in melt and solution	Insulators in both solid and melt	Good conductors through electron transport	Insulators
Optical	Absorption is same as that of individual ions	High refractive index in solid; absorption differs in three phases	Liquid and solid both opaque	Absorption is similar in three phases
Example	NaCl	Diamond	Copper	Inert gases

acceptance of this concept was, in fact, probably one of the greatest advances in the study of molecular structure. Much of the effort of present-day scientific research, both theoretical and experimental, is directed toward an elucidation of the forces responsible for the chemical bond.

From an experimental point of view, it is convenient to view the chemical bond in the light of four idealized types: ionic, covalent, metallic, and van der Waals. The physical properties associated with crystals in which the individual bond types predominate are summarized in Table 1-1. Such a classification is extremely useful, and is firmly entrenched in modern terminology, but it must be realized that, in practice, relatively few bonds approach these idealized types. Most bonds are of an intermediate type as shown in the triangle diagram, due to Ketelaar, in Fig. 1-1. It should also be recognized that the classification is largely an empirical one and results, to some extent, from a limited comprehension of the forces involved.

In spite of this limitation we can still make deductions regarding the general nature of the forces involved. Consider, for example, the forces acting between two atoms X and Y, which are capable of forming a diatomic molecule XY. For bond formation to be possible, it is clear that there must be present attractive

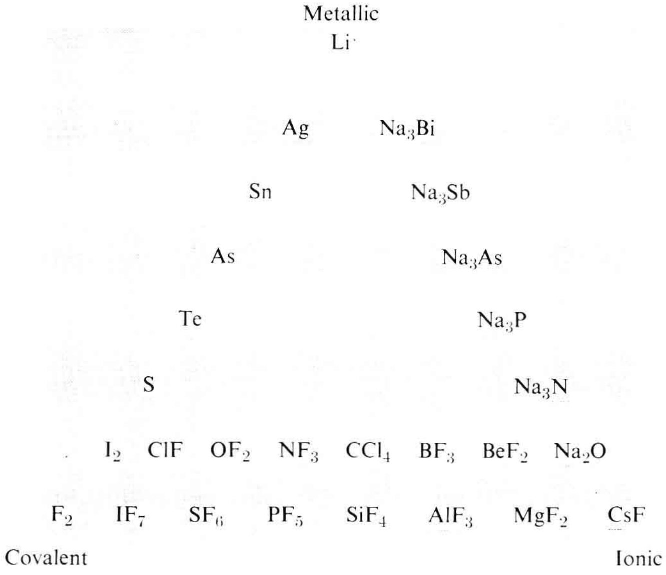
Metallic
Li
Ag
Na$_3$Bi
Sn
Na$_3$Sb
As
Na$_3$As
Te
Na$_3$P
S
Na$_3$N
I$_2$ ClF OF$_2$ NF$_3$ CCl$_4$ BF$_3$ BeF$_2$ Na$_2$O
F$_2$ IF$_7$ SF$_6$ PF$_5$ SiF$_4$ AlF$_3$ MgF$_2$ CsF
Covalent
Ionic

FIG. 1–1. Triangle diagram illustrating the transitions between ionic, covalent, and metallic bonding. (Reproduced from *Chemical Constitution*, by J. A. A. Ketelaar, Elsevier Publishing Company, Amsterdam.)

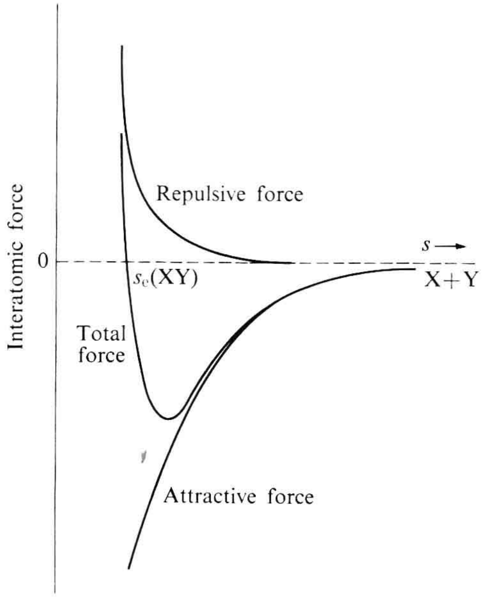

FIG. 1–2. Forces acting between atoms X and Y in the process of bond formation.

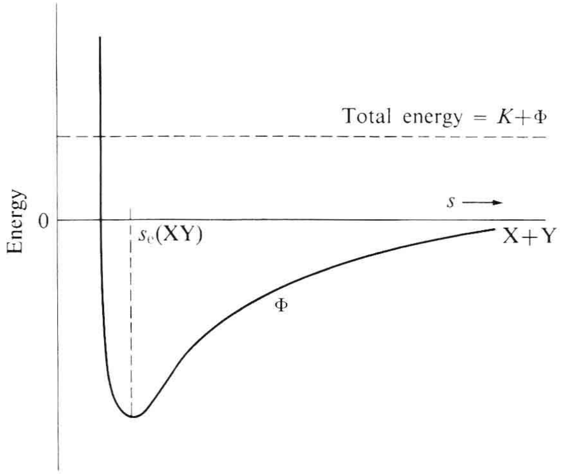

FIG. 1-3. Variation of potential energy Φ with internuclear separation s in the formation of the diatomic molecule XY.

forces that depend inversely on the separation of the atoms. At the same time, since the nuclei do not coalesce, there must be repulsive forces, also inversely dependent on the atomic separation. Furthermore, if a stable configuration is to result, the repulsive forces must act over a shorter distance and exhibit a much higher functional dependence on the separation s. In other words, the repulsive forces will be very small for larger values of s but will increase very rapidly in the region of the equilibrium internuclear distance s_e as s decreases. At s_e, the attractive and repulsive forces are equal so that the net force is zero. This relationship is shown clearly in Fig. 1-2.

The energetics of bond formation may be pictured in the same way. A rigorous treatment would require the application of quantum mechanics but, apart from quantization of the energy, the situation would be much the same as depicted classically in Fig. 1-3. For large values of s, the potential energy of interaction Φ will be negligible so that the total energy E will be kinetic energy K, and given by the expression

$$E = K + \Phi = \tfrac{1}{2}m_X v_X^2 + \tfrac{1}{2}m_Y v_Y^2.$$

For smaller values of s, Φ will no longer be negligible but will decrease and pass through a minimum for $s = s_e$. Past this point it increases rapidly as the repulsive forces take over. In the absence of an additional phenomenon, the total energy E will remain constant so that as s decreases, K must increase and pass through a maximum at s_e. For smaller values of s, K decreases and becomes zero when $\Phi = E$. It will be clear that, if a bond is to be formed, the total energy must be reduced during the process of interaction. If this does not occur, the atoms will simply move apart again, retaining their initial kinetic energy.

There are many ways in which energy may be removed or dissipated, however. It might, for example, be emitted in the form of radiation (chemiluminescence) or transferred through collision to other atoms or molecules or to the wall of the containing vessel. If this occurs, the atoms will be contained within the potential well and a bond will be formed.

Valid as they are, these deductions concerning the properties of interatomic forces still leave unanswered the question as to their origin. A substantial portion of this book will be devoted to answering this question in a manner which will allow us to predict, to a certain extent, chemical behavior in terms of fundamental properties.

(b) The process of reaction

In considering the reactive process between chemical species, several factors must be taken into account. First, there is the question of whether a reaction will occur at all and, if so, to what extent it will go to completion. Second, we shall be concerned with the speed, or the rate, at which the reaction occurs. Finally, and perhaps most important, we will wish to know the mechanism through which the reaction proceeds.

As our discussion of bond formation has indicated, the question of whether or not a reaction will occur is largely one of energetics. If the energy of the products is less than that of the reactants, then, under normal conditions, a reaction may reasonably be expected to take place. The complete answer is more complex, however, and requires consideration of entropy as well as energy changes. The principles involved are well understood, and thermodynamics enables us to establish the desired relationship between the pertinent parameters and the equilibrium constant, which is the quantitative expression of the extent of reaction.

The mechanism and rate of a reaction are intimately associated and are obviously related to the process of bond formation. Most chemical reactions are far more complex than the atom combination of Section 1–2(a), however, and the term "mechanism" is usually applied to the role played by individual chemical species. This role is often far from simple, as is well illustrated by the photochemically induced reaction of hydrogen and chlorine to form hydrogen chloride:

$$\mathrm{H_2 + Cl_2 \rightarrow 2HCl.}$$

The first step in the reaction is the dissociation of Cl_2 through the absorption of a photon or light quantum of energy $h\nu'$ according to the equation

$$\mathrm{Cl_2} + h\nu' \rightarrow \mathrm{2Cl.} \tag{1–1}$$

This is in turn followed by the reactions

$$\mathrm{Cl + H_2 \rightarrow HCl + H,} \tag{1–2}$$

and

$$\mathrm{H + Cl_2 \rightarrow HCl + Cl,} \tag{1–3}$$

to produce not only the end product HCl but a chlorine atom. The reaction is

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