CHEMICAL BONDS AND BOND ENERGY

Second Edition

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Preface

The first edition of this book contained a fully detailed account of bond energy calculation based on fundamental properties of atoms. On the basis of a simple concept of polar covalence, it provided a means of accounting quantitatively for heats of formation and reaction. Thus the book did much to reveal the beautiful cause-and-effect relationship between the qualities of atoms and the physical and chemical properties of their chemical combinations. It also presented new and valuable insights into the nature of bond multiplicity and the "lone pair bond weakening effects" that appears so significant in the chemistry of elements of the periodic groups M5, M6, and M7.

Regretfully but deliberately omitted from the first edition was any explanation of the well-known fact that the bond energy mentioned above is usually not at all the same as the energy required to break the bond if there is more than one bond per molecule. The two kinds of bond energy may be distinguished by calling the former the *contributing bond energy* (CBE) and the latter, as usual, the *bond dissociation energy* (BDE). Much more has now been learned which is included in this second edition. The CBE is closely related to the BDE, being an important part of it, the remainder being the reorganizational energy (E_R) of the radicals created when the bond is broken: BDE = CBE + E_R. E_R has been evaluated for each of many common radicals, as detailed herein. These values are useful if not indispensable in the interpretation of important phenomena such as reaction mechanisms and product distribution, of special interest to organic chemists but also to inorganic chemists.

Further research on bond lengths, successful for binary compounds, is reported herein, along with new material on bond energies in solids and molecular addition compounds.

The challenge of holding this edition to a reasonable size was met by eliminating some of the details of individual bond energy calculations and finding more efficient means of presenting the information. The book has been rewritten almost completely. The average reader should still be able to test thoroughly any of the material in this book or from elsewhere, using the basic information contained herein. The author will welcome inquiries or suggestions from readers.

In a world, even in a scientific world, where censorship remains an approved means of expressing disagreement, it is refreshing to be able to acknowledge the existence of openmindedness. In particular, I should like to express my deep appreciation to Professor Leland C. Allen of Princeton and Professor Robert G. Parr of the University of North Carolina for their kind and generous encouragement. Finally, my thanks to my nearly nonagenarian mother, who has no need of understanding this book to know it is a good one.

Preface to First Edition

The ultimate goal of theoretical chemistry is the attainment of so thorough an understanding of atoms that their complete behavior under all conditions of chemical interest can be predicted, together with the physical and chemical properties of all substances and their mixtures. In other words, the cause-and-effect relationship between the nature of atoms and the nature of their combinations should become perfectly revealed.

One of the central problems in the pursuit of this unattainable yet irresistibly challenging goal has been to understand the nature of chemical bonds. To understand bonds, one must be able to calculate their energies. This book tells how. It reports the first generally successful calculation of more than 850 kinds of bonds in more than 500 compounds. Such calculations provide fascinating new insights regarding the nature of bonds. In turn, these insights permit the first successful explanations of many previously puzzling phenomena, which are also included. I find these ideas immensely helpful in the classroom, and hope my fellow teachers will share this experience. The work should be equally useful to students and practicing chemists.

The advent of quantum mechanics stirred high hopes that the whole of chemical science could be created from fundamental theory. An abysmal gap soon became evident, however, between principle and practice. Quantum mechanics has been of indispensable assistance in the development of modern chemical theories of atomic structure, and atomic and molecular spectroscopy, and in many other areas. But even the heaviest artillery of quantum mechanics, brought to fullest effect over a period of forty years through the medium of modern computers, has scarcely dented the problem of bond energy calculation.

There are two good reasons for this failure. One is the immense complexity of the practically insoluble problem of calculating all the interactions among all the component particles of an atom. The other is the fact that the energies of interactions among atoms are usually far smaller than the total energies of the atoms. The logical calculation of bonding energy as a difference between the total energy of a molecule and the total energy of its atoms is therefore subject to the difficulty of obtaining accurately very small differences between very large values. Compare, for example, the energies of two oxygen atoms (obtained as the sum of the successive ionization energies), roughly 94,000 kcal per mole, with the O_2 bond energy of 119. Even very good approximate solutions of the many-body problem could hardly be expected to provide reliable bond energies.

The approach I have taken, therefore, over the past twenty years, has been to accept the findings of quantum mechanics to the limit of their usefulness, and then deliberately to avoid the insoluble many-particle problem by attempting to identify those qualities of an atom which in a sense summarize, or are the resultant of, all its interelectronic and electron-nuclear interactions. I have now identified these qualities as the covalent radius, the electronegativity, and the homonuclear bond energy, and have shown how the latter two are interrelated and can be obtained one from the other. These atomic properties, plus the bond length, are the basic data for bond energy calculations as described herein.

This work has revealed many questions needing answer, which I hope many readers will become interested in pursuing.

For financial support, I am indebted to the University of Iowa and especially to Arizona State University for having provided me with a steady salary and comfortable working conditions. For their moral support I am grateful to my wife Bernice and my son Bob, and to my respected colleagues Dr. LeRoy Eyring, Dr. Sheng Lin, and Dr. Paul Stutsman, who have sympathetically strengthened my philosophical endurance of the frustrations of frequent opposition.

None of this work would have been possible without the help of contributions from both experimental and theoretical chemists far too numerous to acknowledge individually, but nonetheless deeply appreciated. Their data and ideas have been a constant source of inspiration.

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The Delightful Science of Chemistry: A Preview of a New View

This chapter allows a sort of quick peek, or sneak preview, into matters that will be presented in considerable detail throughout the remainder of the book. Whether the view will be considered new must depend somewhat on what is meant by view, on what is meant by new, and on what may be new to the viewer. One may sit on a hilltop and watch the valley below. Initially it is completely covered with low-hanging clouds that obscure all but the grossest features of the valley. Slowly and gradually the clouds thin, revealing a small detail here, another there. Hints of scenic continuity begin to be recognized, but not until a substantial portion of the cloud cover has been dissipated can one begin to perceive what is really there. Step by step, one's imagination of the unseen becomes reinforced by reality, or proven absurd, by revelation of additional areas previously covered. And finally the last wisp of vapor becomes dispersed, and the whole valley lies appealingly before one's eyes. At what point in the disappearance of the clouds does the valley appear?

The fundamental nature of chemistry has lain under such a blanket of fog for years and years. The fog persists to this day concealing what one assumes to be the full beauty and exquisite system of chemical change and of physical and chemical properties. Over the years, spots of cloud have worn thin or been removed here and there allowing clear perception of portions of the landscape, but the full coherence of the scene still remains interrupted by areas of undissipated aerosol. Shall we withhold our enjoyment until the last vestige of fog has disappeared? Or shall we take pleasure in it now, letting our imaginations tentatively fill in those areas still blotted from our view? I think we should reserve our highest admiration for the impossible but, meanwhile, appreciate to the fullest that which we have.

For me, the fog has been slowly clearing throughout 45 years as a student of chemistry. Although it still clings with tantalizing tenacity to many mysterious places, sufficient of the whole has been revealed to allow, for the simple mind at least, a more satisfying understanding of chemistry than has ever before been possible. I have ample reason to suspect that their preoccupation with other important and fascinating matters has thus far kept my fellow chemists from developing a full appreciation of the rather remarkable progress toward understanding that is described in this book. I hope that the contents of this chapter may stimulate your curiosity, even whet your appetite, to examine the remainder of the book with a critical but open-minded attitude.

Two examples are our practical limit here. With only two we cannot begin to be comprehensive, but it is possible to become aware of some of the more interesting and exciting implications of this work. Let us therefore engage in a fairly detailed analysis of some of the more relevant chemistry of two common compounds, potassium chloride and carbon dioxide. In preparation for that, we may need reminding of the periodic law.

THE PERIODIC LAW

The basis of the periodic law is generally considered to be the **periodicity of electronic configurations** that characterizes the build-up of the chemical elements in succession of increasing atomic number. Only one step less fundamental, and at least equally important, is the effect of electronic configuration on the **extent to which nuclear charge can be felt.** The effectiveness of the positive charge of the nucleus, as sensed at the periphery of the atom, is called the **effective nuclear charge.** All that the *structure* tells us about bonding is which electrons are so located that they have the possibility of being shared with another atom and which orbitals have vacancies that might accommodate electrons of other atoms. *Effective nuclear charge,* however, determines *how readily* the electrons of the atom might be shared by another atom and *how strongly* the electrons of another atom might be attracted. Taken together, the atomic structure and the effective nuclear charge are the principal factors that govern the behavior of atoms when they come into contact. They consequently tend strongly to predetermine the results of interatomic interactions. These results include, of course, the nature of the physical and chemical properties of any compounds that are formed.

Consider the changes that occur from left to right across the major group elements within a period of the periodic table. The number of outermost electrons changes from 1 to 8. The number of orbital vacancies correspondingly decreases from 7 to 0. To the significant extent that the number of covalent bonds an atom can form is determined by the number of possible half-filled outermost orbitals, then for the first four groups the number of bonds, or valence, is limited by the number of outermost *electrons,* but the valence of the last four groups is limited by the number of outermost *vacancies*: 1–2–3–4–3–2–1–0. Broadly speaking, the question of whether like atoms will join together through covalence or by metallic bonding is largely a function of the ratio of outer electrons to outer vacancies. When the ratio is less than one, all the elements are metals with the single exception of the maverick boron. The small size of the boron atom seems to involve holding the outermost electrons too tightly for effective delocalization of the type characteristic of metals. When the ratio is greater than one, some metallic properties may be observed, for reasons requiring no discussion here, but most such elements are clearly nonmetals.

The outermost principal quantum level of an atom differentiates electrons from those lying in lower levels in the following manner. Whereas ***underlying*** electrons are quite effective in shielding the nuclear charge on an almost one-to-one basis, the *outermost* electrons appear too busy keeping out of each other's way to intervene between one another and the nucleus. Consequently they are very ineffective in blocking off nuclear charge, being roughly only about one-third efficient. This means that adding one positive charge to the nucleus while adding one electron to the outermost level produces an increase of about two-thirds of a protonic charge in the effective nuclear charge. Therefore filling of the outermost shell from one to eight electrons, in the building up of the chemical elements, is accompanied by a steady **increase** in effective nuclear charge.

The size of an electronic cloud surrounding an atomic nucleus, vaguely though this size must be defined, is a function of a balance between the interelectronic repulsions and the attractions between electrons and nucleus. Increasing effective nuclear charge must therefore cause contraction of the cloud, and the atomic radius **decreases** as the number of outermost electrons is increased from one to eight.

The electronegativity of an atom is proportional to the coulombic force between the effective nuclear charge and an electron in an outermost orbital. Therefore increasing the number of outermost electrons must **increase** the electronegativity, since it increases the effective nuclear charge and diminishes the distance over which it must be effective.

Ionization energies of the outermost electrons are of course influenced by orbital type and whether the electron is paired or unpaired in its orbital. But the general trend **upward** from left to right is the expected result of a steadily increasing effective nuclear charge.

Electron affinities are likewise determined by the effective nuclear charge and the distance over which it must act. A trend of **increasing** electron affinity is therefore expected as the number of electrons in the outermost level increases.

In summary, the numerical valence of an atom is determined by the electronic configuration; but the characterization as metal or nonmetal, oxidizing or reducing agent, and the general nature of its combinations with other atoms, both like and different, all reflect the extent to which the nuclear charge is able to control the conditions of both the outermost electrons and the outermost vacancies. With these principles in mind, it is then possible to examine the atoms of specific elements with a reasonably reliable preconceived concept of *what* these atoms must be like and *why* this should be so.

POTASSIUM AND CHLORINE

The central theme of this analysis is that **the properties of compounds must be predetermined by the nature of the atoms which compose them.** In that sense we should be able to predict, or at least enjoy the comfortable feeling, that the properties of atoms are responsible for the properties of compounds, and a sufficient understanding of atoms should lead logically to an adequate understanding of compound properties.

Potassium

One glance at the electronic configuration of potassium, as abbreviated by 2–8–8–1, should suffice to inform us that there is only one electron, and therefore seven vacancies, in the outermost principal quantum level of the potassium atom. The preceding element, argon 2–8–8, exhibits no appreciable effective nuclear charge from the viewpoint of using orbitals in the fourth principal level, for argon is essentially inert. In order to persuade this atom to accept an electron and hold on to it, it is necessary to increase its nuclear charge by one. Even so, this charge is largely blocked by the very symmetrical electronic cloud that surrounds it, so that the added electron (which makes the atom into one of potassium) is not very strongly held. This should imply several related bits of information about potassium atoms:

(1) The atoms should be relatively large, in fact the largest of all atoms in the period that potassium begins. We have experimental evidence of this size in the bond length observed for the K_2 molecule. This length, 3.92 Å, implies an effective radius in the bond direction of 1.96 Å for the potassium atom. Other evidences of relatively large size are to be found in consideration of the solid element, as will be discussed shortly.

(2) The atoms do not hold the outermost electron very strongly. In fact, the ionization energy of potassium is only 102 kpm (kilocalories per mole), which is lower than for any other elements except rubidium, cesium, and francium.

(3) If an atom cannot hold its own electrons tightly, then it certainly cannot be expected to attract outside electrons strongly. In an atom of potassium the effective nuclear charge is small and it is required to operate over a relatively large distance, which means that the electronegativity of the atom is very low. A value of 0.42 has been determined from a consideration of the average density of the electronic sphere, which shows on the average fewer electrons per unit volume of the sphere than in any other elements except the heavier ones of this group.

(4) If an argon atom cannot acquire an extra electron favorably, then certainly an atom of potassium cannot be expected to do so. This is equivalent to saying that the electron affinity must be energy absorbed, not evolved.

We are now ready to consider bringing potassium atoms together. Each has one outermost half-filled orbital and thus the requisites for the formation of one single covalent bond. It is therefore easy to predict with assurance that the covalency of potassium cannot exceed one and that two potassium atoms might join together by a single covalent bond to form a diatomic molecule K_2, fully using the covalent capacity of each atom. Since bonding forces involve attractions that increase with decreasing distance and since the potassium atoms are relatively large, the large distance would be expected to correspond to weak bonding. Furthermore, since the bonding results from the mutual attraction of both nuclei for the same two shared electrons and the low electronegativity shows that neither nucleus can attract such electrons very strongly, we can predict weak bonding for this reason also. The dissociation energy of the K_2 molecule has been measured to have the very low value of 13.2 kpm. In fact, this value can be calculated from a simple linear relationship that occurs between homonuclear bond energy and nonpolar radius and the electronegativity: $E = CrS$. Electronegativity is proportional to the coulomb *force* between the effective nuclear charge and an electron at the distance of the covalent radius. Homonuclear bond energy is proportional to the coulomb *energy* between the effective nuclear charge and the bonding electrons in their average position halfway between the two nuclei, which is also the distance of the covalent radius. Coulombic force is charge product divided by distance squared, and coulombic energy is charge product divided by distance. Hence the relationship, $E = CrS$. It is interesting to note here that whereas electronegativity has usually been invoked solely to explain *uneven* sharing of bonding electrons in covalent bonds between *unlike* atoms, **it also plays an equally vital, though much less appreciated, role in the even sharing characteristic of nonpolar covalence between like atoms.**

Only a very small concentration of K_2 molecules has been observed in the vapor above 760°C, the boiling point of potassium, most of the vapor being monatomic. It is not surprising that most of the weakly bonded K_2 molecules are dissociated at so high a temperature. Below 760°C the element exists as a lustrous liquid, which solidifies at 63.7°C to a typically metallic-appearing solid. We can explain this failure of the K_2 molecules to persist—studies of the solid show that they are no longer present as such—on the basis of the atomic structure of the potassium. Examination of the K_2 molecule shows us that once the single covalent bond has been formed, neither atom retains any ability to form additional covalent bonds. It also shows us that each atom has relatively low energy orbitals that are not engaged in the bonding. Under such circumstances, it is generally observed that the bonding electrons tend to become *delocalized*, abandoning their concentrated position in the internuclear region between just one pair of atoms in order to spread out among many atoms. This kind of delocalization of outer electrons into all available orbitals, minimizing the repulsions among electrons, is the distinguishing characteristic of the metallic state. Knowing this, we should then accept the familiar existence of elemental potassium as a metal, rather than a diatomic gas, as the expected behavior of atoms having the general nature exhibited by atoms of potassium.

The advantage to potassium of condensing from the diatomic gas to the metallic solid is evidenced by the atomization energy of potassium metal, which is found to be 21.4 kpm. This is to be compared with the energy to liberate one mole of potassium atoms from the diatomic molecules, which is half of 13.2, or 6.6 kpm. In other words, potassium atoms in the metallic state are subjected to cohesive forces more than three times greater than in the diatomic molecule. From the study of the structure of potassium, it is known that the atoms form the body-centered cubic lattice in which each interior atom is in direct contact with eight neighbors at the corners of an enclosing cube and about 15% farther away from the central atoms of the six adjacent cubes. Clearly the bonding forces per atom pair must be less than in the diatomic molecule, which would therefore cause the atoms to be farther apart in the solid. The metallic radius of potassium is found to be 2.35 Å, in contrast to the nonpolar covalent radius of only 1.96 Å. But potassium atoms are relatively low in atomic weight, and the metal must therefore be quite low in density. In fact, the density is only 0.86 g/ml. From this we find that the volume occupied by one mole of potassium atoms, or the atomic volume, is 45.3 ml, larger than for most of the other chemical elements and certainly most of the closely packed metals.

In summary, thus far we have seen that the potassium atom has qualities entirely consistent with its special electronic configuration and with the properties of potassium atoms joined together by covalent or metallic bonds. Although we are not yet able to predict the exact temperature of melting or boiling or the exact energies involved in phase changes, we can nevertheless appreciate that most if not all of what is known about potassium metal is consistent with what is known about potassium atoms.

Chlorine

In contrast to potassium atoms, chlorine atoms come at almost the end of their period. By this time the outermost shell has been provided with seven of the eight possible electrons, leaving but one vacancy and therefore one half-filled orbital. Whereas potassium is barely beyond the point of practically zero effective nuclear charge, chlorine represents the maximum effective nuclear charge in its period. The increase in atomic number from sodium, 11, to chlorine, 17, involves addition of outermost electrons while increasing nuclear charge, but the increased charge is not effectively blocked by the additional electrons. Chlorine being six steps beyond sodium and the effective nuclear charge having increased by about two-thirds with each step, the final effective nuclear charge of chlorine must be about 4 greater than of sodium. Therefore the atom must have a much more compact electronic cloud in chlorine than in sodium. Furthermore, the much *larger* effective nuclear charge now acts over a *shorter* distance, which increases the electronegativity. If chlorine atoms are smaller and more electronegative than sodium atoms, they are certainly smaller and more electronegative than potassium atoms. In fact the covalent radius, determined as half the bond length in the diatomic molecule, is 0.99 Å, only about half that of the potassium atom. The electronegativity is 4.93, much larger than in potassium.

Just as in the case of potassium, it is easy to predict that with one half-filled outer orbital per atom, chlorine will unite by single covalent bonds to form diatomic molecules. Unlike potassium, however, chlorine has lone pairs of electrons in the remaining orbitals, not vacancies. Therefore there is no possibility of Cl_2 molecules undergoing further combination, their only interattraction being weak van der Waals. The weakness of these forces prevents chlorine from condensing at ordinary conditions. It remains a diatomic molecular gas until cooled to about −34°C. At this temperature the van der Waals forces become sufficiently effective to liquify it.

We should expect the bond in Cl_2 to be much stronger than in K_2, since the effective nuclear charge in chlorine is much larger than in potassium and acts over only about half the distance. In fact, the experimental dissociation energy of Cl_2 is about 58 kpm. If we calculated this according to the $E = CrS$ relationship, E would be about 78, or 20 kpm higher. As we shall see later, both quantities are valid and have their special applications. Our present purposes are adequately cared for by the experimental value 58.

The experimental bond length in Cl_2 is 1.98 Å, making the covalent radius 0.99 Å. The combination of small radius and high electronegativity, together with the presence of the essential vacancy in the outermost principal quantum level, should give chlorine atoms both a strong hold on their own electrons and a strong attraction for an additional electron from some other atom. Consistent with these predictions are the ionization energy, 301 compared to only 102 for potassium, and the electron affinity. When a gaseous chlorine atom acquires an extra electron to become a gaseous chloride ion, about 86 kpm is released as the electron affinity.

In summary, chlorine as the free, elemental gas has properties quite consistent with the nature of chlorine atoms as we know it. The wide differences between metallic potassium and gaseous chlorine are easily rationalized in terms of the differences between potassium atoms and chlorine atoms. Potassium atoms, which are large, hold their outermost electrons only weakly and have very low electronegativity. Chlorine atoms, which are small, hold their outermost electrons very tightly and have very high electronegativity. These differences are easily interpreted on the basis of atomic structure and of its effect on how strongly the nuclear charge is evident within the outermost orbitals of the atom.

POTASSIUM CHLORIDE

KCl Gas Molecules

We have seen that potassium atoms are held together in metallic potassium with sufficient force that it takes 21.4 kpm to liberate them. Furthermore, chlorine