PRINCIPLES
OF
ORGANIC
CHEMISTRY

ABERNETHY

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CHEMISTRY

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PREFACE

🎔 This textbook is intended for the normal one-semester course of three lectures a week or its equivalent. Out of the conviction that during the first semester a textbook should be used as such the author has made a careful selection of topics, eliminating much of the material that, when included, tends to make organic textbooks encyclopedic sources of information, discouraging to the beginning student.

With a brief discussion of electronic structure as a starting point, the book proceeds to an elementary explanation of the chemical bond and the significance of the tetracovalence of carbon. A development of the functional groups follows. The author feels that it is important for the beginning student to draw a sharp line of demarcation between aliphatic and aromatic substances. Emphasis is placed on the importance of the understanding of the fundamentals of nomenclature. Throughout the book such theories and laws as are necessary to correlate the subject matter are given.

With as few exceptions as possible, no compounds are discussed before presenting the class to which they belong. Hence if an aldehyde can be oxidized to an acid, this type of reaction is given without further discussion of acids until those substances are treated.

The Wurtz reaction is given as a decided teaching aid in right thinking in structure, reactions and by-products of a reaction, especially as it is a reasonably simple reaction that can be understood very early in the course. In order to clarify the meaning of organic bases, the mechanism of ester formation is included so that alcohols are not related to inorganic hydroxides. The hydrogen bond is stressed and the similarity between ammonium hydroxide and alkylammonium hydroxides is a convenient correlation. Other special topics fit into their appropriate places. An entire brief chapter is devoted to the Grignard reagent because many condensation

reactions must be omitted and this reagent is so versatile. The final chapter on oxidation and reduction correlates a number of reactions seemingly unrelated and permits quantitative calculations from these reactions. Many biological compounds are discussed because of their permanent significance.

Gratitude is expressed to the author's former associates in graduate school, Professors Arthur S. Roe of the University of North Carolina, E. E. Campaigne of Indiana University, and Bernard Nelson of Wheaton College, Illinois, for criticizing the manuscript in its early development. For detailed criticism the author is indebted to Professor Charles D. Hurd of Northwestern University and Professor L. J. Desha of Washington and Lee University. Dr. Vladimir Haensel supplied information on triptane and Professor H. I. Schlesinger gave the information on the hydrides of the elements of Period II of the periodic table. The chapter on oxidation and reduction owes its origin to discussions with Professor Byron Riegel. The author wishes to thank Mr. J. P. Stewart and Mr. and Mrs. John Husted for other assistance. The ketene generator was diagrammed from an apparatus constructed under the supervision of Professor Glenn T. Seaborg of the University of California at Berkeley, as designed by Professor Choh Hao Li of the same institution. The author's thanks are also due to the W. B. Saunders Company and to the critics who examined the manuscript for them before publication.

<div align="right">JOHN LEO ABERNETHY</div>

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CHAPTER 1

The Meaning of Organic Chemistry

Chemical substances are commonly classified into two great divisions, namely, inorganic and organic compounds. Originally the term inorganic was applied to those compounds which were considered to be obtained only from lifeless materials, while compounds isolated from biological materials, that is, those of plant or animal origin, were called organic. Inorganic chemistry developed to a greater extent at first. Investigation of organic compounds was somewhat restricted since a certain amount of mystery was attached to them because of their relation to life processes.

Ultimately it became evident that this simple classification required revision. With respect to inorganic compounds, it was known, for example, that water and sodium chloride could be found in the biological source of perspiration, yet both certainly occurred in nature as inorganic compounds. Furthermore, Friedrich Wöhler at the University of Göttingen, in a historic experiment in 1828, prepared urea from ammonium cyanate. Urea had been previously extracted from urine and identified as organic, whereas ammonium cyanate had been made in the laboratory, independent of any natural organic source. This experiment slowly caused the removal of the cloak of mystery surrounding organic chemistry. Further investigation disclosed that most compounds formed in life processes contained carbon. Therefore new definitions of organic and inorganic chemistry were necessary. In modern terminology *organic chemistry* is understood to mean the chemistry of carbon and its compounds regardless of whether or not they are found in nature and *inorganic chemistry* is concerned with any of the other elements and their compounds, excluding those formed by their combination with carbon.

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Other than this, no fine line of demarcation can be drawn between these two fields. There are certain distinctive features of organic chemistry, however, which should be noted. First, organic reactions are often slow, whereas inorganic are comparatively rapid. For instance, silver nitrate reacts instantaneously with hydrochloric acid to form silver chloride but ethyl alcohol and acetic acid often require a period of an hour or more in contact with a catalyst to reach equilibrium with ethyl acetate, an industrial solvent. Second, organic substances are frequently insoluble in water and soluble in organic solvents, in contrast to the reverse order of solubility of inorganic compounds. Third, organic compounds have low melting and boiling points, compared to inorganic substances. Fourth,

HYDRIDES OF ELEMENTS OF PERIOD II			
Element	Number of Compounds	Formulas of Compounds	Names of Compounds
He	0	none	none
Li	1	LiH	lithium hydride
Be	0	none	none
B	6*	B_2H_6 B_4H_{10} B_5H_9 B_5H_{11} B_6H_{10} $B_{10}H_{14}$	diborane dihydrotetraborane pentaborane dihydropentaborane hexaborane decaborane
C	thousands	. . . . . .	. . . . . .
N	3	NH_3 N_2H_4 N_3H	ammonia hydrazine hydrazoic acid
O	2	OH_2 O_2H_2	water hydrogen peroxide
F	1	HF (and polymers)	hydrogen fluoride

* Only those are listed for which molecular weights have been determined.

there is a tremendous number of compounds of carbon compared to those of any of the other elements. There are actually some 400,000 known carbon compounds; this is more than those formed by inter-combinations of all of the other elements. The hydrides of the second period of the periodic table serve to emphasize the vast number of compounds of carbon.

These differences are partially attributed to the ability of carbon to produce *covalent substances*, whereas other elements tend to yield *electrovalent compounds* to a large extent. It will be recalled that covalent molecules are formed through a process of sharing electrons between atoms, while electrovalent molecules are produced by a transfer of electrons from one atom to another.

Atomic Structure

The fundamental particles of the atom are the *proton*, the *neutron* and the *electron;* all are listed below with their corresponding masses and charges, assuming a unit negative charge for the electron.
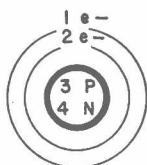
FUNDAMENTAL PARTICLES OF THE ATOM			
Particle	Mass	Charge	Symbol
Proton	1 × Hydrogen Atom	+1	P
Neutron	1 × Hydrogen Atom	0	N
Electron	(1/1845) × Hydrogen Atom	−1	e^-

The center of mass of an atom is located in the *nucleus*. This contains the protons and neutrons, while the electrons move about the nucleus in various *orbits*. When the number of protons in the nucleus and the number of electrons moving about it are equal there is a balance of charges in the atom and it is said to be *neutral*. The maximum numbers of electrons moving in the orbits that fit into the first, second and third shells of the elements of lower atomic weight are 2, 8, and 8, respectively, and when these maximum numbers are attained the shells are said to be complete. *Shells* are rather flexible zones of similar energy content about the nucleus. The *atomic num-*
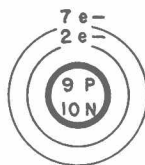
ber of an atom corresponds to the number of protons in its nucleus, and the *atomic weight* is equal to the number of protons plus neutrons. Diagrams of the neutral atoms, helium, lithium, fluorine, neon and sulfur are shown below.
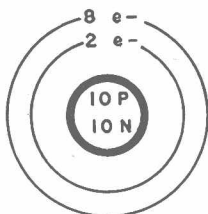
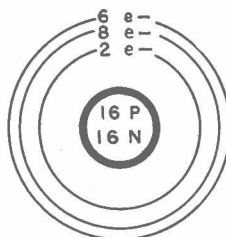|		
2 e— 2 P 2 N	1 e— 2 e— 3 P 4 N	7 e— 2 e— 9 P 10 N
At. No. 2 At. Wt. 4 He	At. No. 3 At. Wt. 7 Li	At. No. 9 At. Wt. 19 F

|	
8 e— 2 e— 10 P 10 N	6 e— 8 e— 2 e— 16 P 16 N
At. No. 10 At. Wt. 20 Ne	At. No. 16 At. Wt. 32 S

There is a strong tendency for atoms to take on the electronic structure of inert elements such as helium and neon, which have completed shells. This can be accomplished either by a transfer of electrons from one atom to another, or by the sharing of electrons between atoms. When lithium combines with fluorine to form the electrovalent compound lithium fluoride, fluorine acquires one electron from the lithium atom to complete its outer shell, thereby assuming the electronic configuration of neon, and lithium, losing one electron, takes the configuration of helium. This reaction, in which there is a transfer of electrons, can be represented readily by means of diagrams, electrons and shells being indicated by dots and circles, respectively.

Li   +   F   ⟶   Li$^+$ F$^-$
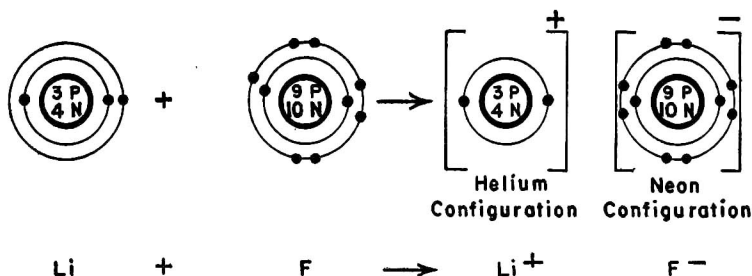
In the formation of lithium sulfide, two atoms of lithium are required to supply the two electrons necessary to complete the outer shell of the sulfur atom. The outer shell of each lithium atom gives up its single electron.
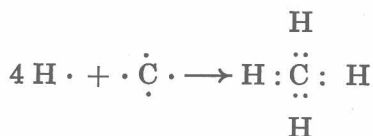

2 Li   +   S   ⟶   Li$_2^+$ S$^=$
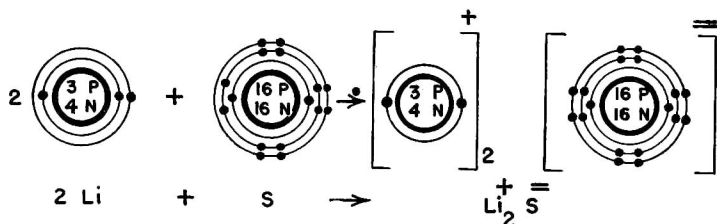
An excess of one proton over the number of electrons in the lithium ion gives it a charge of $+1$, while the -1 charge of the fluoride ion and the -2 charge of the sulfide ion are provided by the excesses of one and two electrons, respectively, over the number of protons in the nucleus. An *ion*, of course, is a charged atom or group of atoms.

Carbon occupies an unusual position in the periodic table because of its electronic structure. This structure is responsible for its covalent nature. Carbon has the atomic number 6 and its outer, or valence, shell contains four electrons. Therefore carbon needs four more electrons to complete this outer shell, or it must lose four electrons in order to drop to the completed lower shell containing two electrons. Actually it neither gains nor loses by transfer, but instead completes its outer shell by sharing electrons with other atoms. Carbon combines with fluorine, for example, by sharing electrons, forming the covalent compound carbon tetrafluoride.

$$C \quad + \quad 4 \quad F \quad \longrightarrow$$
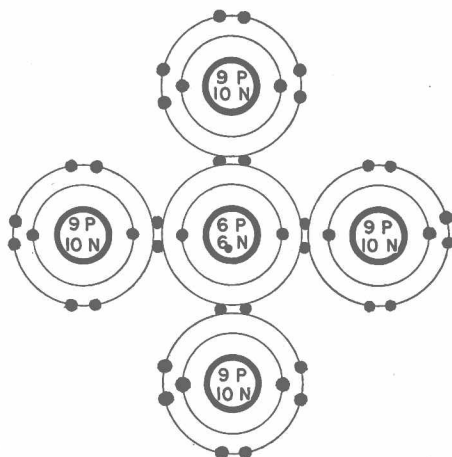
CF_4

Carbon and fluorine now have their required eight outer-shell electrons, but no charged atoms exist because there has been no transfer of electrons.

According to the scheme of abbreviations devised by G. N. Lewis, the symbol of the element is given with the electrons in the outermost shell represented by dots surrounding that symbol. Thus the reaction of four atoms of hydrogen with one of carbon to form a molecule of methane is represented as

$$4\,H\cdot\; +\; \cdot\overset{\displaystyle\cdot}{\underset{\displaystyle\cdot}{C}}\cdot\; \longrightarrow\; H:\overset{\displaystyle\cdot\cdot}{\underset{\displaystyle\cdot\cdot}{C}}:\,H$$

with an H above and an H below the central carbon.

and the combination of two atoms of oxygen with one of carbon to form a molecule of carbon dioxide is indicated by the equation

$$2 : \overset{..}{O} : + \cdot \overset{.}{\underset{.}{C}} \cdot \longrightarrow \; : \overset{..}{O} : : C : : \overset{..}{O} :$$

In each product all atoms have the necessary number of electrons to complete their outer, or valence, shells, without any electrons having been transferred from one atom to another.

Whenever four atoms or groups are attached to a given carbon atom, they become symmetrically distributed about that carbon and the molecule assumes a tetrahedral structure, with carbon in the center of the tetrahedron. Methane has the structure

or
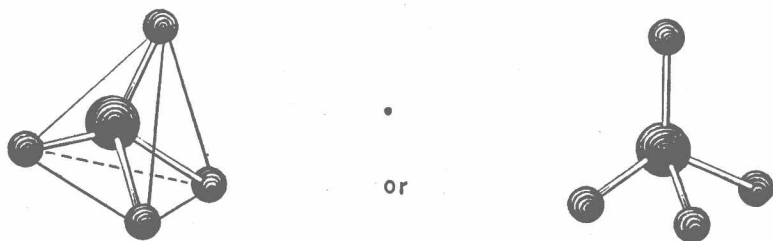
In the common parlance of the organic chemist each pair of electrons shared between two atoms constitutes a *chemical bond* and each bond is represented in a formula by a single line. Since representation of the tetrahedral molecule is awkward, the structures are ordinarily indicated by two dimensional figures, so that the formulas of methane and carbon dioxide become

H
|
become H—C—H and O=C=O, respectively. With very few
|
H
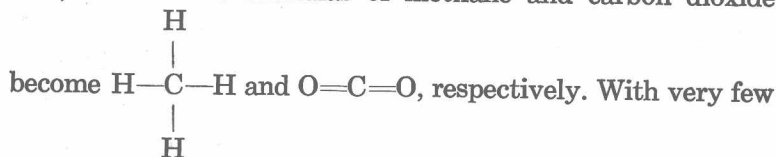
exceptions, carbon exhibits *tetracovalence;* that is, four bonds and no more link a carbon atom to other atoms. In a given compound there may be numerous carbon to carbon bonds and many possible atomic arrangements. Because of this fact the analysis of organic substances is frequently an ingenious process.

Determination of Structure

In the proof of the structure of a compound a qualitative analysis must be accomplished first, in order to determine the elements present. Next, a quantitative analysis is conducted to establish the percentage composition and with this information the *empirical formula*, which represents the smallest whole number ratio of atoms in the molecule, can be found. Then, if the approximate molecular weight is known, the actual number of atoms in the molecule can be determined and represented by a *molecular formula*. Establishment of the *structural formula*, which gives the sequence of atoms with respect to one another, frequently requires knowledge of many kinds of organic reactions. When the sequence of the atoms is known it may be necessary also to establish their relative spatial positions, which can be expressed in a *configurational formula*. The sequence of bonded atoms can be the same and still those atoms may have different relative spatial positions.

Ethylene may be used as an example. Analysis of this substance shows 85.71 per cent carbon by weight, the remainder being hydrogen. If the approximate molecular weight is 29, the empirical formula can be determined as follows:

DETERMINATION OF THE EMPIRICAL FORMULA OF ETHYLENE				
Element	Grams in 100 Grams of Compound	Gram Atoms	Atoms	Smallest Whole Number Ratio of Atoms
H	14.28	$14.28/1 = 14.28$	$14.28 \times 6.06 \times 10^{23}$	2
C	85.71	$85.71/12 = 7.14$	$7.14 \times 6.06 \times 10^{23}$	1

The empirical formula is CH_2 and the molecular formula must be either CH_2 or some whole number multiple of CH_2. From the approximate molecular weight this can be determined:

$$CH_2 \times 1 = 14$$
$$CH_2 \times 2 = 28$$
$$CH_2 \times 3 = 42$$

Therefore, the molecular formula is C_2H_4 because the approximate molecular weight corresponds most closely to $CH_2 \times 2$. Determination of the structural formula usually depends on investigation of the chemical reactions of the substance, although in this particular compound it does not because only one stable arrangement of atoms is possible.

Analysis of Organic Compounds

Quantitative analysis of organic substances usually deals with the elements carbon, hydrogen, sulfur, nitrogen, and the halogens. Carbon and hydrogen are determined by a *combustion analysis* which involves a slow oxidation of a precisely weighed portion of the compound in the presence of excess oxygen at elevated temperatures to form carbon dioxide and water. Gaseous water and carbon dioxide are then conveyed by the stream of oxygen into absorbents, which absorb the water and carbon dioxide independently. By weighing the quantities of these two substances formed, hydrogen and carbon can then be determined. For example, if 0.900 g. of water is formed, $2/18 \times 0.900$, or 0.100 g. of hydrogen is present.

A *halogen* is analyzed by fusion of the organic compound with a substance which converts the halogen into a soluble inorganic halide. Through precipitation and weighing, as for example in the form of a silver halide, the weight of the halogen can be found. Organic *sulfur* is oxidized by means of sodium peroxide to a soluble sulfate. This is precipitated as barium sulfate, weighed, and the weight of sulfur obtained. *Nitrogen* often can be reduced to ammonia, with subsequent acid-base titration procedures. An alternative in many instances involves the formation of gaseous nitrogen and measurement of the volume of gas at the experimental conditions of temperature and pressure. By means of the gas laws the number of moles of nitrogen can be found and thereby the weight of nitrogen.

Oxygen content is found by difference in weights. In other words, after the other elements have been found, the sum of their weights is subtracted from the total weight of compound analyzed and this gives the amount of oxygen.

PROBLEMS

1. Diagram complete atomic structures for the following isotopes of elements:

	H	C	O	Ne	Na	Al	S	Cl
Atomic Weight	1	12	16	20	23	27	32	36
Atomic Number	1	6	8	10	11	13	16	17

2. Diagram complete ionic structures for Na^+, Al^{+++}, Cl^- and $S^=$.

3. Give simplified Lewis structures for the atoms and ions listed in problems 1 and 2.

4. Give simplified Lewis structures for: (a) H_2O; (b) NH_3; (c) CCl_4; (d) C_2H_4, all of which are covalent.

5. Determine the empirical and molecular formulas of the substances for which data are given below:

	Elements	Percentage Composition	Approximate Molecular Weight
(a)	C	80.00	
	H	20.00	31
(b)	C	40.00 .	
	H	6.66	
	O	53.33	185

6. A gaseous compound of carbon and hydrogen has a density of 2.6 g. per liter at standard temperature and pressure and contains 82.76 per cent carbon by weight. Determine the molecular formula of the compound. The Gram Molecular Volume is 22.4 liters.

7. Show that benzene, C_6H_6, vinylacetylene, C_4H_4, and acetylene, C_2H_2, all have the same percentage composition and same empirical formula.

8. Define or explain:
   (a) organic chemistry
   (b) Lewis structure
   (c) covalent compound
   (d) electrovalent compound
   (e) tetracovalence of carbon
   (f) empirical formula
   (g) molecular formula
   (h) structural formula
   (i) configurational formula
   (j) shell

9. The approximate molecular weight of a compound, dichloroethylene, is 95. Combustion of 0.970 g. of the substance with appropriate removal of halogen, produced 0.180 g. of water and 0.880 g. of carbon dioxide. Another portion of 0.582 g. of this same compound was subjected to a fusion process to form a soluble inorganic chloride and addition of excess silver nitrate to an acidified portion of the solution yielded 1.721 g. of silver chloride. Determine the empirical formula of the compound and its molecular formula. Notice that different weights of compound are used in the two analyses.