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Chapter IX

CHEMISTRY*

INTRODUCTION

Chemistry is a study of the forms and activities of matter or substance. It is particularly concerned with the structure of substances and the interaction between substances in a quantitative as well as a qualitative sense.

This chapter is offered not as a comprehensive chemistry course which might be given to science majors. Rather, an attempt has been made to reveal, in a general way, some of the characteristic properties and reactions of the more common elements, especially as they relate to the fields of medicine and industry.

For those corpsmen who would like to develop a more complete understanding of the subject, attention is directed to the references at the end of this section and the subsequent section entitled Organic Chemistry, and to other standard texts of chemistry available in most Navy libraries.

MATTER, ITS CLASSIFICATION AND COMPOSITION

Matter is anything that occupies space and has mass (weight). *In all ordinary changes, matter can neither be created nor destroyed, although it can be changed from one form to another.* This is the law of conservation of matter. Within recent years, however, it has been demonstrated that under certain extraordinary conditions matter can be converted to energy, as is done in nuclear-powered submarines and surface vessels.

Matter may exist in any of three states: gaseous, liquid, or solid. *Solids* are rigid and retain their form; *liquids* flow and tend to assume the shape of the container in which they are placed; and *gases* diffuse to fill completely the container in which they are placed.

The particular state of matter at any given time usually depends upon two conditions: the temperature of its surroundings and the pressure which is exerted upon it. For example, at ordinary temperatures and pressures, water is a liquid. But, if the temperature is increased beyond a certain point, the water changes to steam, a gas. On the other hand, if the temperature is decreased, the water will change, at its freezing point, to ice, a solid.

Matter that is homogeneous and that has a definite chemical composition is called a substance. Pure substances, for example, are salt, iron, copper, water, oxygen, sugar, and quartz.

Classification of Matter

A pure substance may be placed in one of two classifications. It may be classified either as an element or as a compound. An element is a substance that cannot be decomposed into two or more simpler substances by present, ordinary, chemical methods. Examples are iron, oxygen, chlorine, mercury, carbon, lead, and the other elements listed in Table I. A compound is a substance composed of two or more elements combined chemically in definite proportions by weight. It may be decomposed or separated into two or more substances or elements by chemical means. The constituents of a compound lose their original properties upon combination. For example, hydrogen and oxygen are gases in the free state, yet combined they form water.

Hydrogen burns and oxygen supports combustion; yet water, composed of these two elements, is universally used to combat fire. Sodium and chlorine, two violently poisonous elements, combine to form salt, a compound that is absolutely essential to life.

Substances which are not pure are called mixtures. They are heterogeneous materials consisting of two or more parts with different properties. The components of a mixture are not chemically combined nor need they be present

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in definite proportion. They may be separated by mechanical means such as sedimentation, evaporation, distillation, and precipitation. The properties of the mixture are a composite of the individual properties of its components. An example is a mixture of salt and water which may be anything from wet salt to salty water (composition indefinite—individual properties retained) and which may be separated into its components simply by distilling the water from the mixture.

Properties—Identification of Matter

The characteristic qualities of a substance are termed its properties. Again there are two broad classes of properties: physical and chemical. Physical properties can be observed without changing the substance into another substance. They include color, solubility, density (weight per unit volume), boiling point, melting point, freezing point, and cleavage along crystal faces.

Chemical properties relate to the participation of substances in chemical reactions. Chemical reactions are the processes that convert substances into other substances. The ability of iron to combine with oxygen is a chemical property of iron. The combination of iron with oxygen in moist air to form rust (a partially hydrated ferric oxide) is actually a chemical reaction. It is through the systematic study of these chemical and physical properties that a substance may be isolated, identified, and quantitated.

ENERGY

Energy is a concept that is difficult to define. It is involved in doing work, or in heating an object. It exists in many different forms and may be translated from one form to another, either wholly or in part. *When one form of energy disappears, an equivalent amount of energy in other forms is produced.* This is the law of conservation of energy.

Classification of Energy

All forms of energy fall into one or more of three basic forms:

Potential energy is energy stored in a body because of its position or the arrangement of its parts. It is caused by attractive or repulsive forces between members of a group of bodies.

Examples are a stone on a mountain top, a coiled spring, and electromagnetic attraction.

Kinetic energy is the energy of motion. Examples are the stone rolling down the mountain side, a pendulum as it swings, and an electric current running through a wire.

Radiant energy is any sort of energy that travels through space at a speed of 3×10^{10} cm./sec. (186,000 miles per second). Examples are the light of the sun, light from an electric light bulb or flame, and the X-rays.

Heat is kinetic energy and the form into which all other forms of energy tend to be converted. This conversion may be complete. The reverse, however, is not true, only partial conversion of heat to other forms of energy is possible.

ATOMS AND ATOMIC STRUCTURE

The atom is the smallest particle of an element which may take place in a chemical reaction. The concept of the atom was first glimpsed by the early Greek philosophers over 2,500 years ago, but it was not until 1803 that the concept was given precision and chemical significance by John Dalton. His theory has been modified and many exceptions have been made, but the following concepts have survived:

1. There are as many different kinds of atoms as there are different elements (102 as of 1962).
2. When atoms either of different or of the same elements combine, they form molecules. Molecules are the smallest particle of an element or compound that has the chemical properties of the substance.
3. *Every molecule contains a definite whole number of atoms of each of the elements contained in it.* This is the law of simple multiple proportion.

Atomic Weights

The masses or weights of different kinds of atoms have been determined by comparison with one another and are expressed as relative weights. The relative relationships may be determined in a very exact analysis of the least amount of an element which may be found in combination with other elements. For many years oxygen with atomic weight 16 was used as the standard element to which the atomic weights of all other elements were compared. For example, since the sulfur atom weighs approximately twice as much

as the oxygen atom, the atomic weight of sulfur was computed as 2×16 , or approximately 32. However, most naturally occurring elements have isotopes* and many of these elements have several isotopes existing together. Using the oxygen 16-scale, the atomic weight of naturally occurring sulfur is 32.066 because atomic weights of 33, 34, and 36 occur as well as 32, although 95.06 percent of naturally occurring sulfur has an atomic weight of 32.

Unfortunately, naturally occurring oxygen also contains isotopes (studies carried out in the laboratory show that the atomic weight of natural oxygen is not exactly 16). This variation in weight caused difficulty in physical experiments, and moved the physical sciences to adopt an atomic weight scale suitable for their own purposes.

TABLE I.—Table of Atomic Weights Listed Alphabetically by Names of Elements (Based upon Carbon-12)¹

Element	Symbol	Atomic No.	Atomic Weight ²
Actinium.....	Ac	89	(227)
Aluminum.....	Al	13	26.9815
Americium.....	Am	95	(243)
Antimony.....	Sb	51	121.75
Argon.....	Ar	18	39.948
Arsenic.....	As	33	74.9216
Astatine.....	At	85	(210)
Barium.....	Ba	56	137.34
Berkelium.....	Bk	97	(247)
Beryllium.....	Be	4	9.0122
Bismuth.....	Bi	83	208.980
Boron.....	B	5	10.811
Bromine.....	Br	35	79.909
Cadmium.....	Cd	48	112.40
Calcium.....	Ca	20	40.08
Californium.....	Cf	98	(249)
Carbon.....	C	6	12.01115
Cerium.....	Ce	58	140.12
Cesium.....	Cs	55	132.905
Chlorine.....	Cl	17	35.453
Chromium.....	Cr	24	51.996
Cobalt.....	Co	27	58.9332
Copper.....	Cu	29	63.54
Curium.....	Cm	96	(247)
Dysprosium.....	Dy	66	162.50
Einsteinium.....	Es	99	(254)
Erbium.....	Er	68	167.26
Europium.....	Eu	63	151.96
Fermium.....	Fm	100	(253)
Fluorine.....	F	9	18.9984
Francium.....	Fr	87	(223)
Gadolinium.....	Gd	64	157.25
Gallium.....	Ga	31	69.72
Germanium.....	Ge	32	72.59
Gold.....	Au	79	196.967
Hafnium.....	Hf	72	178.49
Helium.....	He	2	4.0026
Holmium.....	Ho	67	164.930

* Atoms of the same element that differ in atomic weight but maintain the same atomic number are isotopes.

TABLE I.—Table of Atomic Weights Listed Alphabetically by Names of Elements¹—Continued

Element	Symbol	Atomic No.	Atomic Weight ²
Hydrogen.....	H	1	1.00797
Indium.....	In	49	114.82
Iodine.....	I	53	126.9044
Iridium.....	Ir	77	192.2
Iron.....	Fe	26	55.847
Krypton.....	Kr	36	83.80
Lanthanum.....	La	57	138.91
Lead.....	Pb	82	207.19
Lithium.....	Li	3	6.939
Lutetium.....	Lu	71	174.97
Magnesium.....	Mg	12	24.312
Manganese.....	Mn	25	54.9380
Mendelevium.....	Md	101	(256)
Mercury.....	Hg	80	200.59
Molybdenum.....	Mo	42	95.94
Neodymium.....	Nd	60	144.24
Neon.....	Ne	10	20.183
Neptunium.....	Np	93	(237)
Nickel.....	Ni	28	58.71
Niobium.....	Nb	41	92.906
Nitrogen.....	N	7	14.0067
Nobelium.....	No	102	
Osmium.....	Os	76	190.2
Oxygen.....	O	8	15.9994
Palladium.....	Pd	46	106.4
Phosphorus.....	P	15	30.9738
Platinum.....	Pt	78	195.09
Plutonium.....	Pu	94	(242)
Polonium.....	Po	84	(210)
Potassium.....	K	19	39.102
Praseodymium.....	Pr	59	140.907
Promethium.....	Pm	61	(147)
Protactinium.....	Pa	91	(231)
Radium.....	Ra	88	(226)
Radon.....	Rn	86	(222)
Rhenium.....	Re	75	186.2
Rhodium.....	Rh	45	102.905
Rubidium.....	Rb	37	85.47
Ruthenium.....	Ru	44	101.07
Samarium.....	Sm	62	150.35
Scandium.....	Sc	21	44.956
Selenium.....	Se	34	78.96
Silicon.....	Si	14	28.086
Silver.....	Ag	47	107.870
Sodium.....	Na	11	22.9898
Strontium.....	Sr	38	87.62
Sulfur.....	S	16	32.064
Tantalum.....	Ta	73	180.948
Technetium.....	Tc	43	(97)
Tellurium.....	Te	52	127.60
Terbium.....	Tb	65	158.924
Thallium.....	Tl	81	204.37
Thorium.....	Th	90	(232)
Thulium.....	Tm	69	168.934
Tin.....	Sn	50	118.69
Titanium.....	Ti	22	47.90
Tungsten.....	W	74	183.85
Uranium.....	U	92	(238)
Vanadium.....	V	23	50.942
Xenon.....	Xe	54	131.30
Ytterbium.....	Yb	70	173.04
Yttrium.....	Y	39	88.905
Zinc.....	Zn	30	65.37
Zirconium.....	Zr	40	91.22

¹ Courtesy of National Bureau of Standards, U.S. Department of Commerce, 1962.

² The weight enclosed in parentheses is the mass number of the most stable isotope of the element.

In 1961, the Commission on Atomic Weights of the International Union of Pure and Applied Chemistry adopted a new scale of atomic weights based on carbon with atomic weight 12. This scale is suitable to both the physical and chemical sciences.

Table I presents the adjusted atomic weights of all known elements as adopted by the 1961 convention.

ELECTRONIC STRUCTURE

The mass (weight) of an atom of a particular element is due almost entirely to the protons and neutrons contained in it. The mass of the electron is negligible (see below). Nearly all of the weight of an atom is concentrated in its nucleus or center. The nucleus is comprised of protons and neutrons.

The *proton* is a particle having unit positive charge and a mass of approximately one on the atomic weight scale. It is identical with a hydrogen atom which has lost its electron and which has a positive charge, H^+ .

The *neutron* is a neutral particle bearing no electric charge. Its mass is approximately the same as that of the proton. The neutron is a major contributor to the weight of an atom. The number of neutrons in the nucleus may be determined by subtracting the atomic number from the atomic weight. For example, there are 118 neutrons in an atom of gold:

$$\begin{array}{r} 197 \text{ (atomic weight of gold)} \\ -79 \text{ (atomic number of gold)} \\ \hline 118 \text{ (number of neutrons)} \end{array}$$

The *electron* is a particle of negative unit charge. Its mass is approximately $1/1,838$ of the mass of a proton. The electrons travel in paths about the nucleus. An oversimplified but pictorial analogy is the travel of the planets about the sun. In any atom there are exactly as many electrons as there are protons in its nucleus. As the number of protons increase (increase in atomic number), the electrons are added outside the nucleus into various energy levels or principle quantum numbers referred to as shells. As these shells progress from the nucleus, the number of possible electrons in the shell increases. The number of electrons possible in the first four shells are shown in Table II, starting with K, the innermost shell.

TABLE II.—*Electron Capacities of the First 4 Electron Shells*

Principal Quantum Number	Shell Name	Maximum Number of Possible Electrons
1	K	2
2	L	8
3	M	18
4	N	32

For example, carbon has an atomic number of 6, therefore it has 6 protons in the nucleus and 6 electrons in the electron shells (2 in the K shell and 4 in the L shell); nitrogen has an atomic number of 7, therefore it has 7 protons in the

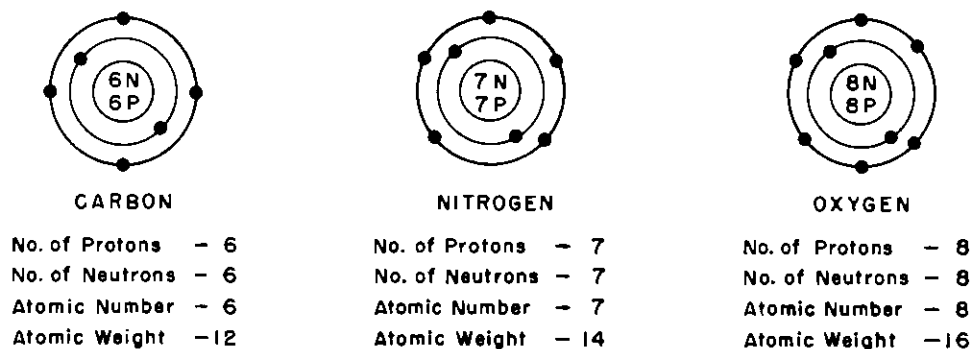


Figure 1.—Diagram of Atoms of Carbon, Nitrogen, and Oxygen.

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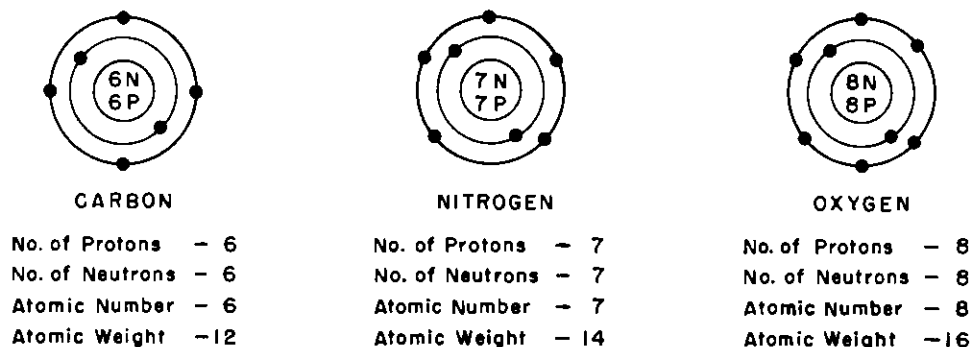


Figure 1.—Diagram of Atoms of Carbon, Nitrogen, and Oxygen.

nucleus and 7 electrons in the electron shells (2 in the K shell and 5 in the L shell, or 1 more electron in the L shell than carbon). Figure 1 presents a diagrammatic representation of the carbon, nitrogen, and oxygen atoms.

Again, the atom having the next higher atomic number, oxygen, has 1 more electron in the L shell than nitrogen; i.e., 6 electrons. This simple, orderly addition is maintained for the first 18 atomic numbers. After that the energy levels within the shells follow a more complicated progression so that the addition of the electrons also follow a more complicated order.

The electron content of the shells of the various elements need not be discussed further at this time except to point out that the outermost shell usually contains no more than 8 electrons with the exception of the K shell which is saturated with 2 electrons. The inner shells may be built up until they reach their saturation number, i.e., 18 for the M shell when it is an inner shell (see Table III). Atoms having 8 electrons in the outermost shell are stable and do not react chemically. These elements are called the noble gases and include helium, neon, argon, krypton, xenon, and radon. Helium, of course, has only 2 electrons in the K shell, the outermost shell. But since it is the K shell, it is saturated and therefore stable. The electrons in the outermost shell influence the properties and reactions of the atom.

TABLE III.—*Electron Structure of Several Elements*

Atomic No.	Element	Shell Electron Distribution					
		K	L	M	N	O	P
2	Helium (He)	2					
10	Neon (Ne)	2	8				
17	Chlorine (Cl)	2	8	7			
18	Argon (Ar)	2	8	8			
19	Potassium (K)	2	8	8	1		
24	Chromium (Cr)	2	8	13	1		
30	Zinc (Zn)	2	8	18	2		
36	Krypton (Kr)	2	8	18	8		
54	Xenon (Xe)	2	8	18	18	8	
86	Radon (Rn)	2	8	18	32	18	8

PERIODIC TABLE AND FAMILIES OF ELEMENTS

Properties of the elements vary as a periodic function of their atomic numbers. When elements are listed in the order of increasing atomic number, a periodic recurrence of similar chemical properties

may be noted. It may also be noted that when each period, or series, is placed below the previous period, elements of similar properties will fall in columns while preserving the arrangement according to atomic number. Thus, it is possible to predict the chemical properties of the element with a fair degree of accuracy from its position in the periodic table and from a knowledge of the properties of the other elements falling in the same group.

The essential development of the periodic table as it is known today was proposed in 1869 by Mendelyev. From the table he was able to predict the atomic number, atomic weight, and certain chemical properties of elements which had not been discovered at the time. His predictions have proved astonishingly correct. A modern, long-form, periodic table is presented here for study (Table IV).

The following information may be readily obtained from the periodic table:

1. The chemical symbols of the elements.
2. The atomic number.
3. The atomic weight.
4. The electron structure.
5. Possible valences.

The horizontal rows of the periodic table are called *periods*. The first period is very short and contains only hydrogen and helium (atomic Nos. 1 and 2), then in succession—2 short periods of 8 elements each, 2 longer periods of 18 elements each, a very long period of 32 elements (note that rare earths—the lanthanides—atomic Nos. 57–71, are set out at the bottom of the table), and an incomplete period (rare earths—the actinides—atomic Nos. 89–102, are also set out at the bottom of the table).

The vertical columns of the periodic table are called *groups*. Elements in the A group (1a through 7a) are much alike in their chemical behavior and form a definite chemical family. It will be observed that the number of the group corresponds to the number of electrons in the outermost shell of the respective atom.

In the B group (1b through 7b) there is a strong resemblance between elements in the same group, but this resemblance diminishes toward the center of the table. Here are the transition metals, the lanthanides, and the actinides. In these the inner electron shells are built up to capacity.

Table IV - Periodic

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RARE

Lanthanum Series	La 57 138.91 2 8 18 18 8 2	Ce 58 140.12 2 8 18 20 8 2	Pr 59 140.907 2 8 18 21 8 2	Nd 60 144.24 2 8 18 22 8 2	Pm 61 [147] 2 8 18 23 8 2	Sm 62 150.35 2 8 18 24 8 2	Eu 63 151.96 2 8 18 25 8 2
	3+	3+ 4+	3+	3+	3+	3+	3+
Actinium Series	Ac 89 [227] 2 8 18 32 18 9 2	Th 90 [232] 2 8 18 32 18 10 2	Pa 91 [231] 2 8 18 32 20 9 2	U 92 [238] 2 8 18 32 21 9 2	Np 93 [237] 2 8 18 32 23 9 2	Pu 94 [242] 2 8 18 32 24 8 2	Am 95 [243] 2 8 18 32 25 8 2
	3+	4+	5+	6+	6+	6+	6+

Table of the Elements

										7a	0				
										H 1	He 2				
										1.00797 1	4.0026 2				
										1-	0				
										1+	0				
										3a	4a	5a	6a	7a	0
										B 5	C 6	N 7	O 8	F 9	Ne 10
										10.811 2 3	12.01115 2 4	14.0067 2 5	15.9994 2 6	18.9984 2 7	20.183 2 8
										3+	2± 4±	3- 3+ 4+ 5+	1- 2-	1-	0
										Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
										26.9815 2 8 3	28.086 2 8 4	30.9738 2 8 5	32.064 2 8 6	35.453 2 8 7	39.948 2 8 8
										3+	2± 4±	3- 3+ 5+	2- 4+ 6+	1- 1+ 5+ 7+	0
10b	1b	2b													
Ni 28 58.71 2 8 16 2	Cu 29 63.54 2 8 10 1	Zn 30 65.37 2 8 18 2	Ga 31 69.72 2 8 18 3	Ge 32 72.59 2 8 18 4	As 33 74.9216 2 8 18 5	Se 34 78.96 2 8 18 6	Br 35 79.909 2 8 18 7	Kr 36 83.80 2 8 18 8							
2+	1+ 2+	2+	3+	2+ 4+	3- 3+ 5+	2- 4+ 6+	1- 1+ 5+	0							
Pd 46 106.4 2 8 18 18	Ag 47 107.870 2 8 18 1	Cd 48 112.40 2 8 18 2	In 49 114.82 2 8 18 3	Sn 50 118.69 2 8 18 4	Sb 51 121.75 2 8 18 5	Te 52 127.60 2 8 18 6	I 53 126.9044 2 8 18 7	Xe 54 131.30 2 8 18 8							
2+ 4+	1+	2+	3+	2+ 4+	3- 3+ 5+	4+ 6+	1- 1+ 5+ 7+	0							
Pt 78 195.09 2 8 18 32 17 1	Au 79 196.967 2 8 18 32 1	Hg 80 200.59 2 8 18 32 2	Tl 81 204.37 2 8 18 32 3	Pb 82 207.19 2 8 18 32 4	Bi 83 208.980 2 8 18 32 5	Po 84 [210] 2 8 18 32 6	At 85 [210] 2 8 18 32 7	Rn 86 [222] 2 8 18 32 8							
2+ 4+	1+ 3+	1+ 2+	1+ 3+ 4+	2+ 4+	3+	2+	2+	0							

EARTHS

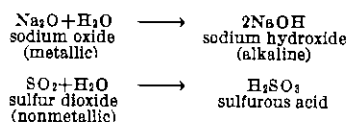
Gd 64 157.25 2 8 18 25 9 2	Tb 65 158.924 2 8 18 27 8 2	Dy 66 162.50 2 8 18 28 6 2	Ho 67 164.930 2 8 18 29 8 2	Er 68 167.26 2 8 18 30 8 2	Tm 69 168.934 2 8 18 31 9 2	Yb 70 173.04 2 8 18 32 8 2	Lu 71 174.97 2 8 18 32 9 2
3+	3+	3+	3+	3+	3+	2+ 3+	3+
Cm 96 [247] 2 8 18 32 25 9 2	Bk 97 [247] 2 8 18 32 27 8 2	Cf 98 [249] 2 8 18 32 28 8 2	Es 99 [254] 2 8 18 32 29 8 2	Fm 100 [253] 2 8 18 32 30 8 2	Md 101 [256] 2 8 18 32 31 8 2	No 102 [256] 2 8 18 32 32 8 2	
3+	3+ 4+	3+	3+	3+	3+	3+	

At the extreme left of the table are two columns of light metals, some of which (1a) are lighter than water. In the upper right-hand corner are the nonmetals and the inert or noble gases.

Elements are classified as metals and nonmetals. Most of the metals, 77 in number, are good conductors of heat and of electricity. They often have a bright, mirrorlike, "metallic" luster. Many of the metals are also very malleable (capable of being hammered or rolled into sheets) and very ductile (capable of being drawn into wire).

The remaining 21 elements are nonmetals. At room temperature they are gases or brittle solids (except bromine which is a liquid). They are poor conductors of heat and of electricity.

The most important distinctions between metals and nonmetals are found in their chemical properties. One example is the behavior of oxides—compounds formed from oxygen and another element. *The metallic oxides form alkaline solutions when dissolved in water. Nonmetallic oxides form acid solutions when dissolved in water.*



The halogens are an important group of nonmetals. They occur as the first four elements in group 7a, i. e., fluorine, chlorine, bromine, iodine. These, as well as the oxides, will be discussed later.

ISOTOPES

All of the atoms of any given element have the same atomic number which is characteristic for that particular element. However, an element may have atoms with different atomic weights, but with the same chemical properties. In a particular element, atoms with different atomic weights (but with the same atomic number and chemical properties) are called isotopes of that particular element. The only way in which the weight of an atom can vary without changing the atomic number is to vary the number of neutrons in the nucleus. Therefore, the only difference between the isotopes of an element is the number of neutrons in the nucleus. The

number of electrons in the isotopes of an element will remain the same.

The isotopes of an element, having like chemical properties, can only be separated by physical means such as diffusion.

MOLECULES, IONS, AND VALENCE

MOLECULES AND MOLECULAR WEIGHT

A molecule is a group of atoms bonded to one another in a definite ratio and acting as a chemical and physical entity. All the molecules of a chemically pure substance are identical. Oxygen gas is composed of molecules containing 2 atoms of the element oxygen; water molecules consist of 2 atoms of the element hydrogen and 1 of oxygen. The *molecular weight* of a substance is the sum of the multiples of the atomic weights of the elements present in the molecule. Thus the molecular weight of O_2 is 32 and that of H_2O is 18 ($2 \times 1 + 16$). (While the new value for oxygen is 15.9994 and for hydrogen 1.00797, for purposes of quick computation these figures have been rounded to 16 and 1, respectively.)

Types of Formulas

A *molecular* formula indicates the assortment of elements and the number of each which appears in an aggregation. This aggregation behaves chemically as a unit and is called a molecule. For water, the formula is H_2O , sometimes expressed as HOH , and means that 1 molecule of water contains 2 atoms of hydrogen and 1 atom of oxygen; for oxygen gas, the formula is O_2 .

The *empirical* formula merely represents the simplest possible formula for a compound. It may or may not represent a compound in its molecular form. Mercurous chloride has a molecular formula of Hg_2Cl_2 and an empirical formula of HgCl . Similarly the molecular formula of oxygen is O_2 ; the empirical is O . On the other hand, both the molecular and empirical formula for water is H_2O , and for sodium chloride it is NaCl . In these and many other compounds the empirical formula is identical with the molecular one. However, the molecules of many gases and organic compounds exist as a multiple of the simplest possible ratio of participating atoms.

In the study of chemical reactions, the molecular formula is used except in cases of macromolecules

and polymers* such as starch where the exact molecular weight is not known, but the building units are. For example, the formula for starch is written as $(C_6H_{12}O_6)_n$. The subscript "n" indicates an unknown number of glucose molecules ($C_6H_{12}O_6$) bound together to form a starch molecule.

IONIZATION

An *ion* is an atom or group of atoms that is not electrically neutral, but instead carries a positive or negative electric charge. An atom (or group of atoms) is neutral when the number of protons in the nucleus equals the number of electrons in the shells. It is a positive ion if the number of electrons is less than the number of protons; conversely, an ion is negative if the number of electrons is larger than the number of protons.

Ionization is the process of producing ions from neutral atoms or molecules by changing the balance of electrons and protons. Common examples are the ionization of salts, acids, and bases when dissolved in water. For discussion of Acids, Bases, and Salts, see page 14 this chapter.

VALENCE

Valence is the combining capacity of an element. It is the number of bonds that an atom of an element may form with other atoms. Elements which are more complex in their behavior may exhibit any one of two or more combining capacities. Knowledge of these characteristic valences of the elements will be of great assistance in memorizing the formulas for the infinite number of compounds possible in chemical combination. For example, the molecular formula of water is H_2O with the following valence-bond structure:



Hydrogen has 1 valence bond and its valence is 1; oxygen has 2 bonds and its valence is 2. These are the usual valences for hydrogen and for oxygen.

*Macromolecules are large molecules containing a definite number of each member compound and a particular arrangement of them. Proteins and nucleic acids are macromolecules.

Polymers are large molecules composed of one compound (or possibly several kinds of compounds) joined in repetition. The size of the polymer varies according to the conditions under which it is formed—starch, glycogen, and resin are examples.

Other examples are hydrogen chloride, HCl , in which hydrogen has a valence of 1 and chlorine of 1; sodium chloride, $NaCl$, in which sodium has a valence of 1 and chlorine of 1; ammonia, NH_3 , in which nitrogen has a valence of 3 and hydrogen of 1; and carbon dioxide, CO_2 , in which carbon has a valence of 4 and oxygen, 2.

TABLE V.—Combining Capacities of Elements, By Groups

Number of Group	Electrons in Outer Shell	Valence	Number of Electrons Given or Accepted
1a-----	1	+1	1 given.
2a-----	2	+2	2 given.
3a-----	3	+3	3 given.
4a-----	4	± 4	4 given or accepted.
5a-----	5	-3	3 accepted.
6a-----	6	-2	2 accepted.
7a-----	7	-1	1 accepted.
0-----	8	0	None given or accepted.

There are several types of valence bonds, two of which will be discussed here—ionic valence and covalence. In *ionic valence* bonds, the elements combine to form compounds because of an electrostatic attraction between the charges on the atoms. Any atom (or group of atoms) that acquires more than its normal quota of electrons (equivalent to the atomic number) becomes a negatively charged ion. Any atom that loses a part of its normal quota of electrons and as a result is left with a surplus of positive electricity (protons), becomes a positively charged ion. When atoms combine in chemical combination, the valence electrons (the electrons in the outer shell) of the atoms show a tendency to assume the stable configuration of an inert gas. Thus in sodium, only 1 electron is present in the outer shell. The tendency of the sodium (Na) atom is to lose this electron and, if it does, it then acquires a positive charge of 1^+ because the atom now has 11 protons and 10 electrons.

Similarly, chlorine has 7 electrons in its outer shell and has a tendency to attract an electron to complete the stable configuration of 8 electrons. When this happens the chlorine (Cl) atom acquires a negative charge of 1^- because the atom now has 17 protons and 18 electrons. Thus a sodium atom will contribute an electron to a chlorine atom to form a positive sodium ion and a negative chlorine ion. The attraction between the opposite charges is strong and will hold the sodium and chloride ions

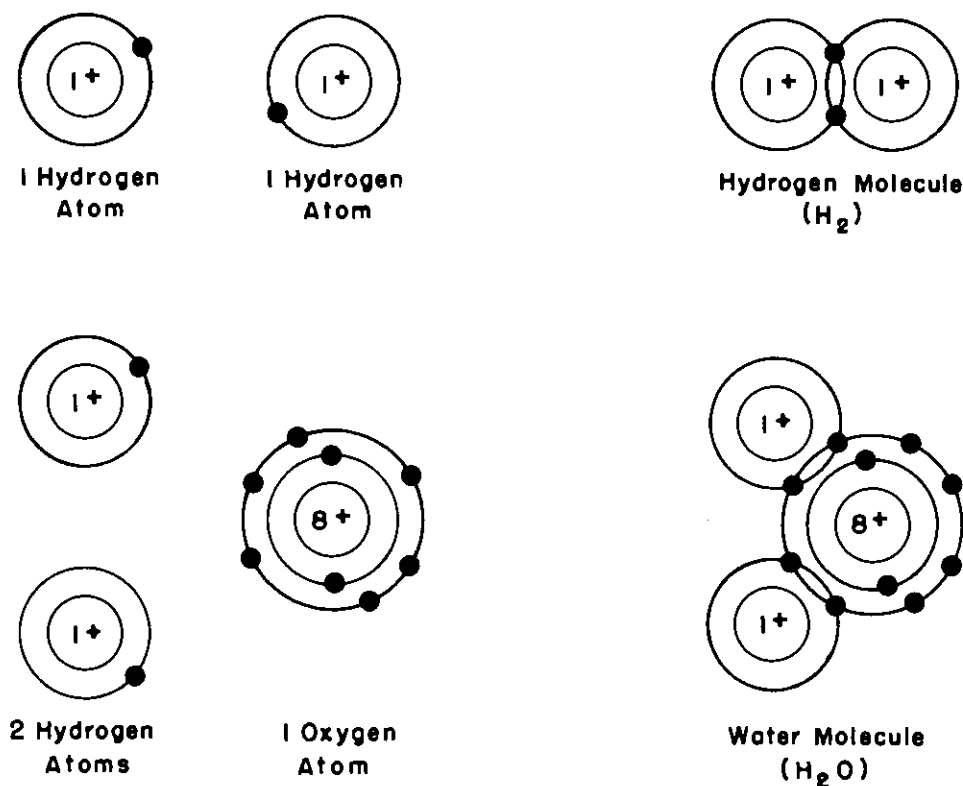


Figure 2.—Diagram of the Covalent Bond in the Hydrogen Molecule and in the Water Molecule.

sufficiently close to form a molecule of sodium chloride ($NaCl$). Thus sodium has a positive ionic valence of 1, while chlorine has a negative valence of 1.

An atom which transfers 2 electrons has a positive ionic valence of 2; if it accepts 2 electrons, it has a negative ionic valence of 2. In magnesium chloride, the magnesium atom has a positive ionic valence of 2 and chlorine has a negative ionic valence of 1; therefore, the molecular formula requires 2 atoms of chlorine to receive the 2 electrons from 1 atom of magnesium or $MgCl_2$. It can be seen that the ionic valence is equal to the number of electrons gained or lost by an atom when it is converted into an ion. Ionic compounds are found in the inorganic acids, bases, and salts. They will conduct electricity when in aqueous solution and are therefore referred to as electrolytes.

Compounds which are not held together by electrostatic forces may be linked by covalent bonds. A *covalent bond* consists of a pair of electrons shared between two atoms in such a way that the outermost shells of both are satisfied. For example, the hydrogen molecule, H_2 , has covalent

linkage. Here a hydrogen atom shares its one outer electron (in the K shell) with the other hydrogen atom, both thereby acquiring the stable or electron-saturated state of 2 for the outermost shell (fig. 2). In water, which is a compound of hydrogen and oxygen, H_2O , the sharing of electrons is shown in figure 2.

The oxygen atom in this compound has 6 electrons in the outer shell and attains its stable configuration of 8 by sharing the 1 electron from 2 hydrogen atoms. These each in turn share 1 of the 6 electrons of the oxygen atom to acquire the stable configuration of 2 electrons.

This type of linkage is very important in organic chemistry and is encountered in thousands of carbon compounds. The carbon atom usually has an electron valence of 4 and must share in 4 pair of electrons to complete its octet. The shared pair may be represented by a straight line (which is called a single bond) in structural formula, such as



for CH_4 which is methane.

Pure covalent compounds do not conduct electricity. Pure water itself is not an electrical conductor; it is the impurities which are dissolved in water that carry the electric current.

Many compounds are neither completely electrovalent nor completely covalent compounds; often they are combinations or modifications of both. What has been presented above merely demonstrates the basic rules for two types of linkages in the formation of chemical compounds.

RADICALS

When certain compounds, such as sulfuric acid, (H_2SO_4), and potassium cyanide, (KCN), undergo chemical changes, some of their atoms remain grouped together. These groups, called radicals or sometimes complex ions, are more or less resistant to change. Since radicals tend to retain their characteristics and are generally transferred from their compounds as a unit, it is convenient to write them as a unit in a formula. This is done by including the radicals in parentheses:

Calcium hydroxide.... $\text{Ca}(\text{OH})_2$ instead of CaO_2H_2 .
 Aluminum sulfate.... $\text{Al}_2(\text{SO}_4)_3$ instead of $\text{Al}_2\text{S}_3\text{O}_{12}$.
 Ammonium sulfide.... $(\text{NH}_4)_2\text{S}$ instead of $\text{N}_2\text{H}_8\text{S}$.

The subscript number indicates the number of times the radical occurs in one molecule of the substance.

CHEMICAL REACTIONS

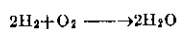
In any investigation of a chemical reaction, the following laws of chemical change must be considered:

1. *Law of Conservation of Elements:* Ordinary chemical change never converts one element into another.

2. *Law of Conservation of Mass or Matter:* Ordinary chemical or physical changes never detectably change total mass.

3. *Law of Definite Proportion:* The weights of the reactants and products in any reaction are in definite ratio to one another.

Since there is no conversion of one element to another and there is no loss in matter, it follows that x grams of element "A" reacting with y grams of element "B" will produce products containing x grams of element "A" and y grams of element "B." In other words, in all chemical reactions the reactants must balance with the products. A simple example is the formation of water, H_2O .

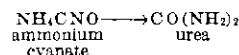


Note there are 4 atoms of hydrogen and 2 atoms of oxygen on both sides of the equation. This equation is said to be balanced.

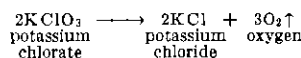
Types of Reactions

A chemical reaction is more easily remembered if recognized as belonging to one of several types:

1. *Internal rearrangement.* In this type, atoms within a molecule or ion are brought into new positions with respect to one another which produces a new compound. For example, urea is formed when a solution of ammonium cyanate is evaporated.

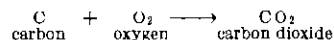


2. *Decomposition.* Here molecules or ions are broken down into simpler compounds or into atoms:

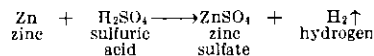


(The arrow pointing upward directs attention to the escape of a gas.)

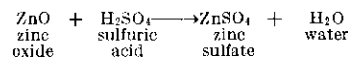
3. *Direct union.* In this type, atoms, molecules, and ions combine to form new substances:



4. *Displacement.* Here an atom or group of atoms, in combining with a molecule or ion, displace one or more atoms already in the molecule:



5. *Exchange.* In this type a part of one molecule, ion, or ion group is exchanged for a part of another.



OXYGEN AND ITS COMPOUNDS

Oxygen in combination with other elements makes up about one half the earth's crust:

1. Oxygen when combined with the nonmetal silicon forms silicon dioxide or silica, SiO_2 , which occurs in nature as a crystalline mineral, quartz. White sand is nearly pure silica.

2. Oxygen in combination with silicon and different metals forms the silicate minerals (mica,

feldspar, clay, and many others) which make up most of the solid rocks on the earth.

3. Other abundant minerals contain oxygen in combination with metals and with the nonmetals, carbon, sulfur or phosphorus, instead of silicon.

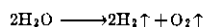
4. An impure form of ferric oxide, Fe_2O_3 , is hematite, the most important ore of iron.

5. Water is about eight-ninths oxygen by weight.

6. In living plants and animals, oxygen is an element of water and of other compounds which are a part of the living tissues.

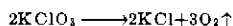
Air at sea level contains about 21 percent oxygen by volume, 78 percent nitrogen, 0.04 percent carbon dioxide, and very small amounts of other gases.

Pure molecular oxygen may be prepared commercially from air. The air is liquefied by cooling under pressure and then, under controlled evaporation, the nitrogen passes off first leaving pure liquid oxygen behind. Another method of obtaining oxygen is from the electrolysis of water in which an electric current is passed through water containing a little sulfuric acid or sodium hydroxide to act as a conductor.



H_2 and O_2 are liberated separately at different electrodes.

In the laboratory, oxygen may be prepared from heating potassium chlorate, leaving potassium chloride behind.



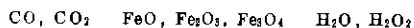
Oxygen is an odorless, nearly colorless gas which in deep layers appears blue. It is liquefied only by very high pressures at temperatures far below the freezing point of water. At atmospheric pressure, liquid oxygen boils at -183° centigrade. Oxygen is only slightly soluble in water, but still is twice as soluble as nitrogen, the chief constituent of air. For this reason, water when exposed to air is richer in oxygen than in nitrogen. Oxygen, from the air, dissolved in water serves as the source of oxygen for respiration of aquatic plants and animals.

OXIDES

All other elements except the inert gases enter into chemical union with oxygen to form com-

pounds called oxides. Some elements (such as hydrogen, phosphorus, sulfur, and iron) combine readily at ordinary temperatures. Other elements such as the "noble metals" (silver, gold, platinum, et cetera) cannot be directly oxidized even by heating in pure oxygen.

There may be several different oxides of the same element, depending upon the conditions under which the oxide is formed, such as amount of oxygen available, heat, pressure, availability of water and catalysts. Some examples of different oxides are:



OXIDATION AND REDUCTION

Chemical union with oxygen is an example of *oxidation*. Examples occurring in nature are burning or combustion, rusting, respiration, and decay. No great increase in temperature is observed in rusting, respiration, and decay, though the quantity of heat set free is precisely the same as it would be if the same chemical changes were accomplished by rapid burning or combustion. The explanation is, of course, that heat is released very slowly in the three processes first named and is transferred to neighboring objects in the atmosphere as fast as it is set free. Thus, the temperature rise is imperceptible.

The reverse of oxidation is termed *reduction*. In a narrow sense, reduction is the removal of oxygen from a compound containing oxygen. Ordinarily, this oxygen is removed by being combined with some other substance that has a strong tendency to combine with oxygen. For example when copper oxide, CuO , is heated in the presence of hydrogen, the oxide is reduced to metallic copper:



The hydrogen removes the oxygen from the copper oxide, gives up electrons and is oxidized to water. At the same time the copper ion takes up electrons and is reduced to metallic copper. The hydrogen is the reducing agent while the copper oxide acts as the oxidizing agent.

Oxidation and reduction also have broader and more useful meanings. Oxidation is any reaction in which a given substance loses electrons or a share in electrons to another substance known as the oxidizing agent which gains these electrons or share in electrons. Conversely, reduction is any

reaction in which a given substance gains electrons or a share in electrons from a substance known as the reducing agent which loses electrons.

Oxidation and reduction always occur together, since the electrons lost by one reactant must be gained by the other. These are called oxidation-reduction reactions or redox reactions.

If a molecule or an ion contains some element which is in its lowest of several valence numbers, the substance is likely to be oxidized and hence is a good reducing agent. So HCl, which contains

Cl with a valence number of -1 (Cl^{-1}) cannot possibly be reduced, but it is easily oxidized to chlorine gas, Cl_2 , with a valence number of zero. Pure elements have a valence of zero even though they may be bound to each other as in the chlorine molecule, Cl_2 , or the oxygen molecule, O_2 .

When an intermediate between the two extremes of valence is considered, whether it will be an oxidizing or reducing agent depends upon the substance with which it is reacting. Some common oxidants and reductants are in Table VI.

TABLE VI.—Some Common Oxidizing and Reducing Agents

Reductant	Formula	Valence	Oxidized Product	Valence	Formula
Metallic sodium	Na	0	Sodium ion	+1	Na^+
Hydrogen gas	H_2	0	Water or hydrogen ion	+1	H_2O or H^+
Stannous ion	Sn^{++}	+2	Stannic ion	+3	Sn^{+++}
Sulfur dioxide	SO_2	+2	Hydrogen sulfate	+6	H_2SO_4
Ferrous ion (light green)	Fe^{++}	+2	Ferric ion (yellow-brown)	+3	Fe^{+++}

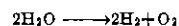
Oxidant	Formula	Valence	Reduced Product	Valence	Formula
Oxygen gas	O_2	0	Water or oxygen ion	-2	H_2O or O^{--}
Chlorine gas	Cl_2	0	Chloride	-1	Cl^-
Nitric acid	HNO_3	+5	Nitrous oxide	+2	NO
			or		or
Sulfuric acid	H_2SO_4	+6	Nitrogen dioxide	+4	NO_2
Permanganate (purple)	MnO_4^-	+7	Sulfur dioxide	+4	SO_2
Dichromate (orange)	$\text{Cr}_2\text{O}_7^{--}$	+6	Manganous ion (colorless)	+3	Mn^{+++}
			Chromic ion (green)	+3	Cr^{+++}

HYDROGEN AND ITS COMPOUNDS

Next to oxygen, hydrogen is the most abundant element in the earth's crust, if we rate abundance by number of atoms rather than by weight. Combined with other elements, it makes up about 1 percent of the weight of the earth's crust. Some of the more important classes of hydrogen compounds are:

Elements	Compounds or Mixtures
H, O	Water, H_2O .
H, N	Ammonia, NH_3 .
H, C	Hydrocarbons (compounds containing H and C only), such as petroleum and its products, terpentine, rubber, and methane.
H, C, O	Woody tissues of plants (cellulose), paper, starches, sugars, fats, alcohols, ethers, aldehydes, organic acids, thousands of organic compounds.
H, C, O, N	The greater part of living plant and animal tissue such as the proteins, alkaloids, dyes, and many medicinal substances.

Commercially, hydrogen is prepared from the electrolysis of water:

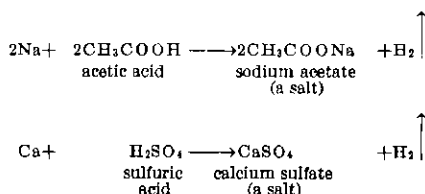


Hydrogen is extremely light, being $1/14$ the weight of air and $1/16$ the weight of oxygen. It is slightly soluble in water. When liquid hydrogen is permitted to evaporate rapidly, a part of it solidifies to a white solid, the melting point of which is only 14° above absolute zero. Absolute zero is that point at which there is no heat and no kinetic motion of the molecule. It is also referred to as 0° Kelvin or 0° K. and corresponds to -273.15° centigrade.

Some of the most important chemical properties of hydrogen are its reactions with metallic oxides (reducing them to metal), and its direct union with many organic compounds in the presence of a catalyst. The direct union of hydrogen with organic compounds is often termed hydrogenation. It is important in many commercial processes such as production of edible fats, motor fuels, nylon, and synthetic rubber.

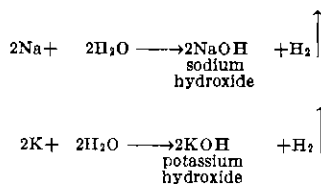
ACIDS, BASES, AND SALTS

A typical acid contains hydrogen, together with a nonmetal or nonmetallic group. When metals react with acids, metallic atoms appear to enter the acid molecules displacing hydrogen. Examples are:



The nongaseous product of the reaction of a metal with an acid is called a salt. A typical salt contains a metal, together with a nonmetal or nonmetallic group.

The product of the reaction of a light metal with water is called a metallic hydroxide (otherwise referred to as an alkali or a strong base).

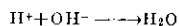


A typical alkali contains a light metal, together with the hydroxyl ion (OH^-). Solutions of the alkalis taste somewhat bitter and puckery and feel slippery. Alkalis turn red litmus paper* blue, whereas all but the least active acids turn blue litmus paper red.

When an acid reacts with a base, both acidic and basic properties disappear as they react with each other to form a salt and water.



Each is said to neutralize the other with the formation of water and may be represented ionically as:

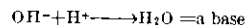
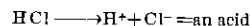


The hydrogen ion or proton of the acid combines with the hydroxyl ion of the base to form water, thereby neutralizing the acidic and basic properties of the two compounds.

The Brönsted definition of acids and bases states that an acid is any compound that loses protons,

*Litmus paper is an indicator to determine roughly the acidity or basicity of a solution. It is red in acid and blue in alkaline solutions.

while a base is any compound that takes up protons.



Some common acids and their salts:

HF	hydrofluoric acid	NaF	sodium fluoride
HCl	hydrochloric acid	KCl	potassium chloride
HBr	hydrobromic acid	NaBr	sodium bromide
HI	hydroiodic acid	KI	potassium iodide
HNO ₃	nitric acid	Ca(NO ₃) ₂	calcium nitrate
H ₂ SO ₄	sulfuric acid	MgSO ₄	magnesium sulfate

HYDROGEN-ION CONCENTRATION: ITS MEASUREMENT AND CONTROL

pH

pH is the symbol of a system devised to indicate the degree of acidity or basicity of a solution. It is a measure of the hydrogen-ion concentration. The pH of a neutral solution is 7. Values from 0 to 7 are found in acid solutions and from 7 to 14 in basic solutions.

Titration

Titration is a method of analysis. It is the process of determining the amount of a substance present in a solution by measuring the exact volume of some reagent which reacts quantitatively with the substance to be analyzed.

An example is the standardization of normal and molar solutions, particularly acid and base solutions. In order to neutralize the known amount of protons in a given quantity of a standard acid solution, an equal amount of hydroxyl ions from a base must be added. A comparison between the amount and concentration of the standard acid with the amount of base will indicate the concentration of the base.

A small quantity of a substance called an indicator is used in titrations to show when the reaction has reached completion. In acid-base titration, the indicator is either a weak acid or a weak base that changes color at a characteristic pH. Hundreds of different indicators are known, two of which are listed here:

Indicator	pH	Acid Color	Neutral Color	Alkaline Color
Litmus.....	6.5	Red.....	Violet....	Blue.
Phenolphthalein...	9.0	Colorless..	Colorless..	Red.

The use of dyes which exhibit changes in color and act as indicators of the pH is known as the colorimetric method. More precise measurement can be obtained by the use of a pH meter (electrometric method).

Buffers

It is sometimes important to keep the pH of a solution constant in spite of chance impurities or side reactions that tend to alter it. This may be accomplished by the addition of buffer mixtures. A buffer is comprised of a weakly ionized acid or base and its salt. It has a characteristic pH which is maintained when acid or base is added to the mixture and therefore acts as a buffer against pH change. Phosphate and acetate buffers are widely used in biologic systems.

Buffers play an important part in nature. Most of the juice of ordinary fruits and vegetables have a slight acidity which is held constant by buffer salts. The blood is faintly alkaline ($\text{pH}=7.33$) and maintains this pH with the greatest precision chiefly through buffering action of the blood serum proteins, carbonates, and phosphates. Solutions to be injected intravenously must be adjusted to the pH of the blood.

Milk is buffered (slightly alkaline) and curdling by bacteria that convert milk sugar into lactic acid is thereby retarded. All of the life processes take place in buffered mediums. Even the soil is buffered to encourage the living organisms within it and the plants that grow in it.

The control of pH is used in the yeast, cheese, wine, and beer industries to insure premium quality and maximum yield. Many other chemical reactions which do not include growing organisms must have rigid pH control.

CARBON AND ITS COMPOUNDS

In nature carbon occurs chiefly as—

1. Carbon dioxide of the atmosphere and the vastly greater supply of dissolved carbon dioxide in the ocean.
2. Carbon compounds in all living animals and vegetable matter.
3. Peat, coal, natural gas, and petroleum.
4. Chalk, limestone, and marble (chiefly calcium carbonate) of which there are inexhaustible deposits; as magnesite (magnesium carbonate) and dolomite (a double salt $\text{CaCO}_3:\text{MgCO}_3$); and as

sodium carbonate found in the beds of evaporated alkali lakes.

Charcoal is formed when wood or coal is heated with the exclusion of air. Activated charcoal is fairly dense charcoal that has been treated with superheated steam to remove the tarry materials that clog the pores of ordinary charcoal. During this process, submicroscopic crystals are formed which greatly increase the surface area. This large surface area endows activated charcoal with its very useful property of high adsorption. It is used in gas masks to adsorb gases, to decolorize solutions, and to purify solvents; medicinally, it is an important component of the universal antidote wherein it plays a role in reducing toxicity of certain poisons.

Crystalline forms of carbon are graphite and diamond. Graphite is found in nature, or may be made by heating coke to a high temperature in an electric furnace. It is a soft, black solid which has a shiny, metallic appearance and a greasy feeling. Graphite is a good conductor of electricity and is nonabrasive. It is used as the brushes in electric generators, in carbon arcs, furnace electrodes, lubricants and, of course, it is used as the core of "lead" pencils. Diamond is the hardest known naturally occurring substance and is used commercially as tips in cutting and drilling tools.

Carbon cannot be melted; but it sublimes* at $3,600^\circ$ centigrade. The position of carbon in the periodic table shows that it possesses 4 valence electrons. Since it has a small atomic radius, its valence electrons are strongly held by the positive charge on the nucleus and not readily transferred to other atoms. On the contrary, carbon tends to become linked with other atoms in covalent union. The ability of carbon atoms to become linked with one another accounts for the extraordinary number of carbon compounds constituting the field of organic chemistry.

Carbon monoxide, CO , is produced when carbon is burned in a limited supply of air or when carbon dioxide, CO_2 , is brought into contact with highly heated carbon or other good reducing agents. It is deadly poisonous, for it combines much more readily than oxygen with the hemoglobin of the red blood cells and thus deprives the blood of its

*Sublimation is the process whereby a solid substance passes into the gaseous state without first passing through the liquid phase.

role as the carrier of oxygen to all parts of the body. The combination of carbon monoxide with hemoglobin may be reversed by the presence of an excess of oxygen. Treatment of carbon monoxide poisoning includes breathing of oxygen containing 5 percent carbon dioxide. Charcoal is not a suitable adsorbent for carbon monoxide. A gas mask designed for use in carbon monoxide contaminated atmospheres should contain a mixture of metallic oxides.

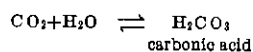
Carbon monoxide is none the less very important in the progress of science and industry. It is the most important reducing agent in industry. For example, iron ore is reduced to metallic iron by the action of carbon monoxide:



Other useful metals are obtained in a similar manner. Carbon monoxide is also an important component of many fuels such as producer gas and water gas.

Carbon dioxide is a gas that is one and one-half times as heavy as air and is soluble in water. It is easily liquefied by pressure. Commercially carbon dioxide may be produced by alcoholic fermentation, by burning carbon in excess of air or oxygen, by heating limestone, and from certain gas wells. Liquid carbon dioxide has a high vapor pressure. This property is put to use in aviation. Bottles of liquid carbon dioxide are used as a source of emergency energy to lower landing gear, apply brakes, or open bomb doors when the usual sources of energy fail. It is also used to inflate life rafts and belts. Solid carbon dioxide (temperature $-79^\circ\text{C}.$) is known as "dry ice" because it is a very cold solid which forms no liquid on being warmed; it passes directly from the solid to the gaseous state. As the gas forms it surrounds the material with an insulating layer of dry gas and is, therefore, extensively used as a refrigerant. Gaseous carbon dioxide is used to make carbonated beverages and in the preparation of carbonates. Because it is heavier than air and incombustible, it makes an excellent fire extinguisher.

Solutions of carbon dioxide in water are acid because of the reversible union of the dissolved gas with water to form the unstable carbonic acid.



There are two available hydrogen ions in carbonic acid which allow the formation of two different salts, hydrogen carbonate (also referred to as acid carbonate and bicarbonate), having the hydrogen carbonate ion, HCO_3^- and carbonates, having the carbonate ion, CO_3^{--} . Examples are sodium bicarbonate, NaHCO_3 , and sodium carbonate, Na_2CO_3 .

NITROGEN AND MEMBERS OF THE 5a FAMILY

Nitrogen, phosphorus, arsenic, antimony, and bismuth are members of the 5a family (see Periodic Table of the Elements), yet their properties vary strikingly. Nitrogen, the lightest member, is a gas of low reactivity whose oxides are exclusively acidic in nature, while bismuth, the heaviest, is a metal of moderate to strong activity whose lower oxide is almost exclusively basic in its behavior. The intervening elements bridge the gap between these extremes.

NITROGEN AND ITS COMPOUNDS

An inexhaustible supply of elemental nitrogen is found in the atmosphere which is about three-fourths nitrogen by weight. There are about 20 million tons of it in the air above each square mile of the earth's surface. Great deposits of sodium nitrate and calcium nitrate occur in various parts of the world, notably in Chile and South Africa.

Nitrogen is found in all plant and animal matter, mostly in the form of protein. The nitrogen of the atmosphere is converted into nitrates by soil bacteria. Green plants take up nitrates and convert them into proteins. Plant proteins are eaten by animals and converted into their own species-specific protein. When the plants and animals die, their protein is broken down by microorganisms, mainly bacteria and fungi, into simpler proteins and finally to ammonia and nitrogen gases. Nitrates are built up again by special types of soil bacteria: nitrogen-fixing and nitrifying bacteria. The nitrates are then utilized by green plants, forming protein, which in turn provide animals with food. The conversion of nitrogen to plant and animal materials and the return to nitrogen is known as the *nitrogen cycle*.

AMMONIA

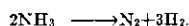
Ammonia (NH_3) is a colorless, readily soluble, easily liquefied gas, about half as dense as air. It is a compound of nitrogen. Its pungent odor enables it to be detected when present in the atmosphere to the extent of one volume in a thousand.

Ammonia is readily liquefied by pressure and has a high heat of vaporization. Because of these properties, it is used as a refrigerant and in the manufacture of ice. Liquid ammonia (with no water present) is a good solvent for many salts and resins. When ammonia is oxidized, under certain conditions, nitric acid is made. Nitric acid has many uses among them the making of silver nitrate, a germicide, and ammonium nitrate, a fertilizer.

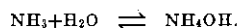
As little as 1 percent of ammonia gas makes air dangerous to breathe. Ammonia gas should never be inhaled unnecessarily or incautiously, for it may produce cardiac arrest.

The chemical properties of ammonia may be summarized by the following reactions:

1. Ammonia is decomposed by moderate heating

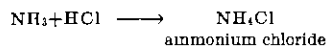


2. Ammonia combines with water to form a solution of ammonium hydroxide, conventionally represented as NH_4OH



This solution is alkaline and conducts electricity as it is also ionic.

3. Ammonia combines directly with acid to form ammonium salts.



The white cloud observed when ammonia fumes and hydrochloric acid fumes are brought together is due to the formation of ammonium chloride. A simple, widely used test for nitrogen in biologic materials uses Nessler's reagent which contains a complex salt. The nitrogen is converted to ammonia which forms an orange-yellow color with this reagent. The intensity of the color is a quantitative increase of the amount of NH_3 present.

NITRIC ACID

An important nitrogen compound is nitric acid, HNO_3 . It is a strong acid which is a colorless fum-

ing liquid when pure. It is usually obtained in a concentrated solution containing about 67 percent HNO_3 . The concentrated acid is always colored faintly yellow from the dissolved nitrogen dioxide, NO_2 , formed by decomposition. This acid is corrosive and will burn the skin, causing it to become hard and yellow. It has been used to remove warts. A mixture of nitric and hydrochloric acids is known as "aqua regia," famed for its ability to dissolve gold.

In combination with sulfuric acid, nitric acid introduces nitrate groups into cellulose to give nitrocellulose (pyroxylin or guncotton). By varying the strengths of the acids and the temperatures, among other factors, products of widely different properties may be obtained. Some are used in the manufacture of plastics and fast-drying lacquers, others in propellant explosives. Reacting with other organic compounds, nitric acid introduces nitro groups, $-\text{NO}_2$, and forms compounds used in dyes and perfumes, and high explosives such as trinitrotoluene (TNT).

PHOSPHORUS

Phosphorus is quite as necessary to life as nitrogen itself. The bony framework and teeth of vertebrates contain a large proportion of modified calcium phosphate. The brain and nervous tissue contain phosphoproteins. In fact, a minute amount of phosphorus is contained in every cell of every living plant and animal.

The oxides of phosphorus react with water to form phosphoric acids. The salts of these acids are used extensively in industry as water softeners, detergents, and fertilizers.

ARSENIC

Arsenic is added to lead to harden it as in making shot, and to brass and other alloys to improve their strength. Arsenic trioxide, As_2O_3 , is a component of various glasses and decorative enamels. Arsenicals in the form of trioxides and pentoxides, chlorides, and arsenates are extremely poisonous. They have been widely employed in the manufacture of insecticides and rodenticides and, unfortunately, used as a means of committing murder. Arsenic compounds in proper amounts have been used in medications for treatment of anemia, skin diseases, and debility. However, their values are doubtful. Arsphenamine (Salvar-

san or 606) is an organic arsenical which was used for many years in the treatment of syphilis.

ANTIMONY AND BISMUTH

Elemental antimony is used principally for alloying with other metals to produce bearing metal, type metal, metal sheathing for cables, and battery plates. Its presence causes most of these alloys to expand upon cooling, a property which is particularly useful in type metal. Tartar emetic (potassium antimonyl tartrate) is used medicinally as an agent to cause vomiting.

Bismuth finds its principal use in preparation of low-melting-point alloys which are used in fuses and safety plugs for boilers, sprinkler systems for fire extinguishing, etc. Compounds of the element are used medicinally. Bismuth subnitrate is used to counteract acidity in the stomach, to coat and heal gastric ulcers, and to check diarrhea. Other compounds are used in preparation of paints, pottery glazes, and some types of glasses.

SILICON AND ITS COMPOUNDS

Silicon is found everywhere in the forms of rocks and sand. Solid rocks have an average composition approximating salts of the hypothetical metasilicic acid, H_2SiO_3 . Rocks, for the most part, are not definite chemical compounds—though, if cooled slowly enough, they may contain crystals of definite compounds.

The most important crystalline form of silica is quartz (SiO_2). It is found in large transparent crystals which are hard enough to scratch glass. As a mineral, quartz is second only to the feldspars in abundance and is estimated to compose about 12 percent of all the igneous rocks of the earth. Feldspars are polysilicate salts and make up about 60 percent of igneous rock.

Certain minute aquatic organisms and sponges develop siliceous skeletons which accumulate in the bottom of the ocean when the organisms die. This material has accumulated in deposits up to a thousand feet in depth and is called diatomaceous earth. It is used as a scouring powder and as an adsorbent.

Fused silica is made by melting sand in a vacuum in an electric furnace. Its advantage over glass is that it will transmit both visible

and ultraviolet light. It has a small coefficient of expansion and may be heated red-hot and then plunged into cold water without being damaged.

Silicon carbide, SiC , is prepared by heating silica with excess coke to about $1,800^\circ$ centigrade. A trade name is Carborundum. An examination of silicon carbide with X-rays reveals that it has the closely knit, rigid structure of the diamond, except that every other atom of carbon is replaced with an atom of silicon.

Silica gel is a hydrous gelatinous silica which is used as an adsorbent, particularly as a desiccant in the laboratory. (A desiccant is a substance with such a high affinity for water that it will adsorb the water in an enclosed atmosphere and thereby dry other substances in the enclosed area.)

Asbestos, talc, mica, some semiprecious stones, and waterglass are examples of silicates. Many glasses are composed of silicates, for example, ordinary window and bottle glass called soda-lime or soft glass are sodium-calcium silicates. Optical glass must be almost colorless, of uniform composition, and free from flow defects and air bubbles. Modern optical glass, therefore, contains little or no silicates; instead boric or phosphoric oxides are used in its manufacture.

Glasses having a high percentage of silica have a resistance to sudden extreme changes in temperature, similar to fused silica. Pyrex, a sodium borosilicate, belongs to this class of glasses. Vycor, a nearly pure silica glass, will stand the shock of being filled with molten bronze while resting on a block of ice. Glazes and enamels are low-melting glasses. Various metallic oxides provide the color and opacity of glasses and enamels.

SULPHUR AND ITS COMPOUNDS

The elements of the sulfur family occupy column 6a of the periodic table. Sulfur makes up but a mere trace of the earth's crust, yet there are in many parts of the world enormous deposits of free sulfur and sulfides such as zinc blende (ZnS), galena (PbS), chalcopyrite (CuFeS_2), and iron pyrite (FeS). The commonly occurring sulfates are gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which is used in the preparation of plaster of paris, and barium sulfate (BaSO_4) which is used as a white pigment in paint and as a filler in the making of paper, linoleum, rubber goods, among others. Barium

sulfate is also used medicinally. Since it is opaque to X-rays, it casts a shadow on the X-ray film. A slurry (thin suspension of a solid in water) of barium is often given prior to making X-ray films of the digestive tract.

Sulfur is one of 12 or more elements necessary for the life and growth of plants and animals. As a constituent of organic compounds, it is very widely distributed in small amounts in plant and animal matter such as seeds, yolks of eggs, hair, and brain and nervous tissue. Organic sulfur compounds, and hydrogen sulfide in petroleum and natural gas, form sulfuric acid during combustion, leading to the serious problem of corrosion in motors.

The existence of two or more different forms of a solid, stable over different temperature ranges, is known as *allotropy*. Sulfur exists in several such forms. This phenomenon is also known as polymorphism (many forms). Rhombic and monoclinic sulfur are both crystalline forms; plastic sulfur—flowers of sulfur—is amorphous (having no form). At ordinary temperatures, sulfur is usually in the rhombic form. The true molecular formula for sulfur is S_8 . For simplicity, elementary sulfur is represented by S in chemical equations. Sulfur combines directly with most other elements except nitrogen and the inert gases of Group O.

Hydrogen sulfide, H_2S , is a colorless, readily liquefiable, very soluble gas of offensive odor. It is formed in nature whenever plant or animal matter decays in a limited supply of air. The "sulfur waters" of mineral springs owe their taste and disagreeable odor to hydrogen sulfide. Natural gas also frequently contains H_2S .

Gaseous hydrogen sulfide, because of its paralyzing action upon the respiratory nerve centers, is a dangerous poison. Concentrations of 3 to 4 volumes in 2,000 volumes of air will cause death in a short time. As little as 1 volume in 2,000 volumes is toxic if breathed for more than a few minutes and will cause headache, nausea, and fainting.

Sulfur dioxide, SO_2 , is a colorless gas with the pungent odor of burning sulfur. It is readily liquefied and as such is used as a solvent for waxes, resins, and as a selective solvent in refining lubrication oils. Sulfur dioxide combines reversibly with water to form sulfurous acid, H_2SO_3 . It is used as a bleach, a disinfectant, and a reduc-

ing agent. Its sodium salt is used to make sodium thiosulfate or "hypo" which is used as a fixative in photography.

Another sulfur-containing acid is sulfuric acid, H_2SO_4 . Concentrated sulfuric acid contains 96 percent H_2SO_4 and is very corrosive. The concentrated acid can safely be diluted by pouring it into a sufficient excess of water to prevent the mixture from getting very hot. To reverse this procedure and add water to the concentrated acid is to risk being blinded or disfigured, for so much heat is liberated in the early part of the reaction that the acid may splatter violently. Concentrated sulfuric acid is a vigorous dehydrating* and oxidizing agent.

HALOGENS, MEMBERS OF THE 7a FAMILY

The halogens (from a Greek word meaning salt formers) receive their name from their occurrence in common salt and related compounds in sea water. They are typical nonmetals, so active chemically that they are never found free in nature.

Halogens make up column 7a of the periodic table:

Atomic No.	Formula	Element	Physical Properties
9-----	F_2	Fluorine-----	Pale yellow gas.
17-----	Cl_2	Chlorine-----	Greenish yellow gas.
35-----	Br_2	Bromine-----	Dark red liquid.
53-----	I_2	Iodine-----	Purplish black solid.

Fluorine, as the fluoride, is found in several minerals such as fluorspar, cryolite, and apatite. Calcium fluoride is present in the enamel of teeth, sea water, and some fresh water.

Chlorine, as the chloride, is found in inexhaustible quantities in nature. Sea water contains 2.8 percent NaCl and 0.8 percent of other metallic chlorides. Salt beds and lakes are found throughout the world. Volcanic gases contain hydrogen chloride. Hydrochloric acid is secreted by the

*A dehydrating agent removes water from its surroundings, and from other substances. This dehydration may occur as a physical process, as in the drying of foods, or as a chemical process when hydrogen and oxygen, which may be found in varying proportions in substances, are removed from these substances in the proportion of two hydrogen atoms to one of oxygen. This type of dehydration may cause decomposition. One of the reasons for the very severe burns caused by sulfuric acid is the chemical dehydrating effect which it has on tissues with accompanying decomposition.

stomach as a component of the gastric juice—enough in a single day to make a fatal dose if taken in concentrated form.

Bromine, as the bromide, is found in sea water (and in a few sources of fresh water) in sufficient quantity to make it profitable as a commercial source.

Iodine, as the iodide, is found in sea water and is concentrated in the tissues of sea weed from which it is recovered. Sodium iodate, NaIO_3 , occurs as an impurity in sodium nitrate beds. Iodide also occurs in the brines of some petroleum wells.

Hydrogen halides may be prepared by direct union of the halogen with hydrogen. Solutions of the hydrogen halides are all strong acids with the exception of hydrofluoric acid which is weak. However, strong solutions of hydrofluoric acid produce serious burns which are best treated by washing with ice water for at least one-half hour. Hydrofluoric acid is distinguished by its ability to etch glass.

Small quantities of fluorine are found in bones and teeth, and the diet must provide these essential amounts. Dental health seems to be promoted by faint traces of fluorides in drinking water, and in many places it is current dental practice to swab children's teeth with fluoride solution to lessen tooth decay. All soluble inorganic fluorides are intensely poisonous and are sometimes used as disinfectants and fungicides. Fluorine-substituted hydrocarbon compounds are used as refrigerants. They are nontoxic to humans and are often used as insecticides, weedkillers, and cleaning fluids.

Chlorine is used to bleach paper pulp, and cotton and linen fabrics. It is used as a disinfectant in the treatment of domestic water supplies and swimming pools. Anhydrous metallic chlorides, commercial hypochlorites, chlorates, perchlorates, and many organic chlorine compounds are made from chlorine.

Hypochlorates are used in household bleaches. Chlorates and chloric acid are dangerously vigorous oxidants which will explode violently if improperly handled. They are used in the manufacture of matches and fireworks. Pure perchloric acid is also an explosive oxidant.

Bromine is used in the preparation of ethylene dibromide, $\text{C}_2\text{H}_4\text{Br}_2$, an ingredient of ethyl gasoline, and in dye stuffs. Bromides, in medicine, serve as heart depressants and nerve sedatives. Silver bromide is light sensitive and is used to coat photographic plates and film.

Iodine as tincture of iodine (an alcohol solution of iodine) and iodoform (CHI_3) are used as antiseptics to treat wounds and abrasions of the skin. Traces of iodine are necessary in the diets of both man and animals. The average adult human body contains about 12 mg. of iodine bound in thyroxine and related compounds—most of which is localized in the thyroid gland. A deficiency of iodine in the diet leads to disturbances of the thyroid gland, particularly to the development of goiter. In certain areas of the United States where goiter is endemic, iodine is added to table salt in a proportion of 1 part in 10,000 as a preventive measure.

Traces of iodine are readily recognized by the blue color that it forms with starch.

The presence of halogen ions (with the exception of fluorine) may be detected by the appearance of a white (for chlorine) or light yellow (bromine and iodine) precipitate when added to a solution of silver nitrate, AgNO_3 .

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- Deming, Horace G.: *General Chemistry*. 6th ed. New York, John Wiley & Sons, Inc., 1952.
Pauling, Linus: *College Chemistry*. 2d ed. San Francisco, W. H. Freeman & Co., 1955.
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ORGANIC CHEMISTRY

Organic chemistry is the study of carbon compounds. In the early days of this science only natural carbon compounds were known, thus they were called organic. It was thought that com-

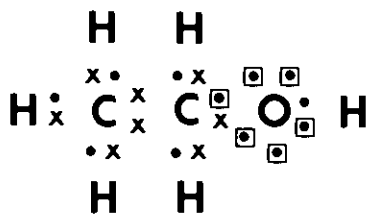
pounds found in living matter were formed through the action of the "life force" and could not be understood or duplicated by man.

In 1828 Whöler, a German scientist, heated an

inorganic compound, ammonium cyanate, and made an organic compound, urea. This synthesis opened up a vast new field of chemistry and thereafter chemists began making other so-called "organic" compounds. Today the number of synthetic organic compounds runs into the hundreds of thousands. Many are either made from, or are closely related to, compounds found in living organisms (or in matter which once had life as wood, coal, petroleum, and natural gas), but many others have no association with life processes. They all do have one thing in common, however, they all contain carbon.

While the work of the modern organic chemist has been outstanding, performing such feats as the total synthesis of morphine, quinine, chlorophyll, and penicillin, he still has not been able to imitate the more noble structures of nature. For many organic compounds the natural source is the only economical source, while for other compounds nature is the only source, particularly in the biochemical field.

The ability of carbon to form a multiplicity of compounds is due to its position in the periodic table; it is at the top and center. Carbon, with four valence solutions, has no more tendency to lose than to gain electrons and tends to resist the acquisition of a charge, positive or negative. These forces lead to a sharing of electrons between carbon and other elements such as sulfur, hydrogen, the halogens, oxygen, or nitrogen, with the formation of a covalent bond and a satisfied octet. The formula for ethyl alcohol, C_2H_5OH , serves as a model.



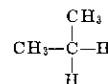
where the x's are electrons from the C atom

where the •'s are electrons from the H atom

where the ◻'s are electrons from the O atom

A formula C_4H_{10} indicates there are 4 carbons joined together in a chain, $C-C-C-C$, and that

there are 10 hydrogen atoms attached to the carbons, 3 to each of the end carbons and 2 to each of the inner carbons, $CH_3-CH_2-CH_2-CH_3$. Note that each carbon has a valence of four and each hydrogen a valence of one. A formula $(CH_3)_2CH_2$ indicates that 1 carbon atom has 2 methyl groups, $-CH_3$, attached to it as well as 2 hydrogen atoms.

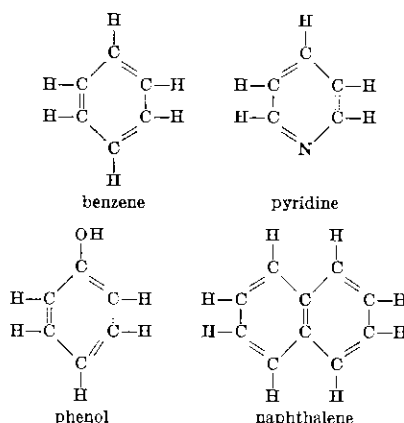


Again the valence requirement of 4 for carbon and 1 for hydrogen is satisfied. In the above example of ethyl alcohol, C_2H_5OH , (CH_3CH_2OH) , 1 carbon is attached to 2 hydrogen, a hydroxyl group ($-OH$) and a methyl group ($-CH_3$).

Chemical formulas in organic chemistry are usually expressed graphically to indicate the active groups and, to some extent, the spatial arrangement of the elements.

ALIPHATIC HYDROCARBONS (ALKYLS)

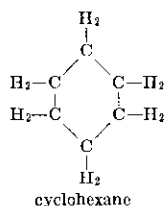
Organic compounds are divided into two general groups, the aliphatics and the aromatics. The aromatics or aryls include those compounds which are related to a benzene type structure such as



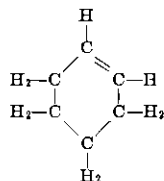
The aliphatics or alkyls include all other compounds and are divided into three groups, the alkanes (paraffins), the alkenes (olefins), and the alkynes (acetylenes). The alkanes are saturated* hydrocarbons such as CH_3CH_3 , ethane; CH_3COOH ,

*No double bonds between carbon atoms.

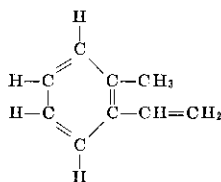
acetic acid; $(\text{CH}_3)_2\text{CH}_2$, propane; $(\text{CH}_3)_2\text{CHOH}$, isopropyl alcohol, and



The alkenes, which are unsaturated, contain double-bonded carbons such as $\text{CH}_2=\text{CH}_2$, ethylene; $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$, butadiene; and cyclohexene:



The alkynes, also unsaturated, contain triple-bonded carbons such as $\text{CH}\equiv\text{CH}$, acetylene, and $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$, ethyl acetylene. A particular compound may be composed of two or more of the general groupings such as o-vinyl toluene,



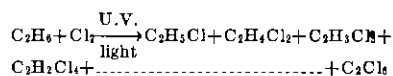
which has an aromatic, an alkane, and an alkene group. The presence of other groups of atoms, such as $-\text{OH}$, $-\text{NH}_2$, $-\text{CHO}$, $-\text{COOH}$, $-\text{Cl}$, $-\text{Br}$, $-\text{F}$, endow the hydrocarbon with increased and varied activity. These groups are referred to as the functional groups and will be discussed individually later.

ALKANES (PARAFFINS)

The lower members of the alkane series are gases at normal temperatures and pressures. The simplest hydrocarbon is methane, CH_4 , which is found in natural gas and in marsh gas. Successively higher members of the alkane or paraffin series are ethane, C_2H_6 ; propane, C_3H_8 ; butane, C_4H_{10} ; pentane, C_5H_{12} ; hexane, C_6H_{14} ; and so forth through 70 or more carbons. These are referred to as straight chain hydrocarbons or alkanes.

As may be seen from deduction, the general formula for the alkanes is $\text{C}_n\text{H}_{2n+2}$, where "n" equals the number of carbon atoms present. Many members of this homologous series are derived from petroleum by means of "cracking," a process for breaking down the larger molecules of higher members of the paraffin series into smaller molecules of the low boiling compounds to be blended into gasoline. Liquid petrolatum is a mixture of liquid paraffins obtained from petroleum.

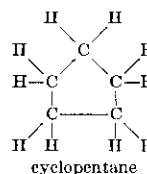
Alkanes, when ignited, burn in the presence of air or oxygen to CO_2 and H_2O , although they are stable to oxygen at ordinary temperatures in the absence of a spark. They also react with chlorine to form mixed alkyl halides.



Most paraffins are relatively stable and are not affected by oxidizing agents such as potassium permanganate. Nor do they readily react with such common reagents as sulfuric, nitric, and hydrochloric acids, sodium hydroxide, and ammonia.

CYCLOALKANES

Cycloalkanes behave much the same as the straight chain alkanes. They are obtained mainly from petroleum products. As the name implies, the carbons are joined in a ring configuration in these compounds:



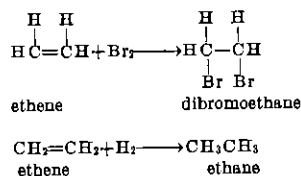
The general formula for the cycloalkanes is C_nH_{2n} . The more common members are cyclopropane, C_3H_6 ; cyclobutane, C_4H_8 ; cyclopentane, C_5H_{10} ; and cyclohexane, C_6H_{12} .

ALKENES (THE OLEFINS)

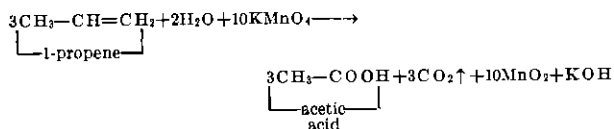
Alkenes or olefins are isomeric with cycloalkanes and have the same general formula C_nH_{2n} . (Isomers are compounds having the same molecular formula but different spatial arrangement.) The alkenes (like the acetylenes which follow this

discussion) are very reactive and play highly significant roles as basic chemicals for the organic chemical industry. Since they are not found in nature, they must be made in large quantities. Fortunately, large amounts are available as by-products from the cracking of petroleum.

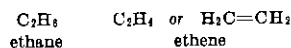
Alkenes are referred to as unsaturated compounds because of the double bond(s) in the molecule. These bonds are more reactive than the single bonds and will add halogens, hydrogen, and mineral acid across these bonds to form single bonds and become a saturated compound (alkane).



The double bond is also easily oxidized by standard oxidizing agents such as potassium permanganate:



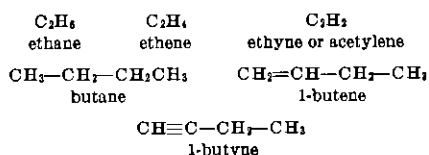
The nomenclature of the alkenes follows that of the alkanes, using the -ene ending rather than the -ane:



ALKYNES (ACETYLENES)

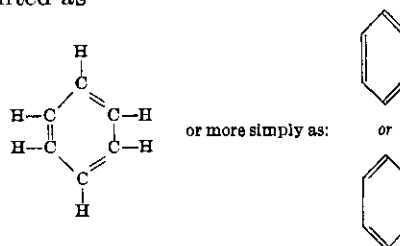
The alkynes or acetylenes contain triple bonds and are even more reactive chemically than alkenes. The first member of this series is acetylene, $\text{HC} \equiv \text{CH}$. The general formula is C_nH_n . Acetylene burns with a very hot flame and is used in welding. It also is used in the manufacture of various polymers such as butadiene, a synthetic rubber.

The nomenclature of the alkynes follows that of the other hydrocarbons, using the -yne ending:



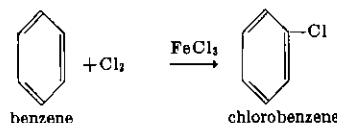
AROMATIC HYDROCARBONS

The simplest aromatic hydrocarbon is benzene, C_6H_6 . It is obtained from the distillation of coal and from the hexane fraction of petroleum in the cracking process. The structure of benzene baffled chemists for many years, for it possessed both saturated and unsaturated properties. In 1865, Kekule proposed the hexagonal ring formula with alternate single and double bonds which was generally accepted as the best way to express the benzene molecule. The structural formula is represented as

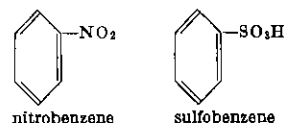


This is merely a graphic representation and does not imply unsaturation as discussed under alkenes. Benzene is a remarkably stable compound due to its structural formation. Reactions with benzene rings behave quite differently in comparison to similar reactions with alkenes.

The benzene ring may be halogenated with the aid of a catalyst. (A catalyst is a substance which when added to a reaction in very small amounts will greatly increase the rate of the reaction and which may be recovered unchanged after the reaction is over.) The chlorination of benzene requires ferric chloride, FeCl_3 , as a catalyst in order to obtain good yields.

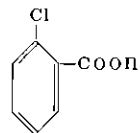


A nitro- or sulfo-derivative may be obtained by treating with nitric or sulfuric acid.

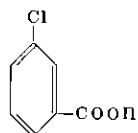


In the nomenclature of aromatic compounds, ortho, meta, and para are used to indicate the position of the second substituent on a benzene

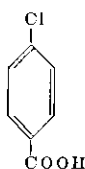
ring. Ortho is in the adjacent position, meta is placed two carbons away and para is three carbons away. Using chlorobenzoic acids to demonstrate this rule:



o-chlorobenzoic acid, ortho form

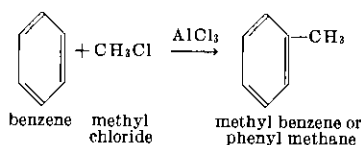


m-chlorobenzoic acid, meta form

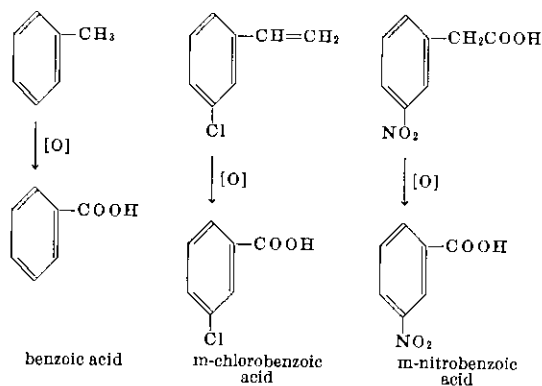


p-chlorobenzoic acid, para form

Alkyl groups may be substituted on the benzene ring by means of the Friedel-Crafts reaction. Aluminum chloride serves as the catalyst. (Friedel-Crafts comes from the names of the two men who developed the reaction.)



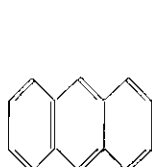
Benzene does not react with ordinary oxidizing agents but any alkyl substituent group will oxidize to —COOH .



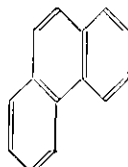
In addition to benzene and its derivatives, other types of aromatic hydrocarbons are known. These are condensed-ring compounds and are usually products of coal tar distillation. Some of the simple forms are:



naphthalene



anthracene

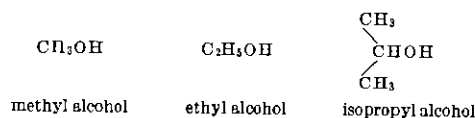


phenanthrene

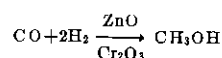
These compounds may form derivatives and have chemical behavior similar to benzene.

ALCOHOLS

Alcohols are alkyl compounds containing the functional hydroxyl (—OH) groups. A few of the more widely used alcohols are:



Methyl alcohol is sometimes called wood alcohol because it is a product of destructive distillation of hard wood. Today most methyl alcohol is made by hydrogenating carbon monoxide:

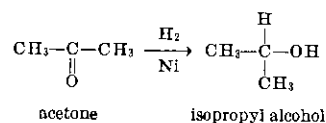


Methyl alcohol is a colorless, volatile liquid with a characteristic odor. It is used as a denaturant for ethyl alcohol, as a solvent for shellacs and resins, as an antifreeze, and as a raw material in organic synthesis. When taken internally, methyl alcohol is very poisonous; even inhalation and absorption through the skin will produce toxic effects. Small doses will cause blindness due to the destruction of the optic nerve; large doses will cause death.

Ethyl alcohol is commonly known as alcohol or grain alcohol and is the intoxicating agent in alcoholic beverages. It is made by the fermentation of sugars and starches. Fermentation is an enzymatic process which may be induced by certain yeasts and bacteria. Industrial ethyl alcohol contains 95 percent alcohol (190 proof) and 5 percent water, and is prepared by fractional distillation of fermentation "beer" or mash. Absolute alcohol is pure ethyl alcohol. The water may be removed from the 95-percent alcohol by distillation from benzene.

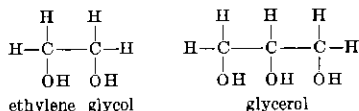
Ethyl alcohol is used as a solvent for many substances and in the preparation of medicines, flavoring extracts, and perfumes. In the hospital it is used as an antiseptic, as a compound to cleanse the body and, since it evaporates rapidly, as a means of reducing body temperature.

Isopropyl alcohol is made by the hydrogenation of acetone.



It is used in many commercial rubbing compounds and cosmetic preparations. Isopropyl alcohol is toxic when taken internally and has no euphoric effect. Serious toxic effects have been reported when used as a coolant to reduce fever in infants.

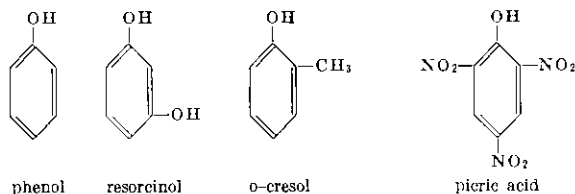
Several polyhydroxyl alcohols are in wide use such as:



Ethylene glycol is used as an antifreeze. Its boiling point is very high compared to methyl and ethyl alcohols. Large quantities of ethylene glycol are used in the preparation of solvents, paint removers, and plasticizers (softeners) used in the paint, varnish, and lacquer industry. Ethylene glycol is very toxic and is converted to oxalic acid in the body. The calcium salt of the acid collects in the kidney and blocks the tubules. Glycerol (glycerin) is a constituent of fats and may be prepared by the saponification of fats in the manufacture of soap. Glycerol is soluble in all proportions of water and alcohol. It is nontoxic and is used as a solvent for medications. Since it takes up moisture from the air, it is used as a moisturizer in cosmetics, lotions, and tobacco. It is also used in the manufacture of resins and photographic film.

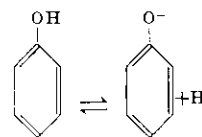
PHENOLS

Phenols are aromatic compounds containing a hydroxyl group on the benzene ring. Examples are:



Phenol is a white crystalline substance which will absorb water from the air. It becomes liquid when mixed with 8 percent water. It has acidic

properties and is referred to commonly as carbolic acid.



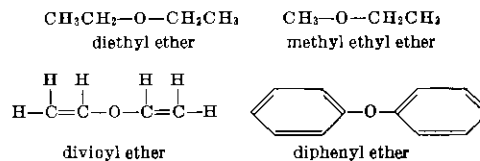
Ionization of phenol to release a proton, giving the compound acidic properties

Phenol is caustic and poisonous, but dilute solutions make effective disinfectants and are still used in hospitals for this purpose. Cresol and other phenols with larger side chain hydrocarbons have even better germicidal properties.

Picric acid or trinitrophenol is a yellow crystalline substance and is a fairly strong acid. It is used in the manufacture of explosives, as a dye, and as a derivative in the identification of organic compounds. It will precipitate proteins, a principle which once found use in ointments compounded for treatment of burns.

ETHERS

Ethers are compounds in which both valence bonds of oxygen are attached to alkyl or aryl groups such as:



Diethyl ether is colorless, insoluble in water, and has a low boiling point. It, as well as some other ethers, is used as an anesthetic. Since ether is extremely volatile, explosive, and flammable, care must be exercised in its use at all times.

Ethers make excellent solvents for fats, gums, resins, and oils, and are used in extraction of these materials.

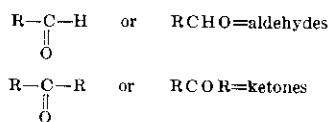
CARBONYL COMPOUNDS

The carbonyl compounds are the aldehydes and the ketones. Both classes of compounds are characterized by the presence of a carbonyl group,

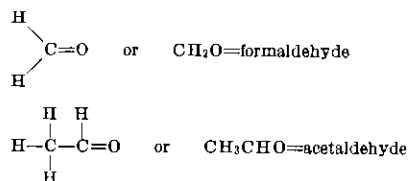


in their structures and are quite reactive.

With "R" denoting any alkyl group:



Some aldehydes of note are:

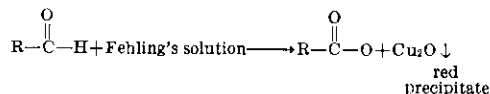


If the carbon is bound to a hydrogen as well as an alkyl or aryl group, it is an aldehyde; if both substituents are alkyl or aryl groups, it is a ketone.

ALDEHYDES

Aldehydes contain the "formyl" or aldehyde group. The word aldehyde itself is a contraction of *alcohol dehydrogenation*, and refers to the product obtained by dehydrogenating a primary alcohol. Dehydrogenation is a form of oxidation; thus aldehydes are oxidation products of primary alcohols.

Formaldehyde is a colorless gas with a sharp, penetrating odor; a 40-percent solution is known as formalin and is used in embalming fluid and to preserve tissue for pathologic examination. It is also used as a fumigant, an insecticide, a disinfectant, and in the manufacture of synthetic resins. It is, of course, quite toxic and the fumes are irritating to the eyes. Acetaldehyde is used in organic synthesis. Benzaldehyde (occurring naturally in the seed of bitter almonds) is the artificial essential oil of bitter almond and is used as a flavoring. Aldehydes and ketones may be oxidized by gentle reagents such as Fehling's solution (a complex copper salt solution).



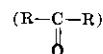
The reduction of the cupric ion is the basis for quantitative determination of "reducing" sugars in blood and urine. A reducing sugar contains an aldehydic or ketonic group.

Somewhat similarly, an ammoniacal silver nitrate solution (Tollens' reagent) reacts with

aldehydes to deposit metallic silver, and is used in silvering mirrors.

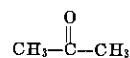
KETONES

Ketones contain a carbonyl group which is attached to two other alkyl or aryl groups

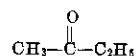


Whereas aldehydes are dehydrogenated primary alcohols, the ketones are the corresponding derivatives of secondary alcohols.

The most widely used ketones are acetone,



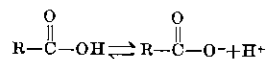
and methyl ethyl ketone,



Both of these are used as solvents in lacquers, plastics, resins, and in the manufacture of synthetic resins and plastics.

ORGANIC ACIDS AND ESTERS

Most organic acids are slightly ionized and therefore weak acids. They contain the carboxylic acid radical, $-\text{COOH}$, which ionizes to release H^+ (protons).



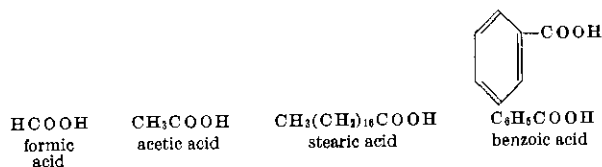
Organic acids may contain more than one carboxylic acid group; those containing one are monobasic acids, those containing two are dibasic acids, those containing three are tribasic, and so forth. Many organic acids contain other functional groups such as the hydroxyl group (hydroxy acids), the amine group (amino acids), the ketone group (keto acids), and the halogen atom (halo acids).

MONOCARBOXYLIC ACIDS

The aliphatic monocarboxylic acids ($\text{R}-\text{CO}_2\text{H}$) are sometimes called *fatty acids*, since they are typical of the acids obtained from the hydrolysis of animal and vegetable fats and oils. The aromatic analogs are also important, but do not

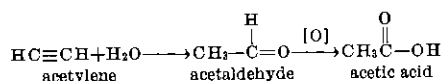
constitute as large a group. Formic acid is the most simple aliphatic carboxylic acid, while benzoic acid is the most simple aromatic example. The fatty acids are aliphatic carboxylic acids which contain an even number of carbon atoms, ranging from 2 to 18, for the more common members of the series.

Examples of monobasic acids are:



Formic acid is a colorless liquid with a sharp, irritating odor. It is one of the strongest acids of the carboxylic type and will blister skin upon contact. Formic acid is named after the ant, *formica*, which secretes the acid. The irritation produced by stings of ants, bees, and stinging nettles is due to formic acid.

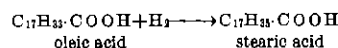
Acetic acid is an essential component of vinegar, being the source of its sour flavor and pickling properties. Commercially produced acetic acid is about 99.5 percent pure and is called glacial acetic acid. It is slightly viscous and will freeze solid on cold days. One commercial process converts acetylene to acetaldehyde which is then oxidized to acetic acid.



It is produced in large quantities and is used extensively in the production of plastics, synthetic fibers, and organic solvents.

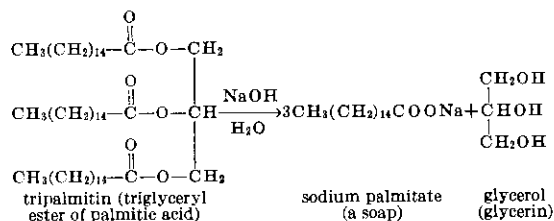
Stearic acid (from the Greek word *stear*, meaning tallow or suet) is a long-chain fatty acid containing 18 carbons and is obtained from fats. Fats are composed of glycerol and fatty acids joined in an ester linkage. Acetic and butyric acids are short-chain fatty acids found in butter. The long-chain fatty acids, such as stearic and palmitic, are found in animal and vegetable fats. Vegetable fats also contain a high percentage of unsaturated fatty acids such as oleic which has one double bond, and linoleic which has two double bonds. Most vegetable fats are liquid at room temperature and are called oils. The low

melting point of the vegetable oils is due to the high concentration of unsaturated fats which are liquid at room temperature. Vegetable oils may be converted into solid fats by addition of hydrogen to the double bonds of the unsaturated fatty acids. As an illustration, we can saturate oleic acid to produce stearic acid:

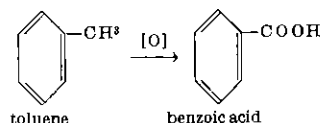


This process is used to prepare butter substitutes and shortening from vegetable oils.

Commercial preparation of fatty acids involves acid hydrolysis* of fats and separation by fractional distillation of the resultant acids. If alkaline hydrolysis is used, the sodium salt of the acids is obtained. The sodium salt of long-chain fatty acids is called soap and the process of manufacture is called saponification. The alkaline hydrolysis of fats is used in the commercial preparation of soap, with glycerin as a byproduct.

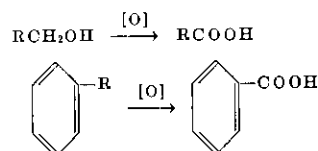


Benzoic acid may be prepared by the oxidation of toluene.



It is used in the synthesis of organic compounds and its sodium salt is used as an antiseptic and food preservative.

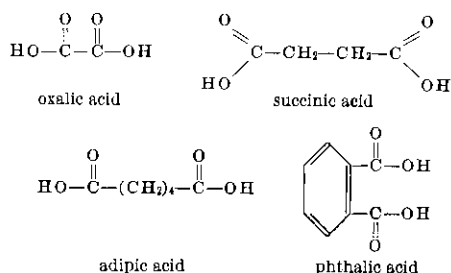
Acids may be prepared from the oxidation of primary alcohols and from the oxidation of alkyl aromatic compounds (R=alkyl group):



*Hydrolysis is a reaction whereby a bond is broken with the aid of water.

DICARBOXYLIC ACIDS

Dibasic acids participate in the same type of reactions as monobasic acids. Examples of dibasic acids are:



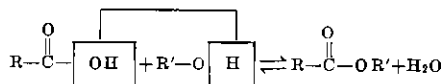
Oxalic acid occurs in the leaves of vegetables such as rhubarb and spinach and is one of the strongest naturally occurring acids. It is easily oxidized and is therefore a strong reductant which is the basis for its bleaching action on rust and ink stains. The ferric compounds are reduced to soluble ferrous compounds.

Succinic acid is important in the metabolism of the body. Adipic acid is used in the manufacture of nylon, and phthalic acid is used in organic synthesis.

Dibasic acids participate in the same type of reactions as monobasic acids.

ESTERS

Acids may react with alcohols to form esters. In this reaction, the —OH part of the carboxyl group combines with the hydrogen of the hydroxyl group in the alcohol to form water and the oxygen in the alcohol is bound to the carbon of the carboxyl group to form the ester.



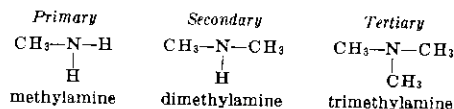
This is a reversible reaction and under proper conditions an acid may be prepared by the hydrolysis of its ester. Most acids are stable toward oxidizing agents.

AMINES AND AMINO ACIDS

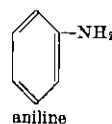
AMINES

Amines are organic derivatives of ammonia in which one or more of the hydrogen atoms have been replaced by an alkyl group. Thus, there are

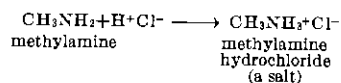
three general classes of amines: primary, secondary, and tertiary.



There are also aromatic amines, of which aniline is the most common:



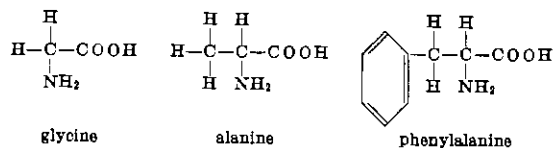
The amines have basic properties and form salts with strong mineral acids.



Using methylamine as an example, the proton of an acid, such as hydrochloric acid, is attracted to the nitrogen of the neutral amine. The resulting ammonium compound thus has a positive charge and will attract the negative chloride ion (from HCl) to form the hydrochloride salt of methylamine. The amines are basic according to the Brönsted theory since they take up protons. Amines have varied commercial uses. They are used in preparation of oil, soluble soaps, pharmaceuticals, cosmetic products such as hair-waving lotions, and one methylamine is produced in great quantities for use in the tanning industry as a dehairing agent.

AMINO ACIDS

The amino acids are an important group of compounds. They are the natural building blocks for the biologically important proteins. An amino acid, as the name implies, is a bifunctional compound which contains both an amino and an acidic group. Most of the naturally occurring amino acids have the amino group (—NH₂) on the carbon atom adjacent to the carboxyl group and are called alpha-amino acids. Some examples are:

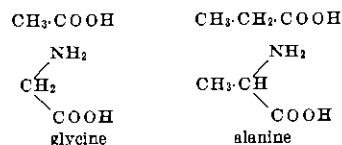


Amino acids may be bonded together through the peptide linkage,

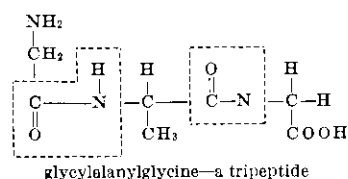


between the $-\text{NH}_2$ groups of one amino acid and the $-\text{COOH}$ of another to form peptides and proteins.

The two simplest amino acids are amino acetic acid (glycine) and amino propionic acid (alanine).



Two molecules of glycine and one of alanine, when united by peptide linkages, might be represented thus (dotted lines indicate peptide linkages).



The peptide linkage between two amino acids results in a compound called a dipeptide, such as glycylalanine which is composed of glycine and alanine. The union of three amino acids would result in a tripeptide, while the combination of several amino acids by the peptide linkage would be called a polypeptide. Proteins are macromolecular polypeptides.

PROTEINS

Amino acids are the building blocks of proteins and are bonded through peptide linkages into large molecules varying in molecular weight from about 5,000 to several million. The particular amino acids, their arrangement and their number, are definite and characteristic for each protein. There is an endless array of different protein molecules, each with its own specific function.

Proteins are one of the main structural elements of the body, being the chief constituent of muscle, cell structure, and connective tissues. Other than water, protein is the chief constituent of blood, and is found in hemoglobin, serum albumin, and globulins. All known enzymes and some

hormones are protein compounds. The functions of protein range from the structural role through buffering activity, osmotic pressure, electrolyte control, and antibody formation, to the highly reactive hormonal and enzymatic activities. The antibodies are generally found in the gamma globulin of serum. Each specific antibody is a little different in molecular structure and form, and in activity. Also, the alpha and beta globulins and albumin of serum are each composed of several proteins. The enzymes are a very large group of proteins which act, each specifically, as the catalytic agents for most of the chemical changes in plants and animals. The complexity of proteins is such that, at the present time, the exact structure of only a few proteins have been elucidated. The first protein to have its molecular structure determined was the hormone, insulin. Up to the present time it has not been possible to synthesize naturally occurring proteins. However, recent developments in this field of research make the synthesis of natural proteins appear imminent.

There are a number of color tests used as an aid in the identification of protein substances. One of these is the biuret test. In this the peptide bond of peptides and proteins forms a violet or reddish-violet color with the cupric ion. Another test, the ninhydrin, is frequently used to quantitate amino acids. In this, a blue color is produced.

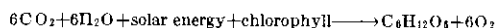
Proteins are easily denatured by heat, change in pH, violent motion, repeated freezing and thawing, and various chemical agents. A denatured protein has an altered geometric arrangement of its molecules and loses its physiologic activity.

A mixture of proteins may be separated by fractional precipitation with salts such as sodium sulfate and ammonium sulfate, and with solvents such as ethyl alcohol which may be used in conjunction with salt fractionation. More elegant methods are electrophoresis, ultracentrifugation, and chromatography.

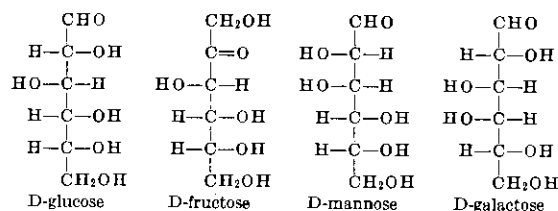
CARBOHYDRATES

Carbohydrates are composed of sugars which are polyhydric alcohols containing an aldehyde or ketone group. Sugars are manufactured in

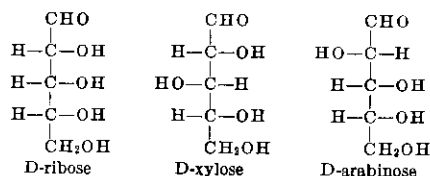
the cells of plants by the fixation of CO_2 in the presence of chlorophyll and solar energy.



$\text{C}_6\text{H}_{12}\text{O}_6$ is the empirical formula for hexose sugars containing 6 carbon atoms. There are six different isomeric hexoses, differing only by the spatial arrangement of the hydroxyl groups. Four of these occur naturally: glucose, mannose, fructose, and galactose. A popular way of writing sugar structures, demonstrating the ketone and aldehyde form, is as follows:



A few pentoses (5 carbon sugars) are found in nature such as:



Sugars form linkages with other sugars to form di- and tri-saccharides, and polysaccharides such as starch and glycogen.

Sucrose, the common table sugar, consists of one molecule of glucose and one molecule of fructose linked through the carbonyl groups. It is a disaccharide.

Starch is a polysaccharide composed of a large number of glucose units. It is the storage form

of glucose in plants and is the main source of food in the world. In man, glucose is stored as glycogen, another glucose polysaccharide. The size of the molecule, and therefore the molecular weight of a particular polysaccharide, may vary over a wide range; i.e., the number of units of sugar will vary. They are not homogenous substances. Polysaccharides differ from each other in the kind of repeating units of sugar, in the type of linkages, and in the degree of branching in the molecule.

The detection of glucose in the blood and in the urine may be qualitatively accomplished with Fehling's solution, a cupric ion complex, which oxidizes the carbonyl group of the sugar and precipitates brick-red cuprous oxide. This test is negative in sucrose because the carbonyl groups of both glucose and fructose have been bound. Sucrose is a nonreducing sugar, meaning it will not reduce Fehling's solution to cuprous oxide.

Cellulose is a glucose polysaccharide which forms the supporting structure of plants and is found in plant fibers such as cotton and flax. The synthetic fiber, rayon, is a cellulose.

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