CHEMISTRY and the CHEMICAL INDUSTRY

A Practical Guide for Non-Chemists

Robert A. Smiley, Ph.D.
Harold L. Jackson, Ph.D.

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Preface

The chemical industry affects virtually all aspects of our lives. Were it to disappear suddenly, we would find ourselves living again in the early nineteenth century without cars, airplanes, television, electric lights, most of our colorful clothing, most perishable food, most drugs and medicine, plastics, and all the rest of the modern conveniences that most of us take for granted.

Consider how the chemical industry contributes to your daily life. For example, when you get up in the morning, you brush your teeth using toothpaste, which is a mixture of chemicals squeezed from a plastic tube onto plastic bristles mounted in a plastic handle. You may take a shower using soap and shampoo, each made by the chemical industry, and finally dry, brush, or comb your hair with other articles made of plastic. While doing this, you will likely be looking into a mirror over a porcelain or cultured marble sink while standing on vinyl plastic floorcovering, tile, or carpeting, all of which are products of the chemical industry. The varnish coating the wooden floors of your house and the paint or wallpaper covering the walls are products of the chemical industry. At breakfast, it is likely that the kitchen counters and table are topped with plastic, as are the chairs. The refrigerator would not work without chemicals either for the refrigeration unit or the insulation in its walls. The interior is plastic lined and the exterior has a durable coating made possible by the chemical industry. Your breakfast food is probably fresh because it was treated with chemical preservatives and/or shipped in a box with a plastic lining. The car or bus that you go to work in is totally chemical dependent, from the anti-corrosion treatment of the metal, the protective paint and the plastic parts and tires to the chemical battery that starts the vehicle, the oil that lubricates it, and the gasoline that fuels it. And so it goes.

The fact that our daily lives are so dependent on the chemical industry does not appear to be widely recognized, even by those working in the chemical industry. And so, as companies are forced in a world economy to become more productive and more quality conscious, as well as having a greater concern for the environment, it becomes essential that their present and future employees understand the basic concepts upon which the chemical industry (indeed, our modern existence) is based. This book is designed to aid in that understanding by reviewing the important aspects of industrial chemistry in a way that can be understood even by those who have not taken any formal chemistry courses.

No mathematics is used and basic physical science is minimized. Why chemicals behave as they do is not explained. It is assumed that the end result of the manufacturing processes presented is the information wanted by the reader and not the science or engineering involved. If needed, the latter information can be obtained from listed sources.

The first chapter begins with a description of the chemical industry and its unique features and branches. The most common terms used in chemistry are defined, using nonscientific analogies where possible. In the following chapters, some basic organic chemistry is presented so that later descriptive explanations of the largest and most important products of the chemical industry can be better understood. The product descriptions include the raw material sources, manufacturing processes, and, of most importance, their commercial uses. Finally, there is a short compilation of general information sources.

The style of the book is to present only a small amount of information on each page with a slide-like illustration using short descriptions and easily understood chemical equations and structures. Under each illustration is additional information or comments with room for the reader to make notes if desired. Although there is obvious continuity, an attempt has been made to make each page subject somewhat independent so that readers can study the contents of the book one page at a time at their own pace. Of necessity, because of this format, there is considerable repetition. We do not consider this bad.

Robert A. Smiley
Harold L. Jackson

Authors

Robert A. Smiley, Ph.D. retired from the DuPont Company in 1990, after which he became an independent consultant in general industrial chemistry. Clients have included ICI, Westinghouse, Clorox, Arco, and many smaller chemical companies. Currently he consults for Dixie Chemical Company where he holds the title of corporate research fellow. He is also the president of Falcon Lab LLC, a company engaged in patent licensing. His fields of expertise include nitrile chemistry, diisocyanate and polyurethane chemistry, nitric acid oxidation, and nitration chemistry and explosives. For many years he gave sponsored seminars on industrial chemistry and polyurethane chemistry both in Europe and the U.S. He received a B.S. degree in industrial chemistry from Case Institute of Technology and a Ph.D. in organic chemistry from Purdue University and joined DuPont as a research chemist in 1954. After a number of successful assignments in the process development of polymer intermediates, he became a research supervisor and then moved on to other positions in technology licensing, business analysis and back to research as research associate and research fellow. He holds 26 U.S. patents and is the author or co-author of 13 publications.

Harold L. Jackson, Ph.D. has 51 years of experience in the chemical industry. After receiving a Ph.D. in organic chemistry from the University of Illinois in 1949, he joined DuPont's central research department where he made significant contributions in the areas of inorganic, organic, and polymer chemistry. He later moved to other research responsibilities in DuPont's chemicals and petrochemicals departments where he studied polymer synthesis and characterization, polymer intermediate development, and solvent chemistry. He has been involved in and assisted with marketing efforts on commercial products resulting from his research work. He retired in 1992 as a research fellow. Dr. Jackson holds 32 U.S. patents and is the author of numerous technical articles. In addition to his industrial activities, Dr. Jackson served as visiting professor of organic chemistry at the University of Kansas.

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1 Introduction

The objective of this chapter is to provide a basis for some understanding of chemistry and the chemical industry. Segments and characteristics of the industry together with important events in chemical history are briefly presented. The "language" of chemistry is introduced and important chemical terms are defined.

CHEMICAL AND ALLIED PRODUCTS INDUSTRIES

IMPORTANT SEGMENTS

Inorganic chemicals
Petrochemicals
Synthetic resins and plastics
Textile fibers
Synthetic rubber
Pharmaceuticals and drugs
Soap, detergents, and cosmetics
Paint, varnishes, and printing inks
Fertilizers and other agricultural chemicals
Adhesives and sealants
Dyes and pigments
Paper
Glass

In terms of total product value, the worldwide shipments of the chemical and allied products industries were almost 1600 billion dollars in 1999. In the U.S. alone, the value was 435 billion dollars (source: *Chemical & Engineering News*, June 26, 2000). The U.S. has the largest chemical economy by far of any country in the world, followed by Japan and Germany as distant second and third.

CHEMICAL INDUSTRY

CHARACTERISTICS

Large, diverse, and complex
Global
Strong technology base
Many segments, highly fragmented
Subject to business cycles
Highly competitive
Capital intensive
Committed to research and development
Advanced in use of computers and computer controls
Over 50% of the products are based on petroleum
Best employee safety record among all major industries
Criticized for many environmental problems

Because of the absolute necessity for chemicals in almost every manufacturing industry, it is difficult to define exactly what the chemical industry is. A good definition, however, is that the chemical industry consists of all companies engaged in converting raw materials obtained from the environment (air, ore, petroleum, trees, crops, etc.) into chemical intermediates plus the companies that convert these intermediates into consumer end products. Chemicals derived from petroleum or natural gas, known as *petrochemicals*, comprise about 55% of the total chemicals produced. Some of the globalization of the chemical industry now taking place is due to the shifting of production by petrochemical producers to energy-rich regions of the world such as Indonesia, Mexico, and the Middle East.

CHEMICAL INDUSTRY

THE BEGINNINGS

Pre-1600	Alchemists sought to turn base metals (iron, zinc, lead) into gold using the four “elements”— earth, fire, air, and water.
About 1600	The idea of the four “elements” was challenged and the chemical era began.
1600s	Robert Boyle worked out scientific experimental methods and published his findings (the scientific method).
1700s	Joseph Priestly discovered oxygen.
	Antoine Lavoisier distinguished between chemical and physical changes and enumerated and verified the fundamental law of the conservation of mass.
1800s	Dmitri Mendeleev published the Periodic Table of the Elements.

Ancient man (prehistoric–600 BC) practiced certain chemical arts such as extraction and working of metals, manufacture of leather, production of alcoholic beverages, and the use of vegetable oils, alkaloids, and narcotics. The Greek philosophers (600–200 BC) speculated on problems in the realm of what we now call chemistry, but they did little or no experimentation. In the Dark and Middle Ages, alchemy flourished and gradually evolved into an experimental science as the result of the thinking of men such as Roger Bacon (1214–1294), Paracelsus (1493–1541), and Francis Bacon (1561–1626). The birth of modern chemistry as an exact science, based on the law of the conservation of mass and on the quantitative study of chemical reactions, is dated from the work of Lavoisier.

CHEMICAL INDUSTRY

RESEARCH AND DEVELOPMENT/ENGINEERING TECHNOLOGY

- Important base for chemical industry:
  - R&D spending for 2000 was over $250 billion.
  - Most of the R&D in the U.S. is funded and carried out by the chemical industry.
  - High investment facilities required with modern (state-of-the-art) scientific equipment.
- R&D activities:
  - Basic chemical research (by trained chemists); much of this is done in universities
  - Improve existing products (e.g., better quality)
  - Improve existing processes (by chemists and engineers), including cost reductions
  - By-product disposal and utilization
  - Solution of environmental problems

The size of today's chemical industry is a result of research and development (R&D) activities that generated new products and processes resulting in rapid industry growth. Over the years, R&D emphasis shifted from basic research aimed at new chemicals and their uses to improvement of existing products and processes. Today, substantial R&D is directed toward solving problems related to the environment and to satisfying governmental regulations.

CHEMICAL INDUSTRY

HISTORY

Pre-1900	Cement, lye, soap, explosives, dyes, paint, fertilizer, chemicals based on coal
1920s–30s	Cellophane and rayon (based on wood), medicinals, photographic chemicals, nylon, plastics
1940s	Synthetic rubber, pesticides, plastic films, chemicals based on petroleum
1950s	Engineering plastics, preservatives, new catalysts
1960s	Foreign investment, lower prices, performance improvements, pollution awareness
1970s	Energy and feedstock problems, higher raw materials costs
1980s	Imports, environment, and health concerns
1990s	Global industry, governmental regulations

Industrial chemistry is barely 100 years old, but tremendous developments were made during that time because of advances in basic chemical and engineering science. These advances resulted from research efforts conducted within chemical industry laboratories as well as in university laboratories. During the 1950s, the nature of the industry changed from emphasis on development of totally new products to refinement of existing types of products. In recent years, product refinements have been guided by concerns about human health and protection of the environment.

LANGUAGE OF CHEMISTRY

- Chemical naming (nomenclature)
  - Systematic
  - *Chemical Abstracts* (American Chemical Society)
  - Common (historical)
  - "Nickname" (acronyms and trade names)
- Relationship of names to chemical structure
- Properties (chemical, physical)
- Chemical formulae (chemical shorthand)
- Pronunciation

To be knowledgeable in chemistry, one must be familiar with its language. This language includes the naming of chemicals, both systematic and common names, and the names and definitions of significant chemical and physical properties. The relationship of chemical names to chemical structures and formulae is also important. And, just as with any language, if one is to talk chemistry, it helps to be able to pronounce the names and other terms. Many of the terms and names needed to understand chemical "language" are introduced and defined throughout this book.

A major part in the language of chemistry is in learning the names of the chemicals (nomenclature). Many chemicals, particularly the more common ones, are known by several different names. For example, the chemical CH_3CH_2OH has the systematic name "ethanol." The publication *Chemical Abstracts* (American Chemical Society) also uses the name "ethanol." The historical or common name is "ethyl alcohol" or "grain alcohol." A "nickname" for it is just "alcohol," and there are various tradenames, depending on the manufacturer. For example, the Eastman Company sells it under the name of Tecsol®. Even trained chemists have trouble with nomenclature, which makes the use of and need for written chemical formulae common among chemists.

CHEMISTRY

PROPERTIES AND CHANGES

Properties	Characteristics of a substance
Physical properties	Observable characteristics such as density, color, smell, hardness, solubility, etc.
Chemical properties	Properties of a substance that cause specific behavior during chemical reactions
Chemical reaction	Any change that alters the chemical properties of a substance or forms a new substance
Reactants	The substances present at the beginning of a chemical reaction
Products	The substances formed in a chemical reaction

One of the important tasks of chemistry is to study how substances can be identified or distinguished from each other, that is, a study of properties. Such studies are also essential in determining how substances can be used in human endeavors.

There are two types of physical properties: *qualitative* properties and *quantitative* properties. Qualitative properties are those that cannot be measured, such as smell or taste. Quantitative properties, on the other hand, can be given precise mathematical values, for example, the weight of a certain volume of a substance (density), the temperature at which the substance boils (boiling point), or electrical conductivity.

Chemical properties depend on the ways in which a substance interacts (reacts) with other substances. Sulfuric acid reacts with iron to form iron sulfate and hydrogen.

$$\text{Iron} + \text{Sulfuric acid} \longrightarrow \text{Iron sulfate} + \text{Hydrogen}$$

This is a chemical reaction. The fact that iron reacts when it comes into contact with sulfuric acid is a chemical property of iron. Conversely, the ability of sulfuric acid to affect iron is a chemical property of sulfuric acid. The sulfuric acid and iron are called *reactants* in the above equation, and the iron sulfate and hydrogen are the *products* of the reaction.

CHEMISTRY

SUBSTANCE STATES

Solid state	The state (or phase) in which a substance has a definite volume and shape
Liquid state	The state in which a substance has a definite volume, but can change shape
Gaseous state	A state in which a substance has no definite volume or shape
Melting	The change of state from solid to liquid
Vaporization	A change of state from liquid to gaseous
Condensation	A change of state from gaseous to liquid
Sublimation	The change of state from solid to gaseous without going through the liquid state

A change of state is a physical change that does not alter chemical properties. It usually takes place by increasing or decreasing the temperature of a substance. The ability to change the state of substances is important in the synthesis and purification of chemicals.

Water from a tap is an example of a chemical in the liquid state, whereas ice is water in a solid state. When liquid water boils, it turns to steam, which is water in the gaseous state. A dripping icicle on a warm winter day is an example of melting, whereby the solid phase of water (ice) is converted back to the liquid state. Droplets of water forming on a cool surface is the result of condensation of gaseous water (steam) back to liquid water. Carbon dioxide, the gas in carbonated beverages, is known as dry ice when it is in the solid state. When dry ice is heated, it goes directly to a gas without first becoming liquid. This is sublimation.

CHEMISTRY

CHEMICAL SUBSTANCES

Matter	All substances
Element	A substance that cannot be split into simpler substances by a chemical reaction
Atom	The smallest particle of an element that retains the chemical properties of that element
Compound	A combination of two or more elements held together in some way. It has different physical and chemical properties from the elements it contains. The proportion of each element in a compound is constant, for example, the compound known as water always contains two atoms of hydrogen and one of oxygen
Molecule	The smallest particle of an element or compound that exists on its own and still retains its properties

All matter is composed of elements. Most matter contains two or more elements and some in the form of compounds contain thousands or even millions of atoms. Water, for example, is a compound that contains two elements: hydrogen and oxygen. The chemical compound we know as sugar contains three elements: carbon, hydrogen, and oxygen. Table salt is composed of the elements sodium and chlorine.

Mixtures are blends of two or more elements and/or compounds that are not chemically bound to each other. Mixtures can usually be separated by physical means.

CHEMISTRY

CHEMICAL REPRESENTATION

Chemical symbol	A way of expressing an *element* in written form. It represents one atom and often is the first one or two letters of the name of the element.
Molecular formula	A combination of symbols representing one *molecule* of an element or compound. It shows which elements are in the molecule and the number of atoms of each element.
Reaction equation	A written expression of a chemical reaction where the reacting chemicals are shown to the left of an arrow pointing to the products of the reaction on the right. Either words or formulae can be used.
Balanced equation	An equation using formulae where the number of atoms of each element involved in the reaction is the same on each side of the arrow.

The language of chemistry is understood better when the symbols of the more common elements are known, such as those shown on the following page. Use of these symbols provides a convenient shorthand method for chemists to represent molecular formulae. In these formulae, the subscript number following the atomic symbol denotes how many atoms of that element are in the molecule, for example, the formula for water is H_2O, which means each molecule of water contains two atoms of hydrogen (symbol H) and one atom of oxygen (symbol O).

The process (chemical reaction) by which a chemical product is made, as depicted by an equation, is called *synthesis*. Working in laboratories, chemists devise new ways to synthesize known chemicals or new chemicals never made before and not found in nature. Synthesis chemists working in industrial laboratories also must find or develop uses for the new chemicals that they synthesize while considering the costs of eventual manufacture.

CHEMISTRY

SYMBOLS OF COMMON ELEMENTS

O	Oxygen	A gaseous element essential to human life; comprises about 20% of the air
H	Hydrogen	The most abundant element in the universe
N	Nitrogen	Necessary element in protein; air is 80% N
C	Carbon	All living matter contains carbon compounds
Cl	Chlorine	Abundant element, always combined in nature with other elements
S	Sulfur	Occurs free in nature
Na	Sodium	Combined with other elements in nature
P	Phosphorous	Combined with other elements in nature; another element essential to life

Chemists know how much by weight of an element or a compound will react exactly with another element or compound because the atoms of each element have an assigned weight called the atomic weight. By scientific agreement, each element's atomic weight is proportional to that of carbon with an assigned weight of 12. In all chemical weight calculations, hydrogen has an atomic weight of 1 (the lightest element), while nitrogen is 14 and oxygen is 16. The molecular weight of a compound is the sum of the weights of all of the atoms in the compound as shown by its chemical formula; for example, the molecular weight of water with the formula H_2O is 2×1 (2 hydrogens) $+ 1 \times 16$ (1 oxygen), which totals 18.

It is desirable for chemical calculations to deal with weighable amounts of various substances that we know contain equal numbers of molecules. For example, the molecular weight of hydrogen is 2 and that of oxygen is 32. This means that 2 g of hydrogen contains the same number of molecules as 32 g of oxygen. These actual weights are called *gram-molecular weights* or *moles*, for short. Thus, a gram-molecular weight (or mole) of any chemical is the quantity of that chemical whose weight is numerically equal to its molecular weight. It has been determined that one gram-molecular weight of a chemical contains 6.023×10^{23} molecules (this is called Avogadro's number).

CHEMISTRY

DIVISIONS

Inorganic	The chemistry of all elements and their compounds except those containing carbon
Organic	The chemistry of all compounds containing carbon
Physical	Applies concepts of physics to chemical phenomena
Analytical	Chemical characterization and identification
Biochemistry	Chemistry of living organisms
Chemical engineering	Design and operation of equipment for the production of chemical products by the use of chemical reactions

No branch of science is broader than chemistry because it deals with all matter in all forms. For convenience, chemistry is usually divided into the above divisions, but there is a great overlap. For example, there are chemicals known that contain inorganic elements and large carbon compound fragments that can be classified as either inorganic or organic. Thus, trained chemists must have a background in all the divisions of chemistry although their work may be in a specialized area such as organic chemistry or analytical chemistry. In the chemical industry, chemical engineers are concerned with the production of bulk materials from basic raw materials by large-scale application of chemical reactions worked out in laboratories. In doing this, they make use of so-called *unit operations* of chemical engineering such as fluid flow, heat transfer, filtration, evaporation, distillation, drying, mixing, adsorption, solvent extraction, and gas absorption.

CHEMISTRY

GENERAL DEFINITIONS

Ion	An atom or group of atoms (molecule) with an electrical charge. Positively charged ions are called *cations* while negatively charged ions are called *anions*.
Acid	A compound containing hydrogen that dissolves in water to produce hydrogen ions. Hydrogen ions are positively charged.
Base	A compound that will react with (*neutralize*) hydrogen ions to produce water. It is the opposite of an acid. A water-soluble base is an *alkali*.
Salt	Substance in addition to water that is produced from the reaction of an acid with a base.
pH	A measurement of hydrogen ion concentration (*acidity*) in water. Pure water has a pH of 7. Acids have a pH less than 7 while the pH of bases is above 7.

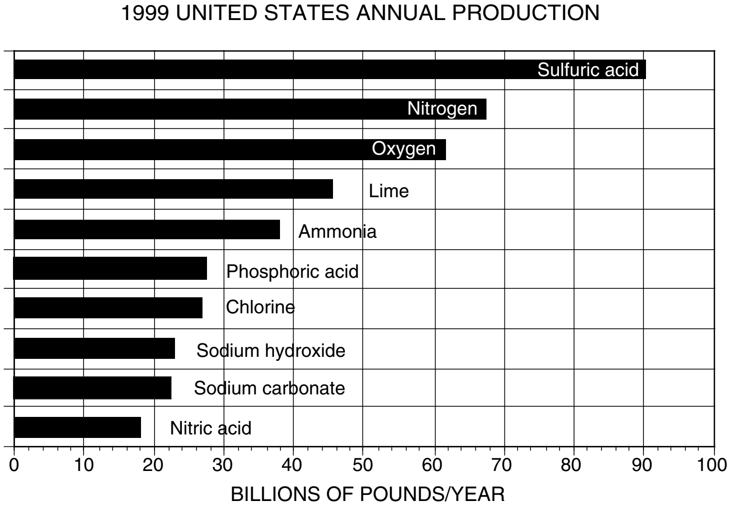
All chemicals, whether inorganic or organic, are either acidic, basic, or neutral. An example of an inorganic acid is sulfuric acid used in automobile batteries, while the acetic acid found in vinegar is an organic acid. Ammonia found in many household cleaners is a base, as are sodium carbonate and sodium hydroxide (lye). Sodium chloride (common salt) is an example of a salt because it is produced by the *neutralization* of hydrochloric acid with sodium hydroxide. A solution of table sugar in water is neutral (pH 7) because it does not contain hydrogen ions nor does it react with bases to produce water.

Control of pH is of critical importance in many industrial operations such as water purification, food and drug preservation, and agriculture.

2 Important Inorganic Chemicals

Inorganic chemicals are derived from minerals in the ground or from the air, not from living matter. Some idea about the importance of this branch of the chemical industry is illustrated by reviewing the ten largest production volume chemicals, their sources, and uses.

IMPORTANT INORGANIC CHEMICALS



The chemical industry is usually viewed as being primarily associated with *organic* (carbon-containing) chemicals, largely because everyday chemical industry products such as plastics, synthetic fibers, drugs, etc. are derived from organic starting materials. But *inorganic chemicals* are the real heart of the industry. If the production of large volume organic chemicals were included in the above list, only one, ethylene, would appear (between oxygen and lime). Four of the above ten are isolated directly or indirectly from the air we breathe, so inexhaustable supplies of those four are available from that source. The other six are also based on readily available, inexhaustable raw materials.

These chemicals have all been produced since the beginning of the chemical industry by various and sometimes changing processes. When process changes were made, it was almost always for economic reasons, that is, to make products at lower cost. It seems unlikely that still lower cost processes will be developed, but there may be future process changes for some of these chemicals because of environmental concerns.

SULFURIC ACID (H_2SO_4)

Also known as “oil of vitriol,” “battery acid,” “oleum”

Properties	100% sulfuric acid is a colorless, odorless, dense, oily, corrosive liquid. When added to water, the mixture becomes hot enough to boil. It is a very hazardous chemical to handle because it is corrosive to all body tissues.
Commercial grades	33.5% in water (battery acid), 62.18% in water (fertilizer acid), 77.67% in water (tower acid), 98% (laboratory reagent grade)
Uses	For making fertilizer, in petroleum refining, synthetic rubber and other plastics, copper leaching, manufacture of inorganic pigments, water treatment chemicals, paints, car batteries, etc.
Manufacture	$\underset{\text{sulfur}}{S} + \underset{\text{oxygen}}{O_2} \xrightarrow{\text{catalyst}} \underset{\text{sulfur dioxide}}{SO_2}$ $\underset{\text{sulfur dioxide}}{SO_2} + \underset{\text{oxygen}}{O_2} \xrightarrow{\text{catalyst}} \underset{\text{sulfur trioxide}}{SO_3}$ $\underset{\text{sulfur trioxide}}{SO_3} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{sulfuric acid}}{H_2SO_4}$
Suppliers	ASARCO, General Chemical, Arch Chemical, Colonial Chemical, Phelps Dodge, Kennecott Corp., Cytec Industries, El Dorado Chemical, many others.

Due to its versatile properties and low cost, sulfuric acid is the most important product of the chemical industry. It is involved somewhere in the production of almost all manufactured products. For many years, sulfuric acid production was used as an indication of the strength of a country’s economy, but now it is more indicative of a country’s agricultural vitality because of its high use in the manufacture of fertilizers.

Although very corrosive, it can be stored and shipped in steel or common alloys at commercial concentrations. In some chemical processes, it is used simply as an acid while in others it is used as a *dehydrating agent* to remove water, as an agent to increase the rate of a chemical reaction (catalyst), or as a solvent for reactions in which it remains unchanged. It rarely ends up in the final product. Waste sulfuric acid can be recycled.

Sulfur is a yellow, relatively low melting solid. Traditionally it has been obtained from underground deposits where it is melted in place with steam and then pumped out in a fairly pure state. Newer sources are metal ores or natural gas where the sulfur exists in a chemically combined state.

In the most common process for making sulfuric acid, sulfur is burned at a very high temperature in dry air to make sulfur dioxide, which is then reacted with more oxygen over a catalyst to make sulfur trioxide. Reaction of sulfur trioxide with water produces sulfuric acid.

NITROGEN (N_2)

Properties	Nitrogen is a colorless, odorless gas making up about 78% of the air. It can be liquified under pressure. At normal temperatures, it is unreactive (inert).
Commercial grades	Various purities (with respect to oxygen content) as gas or liquid.
Uses	Manufacture of ammonia, inert atmosphere for chemical reactions, metal treating, enhanced oil recovery, food processing (freezing), electronics.
Manufacture	Filtered air is compressed and cooled to remove water and carbon dioxide. The oxygen/nitrogen mixture is further cooled in a distillation column and the lower boiling nitrogen distilled from the higher boiling oxygen.
Suppliers	Air Liquide America Corp., Air Products, BOC Gases, Praxair.

Many of nitrogen's uses depend on the fact that it is chemically inert, that is, it does not readily react with other chemicals. The exception to this, and a very important exception, is its reaction with hydrogen at high temperature over a catalyst to make ammonia (NH_3). This is called *nitrogen fixation* and is one of the most important processes in the chemical industry because it provides the nitrogen contained in almost all synthetic chemicals containing chemically combined nitrogen and all nonorganic fertilizer. Thus, the nitrogen compounds, such as ammonia, that farmers use to stimulate crop growth come indirectly from the air.

INORGANIC NITROGEN COMPOUNDS

$H_2 + N_2 \xrightleftharpoons{\text{catalyst}} NH_3$	Ammonia
$NH_3 \xrightarrow{O_2} HNO_3$	Nitric acid
$NH_3 + HNO_3 \longrightarrow NH_4NO_3$	Ammonium nitrate (fertilizer)
$NH_3 + CO_2 \longrightarrow NH_2CONH_2$	Urea (fertilizer)
$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$	Ammonium sulfate (fertilizer)

Source of hydrogen

$$\underset{\text{natural gas}}{CH_4} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{synthesis gas}}{CO + H_2} \xrightarrow{H_2O} \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{hydrogen}}{H_2}$$

These equations show how nitrogen from the air ends up in so many other chemical products. It would be hard to imagine what the world would be like if no one had discovered how to convert nitrogen from the air to usable chemicals.

The hydrogen for reaction with nitrogen in the air is obtained by reacting methane (from natural gas found in underground deposits) with water, as shown in the above equation.

OXYGEN (O_2)

Properties	Oxygen is a colorless, odorless, and tasteless gas, that makes up about 21% of the Earth's atmosphere. It is essential to life for almost all living matter. It is found in nature in combination with all elements except the so-called rare gases (helium, argon, and neon). It can be liquefied under pressure.
Commercial grades	Shipped at a minimum 99.5% purity as a liquid in steel cylinders. Available as pure as 99.995%.
Uses	Metallurgy (e.g., making steel), metal fabrication, chemical manufacture, medical and life-support applications, sewage treatment, rocket propellant, paper bleaching.
Manufacture	By distillation of liquid air, the same as nitrogen. Most oxygen is used captively, less than 20% of production being sold on the merchant market.
Suppliers	Air Liquide America Corp., Air Products and Chemicals, BOC Gases, Praxair.

Chemical reactions in which oxygen atoms become attached to other elements are termed *oxidations*. Such reactions almost always result in the release of energy in the form of heat. Some oxidations are rapid, like the burning of wood or natural gas, with the evolution of heat and light. In this case, the oxygen combines with the carbon in the materials being oxidized (burned) to form carbon dioxide.

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{Heat}$$

Other oxidations, like the rusting of iron at room temperature, proceed slowly with a slow release of heat. In the case of iron, the final product is iron oxide (rust).

$$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$$

If iron is heated in pure oxygen to the point of rapid oxidation, a temperature high enough to melt concrete can be achieved. However, whether the oxidation goes slowly or rapidly, the amount of heat given off in the combination of the same amount of iron with oxygen is the same.

When oxygen is removed from a chemical compound in chemical reactions, instead of being added to it, the reactions are called *reductions*. Thus, oxidation and reduction can be considered to be opposite chemical processes.

LIME (CaO)

Also “quicklime,” “unslaked lime,” and “calcium oxide.” “Hydrated” lime is calcium hydroxide ($Ca(OH)_2$).

Properties	White to grayish-white solid. Reacts with water to form calcium hydroxide.
Commercial grades	Commercial lime is available in lump, pebble, ground, and pulverized forms.
Uses	One of the oldest commercial chemicals. Used in hundreds of applications. The most important uses are for making steel and chemicals, water treatment, pollution control, pulp and paper, and construction.
Manufacture	Limestone (calcium carbonate, $CaCO_3$) from mines or quarries is heated in a kiln (calcined). $\underset{\text{limestone}}{CaCO_3} \xrightarrow{\text{heat}} CaO + \underset{\text{carbon dioxide}}{CO_2}$
Suppliers	Barium & Chemicals, Bruchem, Chemical Lime Co., Coyne Chemical, Kraft Chemical, Austin White Lime Co., Cutler-Magner Co., Mississippi Lime Co., Los Angeles Chemical, others.

Lime has been manufactured for more than 2000 years and was the product of one of the first chemical processes used in the U.S. by the early settlers (the manufacture of rum being another). The many uses of lime are so varied that limestone and lime production are greater than any other natural substance. It is a low-cost commodity in the U.S. because there are limestone deposits in many parts of the country. Lime plants are always close to the limestone source in order to minimize freight costs.

AMMONIA (NH_3)

Properties	Ammonia is a colorless gas with a suffocating, pungent odor. It is readily liquefied under pressure. The gas is very soluble in water to produce ammonium hydroxide, also known as ammonia water or aqua ammonia.
Commercial grades	Shipped as a liquid in steel cylinders under pressure.
Uses	Mainly for the manufacture of nitric acid, urea, and ammonium salts, all of which are used in fertilizers and explosives. Urea is also used in the manufacture of plastics.
Manufacture	$\underset{\text{hydrogen}}{3H_2} + \underset{\text{nitrogen}}{N_2} \xrightleftharpoons{\text{catalyst}} 2NH_3$
Suppliers	There are dozens of suppliers, some of which are Air Products and Chemicals, Cytec Industries, LaRoche Industries, Coyne Chemical, Hill Brothers Chemical, and J.R. Simplot Co.

The production of ammonia is extremely important because of the need to grow ever-increasing amounts of food to feed the world's population. It was first recognized about 1840 that the application of nitrogen-containing chemicals such as nitrates to farmland substantially increases crop yields. There are no abundant nitrate ores from which nitrogen fertilizers can be made. However, in the early 1900s, a German named Haber demonstrated in his laboratory that normally unreactive nitrogen in the air can be combined with hydrogen under pressure over a catalyst to produce ammonia. The first plant to make ammonia by the *Haber process* was started in 1913. Haber received a Nobel Prize in 1919 for his work. About 75% of the synthetic ammonia produced is used in fertilizers, while 20% is used within the chemical industry. The other 5% goes into the manufacture of explosives and gunpowder.

PHOSPHORIC ACID (H_3PO_4)

Also “orthophosphoric acid”

Properties	Pure phosphoric acid is a colorless solid melting at 42°C. Soluble in all proportions in water. Commercial 85% phosphoric acid in water is a colorless, odorless, heavy liquid.
Commercial grades	75%, 89%, 85%, 105–117% in technical, food, and electronic grades.
Uses	The highest value inorganic acid marketed in the U.S. and second in value to sulfuric acid. Used primarily for the preparation of salts used as fertilizers (ammonium and calcium salts), water softeners and detergents, animal feeds, and baking powder. Food-grade phosphoric acid is used to acidify soft drinks, e.g., Coca Cola. Organic phosphates are used in flame retardants.
Manufacture	Mined phosphate rock is reacted with sulfuric acid. The product phosphoric acid is isolated as a 28–35% solution by filtering off the insoluble calcium sulfate co-product. $\underset{\text{phosphate rock}}{Ca_3(PO_4)_2} + \underset{\text{sulfuric acid}}{3H_2SO_4} \longrightarrow 2H_3PO_4 + \underset{\text{gypsum}}{3CaSO_4}$
Suppliers	Albright and Wilson, Coyne Chemical, FMC Corp., General Chemical, Hoechst, Monsanto, Rhone Poulenc, Texas Gulf, others.

The element phosphorus, like nitrogen, is essential to plant and animal life. Although phosphorus was not identified and isolated until 1669, phosphorus-containing materials have been used as fertilizers since ancient times, usually from bird droppings, fish, and bone. The first phosphoric acid was made by treating bone ashes with sulfuric acid. This marked the beginning of the commercial fertilizer industry. Eventually, mined phosphate rock, a poor fertilizer by itself, was substituted for bones as a raw material for phosphoric acid in the mid-1880s.

CHLORINE (Cl_2)

Properties	A greenish-yellow gas with a characteristic pungent odor. Forms compounds with virtually all elements. Strong oxidizer. Slightly soluble in water. Can be readily liquified under pressure. Very toxic.
Commercial grades	Shipped under pressure as a liquid in small and large steel cylinders, tank cars, barges, and pipelines.
Uses	Chlorine is used for water purification and in decreasing amounts for pulp and paper bleaching. Some is used for metallurgical purposes such as metal extraction. Its largest use is for the production of organic compounds used in plastics, pesticides, herbicides, refrigeration fluids, solvents, and others.
Manufacture	Co-produced with sodium hydroxide by the electrolysis of salt brine.

$$\underset{\text{sodium chloride}}{2NaCl} + \underset{\text{water}}{2H_2O} \xrightarrow{\text{electrical current}} 2NaOH + \underset{\text{hydrogen}}{H_2} + \underset{\text{chlorine}}{Cl_2}$$

Suppliers	Dow Chemical, OxyChem, PPG Industries, Formosa Plastics, Olin, Vulcan, Georgia Gulf, LaRouche Industries, Bayer, others.

Chlorine and sodium hydroxide are produced at the same time in a ratio to each other that cannot be changed. This is OK for the manufacturers as long as the demand for each of these products is the same. But that usually is not the case. If the demand for chlorine is low, producers decrease production because it is difficult to store chlorine. This causes sodium hydroxide to be in short supply, and prices rise, causing some users to turn to alternates such as sodium carbonate. When the demand for chlorine is high and sodium hydroxide is plentiful, prices for sodium hydroxide may fall if demand fails to meet supply.

Chlorine is used to make laundry bleach, such as Clorox, by dissolving chlorine in sodium hydroxide to give a weak solution of *sodium hypochlorite*. Sodium hypochlorite slowly releases an active form of oxygen, which reacts with many forms of soil and dirt to destroy them by oxidation. Sodium hypochlorite also rapidly destroys bacteria, viruses, and molds.

SODIUM HYDROXIDE (NaOH)

Commonly known and sold as "caustic soda"

Properties	Pure sodium hydroxide is a white crystalline solid. It dissolves in water with high evolution of heat and is a very strong base. It reacts with certain metals such as aluminum and zinc to produce hydrogen. Extremely hazardous chemical.
Commercial grades	Sold as a solid in pellet and flake forms in several purity grades. Commonly used in commerce as a 50% solution in water.
Uses	Chemical manufacture, soaps and detergents, petroleum, food processing, pulp and paper industry, water treatment, textile manufacture.
Manufacture	Electrolysis of salt brine: $\underset{\text{sodium chloride}}{2NaCl} + \underset{\text{water}}{2H_2O} \xrightarrow{\text{electrical current}} 2NaOH + \underset{\text{hydrogen}}{H_2} + \underset{\text{chlorine}}{Cl_2}$
Suppliers	Arch Chemicals, Brown Chemical, Coyne Chemical, LaRouche Industries, PPG Industries, FMC Corp., many others.

Sodium hydroxide is an important chemical raw material because it readily forms other chemicals (salts), that are soluble in water. It is a type of chemical referred to as a base. Bases are compounds, that react with acids to form water and a salt.

Soap is a salt made by reacting animal fats with lye, another name for a solution of sodium hydroxide in water. In the 1800s, the need for soap as the population expanded created a demand for sodium hydroxide. Thus, sodium hydroxide was another early product of the chemical industry. Other washing compounds can be made by treating phosphoric acid (or boric acid) with sodium hydroxide. Such reactions are called neutralizations, the chemical term for the reaction of an acid with a base to form a salt and water.

$$H_3PO_4 + 3NaOH \longrightarrow Na_3PO_4 + 3H_2O$$

Some metals that are chemically combined with oxygen (metal oxides) also dissolve in sodium hydroxide. For example, aluminum ore (known as bauxite) is treated with sodium hydroxide to isolate pure aluminum oxide, from which pure aluminum is obtained. Sand (silicon dioxide) will also dissolve in sodium hydroxide to form a chemical known as *sodium silicate* or *water glass*.

SODIUM CARBONATE (Na_2CO_3)

Commercially sold as "soda ash"

Properties	Sodium carbonate is a white, powdery solid moderately soluble in water to give a basic solution. It reacts with acids to produce a sodium salt and carbon dioxide.
Commercial grades	Available in many grades such as "lite," "dense," or "fine powdered" in bags and bulk.
Uses	Over 50% is used to make glass. Other uses include the preparation of chemicals (such as sodium silicate and sodium phosphate), soaps and detergents, in the pulp and paper industry, and in water treatment. Substantial amounts are exported.
Manufacture	About 95% of the sodium carbonate used in the U.S. is mined, primarily in Wyoming. The ore is known as "trona" and needs only to be heated to produce commercial "soda ash." Elsewhere in the world it is made by the "Solvay" process, which uses limestone and salt as raw materials. Calcium chloride is a by-product of the Solvay process.
Suppliers	FMC Corp., Solvay Minerals, General Chemical, OCI Wyoming, IMC, TG Soda Ash.

Less than half as much energy is needed to recover sodium carbonate from ores as it is to make it synthetically. The environmental impact is also less. However, because there is a limited distribution of natural soda ash in the world compared to the wide availability of salt and limestone, synthesis will continue to be a source of sodium carbonate outside the U.S.

Sodium carbonate undergoes many of the same reactions as sodium hydroxide, for example, the formation of salts when contacted with acids. In the case of sodium carbonate, carbon dioxide gas is formed along with water.

$$H_2SO_4 + Na_2CO_3 \longrightarrow Na_2SO_4 + H_2O + CO_2$$

In some processes where either sodium hydroxide or sodium carbonate can be used, the latter is sometimes preferred because less heat is liberated or the sodium carbonate costs less.

NITRIC ACID (HNO_3)

Properties	Pure 100% nitric acid is a colorless liquid when first prepared, but turns yellow when exposed to light. Has a choking odor. It is a strong, so-called oxidizing acid which under the right conditions will react energetically with virtually all organic compounds; will usually attack all metals except aluminum and some stainless steels. Very hazardous chemical.
Commercial grades	Reagent grade nitric acid is 68–71% in water. Grades over 80% are called "fuming" nitric acid. Special concentration blends are available.
Uses	The largest use is in the manufacture of fertilizers. It is also used to make one of the raw materials for nylon, virtually all gunpowder and explosives (nitroglycerin, nitrocellulose, TNT, ammonium nitrate, etc.) and the starting materials for polyurethane elastomers and paints.
Manufacture	Ammonia is burned over a catalyst to a mixture of nitrogen oxides which when reacted with water produces nitric acid. $\underset{\text{ammonia}}{NH_3} + \underset{\text{air}}{O_2} \longrightarrow \underset{\text{nitrogen dioxide}}{NO_2} + H_2O$ $NO_2 + H_2O \longrightarrow HNO_3$
Producers	Coyne Chemical, General Chemical, El Dorado Chemical, La Roche Industries, Los Angeles Chemical, J.R. Simplot Co.

Nitric acid is the principal reagent (chemical reactant) used to introduce nitrogen into other chemicals for not only the uses listed but also for dye and pharmaceutical intermediates, agricultural chemicals, and many others. This process is called *nitration*. Under conditions other than those used for nitration, nitric acid is used to introduce oxygen rather than nitrogen into a molecule, for example in the manufacture of adipic acid used to make nylon. This is an example of an oxidation reaction where the nitric acid behaves as an *oxidizer*.

HYDROGEN (H_2)

Properties	Hydrogen is the lightest and most abundant element. It is a colorless, odorless gas that can be liquefied under pressure. It is highly explosive when mixed with air and burns to produce only water.
Commercial grades	Supplied as liquid in steel cylinders and as a gas under pressure in pipelines.
Uses	Production of ammonia and methanol, refining of metals from oxide ores, petroleum refining, hydrogenation of fats and oils, preparation of higher alcohols, and other chemicals. Most of the hydrogen produced is used captively (i.e., by its producer).
Manufacture	$\underset{\text{natural gas}}{CH_4} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{synthesis gas}}{CO + H_2} \xrightarrow{H_2O} \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{hydrogen}}{H_2}$ The hydrogen is separated from the carbon dioxide by contacting the mixture with a liquid chemical (monoethanolamine), which absorbs the carbon dioxide. The latter can be recovered in high purity from the monoethanolamine.
Suppliers	Air Products and Chemicals, Air Liquide America, BOC Gases, Praxair.

The original source of hydrogen for chemical purposes is the splitting of water into its components (oxygen and hydrogen) with electricity (electrolysis); however, using hydrocarbons from natural gas or petroleum is less costly. Because hydrogen is so abundant, there is considerable speculation and research underway on ways to use it as an energy source, for example, in fuel cells to provide electricity for homes, buses, trucks, and automobiles. A *fuel cell* produces electricity when the hydrogen fuel combines with oxygen from the air. The exhaust is only water so fuel cells are *non-polluting*. In some applications, metal cylinders or tanks will be required to store the hydrogen under pressure.

3 Organic Chemistry

Originally, *organic chemistry* referred to the study of chemicals and chemical processes associated with living organisms. Now, however, it is the study of all carbon-containing compounds, with the exception of carbonate salts and carbon oxides which are still included in the study of inorganic compounds. There are well over two million known organic compounds, almost 20 times more than all the other known chemicals combined. This large number is due to the unique capacity of carbon atoms to combine with other carbon atoms to form chains or rings.

ORGANIC CHEMISTRY

The study of compounds containing the element carbon.

- Origin—compounds formed naturally by plants or animals.
- Wöhler (1828) synthesized urea (an organic compound found in human urine) from lead cyanate and ammonium hydroxide, neither of which are found in living matter.
- Organic vs. inorganic is a matter of definition rather than source.

Organic chemistry is the study of compounds containing carbon and one or more other chemical elements. Many years ago the term "organic" was given to those compounds known to be formed by plants or animals. However, in 1828, Frederick Wöhler synthesized urea (an organic compound produced by animal life) from two inorganic compounds, lead cyanate and ammonium hydroxide. This showed that organic compounds do not have to come from a natural source, and, now by definition, organic compounds are those compounds that contain carbon (with the exception of amorphous carbon, graphite, diamond, the gases carbon monoxide and carbon dioxide, metal carbonyls, and inorganic carbonates formed from carbon dioxide).

ORGANIC COMPOUNDS

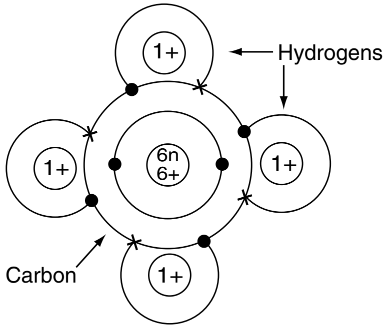
Greater than 95% of all known chemicals contain carbon. Carbon is unique because:

- Each atom combines with four other atoms
- Forms chains of atoms:
    - Open chains
    - Closed chains (rings)
    - Combination of open and closed chains
- Combines with atoms of other elements

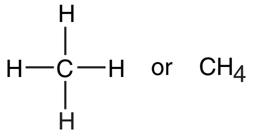
Organic compounds make up more than 95% of all the chemical compounds known to exist. One reason for this is that carbon is unlike all other elements. It can form chemical bonds to connect (become bonded) with four other atoms. This ability to connect with other atoms (form bonds) is called *valence*. Carbon is said to have a valence of 4. The most unique feature of carbon is that it readily forms bonds with other carbon atoms to form what are usually called *carbon chains*. It also readily bonds to other elements, particularly hydrogen, oxygen, and nitrogen.

In addition to forming open chains, closed chains, and combinations thereof, in recent years, it has been found that carbon atoms can even link together to form closed spheres, which have structures resembling soccer balls.

CARBON STRUCTURE



Methane



$$H{-}\overset{\displaystyle H}{\underset{\displaystyle H}{C}}{-}H \quad \text{or} \quad CH_4$$

n	Neutrons
+	Protons
●	Electrons (carbon)
x	Electrons (hydrogen)

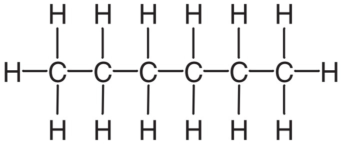
An atom is like a solar system with a heavy nucleus in the middle corresponding to the sun and electrons orbiting the nucleus corresponding to the planets. There are six neutrons and six protons in the nucleus of carbon and two electrons in an inner orbit and four electrons in an outer orbit. The outer orbit needs eight electrons to be stable. Thus, carbon will accept an electron from four other atoms to complete the needed eight. Hydrogen, with one available electron, needs one more electron to stabilize itself with two electrons. So, it can share its one electron with carbon and carbon can share one of its electrons with hydrogen. Thus, four hydrogen atoms, each with one electron, can satisfy the four electrons needed by carbon. The result is a stable simple organic compound known as methane.

The sharing of electrons between carbon and hydrogen is an example of atom to-atom bonding known as *covalency* and the two-electron bond is called a *covalent bond.*

CARBON CHAINS

Carbon atoms bond to each other to form chains, a process known as *catenation*. Open chains:

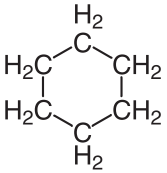
aliphatic compounds



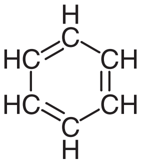
hexane

Closed chains or rings:

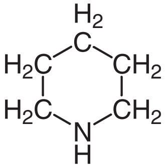
alicyclic or cycloaliphatic



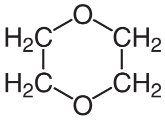
aromatic



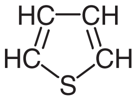
heterocyclic



piperidine



dioxane

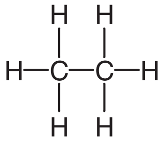


thiophene

Carbon atoms can link up (bond) with other carbon atoms. When two carbons, each with three hydrogens, bond together, it forms a compound called ethane, $H_3C–CH_3$. Carbon atoms like to bond together to form chains — a process called *catenation*. When the carbon chains are open chains, the compounds are called *aliphatic* compounds. Closed chains (rings) are called *alicyclic* compounds, or *cycloaliphatic* compounds. There are special ring compounds, known as aromatic compounds (Chapter 4), or rings containing other elements such as oxygen, nitrogen, or sulfur. Rings containing atoms other than carbon are called *heterocyclic* compounds.

CARBON–CARBON MULTIPLE BONDS

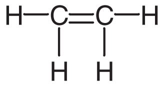
Single bond



$$H-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-H$$

ethane

Double bond



$$H-\underset{H}{C}=\underset{H}{C}-H$$

ethylene

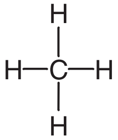
Triple bond $H-C\equiv C-H$ acetylene

Carbon likes to form bonds so well with itself that it can form multiple bonds to satisfy its valence of four. When two carbon atoms are linked with a single bond and their other valencies (three each) are satisfied by hydrogens, the compound is ethane. When two carbons are linked by a double bond (two covalent bonds) and their other valencies (two each) are satisfied by hydrogens, the compound is ethylene. When two carbons are linked by a triple bond (three covalent bonds) and their other valencies (one each) are satisfied by hydrogens, the compound is acetylene.

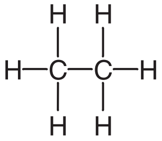
ALIPHATIC HYDROCARBONS

PARAFFINS (ALKANES, SATURATED HYDROCARBONS)

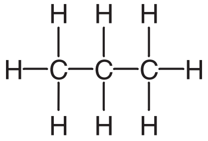
- Contain only carbon and hydrogen, thus the name "hydrocarbon"



- One carbon methane



- Two carbons ethane



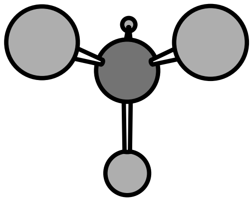
- Three carbons propane
- The general formula is C_nH_{2n+2}, differ by $-CH_2-$

The simplest of the aliphatic hydrocarbons are the paraffins, which are also known as alkanes or saturated hydrocarbons. Paraffins make up the major components of petroleum. The simplest paraffin is methane, CH_4. Next is ethane, C_2H_6; then propane, C_3H_8. Note that each of these differ by CH_2 and that the general formula is C_nH_{2n+2} where n is any whole number. Paraffins may be gases, liquids, or solids; for example, at room temperature and ordinary pressure, CH_4 to C_4H_{10} are gases, C_6H_{14} to $C_{16}H_{34}$ are liquids, and $C_{18}H_{38}$ and higher are waxes or solids.

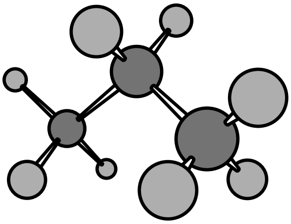
Gasoline is a mixture of aliphatic hydrocarbons containing 6 to 11 carbon atoms (C_6H_{14} to $C_{11}H_{24}$), while kerosene is a higher boiling mixture containing 12 to 16 carbons.

ALIPHATIC HYDROCARBONS

STRUCTURE



Methane molecule



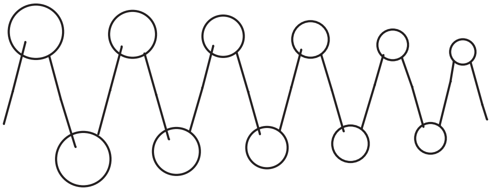
Propane molecule

The valence bonds of carbon have fixed directions and are equidistant in space, pointing from the center to the corners of a tetrahedron forming an angle of 109°. Thus, in propane, which we usually write as $CH_3{-}CH_2{-}CH_3$, the carbon atoms are not connected in a straight line, but are actually as shown in the above three-dimensional diagram.

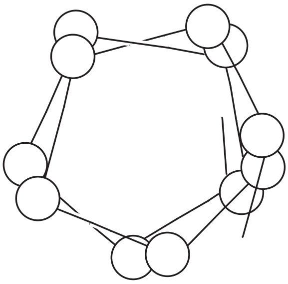
In longer chained hydrocarbons, the carbon atoms have a zig-zag structure. Also, it is important to note that the atoms are free to rotate about any single bond.

ALIPHATIC HYDROCARBONS

STRUCTURE: LONG HYDROCARBON CHAINS



Extended chain of carbon atoms



Coiled chain of carbon atoms

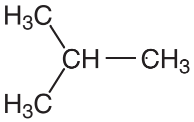
Because of the atoms’ freedom to rotate about single bonds, a chain of carbon atoms can achieve various positions in space. On one extreme is the zig-zag extended chain and on the other is a coil. Such spatial structures become particularly important in determining properties of very long chained compounds known as polymers (Chapter 5).

ISOMERS

Compounds with the same formula but with different structures are called *isomers.*

$CH_3—CH_2—CH_2—CH_3$

C_4H_{10}
normal butane (n-butane)



C_4H_{10}
isobutane (i-butane)

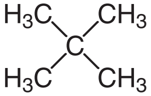
The paraffin hydrocarbon containing four carbon atoms is called butane, but two 4-carbon (C_4) paraffins are possible. The butane with its carbons in a line is known as normal butane or n-butane. The branched chain butane is isobutane or i-butane. Although each compound has the formula C_4H_{10}, they have different properties; for example, n-butane boils at –0.5°C while isobutane boils at −11.7°C. n-Butane and i-butane are *isomers* of each other. The straight-chain paraffin is always called the normal form.

ISOMERS

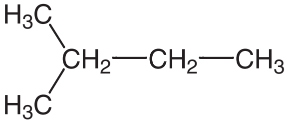
With five carbons in a hydrocarbon molecule, there are three isomers with the molecular formula C_5H_{12}:

$$CH_3—CH_2—CH_2—CH_2—CH_3$$

n-pentane

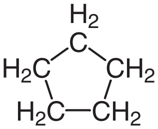


neopentane



isopentane

and a single ring of C_5H_{10}



cyclopentane

As the number of carbon atoms increases, the number of possible isomers becomes larger. Whereas there are only two isomeric butanes, there are three isomeric pentanes. With five carbons, in addition to the open-chain compounds shown, a stable ring compound known as cyclopentane is also possible. Five- and six-membered carbon rings are very stable because the bonds between carbon atoms in these size rings are close to the 109° angle preferred by carbon. Three- and four-membered hydrocarbon rings are also known, but they are less stable because of the required distortion of the bond angle.

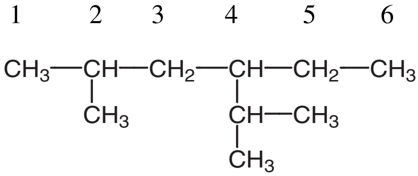
Note that whereas n-, neo-, and isopentanes have the same molecular formula, C_5H_{12}, and are therefore isomers, cyclopentane has the formula C_5H_{10}, and so is not an isomer of the open-chained pentanes.

PARAFFIN NAMES

CH_4	Methane
C_2H_6	Ethane
C_3H_8	Propane
C_4H_{10}	Butane
C_5H_{12}	Pentane
C_6H_{14}	Hexane
C_7H_{16}	Heptane
C_8H_{18}	Octane
C_9H_{20}	Nonane
$C_{10}H_{22}$	Decane
$C_{11}H_{24}$	Undecane
$C_{12}H_{26}$	Dodecane

The ending "ane" in the name denotes a paraffinic hydrocarbon. Alkyl groups are derived from these stand-alone molecules by the removal of one hydrogen. For example, a methyl group, $-CH_3$, is methane with one hydrogen removed. The hexyl group, $-C_6H_{13}$, is hexane with one hydrogen removed. Organic groups are not stand-alone molecules, but are always part of a molecule. The general term for a group derived from a paraffin is alkyl group. A general symbol sometimes used by chemists for an organic group is simply –R. The alkyl groups are named by replacing the "-ane" of the parent paraffinic hydrocarbon with the ending "-yl." Thus, ethyl is the alkyl group derived from eth*ane*, butyl is from but*ane*, decyl is from dec*ane*, etc.

PARAFFIN NAMES



2-methyl-4-isopropyl hexane

Name base: longest straight chain of carbon atoms
Numbered to give the lowest sum
The alkyl groups attached to the carbon base are methyl and isopropyl

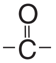
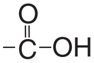
More complicated paraffinic hydrocarbons take their names from the longest chain of carbon atoms. In the name the atoms are numbered so that the sum of the atoms bearing substituent groups (side chains) is the lowest. The side chains (alkyl groups) are described as being attached to a numbered carbon atom. In the above example, the longest straight chain is six carbons, so the compound is a hexane with the isopropyl group attached to carbon atom 4 and the methyl group to carbon atom 2. Had the hexane chain been numbered in reverse, the compound would be 3-isopropyl-5-methyl hexane. However, because the sum of 2 + 4 is less than 3 + 5, the correct name is 2-methyl-4-isopropyl hexane.

PARAFFINS

Boiling Range	*Name*	*Carbons*	*Use*
65–212°F	Ligroin	C_5–C_7	Solvents
180–250°F	Naphtha	C_6–C_8	Paint thinner
160–390°F	Gasoline	C_6–C_{11}	Motor fuel
390–570°F	Kerosene	C_{12}–C_{16}	Heating
Above 570°F	Heavy oil	C_{13}–C_{18}	Fuel oil
	Lubricating oil	C_{16}–C_{20}	Lubricant
	Petroleum jelly	C_{18}–C_{22}	Pharmaceutical
	Paraffin wax	C_{20}–C_{30}	Candles
	Asphaltic bitumen	C_{36}–C_{40}	Asphalt, tar, coke

The chief sources of the paraffins are natural gas and petroleum. Petroleum (also called "crude oil") is a complex mixture of paraffins that can be separated by a process called distillation into fractions according to their boiling range. The C_1–C_4 paraffins under normal conditions are gases, C_5–C_{17} are liquids, and C_{18} and higher are solids. Paraffins serve many uses to help mankind. Perhaps most importantly, they are the building blocks from which most of our industrial organic chemicals are manufactured.

FUNCTIONAL GROUPS

Hydroxyl (alcohol)	–OH
Carbonyl (ketone, aldehyde)	 $-\overset{O}{\overset{\parallel}{C}}-$
Carboxyl (acid)	 $-\overset{O}{\overset{\parallel}{C}}-OH$
Nitrile (cyano)	–CN
Alkoxyl (ether)	–O–R (R is an alkyl group)
Halide (chloride, bromide, iodide)	–Cl, –Br, –I
Amino	$-NH_2$
Nitro	$-NO_2$

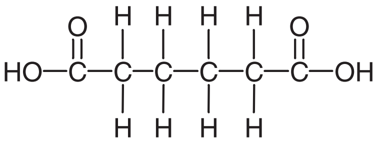
Other atoms or groups of atoms such as oxygen, nitrogen, and chlorine may be substituted for hydrogen in an aliphatic hydrocarbon. If a hydrogen in ethane is substituted with the hydroxyl group (–OH), it becomes ethyl alcohol. If the hydrogen is replaced by chlorine, the compound is ethyl chloride. Likewise, by replacing a hydrogen with an amino group ($-NH_2$), ethyl amine is formed. These groups substituted for a hydrogen are called *functional groups* because they determine most of the chemical properties (functions) of organic compounds.

FORMULAE

Empirical formula — simplest ratio of atoms in a molecule
Molecular formula — actual number of atoms in a molecule
Structural formula — shows the order of atom linkage

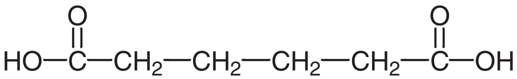
Example: The compound "adipic acid" is used to make nylon and as an acidulant in "Jello"

Empirical formula: $C_3H_5O_2$
Molecular formula: $C_6H_{10}O_4$
Structural formula:



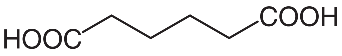
$$HO-\overset{\overset{O}{\|}}{C}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{O}{\|}}{C}-OH$$

$HO_2CCH_2CH_2CH_2CH_2CO_2H$



$$HO-\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}-OH$$

$HO_2C(CH_2)_4CO_2H$

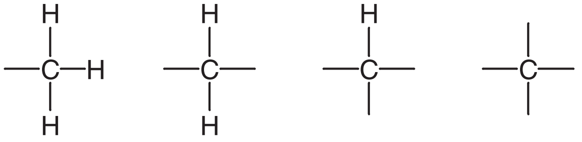


The intersection of lines in the above structural formula is understood to represent a $-CH_2-$

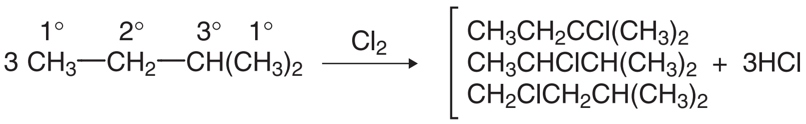
There are so many isomers possible in organic chemistry that molecular formulae alone are essentially useless. Structural formulae are the most useful, but, for ease in printing or writing, generally every bond is not shown. For example, the butanes can be written as $CH_3(CH_2)_2CH_3$ for n-butane and $CH_3CH(CH_3)CH_3$ for isobutane. Various ways of depicting the structural formula of adipic acid are shown above. Although these formulae may appear to differ, careful study shows that they all represent the same compound.

PARAFFINS: CHEMICAL PROPERTIES

TYPES OF CARBON ATOMS



primary (1°) secondary (2°) tertiary (3°) quaternary (4°)



$$\overset{1°}{3\,CH_3}-\overset{2°}{CH_2}-\overset{3°}{CH}\overset{1°}{(CH_3)_2} \xrightarrow{Cl_2} \left[\begin{array}{l} CH_3CH_2CCl(CH_3)_2 \\ CH_3CHClCH(CH_3)_2 \\ CH_2ClCH_2CH(CH_3)_2 \end{array}\right. + 3HCl$$

isopentane

In most paraffins there will be different numbers of hydrogens attached to the carbon atoms. There are four types of carbon atoms with names corresponding to the number of bonds made with other carbon atoms or functional groups. These names are primary, secondary, tertiary, and quaternary, as shown above. In a compound such as isopentane, there are three primary carbon atoms, one secondary, and one tertiary.

Chlorine reacts with a hydrocarbon by substituting for one or more hydrogens. The easiest hydrogen to remove in this manner is from a tertiary carbon, next a secondary, and the least readily from a primary carbon. Where more than one type of carbon is present, as in isopentane, a mixture of compounds containing chlorine will be produced.

PARAFFINS: CHEMICAL PROPERTIES

CHLORINATION

$$C_nH_{2n+2} + Cl_2 \longrightarrow C_nH_{2n+1}Cl + HCl$$

Chlorocarbons from Methane, CH_4

	Name	*Use*	*Boiling Point*
CH_3Cl	Methyl chloride	Refrigerant	–24°C (–15°F)
CH_2Cl_2	Methylene chloride	Paint stripper	45°C (104°F)
$CHCl_3$	Chloroform	Chem. intermed.	61°C (142°F)
CCl_4	Carbon tetrachloride	Chem. intermed.	77°C (175°F)

Paraffins react with chlorine under the influence of light, heat, or catalysts to form chlorocarbons. The chlorocarbons are important in industry because of their own properties and because of their use as chemical intermediates in the synthesis of other compounds. Today, many of the chlorocarbons are regulated by federal and state agencies to limit their use because of detrimental effects on health and the environment.

PARAFFINS: CHEMICAL PROPERTIES

Nitration

$$CH_3CH_2CH_3 \xrightarrow[HNO_3]{400°C} \left[\begin{array}{l} CH_3CH_2CH_2NO_2 \\ CH_3CH(NO_2)CH_3 \\ CH_3CH_2NO_2 \\ CH_3NO_2 \end{array}\right.$$

Oxidation

$$CH_4 + O_2 \longrightarrow CO_2 + 2H_2O$$

Pyrolysis or "Cracking"

$$2CH_3CH_2CH_3 \xrightarrow[500°C]{pressure} \begin{array}{l} CH_3CH{=}CH_2 + H_2 \\ +\ CH_2{=}CH_2 + CH_4 \end{array}$$

Isomerization

$$CH_3CH_2CH_2CH_3 \xrightarrow{catalyst} CH_3CH(CH_3)CH_3$$

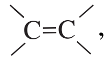
Paraffins react with nitric acid at high temperatures to form a mixture of nitroparaffins which find use as solvents.

Oxidation by reaction with oxygen in the air is a major use of paraffins. Paraffins are converted to more reactive compounds called olefins by "cracking" under pressure at high temperature.

An important reaction in the manufacture of gasoline is *isomerization* of straight-chain paraffins to more highly branched compounds, which have better fuel properties (higher octane rating).

UNSATURATED HYDROCARBONS

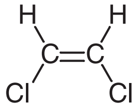
Olefins (alkenes):

- Contain only carbon and hydrogen
- Contain the group  , i.e., carbon atoms joined by two bonds
- The two bonds are called a *double bond*, and the compound is *unsaturated* because it contains less hydrogen atoms than the corresponding paraffin, which is considered *saturated* (with hydrogen)
- $CH_2{=}CH_2$ $CH_2{=}CHCH_3$ $CH_2{=}CHCH_2CH_3$
  ethylene propylene 1-butylene
- General formula is C_nH_{2n}

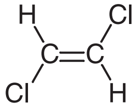
One of the most important reactions in the chemical industry is the "cracking" (removing hydrogen) of paraffins to form *olefins*. Olefins are essential starting materials for many common products that we all use, particularly plastics. The simplest olefin is ethylene, which can be *polymerized* (reacted many times with itself) to give *poly*ethylene used for bottles, dishware, film, etc. The next higher olefin, propylene, can be polymerized to polypropylene used in the manufacture of rugs, toys, kitchenware, and many other plastic objects. Note that the names of olefins end in -*ene*, which denotes the presence of a double bond in the compound.

OLEFINS

- Nomenclature: $CH_2{=}CHCH_2CH_3$ $CH_3CH{=}CHCH_3$
  1-butylene 2-butylene
  1-butene 2-butene
- Multiple double bonds
  $CH_2{=}CHCH{=}CH_2$
  1,3-butadiene or just "butadiene"
- Geometrical isomers



cis-1,2-dichloroethylene

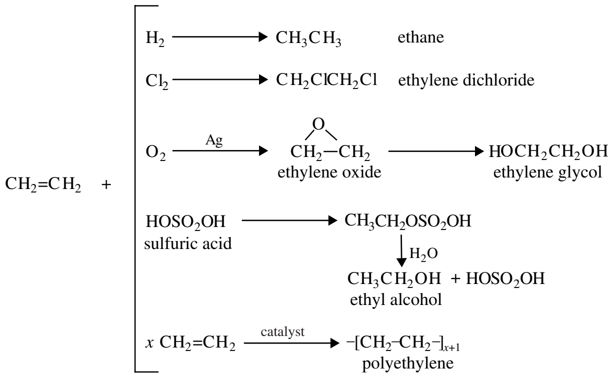


trans-1,2-dichloroethylene

In naming olefins, the prefix number indicates the lower numbered carbon atom involved in the double bond, numbering from one end of the molecule. Two or more double bonds in one molecule are possible with the number of double bonds indicated by "di-" for two double bonds, "tri-" for three, "tetra" for four, etc. before the "-ene" ending (e.g., butadiene). *Buta-* means four carbons and *diene* indicates the presence of two double bonds.

Because a double bond between two carbons prevents the carbons from rotating, isomers involving the atoms bonded to the carbons are possible, as shown above with dichloroethylene. Such isomers are called *geometrical isomers,* in contrast to the *structural isomers* discussed previously. When the substiuent groups are on the same side of the molecule, the compound is designated the "*cis-*" isomer. When the substituent groups are on the opposite side, the compound is the "*trans-*" isomer. Like all isomers, *cis-* and *trans-* isomers have the same molecular formula, but differ in certain physical and chemical properties. For example, *cis*-1,2-dichloroethylene boils at 60°C whereas *trans*-1,2-dichloroethylene boils at 48°C.

OLEFINS: CHEMICAL PROPERTIES



Olefins are very reactive compounds and, thus, are the starting materials for many products of the chemical industry. Shown above are some typical reactions for ethylene. Other olefins undergo similar reactions. The C_4 olefins recovered in petroleum refineries are used to make synthetic rubber, gasoline additives, plastics, and textile fibers.

UNSATURATED HYDROCARBONS

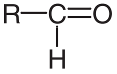
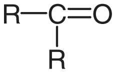
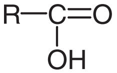
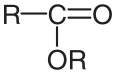
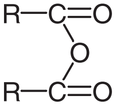
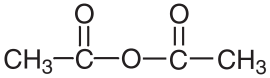
ACETYLENES (ALKYNES):

- Contain only carbon and hydrogen
- Contain the group –C≡C–, i.e., carbon atoms joined by three bonds
- The three bonds are called a triple bond, and the compound is unsaturated because it contains fewer hydrogen atoms than the corresponding paraffin, which is considered saturated (with hydrogen)
$HC\equiv CH$	$HC\equiv C–CH_3$
acetylene	methyl acetylene
ethyne	propyne
- General formula is C_nH_{2n-2}

Acetylenes contain at least one triple bond. The triple bond is even more reactive than a double bond and, therefore, acetylene is used industrially to make other compounds used in rubber and plastics. Acetylene burns in oxygen to produce a very hot flame used for welding and metal cutting (oxyacetylene torch).

Although the current source of acetylene is petroleum, it can be manufactured from calcium carbide, a product of the reaction of limestone and coke (carbon). During World War II, Germany, having a shortage of petroleum, used the latter technology to develop a chemical industry based on acetylene.

OXYGENATED ORGANIC COMPOUNDS

Class	*General Formula*	*Example*
Alcohols	$\mathrm{R{-}OH}$	Ethyl alcohol CH_3CH_2OH
Aldehydes	 $\mathrm{R-\underset{\underset{H}{\vert}}{C}=O}$	Acetaldehyde CH_3CHO
Ketones	 $\mathrm{R-\underset{\underset{R}{\vert}}{C}=O}$	Acetone CH_3COCH_3
Acids	 $\mathrm{R-\underset{\underset{OH}{\vert}}{C}=O}$	Acetic acid CH_3COOH
Esters	 $\mathrm{R-\underset{\underset{OR}{\vert}}{C}=O}$	Ethyl acetate $CH_3COOCH_2CH_3$
Ethers	$\mathrm{R{-}O{-}R}$	Diethyl ether $CH_3CH_2OCH_2CH_3$
Anhydrides	 $\begin{array}{l}\mathrm{R-C{=}O}\\ \quad\ \backslash\\ \qquad \mathrm{O}\\ \quad\ /\\ \mathrm{R-C{=}O}\end{array}$	Acetic anhydride  $\mathrm{CH_3-\overset{\overset{O}{\Vert}}{C}-O-\overset{\overset{O}{\Vert}}{C}-CH_3}$

Oxygen is a constituent of many organic compounds. The most common classes of these oxygen-containing compounds and examples of each are shown above. The letter R– is the shorthand symbol for an organic group such as methyl, ethyl, butyl, etc. The rest of the molecule is the functional group that characterizes the class of compound. For example, –OH (hydroxyl) is the alcohol functional group.

OXIDATION

Partial Oxidation of Paraffins

Paraffins	RCH_2CH_3
Alcohols	RCH_2CH_2OH
Aldehydes	RCH_2CHO
or ketones	$RCOCH_3$
Acids	RCH_2COOH

Increasing Oxidation

Complete Oxidation

$$\text{Organic compounds} + O_2 \longrightarrow CO_2 + H_2O$$

When sufficient oxygen is present, organic compounds can undergo complete oxidation (burning) with the formation of carbon dioxide and water. By controlling the oxidation reaction (i.e., by limiting the amount of oxygen), a series of intermediate oxidation products is obtainable. As the degree of oxidation of a paraffin hydrocarbon progresses, first an alcohol (–C–OH) is produced, then an aldehyde (–CH=O) or ketone ($-\underset{|}{C}=O$), then an acid (–COOH), and finally complete oxidation.

ALCOHOLS

Simple alcohols:

CH_3OH	CH_3CH_2OH	$CH_3CH_2CH_2OH$	$CH_3CHOHCH_3$
methyl alcohol (methanol) (wood alcohol)	ethyl alcohol (ethanol) (grain alcohol)	n-propyl alcohol (propanol)	sec-propyl alcohol (isopropanol) (isopropyl alcohol)

Isomeric alcohols:

Paraffin Isomer	*Type of Carbon Bond to* –OH	*Alcohol*
$CH_3CH_2CH_2CH_3$ n-butane	Primary	$CH_3CH_2CH_2CH_2OH$ 1-butanol
$CH_3CH_2CH_2CH_3$ n-butane	Secondary	$CH_3CH_2CHOHCH_3$ 2-butanol
$CH_3CH(CH_3)CH_3$ isobutane	Primary	$CH_3CH(CH_3)CH_2OH$ isobutyl alcohol
$CH_3CH(CH_3)CH_3$ isobutane	Tertiary	$(CH_3)_3COH$ tertiary butyl alcohol

If one of the hydrogens of a paraffin is replaced by an –OH group, the compound is called an alcohol. The –OH group is known as a *hydroxyl* group in organic chemistry (not to be confused with the hydroxide ion of inorganic chemistry). There are three types of alcohols, depending on how many hydrogens are on the carbon to which the –OH is attached: primary ($-CH_2OH$), secondary (–CHOH), and tertiary (–COH).

POLYALCOHOLS

Dihydric alcohol or glycol (two hydroxyl groups):

CH_2OHCH_2OH

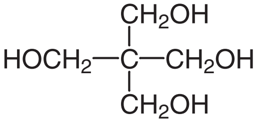
ethylene glycol

Trihydric alcohol (three hydroxyl groups):

$CH_2OHCHOHCH_2OH$

glycerine or glycerol (common name)

Tetrahydric alcohol:



$$HOCH_2-\underset{\displaystyle CH_2OH}{\overset{\displaystyle CH_2OH}{\underset{|}{\overset{|}{C}}}}-CH_2OH$$

pentaerythritol (common name)

There may be more than one hydroxyl group in an organic molecule. Polyalcohols are widely found in nature as all starchs and sugars are polyalcohols including sucrose (table sugar), and all fats, both vegetable and animal, are derivatives of glycerine.

Ethylene glycol is the principal ingredient in automobile antifreeze and is also used to make polyester textile fibers such as "Dacron." Glycerine is recovered as a by-product in the manufacture of soap and is used in cosmetics. Both glycerine and pentaerythritol are also used in the manufacture of paint and explosives.

MANUFACTURE OF ALCOHOLS

Methyl alcohol:

$$(1)\ \text{Wood} \xrightarrow{\text{heat}} CH_3OH$$

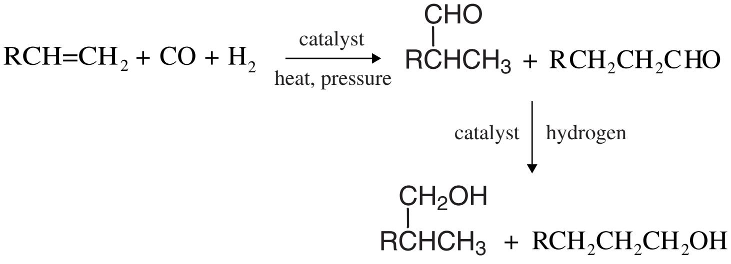
$$(2)\ CO + 2H_2 \xrightarrow[\text{heat, pressure}]{\text{catalyst}} CH_3OH$$

Ethyl alcohol:

$$(1)\ \text{Sugar} \xrightarrow{\text{yeast}} CH_3CH_2OH$$

$$(2)\ CH_2{=}CH_2 + \text{Sulfuric acid} \longrightarrow CH_3CH_2OSO_2OH \xrightarrow{\text{water}} CH_3CH_2OH + \text{Sulfuric acid}$$

Higher alcohols:

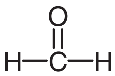


$$RCH{=}CH_2 + CO + H_2 \xrightarrow[\text{heat, pressure}]{\text{catalyst}} \overset{\displaystyle CHO}{\overset{|}{RCHCH_3}} + RCH_2CH_2CHO \xrightarrow[\text{catalyst}]{\text{hydrogen}} \overset{\displaystyle CH_2OH}{\overset{|}{RCHCH_3}} + RCH_2CH_2CH_2OH$$

The simple alcohols were originally prepared from natural products; e.g., the heating of wood in the absence of air (destructive distillation) produced methyl alcohol, hence the name "wood alcohol." It is now made from carbon monoxide and hydrogen at high temperature and pressure over a catalyst. Ethyl alcohol made by the fermentation of sugar in the presence of naturally occurring yeast (making of wine) goes back to the beginning of man's history. It is also made by the fermentation of grain or potatoes from which it gets the name of "grain alcohol." It is also made industrially by the reaction of ethylene with water using sulfuric acid as a catalyst. Higher alcohols are made by reacting olefins with carbon monoxide and hydrogen (a mixture called synthesis gas) to produce a mixture of aldehydes, which are then reacted with hydrogen gas over a catalyst to produce the corresponding alcohols. The latter reaction is called *hydrogenation*.

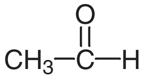
ALDEHYDES

Common aldehydes:



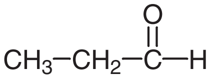
$H-\overset{\overset{O}{\|}}{C}-H$

formaldehyde



$CH_3-\overset{\overset{O}{\|}}{C}-H$

acetaldehyde



$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

propionaldehyde

Manufacture:

$CH_3OH + \text{Air} \longrightarrow HCHO + H_2O$

methanol formaldehyde

$CH{\equiv}CH + H_2O \longrightarrow CH_3CHO$

acetylene acetaldehyde

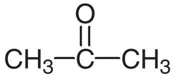
$CH_2{=}CH_2 + \text{Air} \longrightarrow CH_3CHO$

ethylene acetaldehyde

Aldehydes are characterized by a carbonyl group $(-\overset{|}{C}=O)$ at the end of a chain with the carbon of the carbonyl group also bonded to a hydrogen. Aldehydes can be considered to be a dehydrogenated (loss of hydrogen) or oxidized alcohol; for example formaldehyde is formed by the partial oxidation of methanol as shown above and acetaldehyde is formed by the partial oxidation of ethanol. Formaldehyde is a gas and is important as a fumigant. Dissolved in water, it (formalin) is used as a germicide, perservative, and embalming agent. It is also a widely used intermediate in the manufacture of certain plastics and adhesives. Acetaldehyde, a liquid, is an intermediate in the manufacture of acetic acid and acetic anhydride, both important industrial chemicals.

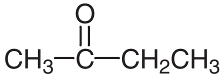
KETONES

Common ketones:



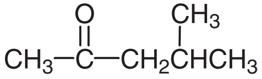
$CH_3-\overset{\overset{O}{\|}}{C}-CH_3$

Acetone



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3$

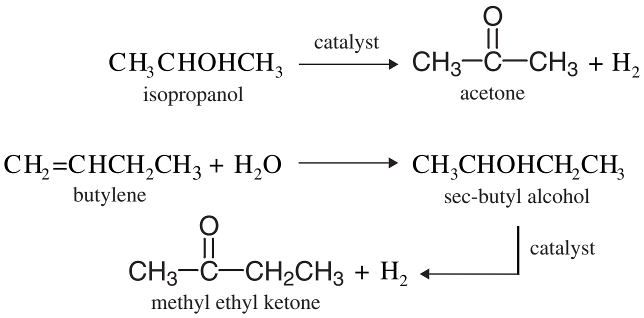
metyl ethyl ketone



$CH_3-\overset{\overset{O}{\|}}{C}-CH_2\overset{\overset{CH_3}{|}}{C}HCH_3$

methyl isobutyl ketone

Manufacture:



$$CH_3CHOHCH_3 \xrightarrow{\text{catalyst}} CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + H_2$$

$$CH_2{=}CHCH_2CH_3 + H_2O \longrightarrow CH_3CHOHCH_2CH_3$$

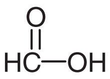
$$CH_3CHOHCH_2CH_3 \xrightarrow{\text{catalyst}} CH_3-\overset{\overset{O}{\|}}{C}-CH_2CH_3 + H_2$$

Ketones are characterized by carbonyl groups anywhere in a chain except at the end, and the carbonyl carbon is bonded only to other carbons. Ketones are particularly important as solvents in paints, particularly methyl ethyl ketone and methyl isobutyl ketone. Most have a penetrating odor and are highly flammable.

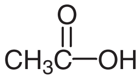
They are also important chemical intermediates. For example, acetone is used to make methyl methacrylate (the starting material for “Plexiglas” and “Lucite” plastics), methyl isobutyl ketone, and Bisphenol A (used in epoxy and polycarbonate resins).

ACIDS

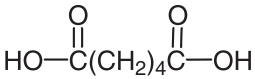
Common acids:


$\mathrm{HC(=O){-}OH}$

formic acid


$\mathrm{CH_3C(=O){-}OH}$

acetic acid

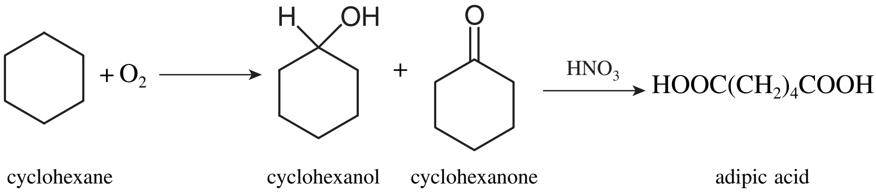

$\mathrm{HO{-}C(=O)(CH_2)_4C(=O){-}OH}$

adipic acid

Manufacture:

$$\underset{\text{acetaldehyde}}{\mathrm{CH_3CHO}} + \text{Air} \longrightarrow \underset{\text{acetic acid}}{\mathrm{CH_3COOH}}$$

$$\underset{\text{methanol}}{\mathrm{CH_3OH}} + \mathrm{CO} \longrightarrow \underset{\text{acetic acid}}{\mathrm{CH_3COOH}}$$



Organic acids, known as carboxylic acids, contain the carboxyl group, COOH. They behave as acids, $\mathrm{CH_3COOH \rightleftharpoons CH_3COO^- + H^+}$ in water and form salts when reacted with an alkaline or basic material such as sodium hydroxide. In salt formation, the hydrogen of the –OH group is replaced by a cation. Most carboxylic acids give a weak acid response in water, but some (e.g., $\mathrm{Cl_3C{-}COOH}$) approach the acidity of inorganic acids.

Carboxylic acids with one acid group are known as *monobasic* acids while those with two acid groups are *dibasic* acids. All acids with more than one acid group are in the class of *polybasic* acids. The simplest organic acid, formic acid, is responsible for the irritation of bee and ant stings. Vinegar is a 5% solution of acetic acid in water. The acetic acid is responsible for the characteristic sour taste. Citric acid, found in citrus fruits and used in soft drinks, is a tribasic acid with three carboxylic acid groups. The dibasic acid, adipic acid, is a major component of nylon.

ACIDS

Reactions:

Salt formation

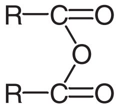
$$R{-}COOH + NaOH \longrightarrow R{-}COONa + H_2O$$

Acid chlorides

$$R{-}COOH + PCl_5 \longrightarrow R{-}COCl + HCl + PCl_3$$

Acid anhydrides

$$R{-}COONa + R\text{-}COCl \longrightarrow$$



$$+ NaCl$$

Esters

$$R{-}COOH + R'{-}OH \longrightarrow R\text{-}COOR' + H_2O$$

A few of the important reactions carboxylic acids undergo are shown above. Soap is made by reacting sodium or potassium hydroxide with long-chain acids such as $C_{17}H_{35}COOH$ (stearic acid). Acid chlorides and acid anhydrides are more reactive than their corresponding carboxylic acids and are used in the chemical industry to make various acid derivatives. A very important industrial reaction is the reaction of carboxylic acids (or the chlorides or anhydrides) with alcohols to form esters.

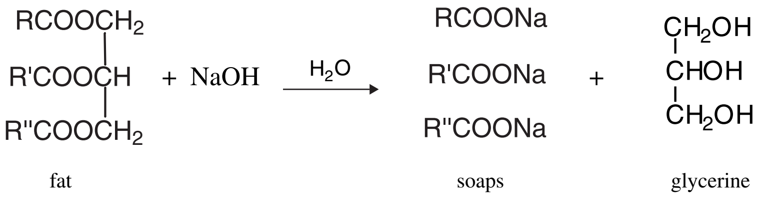
ESTERS

Esters are the reaction product of an acid and an alcohol with the simultaneous formation of water.
Some esters with fruity odors:

$CH_3COOC_4H_9$	butyl acetate	pear
$CH_3COO(CH_2)_2CH(CH_3)_2$	isoamyl acetate	banana
$CH_3CH_2COOCH_2CH(CH_3)_2$	isobutyl propionate	rum
$C_3H_7COOC_4H_9$	butyl butyrate	pineapple

Note that ester names contain first the alcohol, then the acid portion and end in *-ate*. Thus, the ester from the reaction of ethanol with acetic acid is called ethyl acetate.

The whole range of carboxylic acids and alcohols can be reacted to form esters. They are found in a large number of natural and synthetic scents and perfumes because of their pleasant odor. Many are used as solvents for paints and resins. Esters are converted back into the original acids and alcohols by reaction with strong bases in water in a process called *saponification* (soap formation),



or by *hydrolysis* (which means splitting by water).

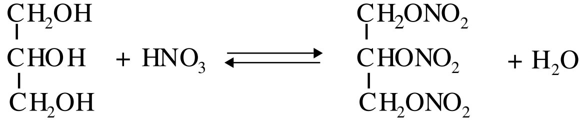
$$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + CH_3CH_2OH$$

ESTERS

Esters from inorganic acids

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{sulfuric acid}}{H_2SO_4} \rightleftharpoons \underset{\text{ethyl sulfate}}{C_2H_5OSO_3H} + H_2O$$

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{nitric acid}}{HNO_3} \rightleftharpoons \underset{\text{ethyl nitrate}}{C_2H_5ONO_2} + H_2O$$



$$\begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} + HNO_3 \rightleftharpoons \begin{array}{l} CH_2ONO_2 \\ | \\ CHONO_2 \\ | \\ CH_2ONO_2 \end{array} + H_2O$$

glycerine

nitroglycerine
(glycerine trinitrate)

Alcohols form esters from inorganic acids as shown above. Like all esterifications, these reactions are reversible; that is, in the presence of water and the right conditions, they revert to the original alcohol and acid. Nitrate esters are mainly used as explosives, but some have found use as diesel fuel additives. Note the difference between a nitrate ester such as ethyl nitrate ($C_2H_5ONO_2$) and an organic nitro compound such as nitroethane ($C_2H_5NO_2$).

ETHERS

R–O–R

Manufacture:

$$2CH_3CH_2OH \longrightarrow CH_3CH_2{-}O{-}CH_2CH_3 + H_2O$$

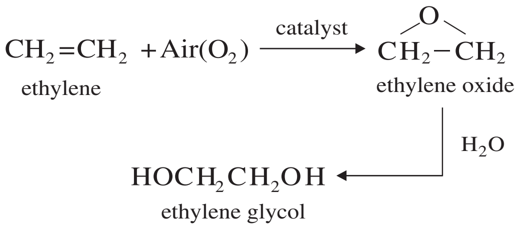
ethyl alcohol ethyl ether

Reactions:

$$CH_3{-}O{-}C_3H_7 + HI \longrightarrow CH_3I + C_3H_7OH$$

methyl propyl ether methyl iodide propanol

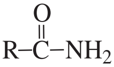
Epoxides (cyclic ethers):



Ethers contain the characteristic linkage –C–O–C–, that is, an oxygen bonded to two carbons. Ethers can be thought of as alcohols in which the hydrogen of the alcohol group is replaced by an alkyl group. The most common ether is ethyl ether, an extremely flammable liquid boiling just above room temperature. It was used for many years as an anesthetic for medical procedures because it causes unconsciousness when breathed, but it has now been replaced by safer chemicals. The simplest ether, methyl ether, is a gas used in certain aerosol sprays. The ether linkage in straight-chain compounds is quite stable, but it can be chemically broken by heating with acids such as hydrogen iodide (HI).

Epoxides are cylic ethers which are highly reactive because of the strained bond angles of a three-membered ring. Because of the high reactivity of epoxides, they are the starting materials for so-called epoxy resins used for high-strength adhesives.

NITROGEN-BASED ORGANIC COMPOUNDS

Class	*General Formula*	*Example*
Amines	$R{-}NH_2$	$CH_3{-}NH_2$ methyl amine
Nitro compounds	$R{-}NO_2$	$CH_3CH_2NO_2$ nitroethane
Nitriles	$R{-}CN$	$CH_3{-}CN$ acetonitrile
Isocyanates	$R{-}N{=}C{=}O$	$CH_3{-}NCO$ methyl isocyanate
Amides	 $R{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}NH_2$	CH_3CONH_2 acetamide

The most important element in organic chemistry after carbon, hydrogen, and oxygen is nitrogen. Generally, nitrogen behaves in organic compounds as if it has a valence of three; that is, each nitrogen is bonded to three other atoms. Amines are derivatives of ammonia (NH_3). Nitro compounds are based on oxides of nitrogen, for example, nitrogen dioxide (NO_2), which is also used to make nitric acid. Nitriles are derivatives of hydrogen cyanide (HCN). Isocyanates contain the group $-N{=}C{=}O$ and are highly reactive, for example, with water. Amides are formed by the reaction of carboxylic acids or their derivatives with ammonia or amines.

AMINES

NH_3	CH_3NH_2	$(CH_3)_2NH$	$(CH_3)_3N$
ammonia	methylamine	dimethylamine	trimethylamine
	(primary)	(secondary)	(tertiary)

Amines are basic and form salts with acids

$$CH_3NH_2 + HCl \longrightarrow \underset{\text{methylamine hydrochloride}}{CH_3NH_4Cl}$$

Tertiary amines react with alkyl halides to form *quaternary ammonium salts*

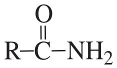
$$(CH_3)_3N + CH_3Br \longrightarrow \underset{\text{tetramethylammonium bromide}}{(CH_3)_4N^+ Br^-}$$

Organic derivatives of ammonia are called amines. Because nitrogen is trivalent, amines can be primary (attached to one carbon), secondary (attached to two carbons), or tertiary. All amines are basic, and their strength as bases increases with the number of alkyl groups attached to the nitrogen; that is, methyl amine is a stronger base than ammonia and trimethylamine is stronger than dimethylamine. Amines can be prepared from ammonia and an alkyl halide:

$$\begin{tikzcd} C_2H_5Br + NH_3 \arrow[r] & C_2H_5NH_3Br \arrow[dl, "NaOH"] \\ C_2H_5NH_2 + NaBr + H_2O & \end{tikzcd}$$

The alkyl halide (ethyl bromide in the above equation) can react further with the primary amine produced to give a secondary amine and with that to form a tertiary amine and finally a quaternary ammonium salt. Quaternary ammonium hydroxides are very strong bases like sodium hydroxide. Tetramethylammonium hydroxide is a very important chemical used in the manufacture of semiconductors and other electronic industry products.

AMIDES

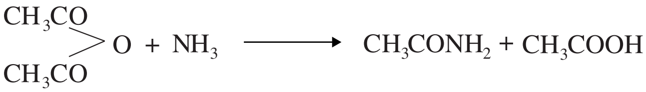


$$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$$

Manufacture:

$$CH_3COOH + NH_3 \longrightarrow \underset{\text{acetamide}}{CH_3CONH_2} + H_2O$$

$$CH_3COCl + NH_3 \longrightarrow CH_3CONH_2 + HCl$$



$$(CH_3CO)_2O + NH_3 \longrightarrow CH_3CONH_2 + CH_3COOH$$

$$CH_3COOC_2H_5 + NH_3 \longrightarrow CH_3CONH_2 + C_2H_5OH$$

When the –OH of a carboxylic acid is replaced by an $-NH_2$, the compound produced is an *amide*. Amides are neutral to mildly basic compounds. They can be made from acids, acid chlorides, acid anhydrides, and esters by reaction with ammonia or primary and secondary amines. The amide linkage is found in polyamide resins such as nylon.

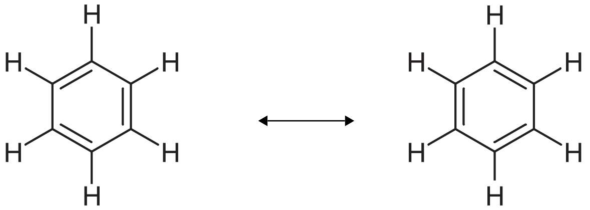
Urea, NH_2CONH_2, is the diamide of carbonic acid, $(HO)_2CO$, and is manufactured in large volume for use in fertilizers and plastics by the reaction of carbon dioxide and ammonia.

4 Aromatic Organic Chemistry

Aromatic organic chemistry is a special branch of organic chemistry because the six-membered carbon rings that define aromatic compounds are exceptionally stable and act as central supports to which other groups can be attached. The name "aromatic" was given to early isolated examples of these compounds because they have characteristic odors.

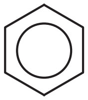
AROMATIC ORGANIC CHEMISTRY

Aromatic chemistry is the chemistry of six-membered carbon rings typified by the parent one-ring compound.



BENZENE

Although the above structures satisfy the molecular formula, double bonds do not in reality exist in aromatic compounds. Thus, aromatic rings are usually depicted by a hexagon with a circle in it. It is understood that a hydrogen is at each corner.



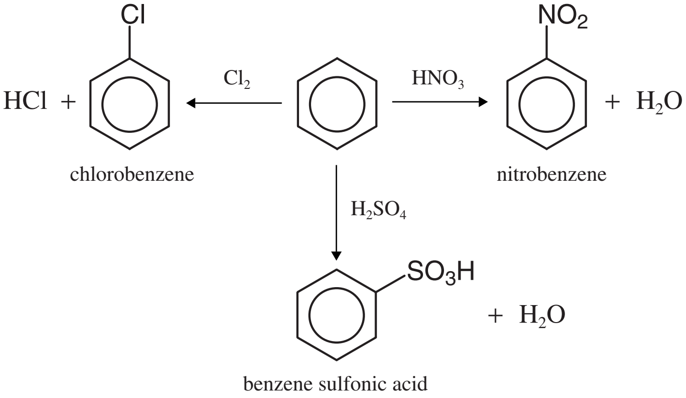
Benzene and related aromatic compounds were first isolated from the gases given off during the heating of coal in the absence of air to produce a form of carbon known as coke, used in the manufacture of steel. That benzene had the molecular formula C_6H_6 was determined in 1825, but it took over a hundred years to prove its structure even though its correct structure was suggested in 1865.

The chemical reactions of benzene and all aromatic compounds, with few exceptions, are unlike those of *unsaturated* aliphatic compounds (olefins); that is, addition reactions do not occur. Instead, the hydrogens on the ring are replaced by other atoms or groups of atoms. The aromatic ring remains unchanged by these *substitution* reactions. All six of the hydrogens in benzene can be replaced by other atoms.

AROMATIC ORGANIC CHEMISTRY

SUBSTITUTED BENZENES

When one hydrogen is replaced in an aromatic compound such as benzene, it is called mono-substitution.



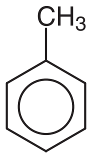
In most cases, the mono-substituted compounds are named as derivatives of benzene.

Replacement of a hydrogen of benzene by chlorine is termed *chlorination*. When one or more hydrogens are replaced by an "$-NO_2$" (nitro group), it is called *nitration*. Reaction of benzene with sulfuric acid, a reaction known as *sulfonation*, leads to a sulfonic acid. Note that in each substitution reaction, a small hydrogen-containing compound is formed.

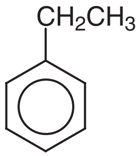
An organic compound can be both aromatic and aliphatic; that is, one or more of the hydrogens of a benzene ring can be replaced by an aliphatic group. Such compounds are always classified as being aromatic.

AROMATIC ORGANIC CHEMISTRY

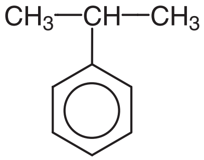
Substituted Benzenes



methylbenzene (toluene)

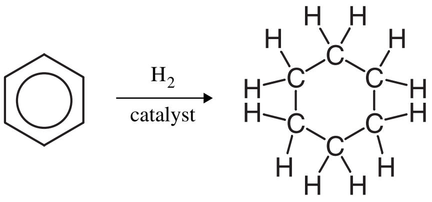


ethylbenzene



isopropylbenzene

Aromatic compounds can be converted to totally aliphatic compounds by reaction with hydrogen.



benzene cyclohexane

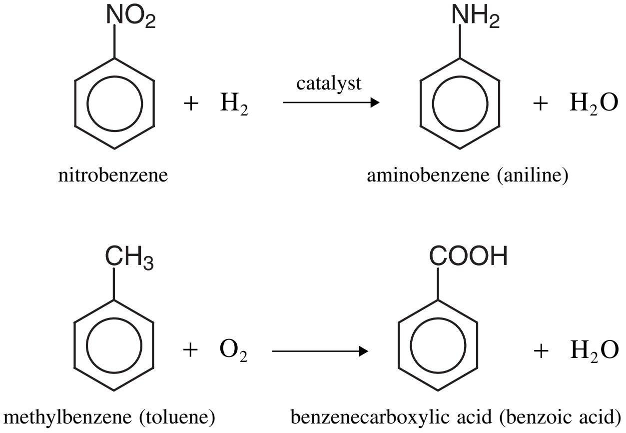
Replacement of an aromatic hydrogen by an aliphatic group is called *alkylation* and the attached group is called an *alkyl* group. Industrially, benzene is alkylated by reaction with an olefinic hydrocarbon such as ethylene to make ethylbenzene, or with propylene to produce isopropylbenzene. The replaced benzene hydrogen becomes part of the attached group.

Reaction of benzene with hydrogen is one of the few cases in which benzene reacts like an aliphatic *olefin*, that is, the hydrogen appears to react as if discrete double bonds were present.

AROMATIC ORGANIC CHEMISTRY

SUBSTITUTED BENZENES

Groups attached to aromatic rings undergo reactions similar to the same groups in aliphatic compounds although the conditions required may be different.

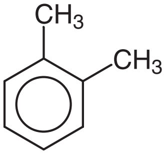


When aromatic compounds are reacted with hydrogen, the catalyst used determines which part of the molecule reacts. Thus, with the right catalyst, a *nitro group* can be converted to an *amine* without adding hydrogen to the ring. In this case the simplest aromatic amine (aniline) is produced.

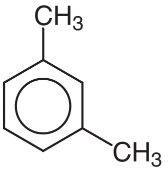
Methyl groups attached to benzene rings can be reacted with oxygen to produce aromatic carboxylic acids. Benzoic acid, the parent aromatic acid, finds wide use as a food preservative and in metal corrosion inhibitors. Aspirin and saccharin are derivatives of benzoic acid.

AROMATIC ORGANIC CHEMISTRY

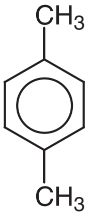
SUBSTITUTED BENZENES



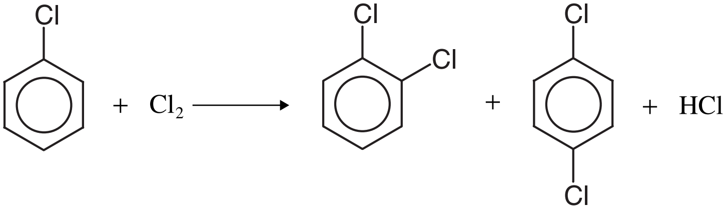
1,2-dimethylbenzene
(*ortho*-xylene)



1,3-dimethylbenzene
(*meta*-xylene)



1,4-dimethylbenzene
(*para*-xylene)



chlorobenzene

1,2-dichlorobenzene
(*ortho*)

1,4-dichlorobenzene
(*para*)

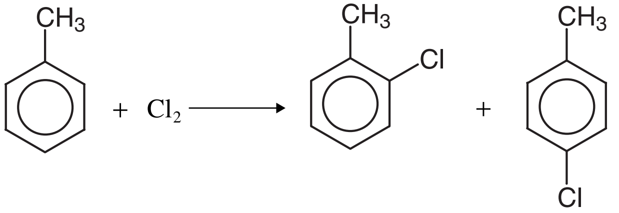
The dimethylbenzenes (xylenes) are very important industrial chemicals recovered during the refining of petroleum. All three xylenes are used to produce the corresponding aromatic dicarboxylic acids by reaction with oxygen over a catalyst.

ortho-Dichlorobenzene is a colorless liquid while *para*-dichlorobenzene (moth balls) is a crystalline white solid.

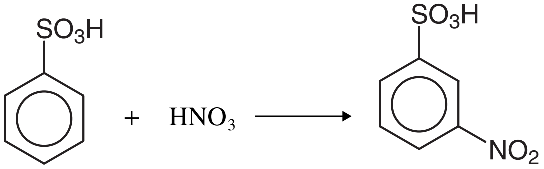
AROMATIC ORGANIC CHEMISTRY

SUBSTITUTED BENZENES

Different groups can be attached to an aromatic ring, for example:



toluene 2-chlorotoluene 4-chlorotoluene



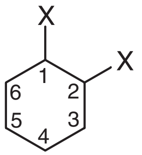
benzenesulfonic acid 3-nitrobenzenesulfonic acid

When the two groups in *disubstituted* benzenes are different, the same three isomers are possible that are possible when the substituents are the same. Compounds with two different substituents are usually named as positional derivatives of a monosubstituted (parent) compound. Above, the common (and commercial) name for methylbenzene is toluene, and the chlorinated derivatives are named as shown above. However, the same two chlorinated derivatives can also be properly named 2-chloromethylbenzene and 4-chloromethylbenzene. In this case, for naming, the parent compound is methylbenzene and it is understood that the methyl group is in the 1-position. The terms "*ortho*-" (1,2-), "*meta*-" (1,3-), and "*para*-" (1,4-) are also sometimes used; for example, 2-chlorotoluene can be called *ortho*-chlorotoluene. This can be very confusing, but in the chemical industry, outside of the research labs, the common names for the parent compounds are almost always used.

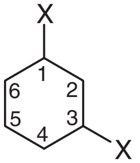
AROMATIC ORGANIC CHEMISTRY

SUBSTITUTED BENZENES

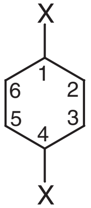
When two hydrogens on a benzene ring are replaced by other elements (disubstitution), there are three possible configurations, as shown here, where X = a substituent group, either the same or different.



1,2- or "*ortho-*" substitution



1,3- or "*meta-*" substitution



1,4- or "*para-*" substitution

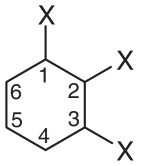
The position of substituents on the ring and their relation to each other corresponds to the number of the carbon to which they are attached.

Substitution of two or more hydrogens in benzene results in "positional isomerism." Positional isomers have the same formula, but different physical and chemical properties. In disubstituted benzene, three positional isomers are possible, as shown above. If the *substituents* are the same or different, one is always listed in the 1-position. If the substituents are different, they are listed alphabetically.

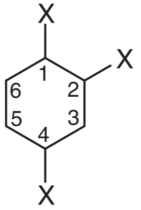
AROMATIC ORGANIC CHEMISTRY

SUBSTITUTED BENZENES

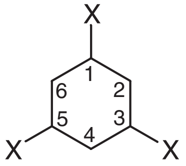
When three hydrogens are replaced by other substituents (trisubstitution), the number of possible configurations is also three.



1,2,3-substitution

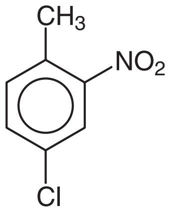


1,2,4-substitution



1,3,5-substitution

When different groups are present, they are numbered in ascending order with the main substituent always in the 1-position.



2-nitro-4-chlorotoluene

With *trisubstitution* by the same or different substituents, the three *positional isomers* shown above are possible. When the substituent groups are the same, the positional numbers are given followed by the suffix "tri-." For example, if the three groups are chlorine, the first isomer above is named 1,2,3-trichlorobenzene. The compound above with different substituents is named as a derivative of the parent compound toluene (methylbenzene) where it is understood that the methyl group is in the 1-position.

Substitution of four benzene hydrogens by the same group (tetrasubstitution) also results in three positional isomers: 1,2,3,4-, 1,2,3,5-, and 1,2,4,5.

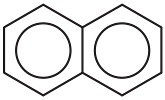
Benzene with five hydrogens replaced are *pentasubstituted*, and when all six hydrogens are replaced, the benzene is *hexasubstituted*.

Polymethyl-substituted benzene isomers usually are referred to by trivial names such as pseudocumene (1,2,4-trimethylbenzene), mesitylene (1,3,5-trimethylbenzene), and durene (1,2,4,5-tetramethylbenzene). These names were given to these compounds when aromatic compounds were first isolated from coal and their structures were as yet not proven.

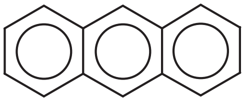
AROMATIC ORGANIC CHEMISTRY

POLYAROMATIC COMPOUNDS

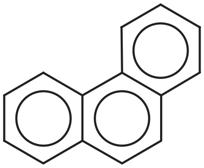
Some aromatic compounds contain multiple benzene rings attached to each other.



naphthalene



anthracene



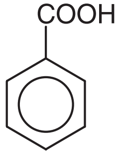
phenanthrene

All three of these industrially important chemicals can be obtained by the *coking* (heating in the absence of air) of coal. Naphthalene is also recovered during petroleum refining. These compounds can be converted in part or completely to aliphatic cyclic compounds by reaction with hydrogen. Like benzene, the hydrogens on these aromatic ring systems can be substituted by other groups.

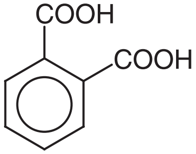
Naphthalene has been used as a moth repellant and an insecticide, but these uses are decreasing due to the increasing use of *para*-dichlorobenzene instead. Derivatives of naphthalene are used in dyes and drugs. An example of the latter is the pain reliever naproxen (sold in drugstores as “Aleve”). Some anthracene derivatives are also used as dyes.

AROMATIC ORGANIC CHEMISTRY

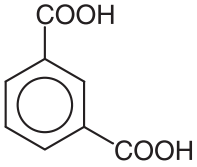
Carboxylic Acids



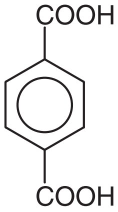
benzene carboxylic acid,
benzoic acid



1,2-benzenedicarboxylic acid,
ortho-benzenedicarboxylic acid,
phthalic acid



isophthalic acid



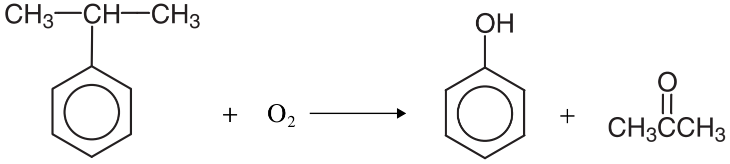
terephthalic acid

Benzoic acid is made by the oxidation of toluene with air (oxygen) at moderate temperatures under conditions whereby the toluene remains as a liquid during the reaction. However, the three benzene diacids are made from the corresponding dimethylbenzenes (xylenes) by oxidation with air (oxygen) over a catalyst at high enough temperature so that the reacting xylenes are in the gaseous state. In the case of the 1,2-derivative (phthalic acid), it is not isolated as free phthalic acid (the structure shown), but rather in the form of a cyclic compound called an *anhydride*, which can occur with the loss of a molecule of water. This anhydride (phthalic anhydride) is used mainly to make high-boiling organic liquids, which, in turn, are used to soften certain types of plastic. These are called *plasticizers*. The odor associated with new cars is caused by these compounds. Isophthalic acid is used to make fire-retardant textile fibers (“Nomex”) while terephthalic acid finds extensive use for the preparation of polyester textile fibers for clothing (“Dacron”), plastic soft drink bottles, transparent film (“Mylar”), and engineering plastics.

AROMATIC ORGANIC CHEMISTRY

PHENOLS

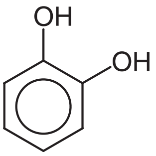
Aromatic rings with attached hydroxyl groups are called phenols.



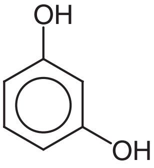
isopropylbenzene, cumene

hydroxybenzene, phenol

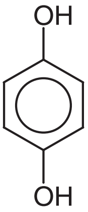
acetone



1,2-dihydroxybenzene, catechol



1,3-dihydroxybenzene, resorcinol



hydroquinone

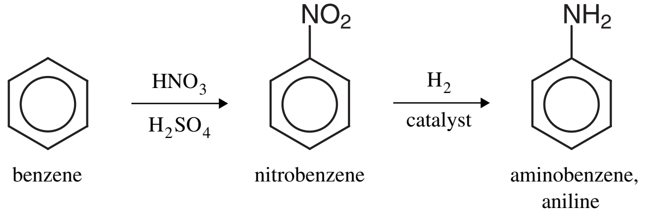
Phenol was originally recovered during the *coking* of coal, essentially being a by-product. Eventually, commercial routes were developed based on benzene (from coal or petroleum); for example, *sulfonation* of benzene to benzenesulfonic acid followed by reaction with water to phenol plus regenerated sulfuric acid. Phenol is used to make plastics (phenol-formaldehyde and epoxy resins) and textile fibers (nylon). Phenol is also used in solution as a general disinfectant for cleaning toilets, stables, floors, drains, etc. and is used both internally and externally as a disinfectant for animals.

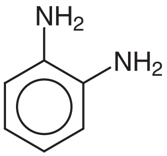
Catechol is also obtained from coal coking and from certain wood residues. Vanillin (synthetic vanilla flavoring) is a catechol derivative. Resorcinol and hydroquinone are currently made by the same type of chemistry used to make phenol. Hydroquinone is an important photographic chemical while resorcinol is widely used in glues for wood (e.g., plywood manufacture).

Although phenols would appear to be alcohols, because they have an –OH group like alcohols, they do not react like alcohols but instead have the chemical properties of acids. For example, they form salts when reacted with a base. This is the reason that the common name for phenol for many years was carbolic acid.

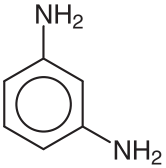
AROMATIC ORGANIC CHEMISTRY

AMINES

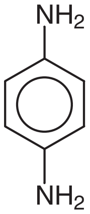




1,2-diaminobenzene,
ortho-phenylene diamine



1,3-diaminobenzene,
meta-phenylene diamine



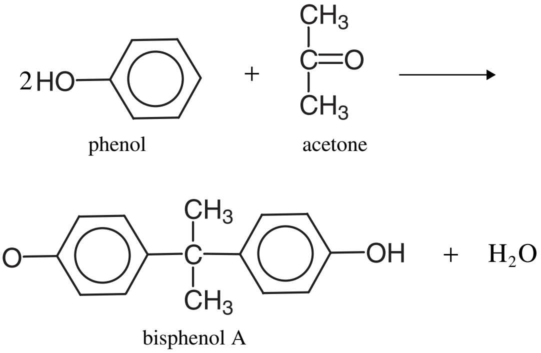
1,4-diaminobenzene,
para-phenylene diamine

The largest use of aniline is for the preparation of chemicals used in the rubber industry.

The diaminobenzenes are made from benzene by a combination chlorination–nitration route although *para*-phenylene diamine is also made directly from aniline. *ortho*-Phenylene diamine is widely used for the preparation of biologically active compounds such as fungicides and veterinarian medicines. The *meta*-diamine is used in fire-retardant textile fibers (“Nomex”) while the *para*-diamine finds use in high-strength textile fibers used for bullet-proof vests, sails, army helmets, and other types of fiber-reinforced plastics (“Kevlar”).

AROMATIC ORGANIC CHEMISTRY

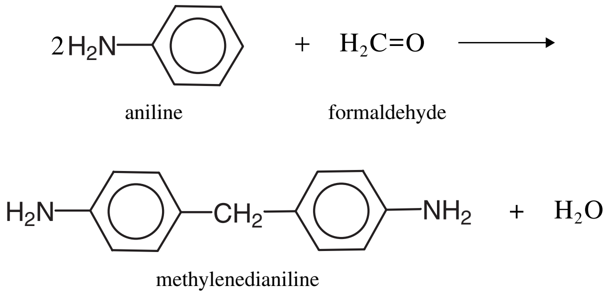
BENZENE-BASED INTERMEDIATES FOR EPOXY RESINS AND POLYCARBONATES



Epoxy resins for printed circuits, castings, rocket motor casings, coatings, and adhesives are almost all made from bisphenol A. Polycarbonates based on bisphenol A are used in glazing applications such as aircraft windows, school windows, and other areas where a combination of toughness and high clarity are required.

AROMATIC ORGANIC CHEMISTRY

BENZENE-BASED INTERMEDIATES TO POLYURETHANES



Methylenedianiline is used to make an intermediate in the manufacture of polyurethane rubber used for making automobile parts, shoe soles, rubber wheels, and insulation foam.

5 Polymer Chemistry

Polymers are very large organic molecules that are either made synthetically or are of natural origin, and find use as plastics, rubber, fibers, and coatings. Polymers were first produced commercially in 1860 by modification of cellulose from wood or cotton, followed by a fully synthetic product made from phenol and formaldehyde in 1910.

POLYMERS

- Giant molecules made up of repeating units called *monomers* or *mers*
- Polymers are also called *macromolecules*
- Differences between ordinary organic compounds and polymers are due mainly to the large size and shape of polymer molecules
- Polymers in nature
- Man-made polymers

All polymers are giant molecules made up of repeating units called monomers or mers. These units may be the same or different. The number of monomers that join to form a polymer or macromolecule is called the degree of polymerization and is theoretically infinite, but, in practice, the number of monomer units is commonly in the range of 1000 to 20,000 if no crosslinks are present.

Polymers have been part of nature since the beginning of life. For example, proteins, nucleic acids, and polysaccharides found in plants and animals are polymers. Today, man-made polymers are part of our lifestyle, providing clothing, paints, furniture, carpets, building materials, etc.

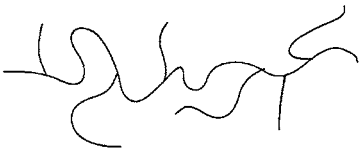
NATURAL POLYMERS

Starch	Homopolymer of glucose
Cellulose	Homopolymer of glucose
Chitin	Polymeric acetamidoglucose
Protein	Copolymer of amino acids
Natural rubber	Polymer of isoprene

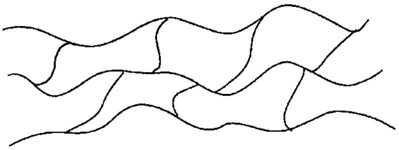
The subject of natural polymers is quite complex because they are involved in the structural, circulatory, transport, protective, and reproductive systems of all living things. *Starch* is a homopolymer of glucose in the alpha-glucoside configuration and serves as an energy reserve for plants and an energy source of animals. *Cellulose*, a structural polymer in plants, is formed by polymerization of glucose in the beta-configuration glucoside. *Chitin* is a cellulose-like biopolymer found in the exoskeletons of many insects and marine invertebrates (shrimp, crabs, etc.). *Proteins*, which are copolymers of up to 20 amino acids, perform a myriad of functions in all living tissue. *Natural rubber* is the only true hydrocarbon polymer found in nature. It requires vulcanization (crosslinking) to give it good elastic properties.

POLYMER STRUCTURE

Branched polymer



Crosslinking



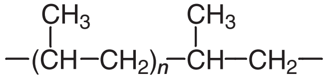
Branching also occurs in polymers. The branches are extensions of linked monomer units that protrude from the polymer trunk chain. Branched polymers can also form random coils, but the branches prevent a highly irregular arrangement and, therefore, less crystallinity results because the molecules cannot line up and pack as well.

Crosslinking means that the polymer molecules are interconnected by some sort of bonding. The bonding can be covalent, ionic, or it can result from intermolecular forces such as hydrogen bonding. With a small degree of crosslinking, a loose network is obtained, such as in vulcanized rubber, in which the crosslinks are formed by sulfur atoms. Highly crosslinked polymers, such as a thermoset plastic, have such a rigid structure that when heated they decompose or burn rather than melt. A crosslinked polymer is one super giant molecule. For example, the polymer in a bowling ball is literally one molecule.

POLYMER STRUCTURE

Linear

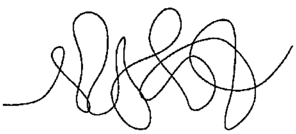
$-(CH_2-CH_2)_n-CH_2-CH_2-$ polyethylene



$$-(\overset{\overset{\large CH_3}{|}}{C}H-CH_2)_n-\overset{\overset{\large CH_3}{|}}{C}H-CH_2-$$

polypropylene

Random coil



The three-dimensional shape or structure of a polymer is dependent on the shape and type of monomer and the ways the monomers are linked together. A linear polymer is one in which the monomers are connected in a chain-like manner. Although called linear, such polymers should not be thought of as straight lines. They form random coils as seen in a plate of spaghetti.

The subscript *n* in the above formulae is a whole number indicating the number of monomer units in the polymer chain. This is called the polymer's degree of polymerization.

POLYMER CRYSTALLINITY

Crystallinity ⟶ property effects
Polymers <100% crystalline
Regularity of structure needed for high crystallinity
  Stretching
  Cold drawing
Branching decreases crystallinity
Crosslinking prevents crystallinity

Crystallinity affects polymer properties, but, unlike small molecules, polymers are not completely crystalline. A basic requirement for crystallinity is regularity of the chain structure. Regularity allows proper alignment of polymer chains so that crystallization can occur. Noncrystalline regions in polymers are called *amorphous*. Regularity can be increased by stretching and cold drawing, because this lines up the molecules. Because branching inhibits regularity, branched polymers tend to be less crystalline. Crosslinking prevents polymers from orienting to achieve the regularity required for crystallization.

POLYMER CLASSES

Thermoplastic vs. thermoset
Step growth vs. chain growth
Resins vs. plastics
Homopolymer vs. copolymer
Block vs. graft vs. alternating vs. random
Linear vs. branched vs. crosslinked
End uses

Terms used in classifying polymers can be quite confusing. As we proceed in our discussion of polymers, we will touch on each of the above terms. First, polymers can be divided into two classes based on their behavior when heated. *Thermoplastics* soften and melt when heated. They make up about 80% of man-made polymers. *Thermosets* maintain their original shape when heated and do not soften or melt. This is due to the crosslinking of polymer chains to form giant three-dimensional molecules. Polymers may be *step growth* or *chain growth,* depending on their mechanism of formation. The terms *resin* and *plastic* refer to polymer products; however, there is much overlap in the usage of those terms. *Resin* is used broadly and covers natural resins (e.g., shellac, amber, etc.) as well as polymers resulting from reaction between two or more substances (e.g., phenol-formaldehyde, silicones, alkyds). *Plastics* are high polymers combined with other ingredients such as plasticizers, accelerants, curatives, etc. and can be formed or molded under heat and pressure. A *homopolymer* is prepared by polymerization of a single monomer while a *copolymer* is prepared from two or more monomers. Copolymers may be *random,* whereby monomer A and monomer B are distributed randomly along the polymer chain; *alternating,* whereby A and B alternate along the polymer chain; *block,* whereby the polymer chains consist of sequences of A connected to sequences of B; or *graft,* whereby chains of B are attached to a backbone chain of A.

POLYMER SYNTHESIS

Polymers are prepared by processes in which small molecules undergo multiple combinations to form very large molecules. There are two principal types of polymerization:

1. S*tep growth polymerization.* Important polymers manufactured by step growth are polyamides (nylons), polyesters, and polyurethanes.
2. *Chain growth polymerization.* Important polymers manufactured by chain growth are polyethylene, polystyrene, polyacrylonitrile, and polymethacrylates.

Conditions that are important to all chemical reactions such as stoichiometry and reactant purity become critical in polymer synthesis. In step growth polymerization, a 2% measuring and/or impurity error cuts the degree of polymerization or the molecular weight in half. In chain growth polymerization, the presence of a small amount of impurity that can react with the growing chain can "kill" the polymerization.

For a polymer molecule, its molecular weight is the number of monomer units that it consists of multiplied by the molecular weight of the monomer unit (minus the molecular weight of any by-products of the polymerization). A molecular weight of at least 5000 is normally required before the polymer displays useful mechanical properties.

STEP GROWTH POLYMERIZATION

Monomer + Monomer $\longrightarrow$ Dimer
Dimer + Monomer $\longrightarrow$ Trimer
Dimer + Dimer $\longrightarrow$ Tetramer
Trimer + Monomer $\longrightarrow$ Tetramer
Trimer + Dimer $\longrightarrow$ Pentamer
⋮ ⋮
30-mer + 21-mer $\longrightarrow$ 51-mer

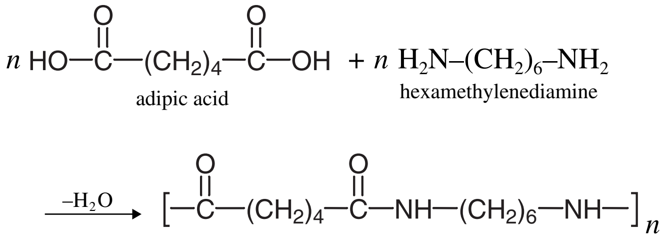
Condensation polymerization is the most common kind of step growth polymerization. In condensation polymerization, the monomers link together with loss of a small molecule such as water.

Step growth polymerization is relatively slow. The reaction can be stopped at any time and low-molecular-weight products (called oligomers) can be isolated. The monomer disappears early in the reaction because of the formation of the low-molecular-weight products (tetramers, pentamers, and oligomers). These low-molecular-weight products continue to react with each other over long reaction times to build up to a fully grown polymer. A range of molecular weights is obtained. The average of this molecular weight range is usually taken as the polymer's molecular weight.

STEP GROWTH POLYMERIZATION

Examples

Polyamide



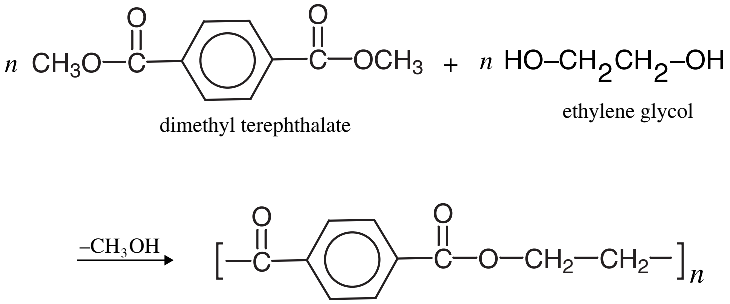
$$n\,HO{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}OH + n\,H_2N{-}(CH_2)_6{-}NH_2 \xrightarrow{-H_2O} \Big[{-}\overset{O}{\overset{\|}{C}}{-}(CH_2)_4{-}\overset{O}{\overset{\|}{C}}{-}NH{-}(CH_2)_6{-}NH{-}\Big]_n$$

adipic acid

hexamethylenediamine

nylon 66

Polyester



dimethyl terephthalate

ethylene glycol

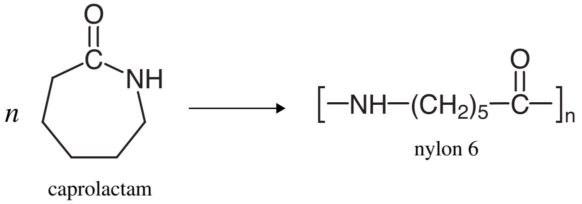
poly(ethylene terephthalate)

The most common form of step growth polymerization is condensation polymerization. Condensation polymers are generally formed from simple reactions involving two different monomers. The monomers are difunctional, having a chemically reactive group on each end of their molecules. Examples of condensation polymerization are the formation of nylon 66, a polyamide, and of poly(ethylene terephthalate), a polyester. Because condensation polymerization proceeds stepwise, the degree of polymerization and average molecular weight increase as the reaction proceeds. The removal of the small molecules formed in the reaction is necessary to drive the reaction to completion and to give high molecular weight. Monomer purity and exact proportions of each monomer are essential to achieve high molecular weight.

STEP GROWTH POLYMERIZATION

EXAMPLES

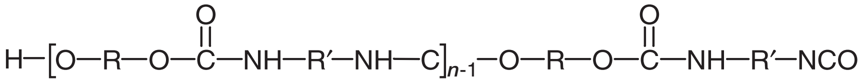
Ring-opening polymerization



$$[\!-\!NH\!-\!(CH_2)_5\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!]_n$$

Polyurethane formation

$$n\ \underset{\text{diol}}{HO\text{–}R\text{–}OH} + n\ \underset{\text{diisocyanate}}{O{=}C{=}N\text{–}R'\text{–}N{=}C{=}O} \longrightarrow$$



$$H\!-\![O\!-\!R\!-\!O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!NH\!-\!R'\!-\!NH\!-\!C]_{n\text{-}1}\!-\!O\!-\!R\!-\!O\!-\!\overset{\overset{\displaystyle O}{\|}}{C}\!-\!NH\!-\!R'\!-\!NCO$$

polyurethane

Step growth polymerization can also take place without splitting out a small molecule. Ring-opening polymerization, such as caprolactam polymerization to nylon 6, is an example. Polyurethane formation from a diol and a diisocyanate is another step growth polymerization in which no small molecule is eliminated.

CHAIN GROWTH (ADDITION) POLYMERIZATION

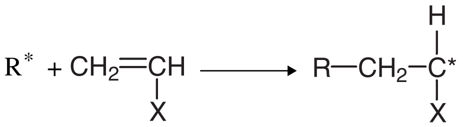
Monomers contain double bonds and add end to end
Requires an initiator
Very fast reaction — up to 10^4 times faster than condensation polymerization
No small molecules split out
Exothermic

Chain growth polymerization, sometimes called *addition polymerization*, involves monomers containing a carbon–carbon double bond, CH_2=CHX. Polymerization occurs by the propagation of the reactive site down a growing chain. The reactive site may be a free radical, an ion, or a metal complex. Once a chain is initiated, monomer units add to the growing chain very rapidly to give a fully-grown polymer chain. During chain growth polymerization, heat is released. Such a reaction that releases heat is said to be *exothermic*.

CHAIN GROWTH (ADDITION) POLYMERIZATION

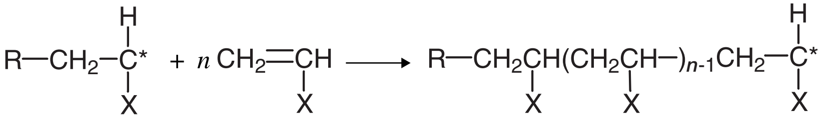
Polymerization steps:

- Initiation



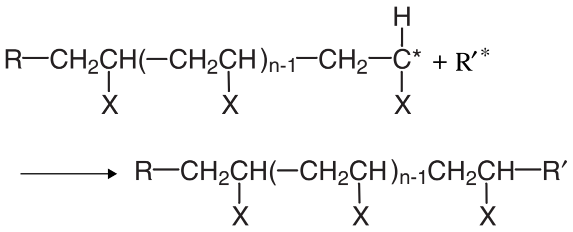
$$R^* + CH_2{=}\underset{\underset{X}{|}}{C}H \longrightarrow R{-}CH_2{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^*$$

- Propagation



$$R{-}CH_2{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^* + n\,CH_2{=}\underset{\underset{X}{|}}{C}H \longrightarrow R{-}CH_2\underset{\underset{X}{|}}{C}H(CH_2\underset{\underset{X}{|}}{C}H{-})_{n\text{-}1}CH_2{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^*$$

- Termination

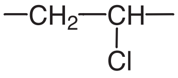
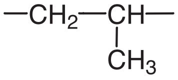
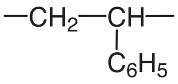
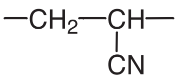
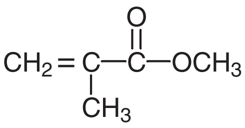
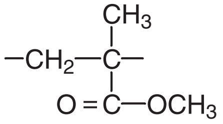


$$R{-}CH_2\underset{\underset{X}{|}}{C}H({-}CH_2\underset{\underset{X}{|}}{C}H)_{n\text{-}1}{-}CH_2{-}\overset{\overset{H}{|}}{\underset{\underset{X}{|}}{C}}{}^* + R'^*$$

$$\longrightarrow R{-}CH_2\underset{\underset{X}{|}}{C}H({-}CH_2\underset{\underset{X}{|}}{C}H)_{n\text{-}1}CH_2\underset{\underset{X}{|}}{C}H{-}R'$$

Chain polymerization involves three steps. To start the reaction, a catalyst that can generate an active site, such as a *free radical* (R*), is used. In the initiation step, the radical adds to the double bond, and the radical site is moved to the end carbon. This new radical reacts with another molecule to give a larger radical, and the propagation reaction is underway. Usually, the number of monomers in the chain is greater than 1000. In the above formulae, X indicates a small substituent, which may be an atom such as hydrogen (H) or chlorine (Cl) or it may be a group such as methyl (CH_3), cyano (CN), carboxyl (COOH), carbomethoxy ($COOCH_3$), etc. The growing chain is terminated by collision with another chain or other radical source or by one of several other mechanisms. The number of monomer units in the polymer chain is the *degree of polymerization*, abbreviated DP. If the degree of polymerization is very low, the product is sometimes referred to as an *oligomer.*

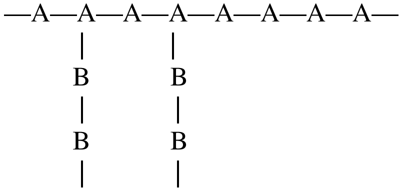
TYPICAL CHAIN GROWTH POLYMERS

Polymer Name	*Monomer*	*Repeating Unit*
Polyethylene	$CH_2{=}CH_2$	$-CH_2-CH_2-$
Poly(vinyl chloride)	$CH_2{=}CHCl$	 $-CH_2-\underset{Cl}{\underset{\mid}{CH}}-$
Polypropylene	$CH_2{=}CH-CH_3$	 $-CH_2-\underset{CH_3}{\underset{\mid}{CH}}-$
Polystyrene	$CH_2{=}CH-C_6H_5$	 $-CH_2-\underset{C_6H_5}{\underset{\mid}{CH}}-$
Polyacrylonitrile	$CH_2{=}CH-CN$	 $-CH_2-\underset{CN}{\underset{\mid}{CH}}-$
Polybutadiene	$CH_2{=}CH-CH{=}CH_2$	$-CH_2CH{=}CHCH_2-$
Poly(methylmethacrylate)	 $CH_2=\underset{CH_3}{\underset{\mid}{C}}-\overset{O}{\overset{\parallel}{C}}-OCH_3$	 $-CH_2-\overset{CH_3}{\overset{\mid}{\underset{O=C-OCH_3}{\underset{\mid}{C}}}}-$
Polytetrafluoroethylene	$CF_2{=}CF_2$	$-CF_2-CF_2-$

Polymers prepared by chain growth polymerization are very important industrially. Polyethylene and polypropylene are used as films and containers. Poly(vinyl chloride) serves as piping and siding for houses. Polystyrene gives very clear, bright bottles and molded articles or may be foamed as hot drink cups. Polyacrylonitrile is made into fibers for clothing. Polybutadiene is used to make auto tires. Poly(methyl methacrylate) is the basis for certain auto paints and for clear glass-like objects such as auto taillights. Polytetrafluoroethylene gives us nonstick cookware.

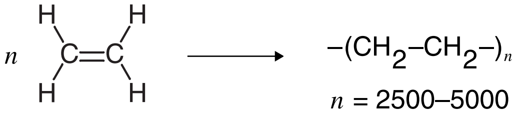
COPOLYMERS

- Polymers made with two or more monomers are copolymers.
- Most step growth polymers are copolymers.
- Chain growth copolymers are made to achieve specific properties.
- Chain growth copolymers may be:

Alternating	—A—B—A—B—A—B—A—B—
Random	—A—A—B—A—B—B—B—A—A—B—
Block	—A—A—B—B—B—B—A—A—A—B—B—
Graft	

Mixtures of two or more monomers can polymerize to form copolymers. Many copolymers have been developed to combine the best features of each monomer. For example, poly(vinyl chloride) (called a *homopolymer* because it is made from a single monomers) is brittle. By copolymerizing vinyl chloride with vinyl acetate, a copolymer is obtained that is flexible. Arrangement of the monomer units in a copolymer depends on the rates at which the monomers react with each other. Graft copolymers are formed when a monomer is initiated by free radical sites created on an already-formed polymer chain.

POLYETHYLENE



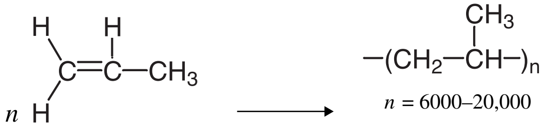
$$n\,H_2C{=}CH_2 \longrightarrow -(CH_2{-}CH_2{-})_n$$

n = 2500–5000

Low-density polyethylene (LDPE): film for food packaging, etc.
High-density polyethylene (HDPE): blow molded into bottles and containers
Linear low-density polyethylene (LLDPE): powder coatings

Polyethylene, a thermoplastic, is the largest selling plastic material. LDPE is a branched polyethylene whose branches prevent close packing and gives low density. HDPE is polyethylene that has essentially no branching, so the molecules pack very well, which leads to high density and high crystallinity. LLDPE is actually a copolymer prepared at low temperature and low pressure from a mixture of ethylene and about 10% of a C_4–C_8 olefin.

POLYPROPYLENE



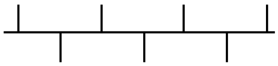
$$n\,\mathrm{CH_2{=}CH{-}CH_3} \longrightarrow -(\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{CH}}}-)_n$$

n = 6000–20,000

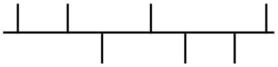
Special catalyst system (Ziegler–Natta) required
Three structures:

Isotactic

Syndiotactic

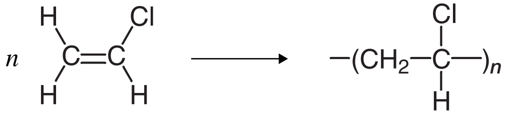


Atactic

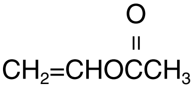


Polypropylene was not developed until the 1950s when Ziegler and Natta invented *coordination catalysts*. The structural difference between polyethylene and polypropylene is the methyl group in the propylene unit. Its presence makes a difference because it makes possible three different polymer structures: *Isotactic*, with all methyl groups in the same plane makes the best plastic; *syndiotactic*, in which the methyl groups alternate in the same plane; and *atactic*, with the methyl groups randomly in and out of the plane is soft and rubbery. Polypropylene is used as film and in many structural forms. It is also used as fibers for carpet manufacture and for thermal clothing.

POLY(VINYL CHLORIDE)



Vinyl chloride polymers and copolymers are called “vinyl resins.” Common comonomers for vinyl chloride are



$CH_2{=}CHOC(=O)CH_3$

vinyl acetate

and

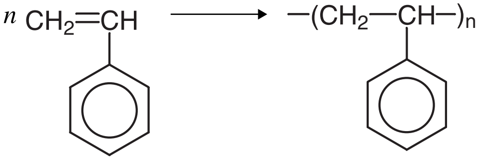
$CH_2{=}CCl_2$

vinylidene chloride

Poly(vinyl chloride) is usually used with a “plasticizer” to make it softer.

Poly(vinyl chloride) (PVC) is a thermoplastic that finds many uses. *Rigid* vinyls (unplasticized or lightly plasticized polymer) are hard and stiff and are used as pipe, house siding, and a variety of parts for construction and appliances. Plasticizers impact flexibility so that plasticized vinyls result in clear packaging films, wire and cable coverings, and upholstery materials. Plasticizers are organic compounds that are added to polymers to facilitate processing and increase flexibility and toughness by solvation of the polymer molecule. Among important plasticizers are nonvolatile organic liquids and low-melting solids, for example, phthalate, adipate, and sebacate esters, tricresyl phosphate, polyols, etc. Large quantities of PVC are used to manufacture household and other consumer goods.

POLYSTYRENE



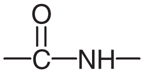
Polystyrene is a glassy, brittle, amorphous polymer.

For many uses, it is foamed and made into egg cartons, disposable plates and cups, food trays, packing materials, etc.

Mixing polystyrene with an elastomer such as polybutadiene makes it tougher. This material is called high-impact polystyrene.

Polystryene is an addition polymer usually made by bulk or by suspension polymerization. Styrene homopolymer has high rigidity, sparkling clarity, and is easy to fabricate. Styrene copolymers are very important commercially. A copolymer containing 25% styrene and 75% butadiene is known as SBR and is used for making tires, hoses, rubber-coated fabrics, and adhesives. ABS, a copolymer of 50% styrene, 20% butadiene, and 30% acrylonitrile, is a plastic that is both tough and hard. It is used to manufacture luggage, high-quality plastic pipe and fittings, telephones, appliance housings, etc.

ENGINEERING RESINS

- Nylon
  Nylon refers to polymers containing the amide,  $-\overset{\overset{\displaystyle O}{\|}}{C}-NH-$, grouping. Nylon 6 and nylon 66 are the most common nylons. They are very tough and wear resistant.
- Polycarbonates
  Polycarbonates are condensation polymers made from phosgene and bisphenol A. They have high impact strength and are used in glazing, helmets, and appliance casings.
- Phenolics
  A thermoset resin used for engineering purposes.

Engineering resins are polymers that have outstanding physical properties such as thermal stability, chemical resistance, self-lubrication, weather resistance, etc. Generally, they are thermoplastics. They are gaining in importance in automobile manufacture as metal replacements to provide lighter weight cars.

FIBERS

- Nylons
  Nylon 66 is a condensation polymer made from adipic acid and hexamethylenediamine. Nylon 6 is made by ring-opening polymerization of caprolactam.
- Polyesters
  The most common polyester fiber is polyethylene terephthalate (PET), prepared from ethylene glycol and terephthalic acid.
- Acrylics
  Polymers of acrylonitrile, $CH_2=CHCN$.
- Polypropylene
  Polypropylene fibers are mainly used in outdoor carpets and in cold-weather clothing.

Fibers are made from thermoplastic polymers. The polymers are made into fiber form, normally by extrusion of molten polymer or a polymer solution through tiny holes. The resulting fiber is stretched to orient the molecules. This orientation of the molecules lines up the polymer molecules and produces the strength and other properties needed in a textile yarn.

6 High-Volume Organic Chemicals

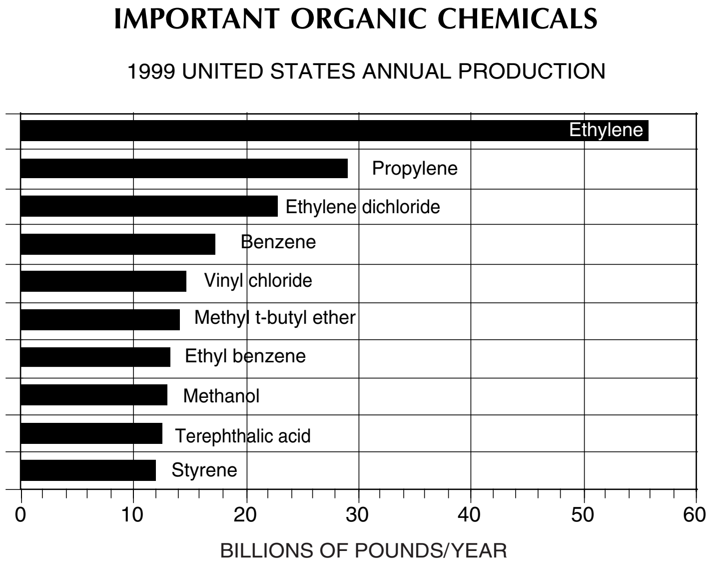
All organic chemicals are, by definition, based on chemicals derived from living matter. Thus, the ten highest-volume commercial organic chemicals are all made from starting materials obtained from petroleum (oil) and natural gas, which are believed to have been formed by the microbial decomposition of ancient marine plants and animals.

HIGH-VOLUME ORGANIC CHEMICALS

Raw Material Sources

1. Petroleum and natural gas
   About 90% of all organic chemicals produced are obtained from petroleum and natural gas. These are nonrenewable sources, so eventually alternate raw materials will have to be utilized.
2. Coal
   Prior to World War II, this was the principal organic chemical raw material. It is more difficult to process than oil, but most European countries and the U.S. have very large coal reserves. However, it is nonrenewable.
3. Biomass (carbohydrates)
   Biomass includes chemicals obtained from wood, sugar, grain, etc. A totally renewable source, it will become more important in the future.
4. Animal and vegetable oils
   Chemicals from animal and vegetable oils are known as "fatty acid" products. Obviously, a renewable source.

After World War II, there was an increasing demand for gasoline and other fuels for transportation. Oil was plentiful and cheap, both in the U.S. and in Europe. New high-capacity processes to refine gasoline made by-products ethylene, propylene, and aromatics available for chemical synthesis at a much lower cost than previous sources, such as biomass and coal. By about 1960, gas and oil surpassed coal as the major source of organic chemicals. The price of oil remained relatively stable while coal increased in price because its recovery is labor intensive. By 1970, the changeover was complete and the petrochemical age had arrived. Now, in the U.S., organic chemical production from coal is insignificant, but it remains of some importance in South Africa.

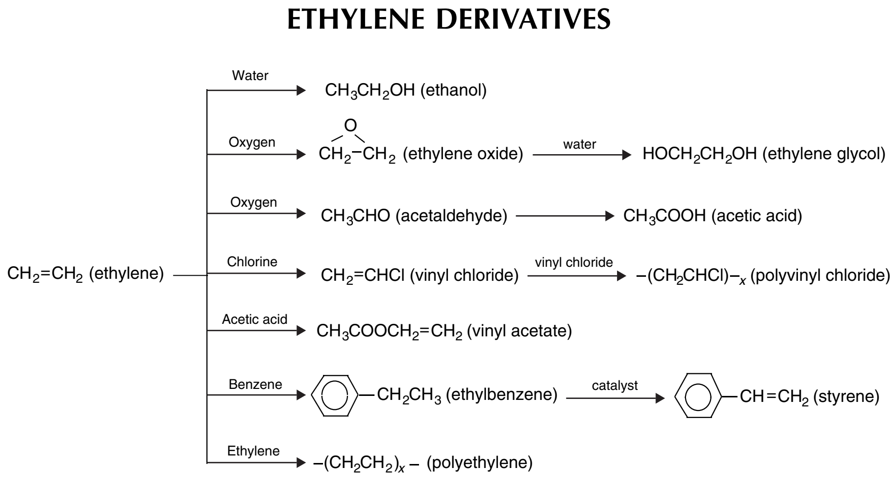


All of the above high-volume organic chemicals are obtained from petroleum or natural gas. This is why the modern organic chemical industry is frequently referred to as the "petrochemical industry." The high-volume status of some of these compounds is due to their use to make others lower on the list. For example, ethylene is used to make ethylene dichloride, which, in turn, is used to make vinyl chloride. Ethyl benzene, made from benzene and ethylene, is used to make styrene. Methyl *t*-butyl ether is made from methanol and butylene, a captive intermediate for which production data is not available.

ETHYLENE ($CH_2{=}CH_2$)

Properties	Colorless, highly flammable gas, boiling point −103.8°C (about −220°F). Reported to have a faint, pleasant odor.
Commercial grades	Available in technical (95%) and polymer (99.9%) grades. Transported as a gas in pipelines, as a liquid in pressurized tank cars and steel cylinders. Difficult to store.
Uses	As the largest volume organic chemical produced, it is used for the preparation of plastics (polyethylene, 50%), ethylene oxide (20%), and other plastic intermediates such as vinyl chloride and styrene.
Manufacture	Made by thermal (high-temperature) cracking in the presence of steam of any available low-cost hydrocarbon such as ethane and propane, naphthas (C_5–C_{10}), and so-called gas oils (C_{10}–C_{30}). Many other organic compounds are produced during the cracking step, depending on the starting material fed to the reactor (cracker). $CH_3{-}CH_3 \longrightarrow CH_2{=}CH_2 + H_2$
Suppliers	BP Amoco, Chevron, DuPont, Exxon Mobil, Equistar, Phillips, Shell, Sunoco, Union Carbide, Huntsman, Dow, and others.

About 100 billion pounds of chemicals and polymers are made from ethylene each year. In fact, over 40% of all organic chemicals produced are based on ethylene. These ethylene-based materials are found in almost every conceivable application encountered in daily life, for example, containers, flooring, adhesives, pharmaceuticals, oil and gasoline additives, paints, surfactants, etc.



About 50% of all the ethylene produced is used to make polyethylene. There are two main types: "high density" or HDPE and "low density" or LDPE. HDPE melts higher and is stiffer and harder than LDPE. It is also opaque, while LDPE is flexible and transparent. HDPE is used for molding bottles, housewares, toys, and for extruding pipe and conduit. LDPE is used mainly for packaging film. HDPE is made by a *catalytic polymerization* at relatively low pressure while LDPE is made by polymerization at very high pressure using a different catalyst.

Vinyl acetate is polymerized to poly(vinyl acetate), (PVAc), which finds use in adhesives and water-based paints. Some PVAc is *hydrolyzed* (reacted with water) to poly(vinyl alcohol) (PVA) for textile sizing, adhesives, and paper coatings. A substantial amount of U.S.-produced vinyl acetate is exported. Prior to 1970, almost all vinyl acetate was made from acetylene. Now none of it is.

ETHYLENE DERIVATIVES

ETHANOL

(Also called ethyl alcohol, grain alcohol, and industrial alcohol)

$$CH_2{=}CH_2 + H_2O \xrightarrow{H_3PO_4} CH_3CH_2OH \quad \text{(ethanol)}$$

Other Methods of Preparation

Fermentation

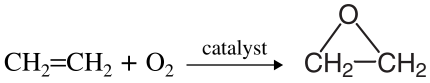
$$\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{enzyme}} CH_3CH_2OH + CO_2$$

Uses	Solvents, chemical intermediates, engine fuel.
Suppliers	Union Carbide, Pharmco Products, Grain Processing Corp. Sasol North America, Midwest Grain Products, and others.

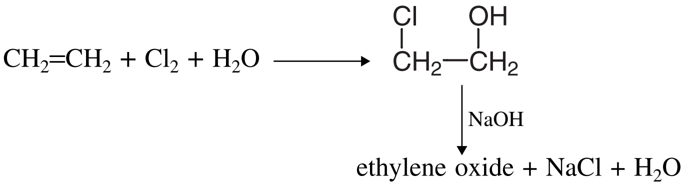
Ethanol is the alcohol found in alcoholic beverages, such as beer, wine, gin, vodka, etc. In that form, it is produced by the *fermentation* equation shown above, as is ethanol for use as fuel in internal combustion engines. The source of carbohydrates for fuel production is corn, so this use is promoted by agricultural interests. In the U.S., ethanol is added to gasoline in amounts up to 10%, but in a few countries, Brazil for example, some car engines have been modified to run on pure ethanol. Ethanol contains less energy than gasoline because it is already partially oxidized (contains oxygen), but it contributes to cleaner burning fuel and less air pollution. About 10 billion pounds of ethanol were produced in the U.S. in 2000.

ETHYLENE DERIVATIVES

Ethylene Oxide



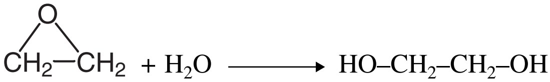
Older Method of Preparation



$$CH_2{=}CH_2 + Cl_2 + H_2O \longrightarrow \overset{Cl}{CH_2}-\overset{OH}{CH_2} \xrightarrow{NaOH} \text{ethylene oxide} + NaCl + H_2O$$

Uses	Preparation of ethylene glycol for antifreeze and synthetic textile fibers (60%), hospital sterilant (15%), surfactants (10%), other chemicals (10%).
Suppliers	BASF Corp., Dow, Huntsman, Eastman Chemical, Old World Trading, Equistar Chemicals, Union Carbide, and others.

Ethylene glycol is made by reacting ethylene oxide with water:



Clothing referred to as *polyester* is made by *polymerizing* ethylene glycol with terephthalic acid and then spinning textile fibers from the resulting polymer. The fibers are woven into cloth from which the clothing is made. Transparent film, tire cord, and carpeting are also made from polyesters based on ethylene glycol. It is also used for the preparation of *polyurethane* ingredients to make inline skate and scooter wheels.

Many laundry and dish detergents as well as shampoos are made from chemicals based on ethylene oxide.

ETHYLENE DERIVATIVES

VINYL CHLORIDE

$$CH_2{=}CH_2 + Cl_2 + O_2 \longrightarrow CH_2{=}CH{-}Cl + H_2O$$

Older Method of Preparation

$$CH_2{=}CH_2 + Cl_2 \longrightarrow \underset{\text{ethylene dichloride}}{Cl{-}CH_2{-}CH_2{-}Cl} \longrightarrow CH_2{=}CH{-}Cl + HCl$$

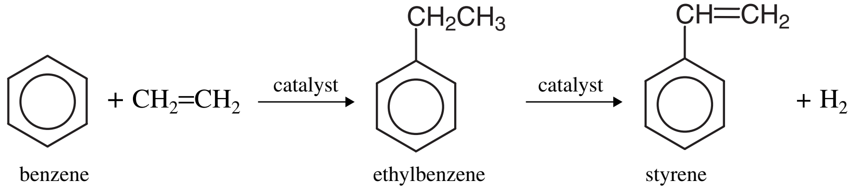
Uses	Vinyl chloride is used exclusively for the preparation of plastics, by homopolymerization to poly(vinyl chloride) (PVC) and by copolymerization with other vinyl ($-CH_2{=}CH-$) compounds. PVC-type polymers are low-cost, fire retardant, and have good structural properties.
Suppliers	OxyVinyls, Dow, Georgia Gulf, Formosa Plastics, Westlake.

About 10% of the ethylene produced in the U.S. is used to make vinyl chloride, which in the chemical trade is usually referred to as "vinyl chloride monomer" or VCM. The largest use of VCM is for polymerization to poly(vinyl chloride) (PVC), a thermoplastic, which in terms of volume is second only to polyethylene. PVC is used in such diverse areas as containers, floor coverings (linoleum), plastic pipes, raincoats, and many, many others. PVC has an evironmental disadvantage over non-chlorine containing plastics in that when it is disposed of by incineration it produces hydrogen chloride, which dissolves in atmospheric water to give hydrochloric acid. Polyethylene does not have this undesirable feature.

VCM is very toxic and is a known cause of a rare form of liver cancer. However, products made from it, such as PVC, pose no health threats.

ETHYLENE DERIVATIVES

ETHYLBENZENE AND STYRENE



This is a two-step reaction. The ethylbenzene is isolated in the first step and then contacted with a different catalyst at high temperature in the second step. Ethylbenzene and styrene plants are usually built together.

Uses	Ethylbenzene is used primarily to make styrene. Styrene is used to make polystyrene, a low-cost and versatile polymer. It is also copolymerized with other vinyl monomers to make rubber (SBR) and moldable plastics (ABS).
Suppliers	Lyondell, Chevron, BP Amoco, Dow, Sterling Chemicals, Nova Chemicals.

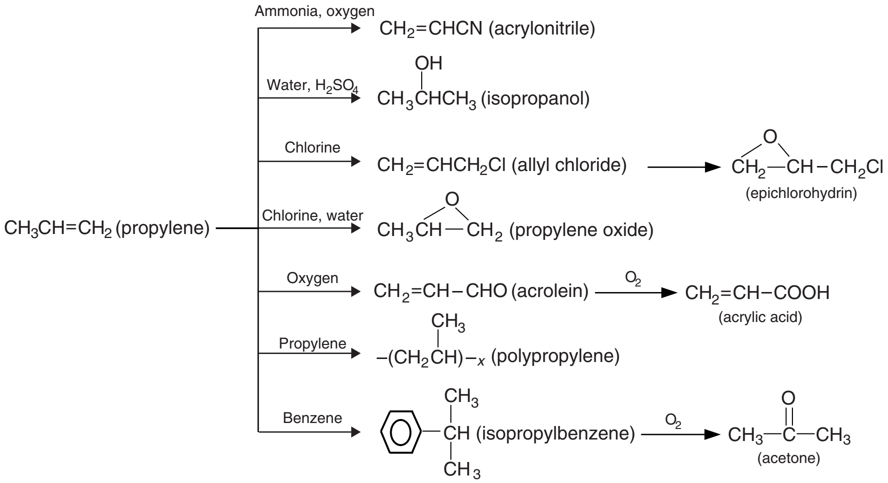
About half of the styrene produced is polymerized to *polystyrene*, an easily molded, low-cost thermoplastic that is somewhat brittle. Foamed polystyrene can be made by polymerizing it in the presence of low-boiling hydrocarbons, which cause bubbles of gas in the solid polymer after which it migrates out and evaporates. Modification and property enhancement of polystyrene-based plastics can be readily accomplished by *copolymerization* with other substituted ethylenes (vinyl monomers); for example, copolymerization with butadiene produces a widely used synthetic rubber.

PROPYLENE ($CH_3CH=CH_2$)

Properties	Colorless, flammable gas boiling at –48°C (about –54°F). Burns with a yellow sooty flame, so it can be substituted for propane in liquid petroleum gas (LPG).
Commercial grades	Available in three grades: refinery (50–70%), chemical (90–92%), and polymer (99%) grade. The remaining percentage in each case is mainly propane. It is shipped as a liquid in pipelines, tank cars, tank trucks, and steel cylinders. Storage is as a liquid at pressures of about 200 psi.
Uses	Used in the petroleum industry to make so-called alkylate for improved octane gasoline. Large quantities are polymerized to polypropylene for carpeting, upholstery, ropes, and other uses. Used in the chemical industry as a starting material for many large-volume chemicals such as acetone, acrylonitrile, and propylene oxide.
Manufacture	Made in exactly the same way ethylene is made, that is, by cracking low-cost hydrocarbons. Plants that produce propylene are always called ethylene plants because that is the principal product.
Producers	BP Amoco, Chevron, DuPont, Exxon Mobil, Equistar, Shell, Huntsman, Phillips, Dow, and others.

The production volume of propylene tracks that of ethylene because they are simultaneously produced in the same plants. Usually, propylene sells for a somewhat lower price than ethylene, but this occasionally varies when derivative demands change. Prices for both stay relatively constant in the 25–30 cent/lb. range.

PROPYLENE DERIVATIVES



The main use of propylene is for *polymerization* to polypropylene, a process similar to the manufacture of high-density polyethylene (i.e., a low-pressure, catalytic process). Textile fibers made from polypropylene are relatively low-cost and have particularly good properties, such as high resistance to abrasion and soiling for use in furniture upholstery and indoor/outdoor carpeting.

Three major non-polymer propylene derivatives are isopropanol, acetone, and acrylic acid. Isopropanol (isopropyl alcohol) is used mainly as a solvent. It has been made from propylene by reaction with sulfuric acid and water for at least the last 75 years, making its manufacture the oldest, still-running commercial organic chemical process. It is used in household rubbing alcohol because, unlike ethanol, it is unfit for human consumption even in small amounts. About 25% of the isopropanol produced is used for making acetone, in competition with a route based on isopropylbenzene.

PROPYLENE DERIVATIVES

ACRYLONITRILE

Uses Acrylic textile fibers are primarily polymers of acrylonitrile. It is copolymerized with styrene and butadiene to make moldable plastics known as SA and ABS resins, respectively. Solutia and others electrolytically dimerize it to adiponitrile, a compound used to make a nylon intermediate. Reaction with water produces a chemical (acrylamide), which is an intermediate for the production of polyacrylamide used in water treatment and oil recovery.

Manufacture Made by the reaction of propylene with ammonia and air (the Sohio process). This is the basis for the production of all of the acrylonitrile made in the world. Recoverable and salable by-products include hydrogen cyanide (HCN) and acetonitrile (CH_3CN).

$$CH_2{=}CH{-}CH_3 + NH_3 + O_2 \xrightarrow{\text{catalyst}} CH_2{=}CH{-}CN + H_2O$$

Suppliers Cytec, BP Amoco, DuPont, Sterling Chemical, Solutia.

The principal use of acrylonitrile since the early 1950s has been in the manufacture of so-called “acrylic” textile fibers. Acrylonitrile is first polymerized to polyacrylonitrile, which is then spun into fiber. The main feature of acrylic fibers is their wool-like characteristic, making them desirable for socks, sweaters, and other types of apparel. However, as with all synthetic textile fibers, fashion dictates the market and acrylic fibers currently seem to be in disfavor, so this outlet for acrylonitrile may be stagnant or declining. The other big uses for acrylonitrile are in copolymers, mainly with styrene. Such copolymers are very useful for the molding of plastic articles with very high impact resistance.

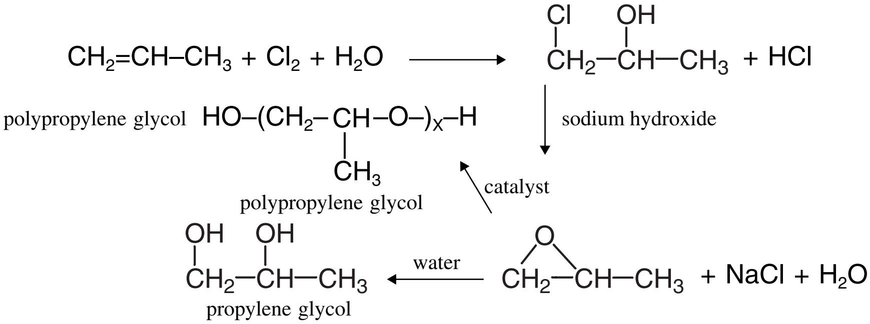
Until the 1960s, acrylonitrile was, like vinyl acetate, made from acetylene (by reaction with hydrogen cyanide), but research on catalysts in the 1950s led to the much less costly route shown above.

PROPYLENE DERIVATIVES

Propylene Oxide

Uses About 60% of the propylene oxide made is polymerized to polypropylene glycol and other polyethers for use in polyurethane foams and adhesives. Propylene glycol is also widely used in polyester resins based on maleic anhydride.

Manufacture



Suppliers Huntsman, Dow Chemical.

Most automobile and furniture seating, foam mattresses, carpet underlayment, and other similar products are made from *polyurethanes* based on polypropylene glycol (PPG). PPG is the preferred raw material for these type of polymers because of the wide variation of possible properties of the end product and the relatively low cost.

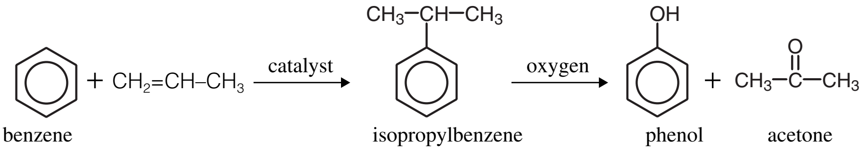
PROPYLENE DERIVATIVES

ISOPROPYLBENZENE

(Commonly called “cumene”)

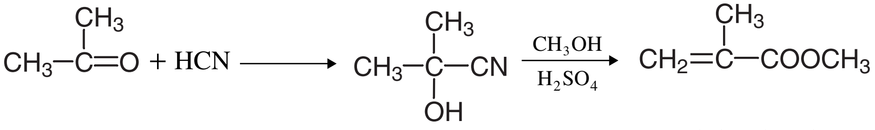
Uses Almost all of the isopropylbenzene produced is used for making phenol and acetone. The largest use of acetone is as a chemical intermediate to methyl methacrylate and along with phenol to make bisphenol A for preparation of polymers. Acetone is also used widely as a solvent.

Manufacture



Suppliers Shell, Sunoco Chemical, Aristech Chemical, Georgia Gulf, Dow Phenolchemie, Union Carbide, and others.

About a billion pounds per year of methyl methacrylate is made from acetone, hydrogen cyanide, and methanol.



$$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=O + HCN \longrightarrow CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CN \xrightarrow[H_2SO_4]{CH_3OH} CH_2=\overset{\overset{\displaystyle CH_3}{|}}{C}-COOCH_3$$

methyl methacrylate

The polymerization of methyl methacrylate produces poly(methyl methacrylate), an exceptionally clear plastic sold under the names “Plexiglas” or “Lucite” as a shatter-proof substitute for glass in windows, doors, and other glazing applications.

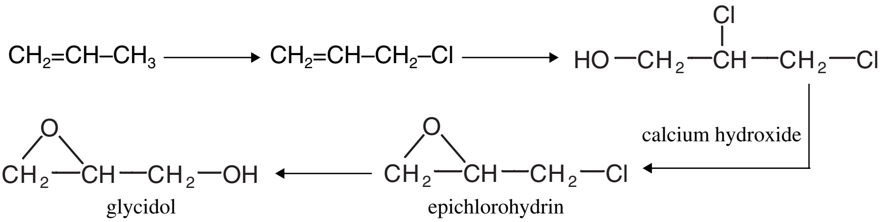
Phenol, along with formaldehyde, is used to produce a very important and versatile group of polymers known as “phenolics” or “phenol-formaldehyde resins.” These resins can be either *thermoplastic* or *thermosetting*, depending on the amount of formaldehyde used. A larger ratio of formaldehyde to phenol promotes *crosslinking* to produce more rigid materials.

PROPYLENE DERIVATIVES

EPICHLOROHYDRIN

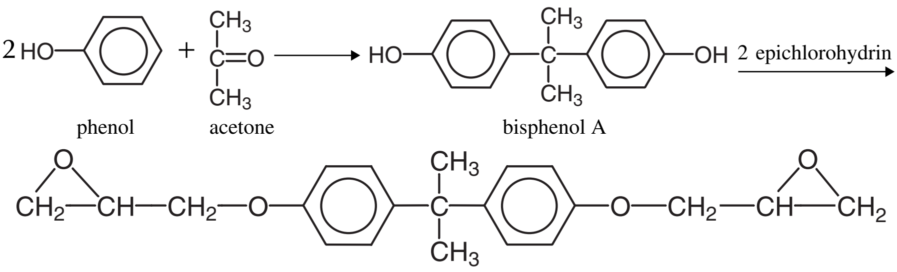
Uses Virtually all epoxy resins are made with starting materials based on epichlorohydrin, principally by reaction with bisphenol A. It is also used for the preparation of resins to increase the wet strength of paper. Both epichlorohydrin and glycidol are used in the manufacture of pharmaceuticals.

Manufacture



Suppliers Dow Chemical, Shell Chemical.

Epoxy resins are widely used in high-strength adhesives, corrosion-resistant coatings, and corrosion-resistant pipes and tanks. The simplest starting material for these thermoset polymers is made from phenol, acetone (to bisphenol A), and epichlorohydrin.



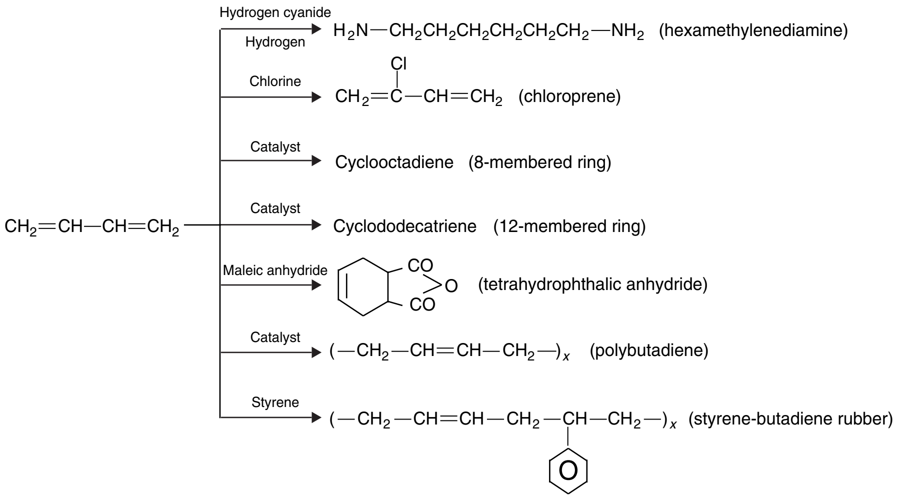
The final resin product is obtained by reacting (curing or crosslinking) the above di-epoxide with acid anhydrides or polyamines. The curing agents (sometimes incorrectly called catalysts) react with the three-membered epoxide rings to produce a highly crosslinked polymer.

BUTADIENE ($CH_2=CH–CH=CH_2$)

Properties	Colorless, odorless, flammable gas, boiling point –4.7°C (23.5°F). Dimerizes thermally and forms explosive peroxides on contact with oxygen.
Commercial grades	Inhibited butadiene is shipped as a liquid in tank trucks, tank cars, and steel cylinders. It is stored cold to prevent dimerization.
Uses	Its largest uses are for polymeriztion to polybutadiene and copolymerization with styrene to make synthetic rubber (SBR) for tires and other rubber uses. Other uses include the preparation of chloroprene for oil-resistant rubber (neoprene) and hexamethylenediamine for the preparation of nylon.
Manufacture	Some of the butadiene produced is recovered from steam crackers along with ethylene and propylene. However, most of it is now produced by the dehydrogenation of butene. $CH_3–CH=CH–CH_3 \xrightarrow{\text{catalyst}} CH_2=CH–CH=CH_2 + H_2$
Suppliers	Equistar, Texas Petrochemicals, Shell Chemical, Huntsman, Exxon Chemicals.

Butadiene is an especially versatile chemical because of its two reactive double bonds. It has been forecast that future butadiene supplies will be plentiful at a stable price due to an anticipated abundance of butenes. This suggests that butenes and butadiene are of major interest in the R&D departments of many large chemical companies.

BUTADIENE DERIVATIVES



Natural *rubber latex*, obtained from rubber trees, is converted to its final form by a process known as "vulcanization," first discovered by Charles Goodyear in 1839. Vulcanization is basically a *crosslinking* reaction of double bonds in the latex structure with sulfur. The polymerization of butadiene with itself or with other vinyl monomers results in a material that like natural latex, still contains double bonds. Thus, *synthetic rubber* made from butadiene can be processed and vulcanized just like natural rubber.

The first use of butadiene to make synthetic rubber was demonstrated in Russia in 1910 by S.V. Lebchev, who also developed a synthesis of butadiene from ethanol obtained by fermentation.

The first important commercial synthetic rubber was poly(chloroprene) which was made available for sale as "Neoprene" by DuPont in 1931. It is still made and sold today because of its superior resistance to oils, sunlight, and oxygen (ozone).

BUTADIENE DERIVATIVES

HEXAMETHYLENEDIAMINE

Uses Most of the hexamethylenediamine produced is used for the manufacture of Type 66 nylon by polymerization with adipic acid. A minor use is for the preparation of hexamethylene diisocyanate used in light-stable polyurethane coatings.

Manufacture

$$\begin{tikzcd} CH_2{=}CH{-}CH{=}CH_2 + 2HCN \arrow[r, "\text{catalyst}"] & \underset{\text{adiponitrile}}{NC{-}CH_2CH_2CH_2CH_2{-}CN} \arrow[dl, "\text{hydrogen}", "\text{catalyst}"'] \\ \underset{\text{hexamethylenediamine}}{H_2N{-}CH_2CH_2CH_2CH_2CH_2CH_2{-}NH_2} & \end{tikzcd}$$

Suppliers BASF Corp., Solutia, DuPont.

Type 66 nylon is a polyamide first commercialized by DuPont just prior to World War II. At that time, the needed hexamethylenediamine was made from adipic acid by reaction with ammonia to adiponitrile followed by reaction with hydrogen. The adipic acid then, like now, was made from cyclohexane. The cyclohexane, however, was derived from benzene obtained from coal. The ammonia was made from nitrogen in the air by reaction with hydrogen from water obtained in the water–gas shift reaction with carbon monoxide from the coal. So, in the 1950s, nylon was honestly advertised by DuPont as being based on coal, air, and water.

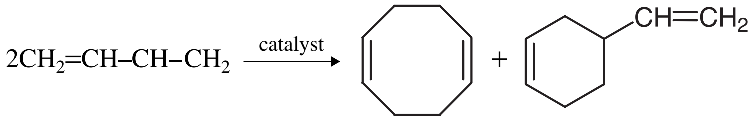
Hexamethylenediamine is now made by three different routes: the original from adipic acid, the electrodimerization of acrylonitrile, and the addition of hydrogen cyanide to butadiene. Thus, the starting material can be cyclohexane, propylene, or butadiene. Currently, the cyclohexane-based route from adipic acid is the most costly and this process is being phased out. The butadiene route is patented by DuPont and requires hydrogen cyanide facilities. Recent new hexamethylenediamine plants, outside DuPont, are based on acrylonitrile from propylene, a readily available commodity.

BUTADIENE DERIVATIVES

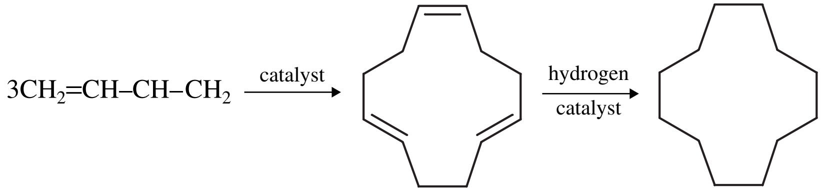
CYCLOOCTADIENE AND CYCLODODECATRIENE

Uses Cyclooctadiene is reacted with bromine to make fire-retardants. Cyclododecane is oxidized with air and then nitric acid to make a diacid containing 12 carbons. This acid is used to prepare some types of nylon, and its esters are used in synthetic lubricating oils.

Manufacture



cyclooctadiene vinylcylohexene



cyclododecatriene cyclododecane

Supplier DuPont.

Whether butadiene reacts with itself to give *linear polymers* or 8- or 12-carbon rings is a function of the catalyst and conditions used. Development of catalysts needed to give the desired products is the job of catalyst research chemists. Although *catalysis* is critically important in the chemical industry and much work has been done on it in research laboratories for many years, catalyst development remains more of an art than a predictable science, and the chemists involved in this type of research use methods they have learned experimentally, not from books or in classrooms.

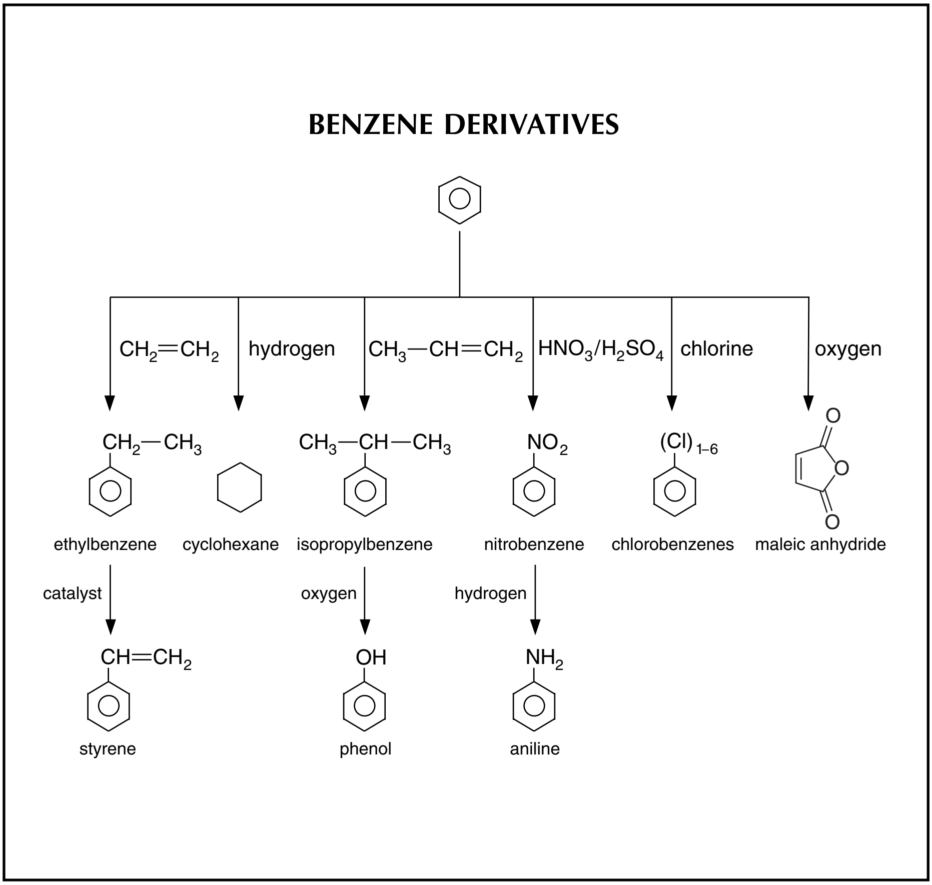
BENZENE (C_6H_6)

Properties	Clear, colorless, flammable liquid that boils at 80°C (176°F) and freezes at 5.5°C (42°F). It has a very characteristic odor. Recently it has been found to be toxic and is suspected of being a human carcinogen. Exposure to it should be very limited or, preferably, avoided.
Commercial grades	Available in three grades: refined-535, refined-485 (nitration grade), and industrial. The numbers following the grade refer to the freezing point specification times 100. It is shipped in steel drums, tank trucks, and tank cars under heavily regulated conditions.
Uses	It is used as a chemical raw material for a myriad of everyday products such as plastics, detergents, textile fibers, drugs, dyes, and insecticides. It is also found in gasoline with other aromatic hydrocarbons.
Manufacture	Benzene used to be made from coal, but it is now made from petroleum by two different routes: catalytic reforming of naptha and hydrodealkylation of toluene. The first route provides toluene as a by-product for the second route.
Producers	ExxonMobil, Chevron Phillips, Equistar, Koch, Dow, Citgo, BP Chemicals, and many others.

Benzene was first isolated in 1825 by Michael Faraday in London, but its structure remained somewhat of a mystery for over a century. In 1865, in what is now thought of as one of the most important pronouncements in the science of chemistry, a German chemist by the name of August Kekule suggested that there are alternating double bonds in the benzene ring and that they continuously trade places with each other. In the 1930s, the late chemist Linus Pauling offered convincing evidence in favor of Kekule's theory using a mathematical treatment known as quantum mechanics.

All steel used to be made by treating iron ore (iron oxides) with carbon. In colonial days, the required carbon (charcoal) was obtained by the heating of wood in the absence of air. The wood was ultimately replaced by coal. To obtain carbon (coke) from coal, the coal was heated to about 2500°F. Gaseous and liquid organics distilled from the coking operation. The gaseous fraction (coal gas) was used for street-lighting in large towns. The high-boiling material (coal tar) was used for roofing and road building. The liquid (coal oil) was about two-thirds benzene along with higher aromatics. All of the benzene used before World War II came from this source. Now, none of it does.

Naphtha is a mixture of aliphatic hydrocarbons isolated from petroleum by distillation. When it is passed over a catalyst under the right conditions, carbon rings are formed, followed by the splitting of hydrogen from the carbon rings to produce benzene, toluene, and other aromatic compounds.

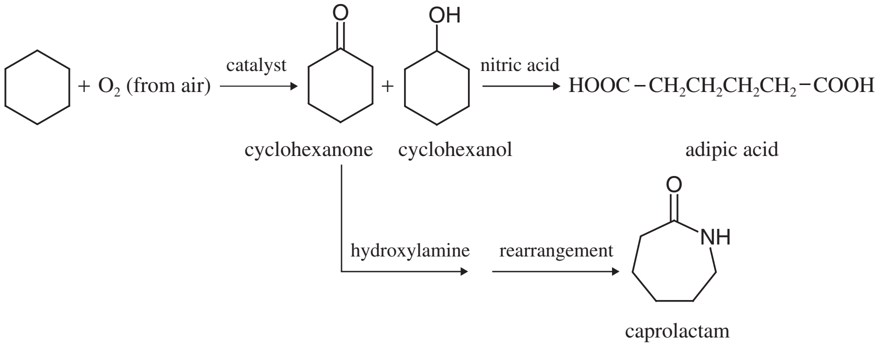


During the 1800s, benzene was of limited commercial value, finding use mainly as a solvent. But after the invention of the internal combustion engine and the automobile, it was found that motors ran better when the fuel contained benzene. This added a new economic incentive to recover all of the benzene possible from the steel industry's coke ovens. However, just prior to World War II, the importance of benzene as a chemical intermediate started to be recognized. These dual incentives (gasoline and chemical intermediate) led to new and improved benzene processes based on petrochemistry rather than coal.

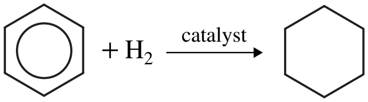
BENZENE DERIVATIVES

CYCLOHEXANE

Uses Over 90% of all the cyclohexane made is used to make nylon intermediates.



Manufacture



Suppliers Huntsman.

The price of *cyclohexane* tracks that of benzene and is only marginally higher because the conversion of benzene to cyclohexane is readily accomplished in very high yield.

The subsequent reaction of cyclohexane with air in the first step to adipic acid is not simple and, actually, is not well understood chemically. Only a small amount of cyclohexane present in the operation is allowed to react before the unreacted cyclohexane is recovered for recycle and the oxygen-containing products isolated for further reaction with nitric acid. Despite decades of research on this chemistry in efforts to increase yields and decrease by-product formation, substantial amounts of the starting cyclohexane do not end up as adipic acid. Some of the by-products are useful, but adipic acid manufacturers produce many millions of pounds per year of organic oils, which are ultimately burned as fuel because no use has been found for them.

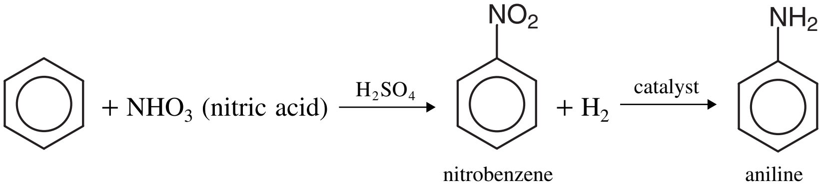
About half of the nylon made in the world is made from the *polymerization* of *caprolactam*. Although the *cyclohexanone* needed to make caprolactam can be made from cyclohexane as shown above, most of it is made from phenol.

BENZENE DERIVATIVES

NITROBENZENE AND ANILINE

Uses Virtually all of the nitrobenzene made is converted to aniline. The most important use of aniline is for the preparation of 4,4′-diaminodiphenyl methane (commonly called methylenedianiline or MDA), an intermediate to one of the main ingredients used to make polyurethane foams and rubber. Aniline is also used to make other rubber chemicals, textile fiber intermediates, dyes, and pharmaceuticals.

Manufacture



Suppliers BASF, Bayer, DuPont, Huntsman, First Chemical.

Up to three of the hydrogens on a benzene ring can be replaced with a nitro ($-NO_2$) group by reaction of nitric acid in sulfuric acid. When two hydrogens are replaced by nitro in this manner (dinitration), one isomer, the *meta*- or 1,3-, predominates. When three hydrogens are replaced (trinitration), the predominant isomer is the 1,3,5-isomer; *meta*-dinitrobenzene is made by this method as a starting material for *meta*-phenylenediamine, one of the components in the manufacture of a heat-resistant nylon sold in the U.S. as “Nomex” by DuPont.

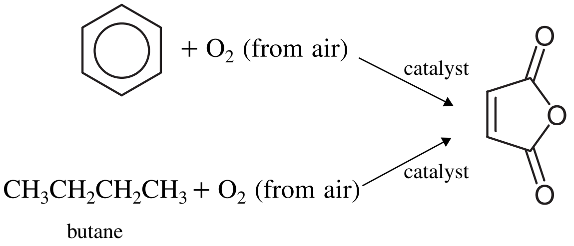
Obviously, polynitro- or polyaminobenzenes other than the *meta*-configuration may be desirable for one reason or another. This is where the skill and training of organic chemists are required because they have learned to be able to know and use the rules of chemistry to manipulate the shape and composition of carbon-containing molecules.

BENZENE DERIVATIVES

MALEIC ANHYDRIDE

Uses The largest single use of maleic anhydride is in the preparation of unsaturated polyester resins. It is first esterified with a polyalcohol (two or more hydroxyls) and then the double bond is copolymerized (crosslinked) with a vinyl monomer such as styrene to form a rigid structure. Such resins are usually reinforced with fiberglass (FRP). Maleic anhydride is also used to make oil additives and agricultural chemicals.

Manufacture



Suppliers Bayer, Huntsman, Ashland, BP Amoco.

For many years the *catalytic air oxidation* of benzene was the main source of maleic anhydride. Obviously, two carbons from each ring are wasted as carbon dioxide in this process. Although some is still made that way, most modern maleic anhydride plants are based on *butane oxidation*. Because butane is forecast to be plentiful and low-cost, new routes to four-carbon chemicals from maleic anhydride are under active development.

Unsaturated polyester resins based on maleic anhydride are widely used in coatings to manufacture boat hulls and truck caps and a variety of other uses where a smooth, weatherproof, hard-surfaced material is desired. Because these resin types are inherently brittle, fiberglass is frequently added for reinforcement. Consumption of unsaturated polyesters in the U.S. is well over a billion pounds per year, with about 50% going into construction and the marine industry.

XYLENES ($C_6H_4(CH_3)_2$)

Properties	There are three xylene isomers, commonly known as *ortho*-xylene, *meta*-xylene, and *para*-xylene. They are all colorless liquids. The *ortho*-isomer boils at 144°C, the *meta*- at 139.1°C, and the *par*a-at 138.5°C.
Commercial grades	Xylenes are available as an isomer mixture (about 10% *ortho*-, 72% *meta*-, and 18% *para*-) and as the pure isomers. The mixed xylenes are priced by the gallon while the pure isomers are priced per pound.
Uses	The mixed xylenes are used as solvents and as octane enhancers in gasoline. The largest use for each of the pure isomers is oxidation to the corresponding dicarboxylic acid.
Manufacture	The xylenes are obtained with benzene (and toluene) from the catalytic reforming of naphtha and separated from the aromatic mixture by distillation. From the mixed isomers, the *ortho*- can be obtained by distillation because its boiling point is sufficiently different. The *meta*- and *para*- are separated by either selective adsorption or by crystallization.
Producers	ExxonMobil, Chevron Phillips, BP Amoco, Citgo, Koch, Hess,

Of the over 4 billion pounds of xylene made each year in the U.S., about 40% is recovered as high-purity *para*-xylene, about 20% as *ortho*-xylene, and the rest used as mixed xylene in gasoline and for solvent purposes. The reason for the large use in gasoline is because xylene (like benzene and toluene) has very high fuel *anti-knock* characteristics (high octane rating). Thus, high-test gasoline has a higher percentage of aromatic hydrocarbons like xylene than regular-grade.

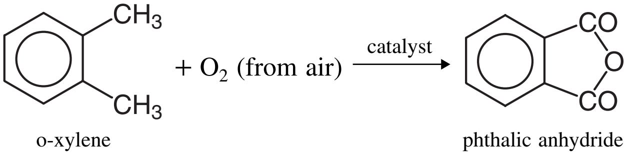
Because *ortho*-xylene is more readily isolated and purified (by distillation), it costs less than *para*-xylene. Like all petrochemicals, prices depend on the price of crude oil; but in early 2001, mixed-xylene was about 17 cents/lb while *para*-xylene was only about 15 cents due to high manufacturing capacity and low demand for use for making terephthalic acid. In the extremely high volumes in which such chemicals are sold, fractions of a penny difference in price can be very important.

XYLENE DERIVATIVES

PHTHALIC ANHYDRIDE (FROM *O*-XYLENE)

Uses A little over half of the phthalic anhydride produced is used for plasticizers in polymers while about 25% is used to manufacture unsaturated polyester resins. Phthalic anhydride also finds wide usage in the manufacture of paints (alkyd resins).

Manufacture



Suppliers Aristech Chemical, ExxonMobil, Koppers, Stepan, Sterling Chemical.

Plasticizers are very high-boiling liquids that when mixed with polymers like poly(vinyl chloride) modify the properties of the polymer to produce a material with added flexibility without losing other desirable properties such as strength. They are commonly made by reacting phthalic anhydride with a long-chain alcohol (typically eight carbons).

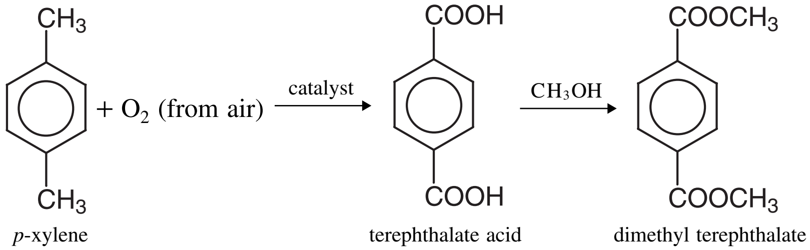
There are over 400 different commercial alkyd resin formulations based on phthalic anhydride used in the coatings business. Alkyd resins for paints are made by reacting phthalic anhydride with a poly-alcohol (usually from naturally occurring sources rather than synthetic) that contains unreacted double bonds. The paint dries by the resin crosslinking through reaction of the double bonds under the influence of oxygen in the air.

XYLENE DERIVATIVES

TEREPHTHALIC ACID AND DIMETHYL TEREPHTHALATE

Uses Both terephthalic acid (TPA) and dimethyl terephthalate (DMT) are used exclusively for the manufacture of polyesters for textile fibers (e.g,. "Dacron"), films, soft-drink bottles, and engineering resins for automotive applications. The glycol used for most TPA-based polyesters is ethylene glycol. The polyester is then known as polyethylene terephthalate, or PET.

Manufacture



Suppliers BP Amoco, DuPont, Eastman Chemical, KoSa.

The manufacture of *polyester* fibers and films requires high-purity starting materials. Terephthalic acid is very difficult to purify because it cannot be distilled and it is not soluble enough in any solvent for other types of purification. The dimethyl ester of terephthalic acid (DMT) can be distilled (although it is a high-melting solid) and so for many years the starting material of choice to make polyester fibers was DMT. However, processes were eventually developed that made very pure terephthalic acid directly so that no purification was needed. Now, either starting material can be, and is, used for making polyesters.

7 Environmental Protection and Waste Disposal

Despite the fact that the chemical industry is absolutely essential to our standard of living, it has a poor image with the majority of people. It is blamed wholly or in part for many problems perceived to adversely affect human health and the environment. These public concerns include destruction of the ozone layer, global warming, cancer-causing pollutants, endrocrine disruptors, poor air quality, poor water quality, etc. Because of these perceptions, the chemical industry has become highly regulated by federal, state, and local laws.

ENVIRONMENTAL PROTECTION

What is the environment?

It is all of the surrounding conditions and influences that affect the development of living things.

What is environmental pollution?

It is any process, natural or man-made, that leads to harmful or objectionable changes to the environment.

What is environmental protection?

It is any action taken to prevent environmental pollution.

The above questions and the answers may seem obvious to most people in view of the current and growing concern for our surroundings, but the terms are used so frequently in the press and on TV without explanation that it seems prudent to know the exact definitions.

TYPES OF POSSIBLE ENVIRONMENTAL POLLUTION BY THE CHEMICAL INDUSTRY

TO THE AIR

1. *Sulfur dioxide*: A toxic and corrosive gas emitted continuously in dilute form, principally from the burning of fossil fuels.
2. *Toxic gas emissions*: Usually concentrated chlorine-containing gases or other harmful vapors released by accident.
3. *Foul-smelling gases*: Sulfur-containing gases such as hydrogen sulfide that have an odor even at low concentrations.
4. *Dust*: Can be anywhere that minerals or finely-divided solids are handled.
5. *Smoke*: Man-made smoke is now mainly controlled in developed countries.
6. *Sprays*: Small liquid droplets in the air that can be caused by process upsets or by high wind.
7. *Radioactivity*: Accidental releases may occur.

TO WATER

1. S*ewage and organic industrial wastes*: This type of pollution adversely affects the oxygen content of water (BOD, biological oxygen demand).
2. *Bacteria and viruses*: Usually from sewage.
3. *Plant nutrients*: From sewage and drainage of fertilized farmland. Causes rapid algae growth that uses up oxygen (eutrophication).
4. *Organic pesticides*: Now mainly controlled by regulation.
5. *Waste minerals and chemicals*: Caused by leaching of mineral and chemical waste heaps and landfills. Can cause enormous damage.
6. *Plant discharge into waterways*: Now strictly regulated by law.
7. *Sediments*: Can cause turbidity and bottom sludge.
8. *Heat*: Changes plant growth rate and amount of dissolved oxygen.

METHODS OF POLLUTION CONTROL

1. *Reduction of effluent volume*: A first step. May require a combination of other control methods.
2. *Total elimination of effluent at the source*: The ultimate goal. Written into some regulations.
3. *Water reuse*: Widely practiced now.
4. *Recovery and recycle of ingredients*: Better utilization of raw materials saves money, natural resources, and the environment.
5. *Recovery of secondary products for sale*: Requires commitment and ingenuity.
6. *Physical separations*: The method that is filling up the landfills.
7. *Chemical treatment*: Widely practiced now. Will increase.
8. *Biological treatment*: Used in all sewage plants and many settling ponds.
9. *Incineration*: The only practical method of disposal for some wastes. Has opposition from many environmental groups.
10. *Dilution*: A widely used method of control in the past. Now unacceptable under many regulations.

POLLUTION CONTROL LAWS AND REGULATIONS

In the U.S., there are local, state, and federal laws regulating health, safety, and the environment. The laws that address the area of pollution control also cover health and safety, toxic substances, noise, transportation, and building site approval.

NATIONAL ENVIRONMENTAL POLICY ACT, 1969 (NEPA)

This act requires that all federal agencies consider the environmental impact of their actions. These agencies must use all practicable means "to achieve a harmonious balance between humanity and nature."

OCCUPATIONAL SAFETY AND HEALTH ACT, 1970 (OSHA)

Under this act, the Department of Labor sets safety standards, inspects workplaces, and sets penalties for violations. This act also established the National Institute for Occupational Safety and Health (NIOSH) to develop and establish health standards.

THE RESOURCE CONSERVATION AND RECOVERY ACT, 1976 (RCRA)

This act governs in detail how the chemical industry must manage hazardous wastes. Generation, handling, transportation, and disposal are included in the regulations.

TOXIC SUBSTANCES CONTROL ACT, 1976 (TSCA)

Requires a federal inventory of existing chemicals in commerce, notification for listing of new chemicals or new uses for existing chemicals, and can require testing of chemicals for toxicity prior to approval for listing.

THE CLEAN AIR ACT, 1970 AND SUBSEQUENT AMENDMENTS

Gives the Environmental Protection Agency (EPA) power to adopt and enforce air pollution standards.

PARTIAL HISTORY OF POLLUTION AND POLLUTION CONTROL BY THE CHEMICAL INDUSTRY

Year	
ca. 2500 BC	The Sumerians used sulfur compounds for insect control.
ca.1500 BC	The Chinese used naturally occurring chemicals to control insects in grain.
>1700	Copper pollution in Palestine due to copper smelting thousands of years before.
1773	Discharge of hydrogen chloride into the air from the manufacture of soda ash. Continued until 1864 when early pollution control laws were passed.
>1900	Sulfuric acid manufacture released both sulfur oxides and arsenic into the environment.
1906	The Pure Food and Drug Act established the Food and Drug Administration (FDA).
1917	Workers making explosives for World War I developed jaundice from dust inhalation.
1921	A chemical nitrate plant in Germany exploded, killing more than 600 people.
1935	The Chemical Manufacturers Association (CMA), a trade group, established a Water Resources Committee to study the effect of their industry on water bodies.
1947	A ship in Texas City, TX, loaded with ammonium nitrate exploded, killing 462 people and injuring more than 3000.
1948	The CMA established an Air Quality Committee to study methods for improving air quality.
1958	The Delaney Amendment to the Food and Drug Act addressed the control of food additives.
1959	Cranberries destroyed by the federal government due to contamination by a weedkiller.
1960	A drug prescribed in the 1950s to prevent miscarriages was reported to cause cancer and other problems in female children of the drug recipients.

1962	A drug prescribed as a tranquilizer for pregnant women caused severe birth defects.
1962	A book indicted DDT and other pesticides for the poisoning of wildlife. DDT was banned in the U.S. in 1972, but it remains in use in developing countries.
1965	Nonbiodegradable detergents were banned when they were found as contaminants in some rivers.
1965	In Japan, 46 people died from eating mercury-contaminated fish from a body of water polluted by a plastics company.
1966	Polychlorinated biphenyls (PCBs), a carcinogen in animals, were found in the environment. The use of PCBs was banned in 1978.
1969	A new artificial sweetener (cyclamate) was banned because it caused cancer in animals when fed in large amounts. Not banned in other countries.
1970	Occupational Safety and Health Act (OSHA) set safety standards for workplaces.
1974	An explosion at a nylon-intermediates plant in England killed 28 people.
1974	Three men working at a poly(vinyl chloride) plant were found to have a rare form of cancer.
1975	Almost half of the workers at a pesticide plant in Virginia were found to be suffering from poisoning. The nearby James River containing oyster beds was found to be contaminated with the same chemical.
1976	A chemical plant in Italy exploded and spread a known animal carcinogen (dioxin) over a large area. No deaths or birth defects were ever shown to be due to this release.
1976	The Toxic Substances Control Act (TSCA) was adopted.
1976	The Resource Conservation and Recovery Act (RCRA) was passed.
1977	Polyacrylonitrile plastic beverage bottles were banned because of possible migration of acrylonitrile (a weak carcinagen) into the bottle contents.
1977	Some employees making a soil fumigant (DBCP) became sterile. It is now banned.
1977	Benzene was linked to high rates of leukemia.

1977	A fire-retardant (Tris) used to treat children's sleepwear was found to be an animal carcinogen.Tris is now banned.
1978	Chlorofluorocarbons banned as aerosol propellants because of potential stratospheric ozone destruction.
1978	An old chemical dump in New York (Love Canal) started to leak into the environment.
1980	Regulation of asbestos insulation in school buildings initiated.
1980	The Comprehensive Environmental Response, Compensation and Liability Act established a "Superfund" to cleanup hazardous landfills.
1983	Over 600 people in Spain died as a result of using contaminated oil sold as "olive oil."
1984	In Bhopal, India, more than 2500 people died from a release of methyl isocyanate.
1985	The chemical industry initiated the "Responsible Care" program to improve the public's perception of the industry. This program promotes environmental, health, and safety performance and total honesty in dealing with the press and the public. Now embraced and practiced by virtually all chemical companies.
1997	According to the U.S. Bureau of Labor Statistics, the lost workday injuries (per 100 employees per year) for the chemical industry was 2.1. The corresponding number for all manufacturing was 4.2. The numbers for other occupations were: agriculture 4.0, mining 3.7, construction 4.4, transportation 4.7, and wholesale and retail trade 2.9.

Information Sources

Sources for information on chemistry and the chemical industry are listed. The type of information available (see keywords) in each source is indicated by the capital letters in parentheses following each listing.

Of these sources, *Kirk-Othmer's Encyclopedia of Chemical Technology* is particularly recommended for questions on chemistry and on end uses. For information on properties and on toxicity and handling hazards, *Patty's Industrial Hygiene*, Material Safety Data Sheets (MSDS), and the Aldrich catalog are very useful. Questions on industrial chemistry should be directed to *Ullman's Encyclopedia of Industrial Chemistry*, and the texts by Chenier, Heaton, and White. *Hawley's Condensed Chemical Dictionary* is valuable as a source for definitions of the terms (language) of chemistry.

INFORMATION SOURCES

A. Industrial Chemistry
B. Organic Chemistry
C. Inorganic Chemistry
D. Polymer Chemistry
E. Properties
F. Nomenclature
G. Environmental
H. Toxicity and Handling Hazards
I. Facts and Figure
J. End Uses

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2. Arpe, H.J. (Ed.), *Ullman's Encyclopedia of Industrial Chemistry,* 5th ed., 37 vols., VCH Publishers, 1997. (A,B,C,D,E,G,I,J)
3. Budavars, S. (Ed.), *The Merck Index,* 12th ed., Merck & Co., 1996. (E,F,H,J)
4. Burdick, D.L. and Leffler, W.L., *Petrochemicals in Nontechnical Language,* John Wiley & Sons, 1986. (A,B,C,D,I,J)
5. Chenier, P.J., *Survey of Industrial Chemistry,* 2nd ed., VCH Publishers, 1992. (A,B,C,D,I)
6. Harris, R. (Ed.), *Patty's Industrial Hygiene,* 5th ed., 4 vols., John Wiley & Sons, 2000. (E,F,G,H,J)
7. Heaton, C.J. (Ed.), *An Introduction to Industrial Chemistry,* Blackie & Son, Ltd., 1991. (A,B,C,D,I,J)
8. Kroschwitz, J.I. et al. (Ed.), *Kirk-Othmer's Encyclopedia of Chemical Technology,* 4th ed., 27 vols., Wiley-Interscience, 1991–1998. (A,B,C,D,E,J)
9. Kroschwitz, J.I. et al. (Ed.), *Kirk-Othmer's Concise Encyclopedia of Chemical Technology,* 4th ed., Wiley-Interscience, 1999. (A,B,C,D,E,J)
10. Lewis, R.J. (Ed.), *Hawley's Condensed Chemical Dictionary,* 13th ed., John Wiley & Sons, 1997. (E,F,H,J)
11. Lide, D.R. (Ed.), *Handbook of Chemistry and Physics,* 81st ed., CRC Press, 2000. (B,C,E,F,H,I)
12. Material Safety Data Sheets (MSDS) — Available from the chemical manufacturer and the marketing agent. Also available online at MSDS-SEARCH.com and at Sigma-Aldrich.com. (E,F,G,H)
13. White, H.L., *Introduction to Industrial Chemistry,* John Wiley & Sons, 1986. (A,B,C,D,I,J)