

CAFFEINE, THEOBROMINE, AND THEOPHYLLINE

Caffeine (melting point: 238°C, sublimates at 178°C; density: 1.23), theobromine, and theophylline are xanthine derivatives classified as central nervous stimulants, but differing markedly in their properties. They can be extracted from a number of natural sources.

Caffeine has been isolated from waste tea and from the decaffeination of coffee by extraction at 70°C, using rotating countercurrent drums and an organic solvent, frequently trichloroethylene. The solvent is drained off, and the beans steamed to remove residual solvent. The extraction solvent is evaporated, and the caffeine is hot-water-extracted from the wax, decolorized with carbon, and recrystallized.

Caffeine is also manufactured synthetically by, for instance, the methylation of theobromine and also total synthesis by methylation and other reactions based upon urea.

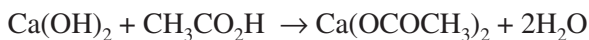
Caffeine is used by the pharmaceutical industry and also by the soft-drink industry for cola-style drinks.

CALCITE

See Calcium Carbonate.

CALCIUM ACETATE

Calcium acetate is manufactured by the reaction of calcium carbonate or calcium hydroxide with acetic acid.



Calcium acetate was formerly used to manufacture acetone by thermal decomposition:

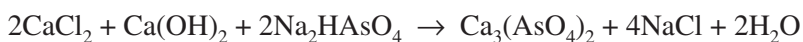


but now it is employed largely in the dyeing of textiles.

See Acetone.

CALCIUM ARSENATE

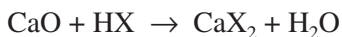
Calcium arsenate is produced by the reaction of calcium chloride, calcium hydroxide, and sodium arsenate or lime and arsenic acid:



Some free lime (CaO) is usually present. Calcium arsenate is used extensively as an insecticide and as a fungicide.

CALCIUM BROMIDE

Calcium bromide (CaBr_2) and calcium iodide (CaI_2) have properties similar to those of calcium chloride (CaCl_2). They are prepared by the action of the halogen acids (HX) on calcium oxide or calcium carbonate.



where X is bromine (Br) or iodine (I).

Calcium bromide and calcium iodide are sold as hexahydrates for use in medicine and photography. Calcium fluoride (CaF_2) occurs naturally as fluorspar.

See Fluorine.

CALCIUM CARBONATE

Calcium carbonate (CaCO_3) occurs naturally as calcite (density: 2.7), a widely distributed mineral. Calcite is a common constituent of sedimentary rocks, as a vein mineral, and as deposits from hot springs and in caves as stalactites and stalagmites. Calcite is white or colorless through shades of gray, red, yellow, green, blue, violet, brown, or even black when charged with impurities; streaked, white; transparent to opaque. It may occasionally show phosphorescence or fluorescence.

Calcium carbonate is one of several important inorganic chemicals (Fig. 1) and is widely used in both its pure and its impure states. As marble chips, it is sold in many sizes as a filler for artificial stone, for the neutralization of acids,

Starting material	Reactant or process	Primary product	Reactant or process	Secondary products
Sulfur	Contact process	Sulfuric acid	Wet process	Aluminum sulfate
				Phosphoric acid
Air	Liquefaction	Liquid nitrogen		Ammonium sulfate
	Liquefaction	Liquid oxygen		Ammonia
Methane	Steam reforming	Synthesis gas	Haber process	Nitric acid
				Ammonium nitrate
Calcium carbonate	Calcining	Carbon dioxide	Water	
Sodium chloride	Solvay process	Calcium oxide		Calcium hydroxide
	Solvay process	Sodium carbonate		Sodium silicate
	Electrolysis	Sodium hydroxide		Silica gel
	Electrolysis	Chlorine		Chlorinated hydrocarbons
				Hydrogen chloride

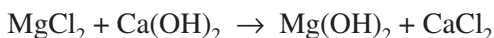
FIGURE 1 Important inorganic chemicals.

and for chicken grit. Marble dust is employed in abrasives and in soaps. Crude, pulverized limestone is used in agriculture to *sweeten* soils, and pulverized arid levigated limestone is used to replace imported chalk and whiting.

Whiting is pure, finely divided calcium carbonate prepared by wet grinding and levigating natural chalk. Whiting mixed with 18% boiled linseed oil yields *putty*, which sets by oxidation and by formation of the calcium salt. Much whiting is consumed in the ceramic industry. Precipitated, or artificial, whiting arises through precipitation, e.g., from reacting a boiling solution of calcium chloride with a boiling solution of sodium carbonate or passing carbon dioxide into a milk-of-lime suspension. Most of the latter form is used in the paint, rubber, pharmaceutical, and paper industries.

CALCIUM CHLORIDE

Calcium chloride is obtained from natural brine that typically contains 14% sodium chloride (NaCl), 9% calcium chloride (CaCl₂), and 3% magnesium chloride (MgCl₂). Evaporation precipitates sodium chloride, and magnesium chloride is removed by adding slaked lime to precipitate magnesium hydroxide.



Calcium chloride is used on roads for dust control in the summer and deicing in the winter, since it is less corrosive to concrete than is sodium chloride. Other applications of calcium chloride include thawing coal, as a component of oil and gas well fluids, and as antifreeze for concrete.

CALCIUM FLUORIDE

See Calcium Bromide, Fluorine.

CALCIUM HYPOCHLORITE

Calcium hypochlorite is manufactured by chlorination of calcium hydroxide $[\text{Ca(OH)}_2]$ followed by the separation of the calcium hypochlorite $[\text{Ca(OCl)}_2]$ through salting out from solution with sodium chloride.



Calcium hypochlorite is also manufactured by the formation under refrigeration of the complex salt $\text{Ca(OCl)}_2 \cdot \text{NaOCl} \cdot \text{NaCl} \cdot 12\text{H}_2\text{O}$, which is prepared by the chlorination of a mixture of sodium hydroxide and calcium hydroxide. The salt is reacted with a chlorinated lime slurry, filtered to remove salt, and dried, resulting finally in a stable product containing 65 to 70% calcium hypochlorite.

The great advantage of calcium hypochlorite is that it does not decompose on standing as does bleaching powder. It is also twice as strong as ordinary bleaching powder and is not hygroscopic.

CALCIUM IODIDE

See Calcium Bromide.

CALCIUM LACTATE

Calcium lactate is manufactured by the reaction of calcium carbonate (CaCO_3) or hydroxide $[\text{Ca}(\text{OH})_2]$ with lactic acid.

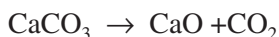


Calcium lactate is sold for use in medicines and in foods as a source of calcium and as an intermediate in the purification of lactic acid from fermentation processes.

CALCIUM OXIDE

Calcium oxide (CaO, lime, quicklime, unslaked lime) is differentiated from calcium hydroxide [Ca(OH)₂, slaked lime, hydrated lime] and limestone (CaCO₃, calcite, calcium carbonate, marble chips, chalk) by formula and by behavior. A saturated solution of calcium oxide in water is called *limewater* and a suspension in water is called *milk of lime*.

Lime is manufactured by *calcining* or heating limestone in a kiln.



Temperatures used in converting limestone into lime are on the order of 1200 to 1300°C.

In the process (Fig. 1), the limestone (CaCO₃) is crushed and screened to a size of approximately 4 to 8 inches. The limestone enters the top of the kiln (Fig. 2) and air enters the bottom and fluidizes the solids for better circulation and reaction. Approximately 98 percent decarbonation is typical.

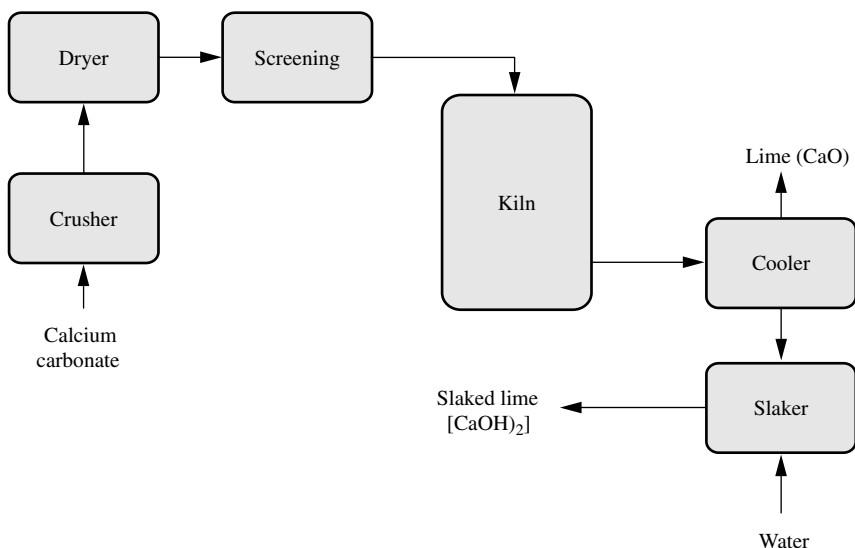
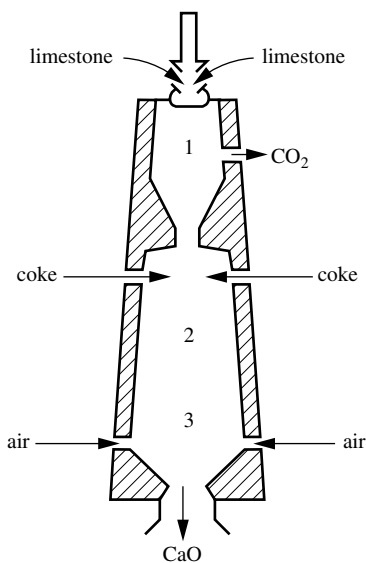


FIGURE 1 Manufacture of lime.



1. *preheating section*

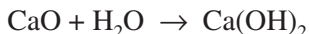
2. *reaction zone*

3. *cooling zone*

FIGURE 2 A lime kiln.

When a kiln is used in conjunction with the Solvay process and the manufacture of soda ash, coke can be fired in the kiln along with limestone to give the larger percentages of carbon dioxide needed for efficient soda ash production. If a purer lime product is desired, the fine lime can be taken from area 4 in (Fig. 2). A less pure product is obtained from the bottom kiln section. Another kind of kiln is the rotating, nearly horizontal type. These can be as much as 12 ft in diameter and 450 ft long. Limestone enters one end. It is heated, rotated, and slowly moves at a slight decline to the other end of the kiln, where lime is obtained.

For most applications slaked lime $[\text{Ca}(\text{OH})_2]$ is sold, since hydration of lime:



is an exothermic reaction and could ignite paper or wood containers of the unslaked material. Slaked lime is slightly soluble in water to give a weakly basic solution.

Lime is used in the metallurgical industry as a flux in the manufacture of steel. Silicon dioxide is a common impurity in iron ore that cannot be

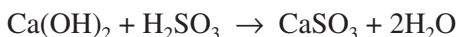
melted unless it combines with another substance first to convert it to a more fluid lava called *slag*. The molten silicate slag is less dense than the molten iron and collects at the top of the reactor, where it can be drawn off.



Lime is used in water treatment to remove calcium and bicarbonate ions.



Lime is also used in pollution control where lime scrubbers in combustion stacks remove sulfur dioxide present in gases from the combustion of high-sulfur coal.



Lime is also used in the kraft pulping process for the purpose of regenerating caustic soda (sodium hydroxide).



The caustic soda is then used in the digestion of wood. The lime is regenerated from the limestone by heating in a lime kiln.

A large part of portland cement is lime-based. Sand, alumina, and iron ore are mixed and heated with limestone to 1500°C. Average percentages of the final materials in the cement and their structures are:

20%	2CaO·SiO ₂	Dicalcium silicate
50	3CaO·SiO ₂	Tricalcium silicate
10	3CaO·Al ₂ O ₃	Tetracalcium aluminate
10	4CaO·Al ₂ O ₃ ·Fe ₂ O ₃	Tetracalcium aluminoferrite
10	MgO	Magnesium oxide

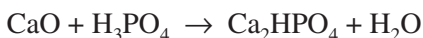
The percentage of dicalcium silicate determines the final strength of the cement, whereas the amount of tricalcium silicate is related to the early strength (7 to 8 days) required of the cement. Tricalcium aluminate relates to the set in the cement, and tetracalcium aluminoferrite reduces the heat necessary in manufacture.

See Cement.

CALCIUM PHOSPHATE

Monobasic calcium phosphate $[\text{Ca}(\text{H}_2\text{PO}_4)_2]$ is manufactured by crystallization after evaporation and cooling of a hot solution of lime $[\text{CaO}$ or $\text{Ca}(\text{OH})_2]$ and strong phosphoric acid (H_3PO_4) . The crystals are centrifuged, and the highly acidic mother liquor returned for reuse. This acid salt is also made by spray drying a slurry of the reaction product of lime and phosphoric acid.

Dibasic calcium phosphate (CaHPO_4) is manufactured from phosphoric acid and lime:



whereas *calcium metaphosphate* is manufactured from phosphate rock, phosphorus pentoxide, and phosphorous acid.



In this process the phosphorus pentoxide contacts the lump rock in a vertical shaft.

This calcium metaphosphate may be regarded as a dehydrated triple superphosphate made directly from phosphate rock. The calcium metaphosphate is quite insoluble, and it must hydrolyze to become effective.



See Lime.

CALCIUM SOAPS

Calcium soaps such as calcium stearate, calcium palmitate, and calcium abietate are made by the action of the sodium salts of the acids on a soluble calcium salt such as calcium chloride (CaCl_2).

Calcium soaps are insoluble in water but are soluble in hydrocarbons. They tend to form jellylike masses and are used as constituents of greases and as waterproofing agents.

CALCIUM SULFATE

Calcium sulfate occurs in large deposits throughout the world as its hydrate (gypsum; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). When heated at moderate temperatures, gypsum loses part of the water to form a semihydrate.



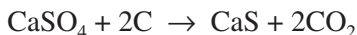
At higher temperatures, gypsum loses all its water and becomes anhydrous calcium sulfate, or *anhydrite*.

Calcined gypsum (the half-water salt) can be made into wall plaster by the addition of a filler material such as asbestos, wood pulp, or sand. Without additions, it is plaster of Paris and is used for making casts and for plaster.

The usual method of calcination of gypsum consists in grinding the mineral and placing it in large calciners holding up to 20 or more tons. The temperature is raised to about 120 to 150°C, with constant agitation to maintain a uniform temperature. The material in the kettle, *plaster of Paris* or *first-settle plaster*, may be withdrawn at this point, or it may be heated further to 190°C to give a material known as *second-settle plaster*. First-settle plaster is approximately the half-hydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$), and the second form is anhydrous (CaSO_4). Gypsum may also be calcined in rotary kilns similar to those used for limestone.

CALCIUM SULFIDE

Calcium sulfide is made by reducing calcium sulfate with coke.



Calcium sulfide is used as a depilatory in the tanning industry and in cosmetics and, in a finely divided form, it is employed in luminous paints. Calcium polysulfides (CaS_n), such as calcium disulfide (CaS_2) and calcium pentasulfide (CaS_5), are made by heating sulfur and calcium hydroxide.



The calcium polysulfides are used as fungicides.

See Calcium Sulfate.

CAPROLACTAM

Caprolactam (melting point: 69.3°C, density: 1.02, flash point 125°C, fire point: 140°C), so named because it is derived from the original name for the C₆ carboxylic acid, caproic acid, is the cyclic amide (lactam) of 6-aminocaproic acid.

Caprolactam is usually manufactured from cyclohexanone, made by the oxidation of cyclohexane or by the hydrogenation/oxidation of phenol (Fig. 1), although the manufacture can be an integrated process with several starting materials (Fig. 2). The cyclohexanol that is also produced with the cyclohexanone can be converted to cyclohexanone by a zinc oxide (ZnO) catalyst at 400°C. The cyclohexanone is converted into the oxime with hydroxylamine, which then undergoes rearrangement to give caprolactam.

Sulfuric acid at 100 to 120°C is often used as the acid catalyst, but phosphoric acid is also used, since after treatment with ammonia the by-product

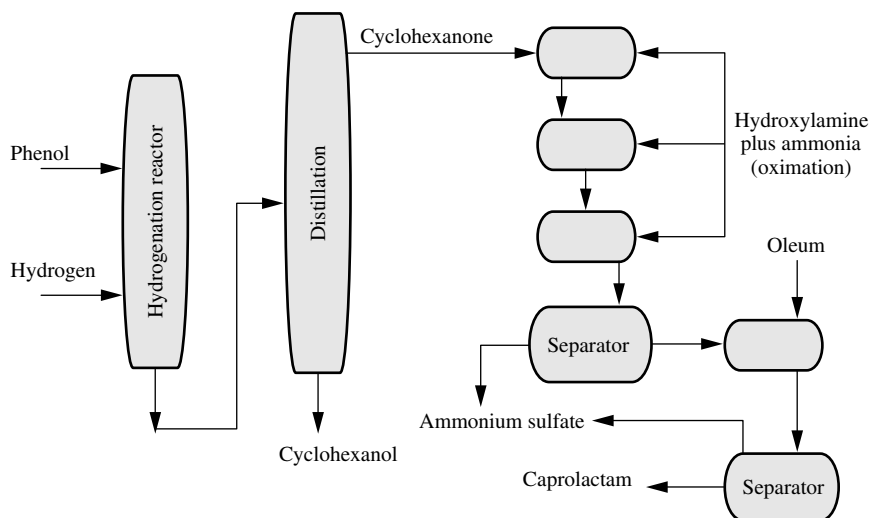


FIGURE 1 Manufacture of caprolactam from phenol.

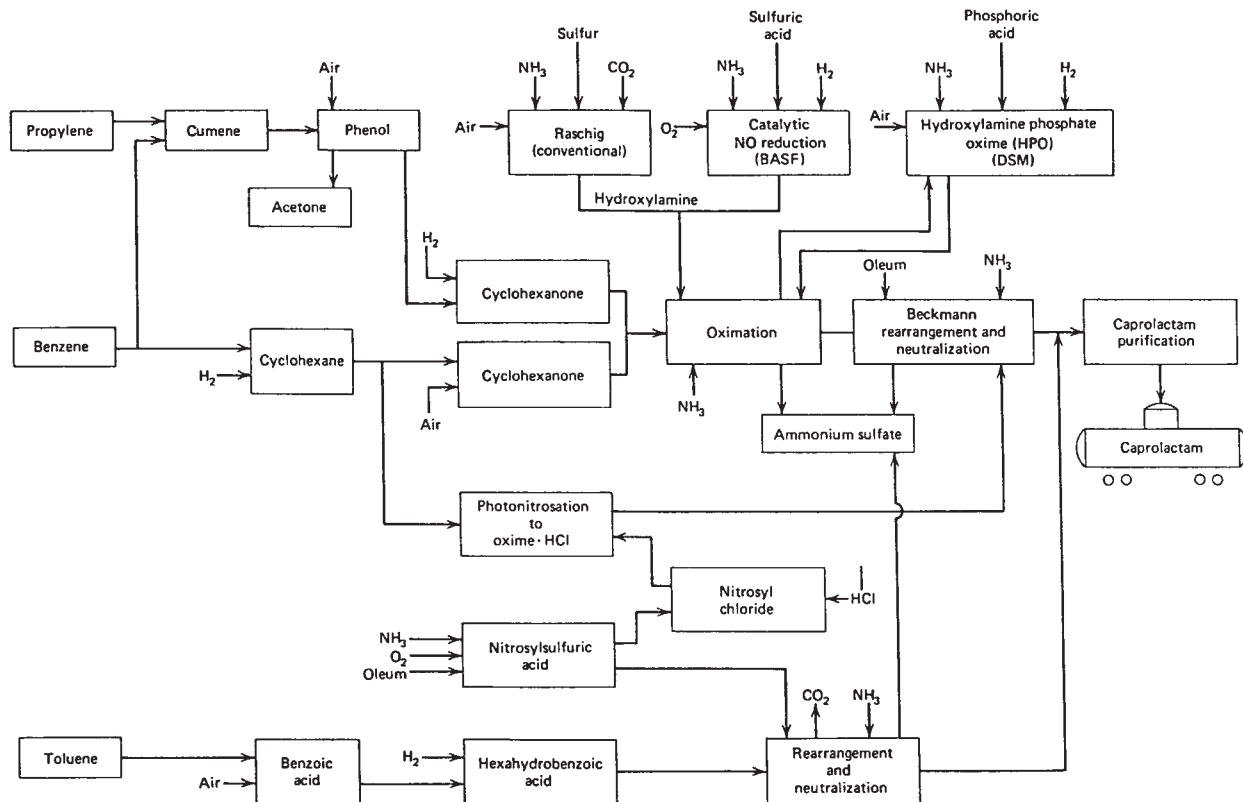


FIGURE 2 Integrated processes for the manufacture of caprolactam from various sources.

becomes ammonium phosphate that can be sold as a fertilizer. The caprolactam can be extracted and vacuum distilled (boiling point: 139°C/12 mmHg) and the overall yield is 90 percent.

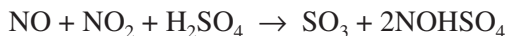
Caprolactam is also manufactured from toluene (Fig. 2) by oxidation of toluene (with air) to benzoic acid at 160°C and 10 atm pressure. The benzoic acid is then hydrogenated under pressure (16 atm) and 170°C in a series of continuous stirred tank reactors. The cyclohexane carboxylic acid is blended with oleum and fed to a multistage reactor, where it is converted to caprolactam by reaction with nitrosyl sulfuric acid.

Another process utilizes a photochemical reaction in which cyclohexane is converted into cyclohexanone oxime hydrochloride (Fig. 2), from which cyclohexanone is produced. The yield of cyclohexanone is estimated at about 86 percent by weight. Then, in a rearrangement reaction, the cyclohexanone oxime hydrochloride is converted to *ε*-caprolactam.

Caprolactam is used for the manufacture of nylon 6, especially fibers and plastic resin and film. Nylon 6 is made directly from caprolactam by heating with a catalytic amount of water.

In one process for nylon manufacture, the feedstock is nitration-grade toluene, air, hydrogen, anhydrous ammonia (NH₃), and sulfuric acid (H₂SO₄). The toluene is oxidized to yield a 30% solution of benzoic acid, plus intermediates and by-products. Pure benzoic acid, after fractionation, is hydrogenated with a palladium catalyst in stirred reactors operated at about 170°C under a pressure of 147 psi (1013 kPa). The product, cyclohexanecarboxylic acid, is mixed with sulfuric acid and then reacted with nitrosylsulfuric acid to yield caprolactam.

The nitrosylsulfuric acid is produced by absorbing mixed nitrogen oxides (NO + NO₂) in sulfuric acid:



The resulting acid solution is neutralized with ammonia to yield ammonium sulfate [(NH₄)₂SO₄] and a layer of crude caprolactam that is purified according to future use.

CARBON

Carbon exists in several forms: lampblack, carbon black, activated carbon, graphite, and industrial diamonds. The first three types of carbon are examples of *amorphous carbon*.

The term *carbon black* includes furnace black, colloidal black, thermal black, channel black, and acetylene black. Carbon black is mostly derived from petroleum and involves partial combustion or a combination of combustion and thermal cracking of hydrocarbons, and to a lesser extent natural gas, at 1200 to 1400°C.

Lampblack, is soot formed by the incomplete burning of carbonaceous solids or liquids. It is gradually being replaced in most uses by *carbon black* that is the product of incomplete combustion. *Activated carbon* is amorphous carbon that has been treated with steam and heat until it has a very great affinity for adsorbing many materials. *Graphite* is a soft, crystalline modification of carbon that differs greatly in properties from amorphous carbon and from diamond. *Industrial diamonds*, both natural and synthetic, are used for drill points, special tools, glass cutters, wire-drawing dies, diamond saws, and many other applications where this hardest of all substances is essential.

Lampblack, or soot, is an old product and is manufactured by the combustion of petroleum or coal-tar by-products in an oxygen-diminished atmosphere. In the process, the soot is collected in large chambers from which the *raw* lampblack is removed, mixed with tar, molded into bricks, or *pugs*, and calcined up to about 1000°C, after which the product is ground to a fine powder.

The four basic *carbon black* manufacturing processes are either of the partial combustion type (the channel, oil furnace, or gas furnace process) or of the cracking type (the thermal process).

The oil furnace process uses aromatic petroleum oils and residues as feedstock and in the *oil furnace process* (Fig. 1), a highly aromatic feedstock oil (usually a refinery catalytic cracker residue or coal tar-derived material) is converted to the desired grade of carbon black by partial combustion and pyrolysis at 1400 to 1650°C in a refractory (mainly alumina) -lined steel reactor.

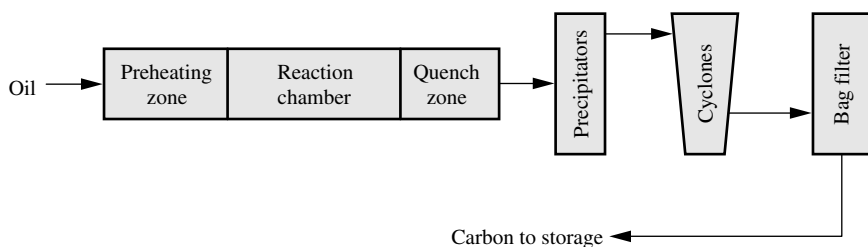


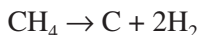
FIGURE 1 Carbon manufacture by the oil furnace process.

The feedstock is atomized and sprayed through a specially designed nozzle into a highly turbulent combustion gas stream formed by preburning natural gas or oil with about a 50 percent excess of air. Insufficient air remains for feedstock combustion, and the oil spray is pyrolyzed in a few microseconds into carbon black with yields (based on carbon) varying from 65 to 70 percent for large carcass-grade types down to about 35 percent for small tread-grade types.

The emissions from the reaction chamber enter the tunnel where it is quenched with water to about 200°C. Tunnel and combustion chamber dimensions vary, but frequently are from 2 to 6 m long and from 0.1 to 1 m in internal diameter. Further downstream, precipitators, cyclones, and to a greater extent bag filters (insulated to remain above 100°C) are used to separate the product black from water vapor and the combustion off-gases. Fiberglass bag filters allow near quantitative yield of the carbon black. Following pulverization and grit removal steps, the loose, fluffy black is normally pelletized for convenient bulk handling and to reduce the tendency to form dust. In the commonly used wet pelletizing process, the black is agitated and mixed with water in a trough containing a rotating shaft with radially projecting pins, which form the pellets. The wet pellets, usually in the 25- to 60-mesh range, are dried in a gas-fired rotating-drum dryer. In the dry pelletizing process, pellets are formed by gentle agitation and rolling of the black in horizontal rotating drums (about 3 m in diameter and 6 to 12 m long) for periods of 12 to 36 hours. An oil pelletizing process is also used, to a minor extent, for specialty applications (e.g., certain ink-grade blacks).

The *channel black process* involves the impingement of natural gas flames on 20- to 25-cm *channel irons* that are slowly reciprocated over scrapers to remove soot deposits. The type of black produced is controlled by burner-tip design, burner-to-channel distance, and air supply (degree of partial combustion).

In the *thermal black process*, natural gas is cracked to carbon black and hydrogen at 1100 to 1650°C in a refractory-lined furnace in a two-cycle (heating and “making,” or decomposition) operation. The reaction is



Yields of carbon are in the range 30 to 45 percent.

The *gas furnace process*, is similar to the oil furnace process but, like the *thermal black process*, uses natural gas as feedstock.

Activated carbon is manufactured from carbonaceous materials, such as petroleum coke, sawdust, lignite, coal, peat, wood, charcoal, nutshells, and fruit pits. Activation is a physical change wherein the surface of the carbon is increased by the removal of hydrocarbons by any one of several methods. The most widely used methods involve treatment of the carbonaceous material with oxidizing gases such as air, steam, or carbon dioxide, and the carbonization of the raw material in the presence of chemical agents such as zinc chloride or phosphoric acid.

After activated carbon has become saturated with a vapor or an adsorbed color, either the vapor can be steamed out, condensed, and recovered (Fig. 2), or the coloration can be destroyed and the carbon made ready for reuse. The oldest example of this process uses the decolorizing carbon long known as *bone char*, or *bone black*. This consists of about 10% carbon deposited on a skeleton of calcium phosphate [$\text{Ca}_3(\text{PO}_4)_2$] and is made by the carbonization of fat-free bones in closed retorts at 750 to 950°C.

Graphite, a naturally occurring form of carbon, has been known for many centuries and occurs throughout the world in deposits of widely

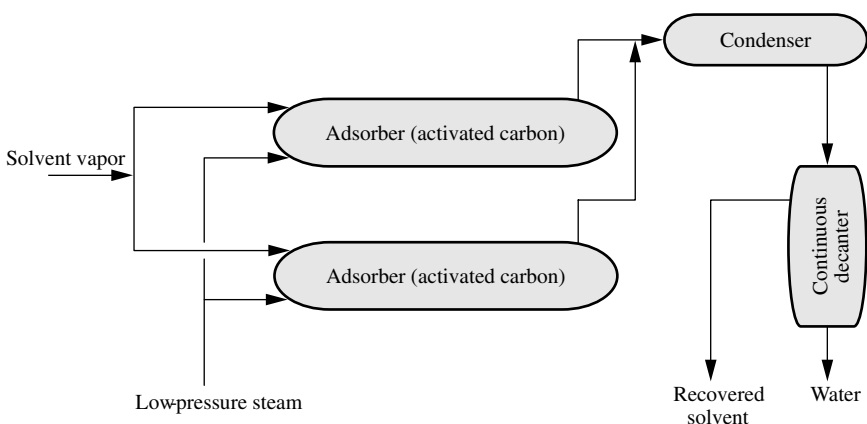
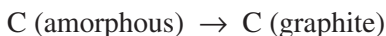


FIGURE 2 Solvent recovery process.

varying purity and crystalline size and perfection. For import purposes, natural graphite is classified as *crystalline* and *amorphous*. The latter is not truly amorphous but has an imperfect lamellar microcrystalline structure.

Graphite is made electrically from retort or petroleum coke (Fig. 3). Temperatures on the order of 2700°C are necessary.



In the process, the carbon feedstock is calcined (1250°C) to volatilize any impurities, after which the calcined products are ground, screened, weighed, mixed with binder, formed by molding or extrusion into green electrodes, and arranged in the furnace (Fig. 4).

In the manufacture of industrial diamonds, the process is a batch process and requires pressures and temperatures in the region of thermodynamic stability for diamond and a molten catalyst-solvent metal consisting of a group VIII metal or alloy. Special ultra high-pressure apparatus is used, the moving members of which are forced together by large hydraulic presses. Different types and sizes of diamond particles, or crystals, require different conditions of pressure, temperature, catalyst-solvent, and reaction time. The crude diamonds are cleaned and graded by size and shape.

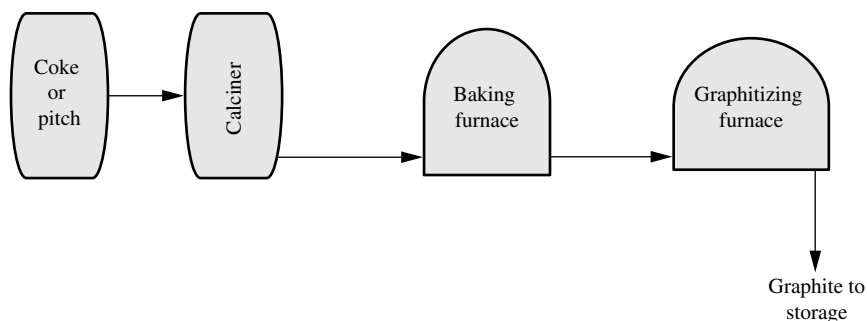


FIGURE 3 Graphite manufacture.

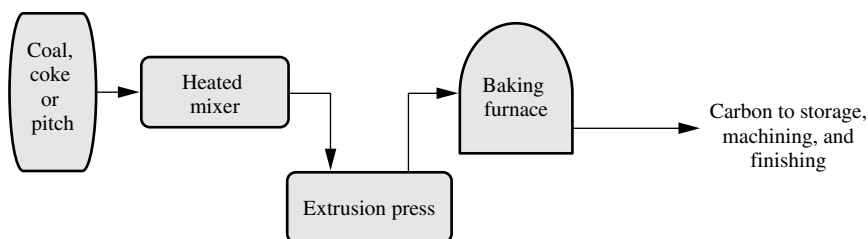


FIGURE 4 Manufacture of carbon electrodes.

Carbon black has uses similar to some inorganic compounds. For example, it is the most widely used black pigment. It is also an important reinforcing agent for various elastomers. It is used in tires and other elastomers and is a leading pigment in inks and paints.

Carbon black is a black pigment, and lampblack, which has a larger particle size, is used for tinting to produce shades of gray. Carbon black is very opaque and has excellent durability, resistance to all types of chemicals, and light fastness.

CARBON BLACK

See Carbon.

CARBON DIOXIDE

Carbon dioxide (CO₂, melting point: −56.6°C at 76 psi – 527 kPa, density: 1.9769 g/L at 0°C) is a colorless, odorless gas. Solid carbon dioxide sublimates at −79°C (critical pressure: 1073 psi, 7397 kPa, critical temperature: 31°C). High concentrations of the gas do cause stupefaction and suffocation because of the displacement of ample oxygen for breathing. Carbon dioxide is soluble in water (approximately 1 volume carbon dioxide in 1 volume water at 15°C), soluble in alcohol, and is rapidly absorbed by most alkaline solutions.

Carbon dioxide is made by steam-reforming hydrocarbons (Fig. 1), and much of the time natural gas is the feedstock.

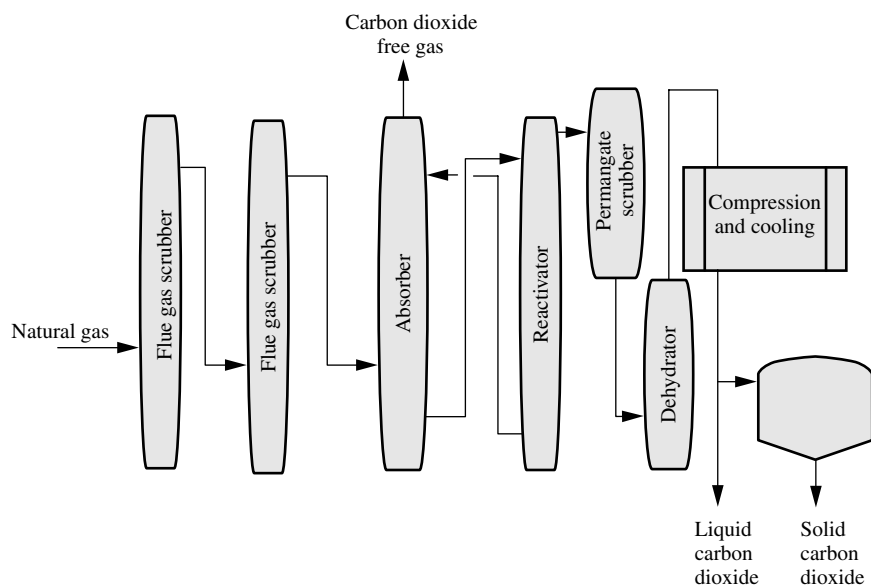
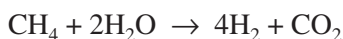


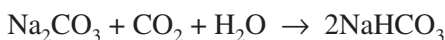
FIGURE 1 Manufacture of carbon dioxide.

A small amount of carbon dioxide is still made from fermentation of grain; ethyl alcohol is the main product (Fig. 2).



Other small amounts are obtained from coke burning, the calcination of lime, in the manufacture of sodium phosphates from soda ash and phosphoric acid, by recovery from synthesis gas in ammonia production, recovery as a by-product in the production of substitute natural gas, and recovery from natural wells.

Although carbon dioxide must be generated on site for some processes, there is a trend toward carbon dioxide recovery where it is a major reaction by-product and, in the past, has been vented to the atmosphere. An absorption system, such as the use of ethanolamines (*q.v.*) or hot carbonate or bicarbonate solutions, is used for concentrating the carbon dioxide to over 99% purity.



In all cases, the almost pure carbon dioxide must be given various chemical treatments for the removal of minor impurities that contaminate it.

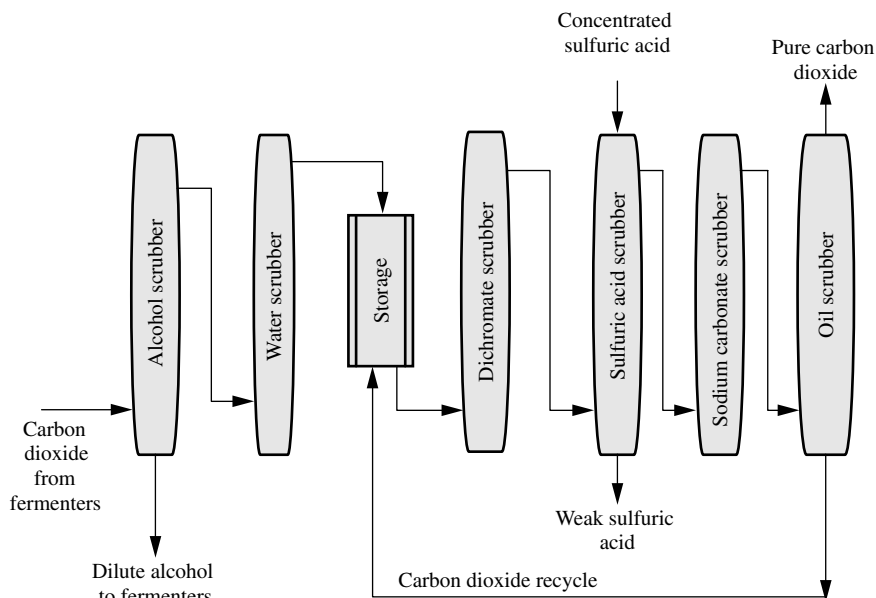


FIGURE 2 Production of carbon dioxide from fermentation processes.

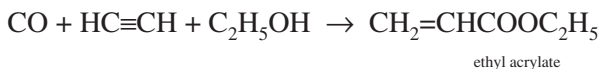
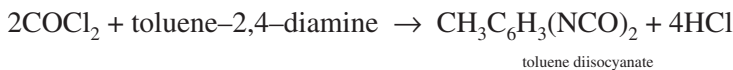
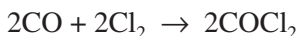
Carbon dioxide, in the solid form, is commonly referred to as *dry ice*. At that temperature it sublimates and changes directly from a solid to a vapor. Because of this property, as well as its noncombustible nature, it is a common refrigerant and inert blanket. Carbon dioxide is also used for enhanced oil recovery.

Other uses include chemical manufacture (especially soda ash), fire extinguishers, and pH control of wastewater. Carbon dioxide is also used as a fumigant for stored grain and has replaced ethylene dibromide in this application.

CARBON MONOXIDE

Carbon monoxide (melting point: -199°C , boiling point: -191.5°C) is one of the chief constituents of synthesis gas (carbon monoxide plus hydrogen). It is obtained in pure form through cryogenic procedures, with hydrogen as a coproduct.

Carbon monoxide is an important raw material in the production of methanol and other alcohols and of hydrocarbons, and it is a powerful poison. It is also used for making diisocyanate and ethyl acrylate.

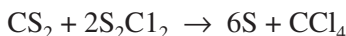
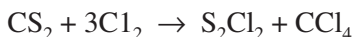


See also Synthesis Gas.

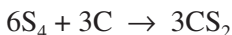
CARBON TETRACHLORIDE

Carbon tetrachloride (melting point: -23°C , boiling point: 76.7°C , density: 1.5947, critical temperature 283.2°C , critical pressure 9714 psi – 67 MPa, solubility 0.08 g in 100 g water) is a heavy, colorless, nonflammable, non-combustible liquid. Dry carbon tetrachloride is noncorrosive to common metals except aluminum. When wet, carbon tetrachloride hydrolyzes and is corrosive to iron, copper, nickel, and alloys containing those elements.

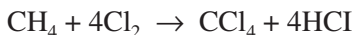
Carbon tetrachloride is manufactured by the reaction of carbon disulfide and chlorine, with sulfur monochloride as an important intermediate.



The reaction must be carried out in a lead-lined reactor in a solution of carbon tetrachloride at 30°C in the presence of iron filings as catalyst. The elemental sulfur can be reconverted to carbon disulfide by reaction with coke.



Chlorination of methane and higher aliphatic hydrocarbons is also used to manufacture carbon tetrachloride.



The chlorination of methane is also used to manufacture partially chlorinated methane derivatives.



The reaction is carried out in the liquid phase at about 35°C , and ultraviolet light is used as a catalyst. The same reaction can be carried out at 475°C without catalyst. The unreacted methane and partially chlorinated products are recycled to control or adjust the yield of carbon tetrachloride.

CELLULOSE

Cellulose is the primary substance of which the walls of vegetable cells are constructed and is largely composed of glucose residues. It may be obtained from wood or derived in very high purity from cotton fibers, which are about 92% pure cellulose.

The important fiber rayon is *regenerated* cellulose from wood pulp that is in a form more easily spun into fibers. Cellophane film is regenerated cellulose made into film. One method of regeneration is formation of xanthate groups from selected hydroxyl groups of cellulose, followed by hydrolysis back to hydroxy groups.

Cellulose acetate and triacetate may be used as plastics or spun into fibers for textiles. They are made by the reaction of cellulose with acetic anhydride.

See Cellulose Acetate, Cellulose Nitrate.

CELLULOSE ACETATE

Fully acetylated cellulose is partly hydrolyzed to give an acetone-soluble product, which is usually between the di- and triester. The esters are mixed with plasticizers, dyes, and pigments and processed in various ways, depending upon the form of plastic desired.

Cellulose acetate is moldable, in contrast to cellulose nitrate, which is not. It, however, has poor resistance to moisture. To overcome this disadvantage, treating the cotton linters with a mixture of butyric acid, acetic acid, and acetic anhydride produces a mixed acetate-butyrate. The plastics made from this material have better moisture resistance and better dimensional stability than cellulose acetate. They also have excellent weathering resistance, high impact strength, moldability, and high dielectric strength.

CELLULOSE NITRATE

Fully nitrated cellulose (nitrocellulose) is unsuited for a plastic base because of its extremely flammable character. Hence, a partly nitrated product is made. Products containing 11% nitrogen are used for plastics, 12% nitrogen for lacquers, and the fully nitrated, or 13% nitrogen, material is used for explosives.

In the process (Fig. 1), the cellulose nitrate is placed in large kneading mixers with solvents and plasticizers and thoroughly mixed. The standard plasticizer is camphor, and the compounded mixture is strained under hydraulic pressure and mixed on rolls with coloring agents. The material is pressed into blocks.

Finally, the plastic is made into sheets, strips, rods, or tubes, seasoned to remove the residual solvent, and polished by pressing under low heat. This plastic possesses excellent workability, water resistance, and toughness. Its chief disadvantage is the ease with which it burns. It also discolors and becomes brittle on aging. The trade name is Celluloid.

See Cellulose, Cellulose Acetate.

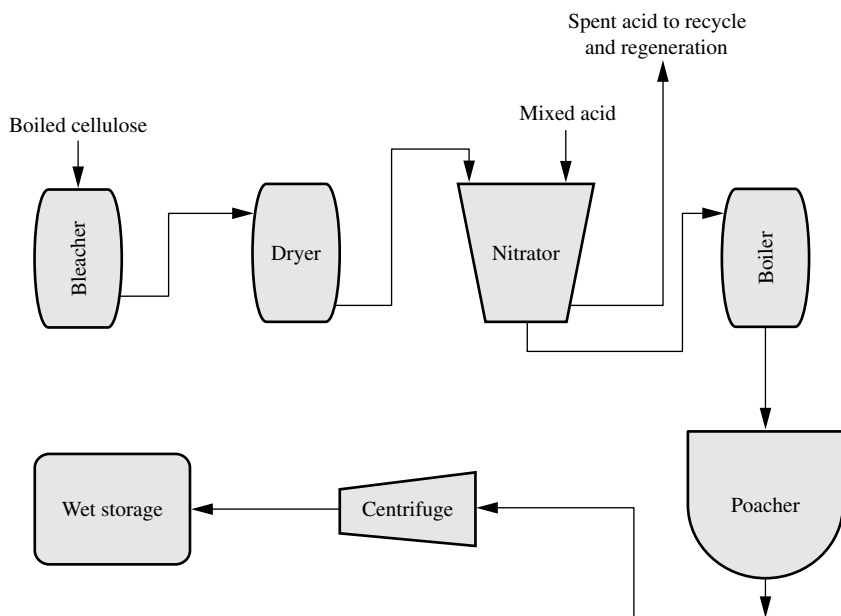


FIGURE 1 Manufacture of cellulose nitrate.

CEMENT

The terms *cement* and *concrete* are not synonymous. Concrete is artificial stone made from a carefully controlled mixture of cement, water, and fine and coarse aggregate (usually sand and coarse rock).

Portland cement is the product obtained by pulverizing clinker consisting essentially of calcium silicate, usually containing one or more forms of calcium sulfate, and there are five types of portland cement:

Type I. Regular portland cements are the usual products for general construction.

Type II. Moderate-heat-of-hardening and *sulfate-resisting* portland cements are for use where moderate heat of hydration is required or for general concrete construction exposed to moderate sulfate action.

Type III. High-early-strength (HES) cements are made from raw materials with a lime-to-silica ratio higher than that of Type I cement and are ground finer than Type I cements. They contain a higher proportion of calcium silicate than regular portland cements.

Type IV. Low-heat portland cements contain a lower percentage of calcium silicate and calcium aluminate, thus lowering the heat evolution.

Type V. Sulfate-resisting portland cements are those that, by their composition or processing, resist sulfates better than the other four types. Type V is used when high sulfate resistance is required.

Two types of materials are necessary for the production of portland cement: one rich in calcium (calcareous), such as limestone or chalk, and one rich in silica (argillaceous) such as clay. These raw materials are finely ground, mixed, and heated (burned) in a rotary kiln to form cement clinker.

Cement clinker is manufactured by both the *dry process* and by the *wet process* (Fig. 1). In both processes *closed-circuit grinding* is preferred to *open-circuit grinding* in preparing the raw materials because, in the former, the fines are passed on and the coarse material returned, whereas in the latter, the raw material is ground continuously until its mean fineness has reached the desired value. The *wet process*, though the original one, is

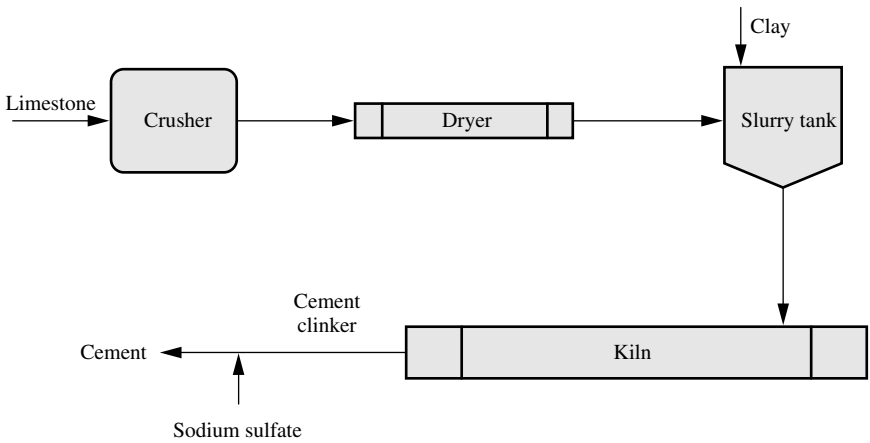


FIGURE 1 Cement manufacture.

being displaced by the *dry process*, especially for new plants, because of the savings in heat and accurate control and mixing of the raw mixture it affords.

The *dry process* is applicable to natural cement rock and to mixtures of limestone and clay, shale, or slate. In this process the materials may be roughly crushed, passed through gyratory and hammer mills, dried, sized, and more finely ground in tube mills, followed by air separators, after which thorough mixing and blending by air takes place. This dry, powdered material is fed directly to rotary kilns that are slightly inclined, so that materials fed in at the upper end travel slowly to the lower firing end, taking from 1 to 3 hours.

In the *wet process*, the solid material, after dry crushing, is reduced to a fine state of division in wet tube or ball mills and passes as a slurry through bowl classifiers or screens. The slurry is pumped to correcting tanks, where rotating arms make the mixture homogeneous and allow the final adjustment in composition to be made.

The final product consists of hard, granular masses from 3 to 20 mm in size, called *clinker*. The clinker is discharged from the rotating kiln into the air-quenching coolers that reduce the temperature to approximately 100 to 200°C while simultaneously preheating the combustion air. Pulverizing, followed by fine grinding in the tube ball mills and automatic packaging, completes the process. During the fine grinding, setting retarders, such as gypsum, plaster, or calcium lignosulfonate, and air-entraining, dispersing, and waterproofing agents are added. The clinker is ground dry by various hookups.

CEPHALOSPORINS

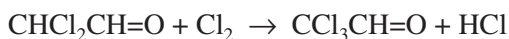
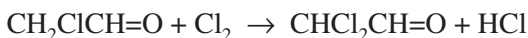
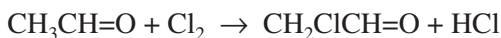
Cephalosporins contain the β -lactams structure, like the penicillins, but instead of a five-membered thiazolidine ring, cephalosporins contain a six-membered dihydrothiazine ring.

Cephalosporin C, which itself is not antibacterial, is obtained from a species of fungus. Chemical modification of this structure to 7-aminocephalosporanic acid by removal of the $R-C=O$ group allows the preparation of the active cephalosporins such as cephalexin and cephaloglycin.

The drugs are orally active because they have an α -amino-containing R group that is stable to the gastric acid in the stomach. Other cephalosporins are easily made by acylation of the 7-amino group with different acids or nucleophilic substitution or reduction of the 3-acetoxy group.

CHLORAL

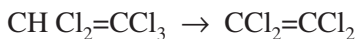
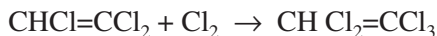
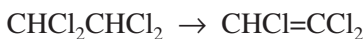
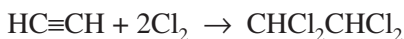
Chloroacetaldehydes are produced by the reaction of acetaldehyde with chlorine by replacement of the hydrogen atoms of the methyl group. Chlorine reacts with acetaldehyde at room temperature to give monochloroacetaldehyde. Increasing the temperature to 70 to 80°C gives dichloroacetaldehyde, and at a temperature of 80 to 90°C trichloroacetaldehyde, (chloral) is formed.



Bromal is formed by an analogous series of reactions.

CHLORINATED SOLVENTS

Originally, successive chlorination and dehydrochlorination of acetylene was the route to trichloroethylene ($\text{Cl}_2\text{C}=\text{CHCl}$):



This route has largely been superseded by a route involving chlorination and dehydrochlorination of ethylene or vinyl chloride and, more recently, by a route involving oxychlorination of two-carbon (C_2) raw materials.

CHLORINE

Chlorine (Cl_2 , melting point: -101°C , boiling point: -34.6°C , density (gas): 3.209 g/L at 0°C) is a pale greenish-yellow gas of marked odor, irritating to the eyes and throat, and poisonous.

Chlorine is produced almost entirely by the electrolysis of aqueous solutions of alkali metal chlorides (Fig. 1), or from fused chlorides. Brine electrolysis produces chlorine at the anode and hydrogen along with the alkali hydroxide at the cathode. At present, three types dominate the industry: the diaphragm cell, the membrane cell, and the mercury cell, and there are many variations of each type.

In production of chlorine by the diaphragm cell process (Fig. 1), salt is dissolved in water and stored as a saturated solution. Chemicals are added to adjust the pH and to precipitate impurities from both the water and the

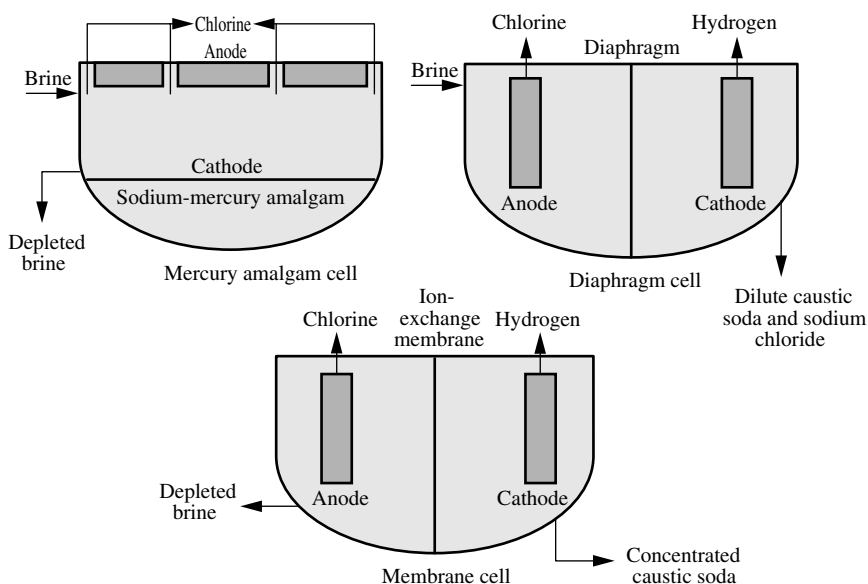


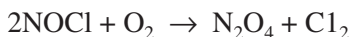
FIGURE 1 Chlorine manufacture by electrolysis.

salt. Recycled salt solution is added. The precipitated impurities are removed by settling and by filtration. The purified, saturated brine is then fed to the cell, which typically is a rectangular box. It uses vertical anodes (ruthenium dioxide with perhaps other rare metal oxides deposited on an expanded titanium support). The cathode is perforated metal that supports the asbestos diaphragm that has been vacuum deposited in a separate operation. The diaphragm serves to separate the anolyte (the feed brine) from the catholyte (brine containing caustic soda). Chlorine is evolved at the anode. It is collected under vacuum, washed with water to cool it, dried with concentrated sulfuric acid, and further scrubbed, if necessary. It is then compressed and sent to process as a gas or liquefied and sent to storage.

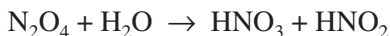
The membrane cell (Fig. 1) uses a cation exchange membrane in place of an asbestos diaphragm. It permits the passage of sodium ions into the catholyte but effectively excludes chloride ions. Thus the concept permits the production of high-purity, high-concentration sodium hydroxide directly.

In the mercury cell process (Fig. 1), chlorine is liberated from a brine solution at the anode. Collection and processing of the chlorine is similar to the techniques employed when diaphragm cells are used. However, the cathode is a flowing bed of mercury. When sodium is released by electrolysis it is immediately amalgamated with the mercury. The mercury amalgam is then decomposed in a separate cell to form sodium hydroxide and the mercury is returned for reuse.

Other processes for making chlorine include sodium manufacture, caustic potash manufacture, hydrogen chloride decomposition, the nitrosyl chloride (NOCl) process, and a process where salt is treated with nitric acid to form sodium nitrate and chlorine with nitrosyl chloride (containing 4 to 10% nitrogen tetroxide) as a by-product. The nitrosyl chloride vapor is placed in contact with oxygen to produce nitrogen tetroxide and chlorine:

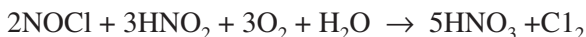


After liquefying and distilling the chlorine out, the nitrogen tetroxide is absorbed in water to make nitric acid and nitrous acids, which are recycled:



The advantage of this process is that it produces chlorine but no caustic soda. The demand for sodium nitrate regulates the amount of chlorine that can be made in this way.





Chlorine is principally used to produce organic compounds. But, in many cases chlorine is used as a route to a final product that contains no chlorine. For instance propylene oxide has traditionally been manufactured by the chlorohydrin process. Modern technology permits abandoning this route in favor of direct oxidation, thus eliminating a need for chlorine.

Chlorine is also used in bleaching and for treating municipal and industrial water supplies, and this use will probably continue. However, some concern has been felt that traces of organic compounds in all water supplies react with the chlorine to form chlorinated organics which are suspected of being carcinogenic. Further, the usefulness of chlorination of municipal wastes has been questioned in some quarters in the light of the fact that such treatment adds chlorinated organics to the waterways.

CHLORINE DIOXIDE

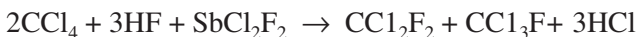
See Sodium Chlorite.

CHLOROACETALDEHYDE

See Chloral.

CHLOROFLUOROCARBONS

Chlorofluorocarbons (CFCs) are manufactured by reacting hydrogen fluoride and carbon tetrachloride in the presence of a partially fluorinated antimony pentachloride catalyst in a continuous, liquid-phase process.



The products dichlorodifluoromethane and trichlorofluoromethane are also known as CFC-12 and CFC-11, respectively.

There are common abbreviations and a numbering system for chlorofluorocarbons and related compounds. The original nomenclature developed in the 1930s is still employed and uses three digits. When the first digit is 0, it is dropped. The first digit is the number of carbon atoms minus 1, the second digit is the number of hydrogen atoms plus 1, and the third digit is the number of fluorine atoms. All other atoms filling the four valences of each carbon are chlorine atoms. Important nonhydrogen-containing chlorofluorocarbons (Freons[®]) are:



Halons, a closely related type of chemical that also contains bromine, are used as fire retardants. Numbering here is more straightforward: first digit, number of carbons; second digit, number of fluorine atoms; third digit, number of chlorines; and fourth digit, number of bromines.

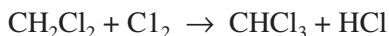
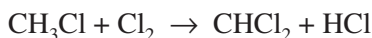
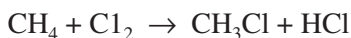
Common Halons are: Halon 1211 (CF_2BrCl), 1301 (CF_3Br), and Halon 2402 ($\text{C}_2\text{F}_4\text{Br}$).

Compared to the same size hydrocarbons, fluorocarbons have higher volatility and lower boiling points, unusual for halides. They are less reactive, more compressible, and more thermally stable than hydrocarbons. They also have low flammability and odor.

Common uses for the fluorocarbons are as refrigerants, foam-blowing agents, solvents, and fluoropolymers. Recent environmental legislation has restricted or banned the use of chlorofluorocarbons.

CHLOROFORM

Chloroform (boiling point: 61.7°C, melting point: -63.5°C, density: 1.4832) is produced by the chlorination of methylene chloride, which in turn is made by the chlorination of methyl chloride and methane.



Chloroform is also produced from acetone and calcium hypochlorite—the reaction is rapid and the yield is high.



Pure chloroform decomposes readily on storing, particularly if exposed to moisture and sunlight, to yield phosgene and other compounds. A small amount (0.5 to 1%) of ethyl alcohol is added to retard this decomposition.

The main use of chloroform is in the manufacture of chlorofluorocarbon refrigerants and polymers.

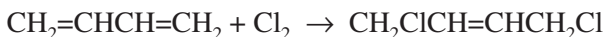
CHLOROPRENE

Chloroprene (boiling point: 59.4°C, density: 0.9583) is, chemically, a chlorovinyl ester of hydrochloric acid and can be manufactured by polymerizing acetylene to vinyl acetylene using a weak solution containing ammonium chloride (NH_4Cl), cuprous chloride (Cu_2Cl_2), and potassium chloride (KCl) as catalyst. The off-gas from the reactor has its water condensed out and is then fractionated. Aqueous hydrochloric acid at 35 to 45°C is then reacted with the vinyl acetylene in the presence of cupric chloride to give chloroprene (2-chloro-1,3-butadiene).

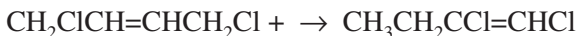


The contact time is about 15 seconds with a 20 percent conversion per pass. An overall yield of approximately 65 percent can be achieved.

Chloroprene is also made by chlorination of butadiene at 300°C followed by dehydrochlorination, using sodium hydroxide at 100°C. Addition of the chlorine to the butadiene occurs at either 1,2 or 1,4 because the intermediate allyl carbocation is delocalized.

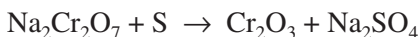


The 1,4-dichloro isomer can be isomerized to the 1,2-dichloro isomer by heating with cuprous chloride.



CHROMIC OXIDE

Chromium oxide (chromic oxide, CrO_3) is one of the oldest known green pigments. It is manufactured by calcining either sodium or potassium dichromate with sulfur in a reverberatory furnace:



Hydrated chromic oxide [$\text{Cr}_2\text{O}(\text{OH})_4$, $\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$] is known as Guignet's green (emerald green) and possesses a much more brilliant green color than the oxide and has good permanency.

Chromic oxide is manufactured by roasting a mixture of sodium dichromate and boric acid at a dull red heat for several hours.

CIMETIDINE

Cimetidine, a highly substituted guanidine, is sold as Tagamet, and is widely used as an antiulcer medication. It acts by blocking the histamine molecules in the stomach from signaling the stomach to secrete acid.

Cimetidine is manufactured by the action of a substituted guanidine on an amino-thio compound in the presence of methyl cyanide.



CINNAMIC ALDEHYDE

Cinnamic aldehyde (boiling point: 253°C with decomposition, melting point: -7.5°C , density: 1.0497) has a cinnamon odor, hence the name. As it oxidizes in air to cinnamic acid, it should be protected from oxidation.

Although this aldehyde is obtained from Chinese cassia oils, it is synthesized by action of alkali upon a mixture of benzaldehyde and acetaldehyde (Fig. 1).



This and most other products for fragrances must be purified by, for example, vacuum fractionation.

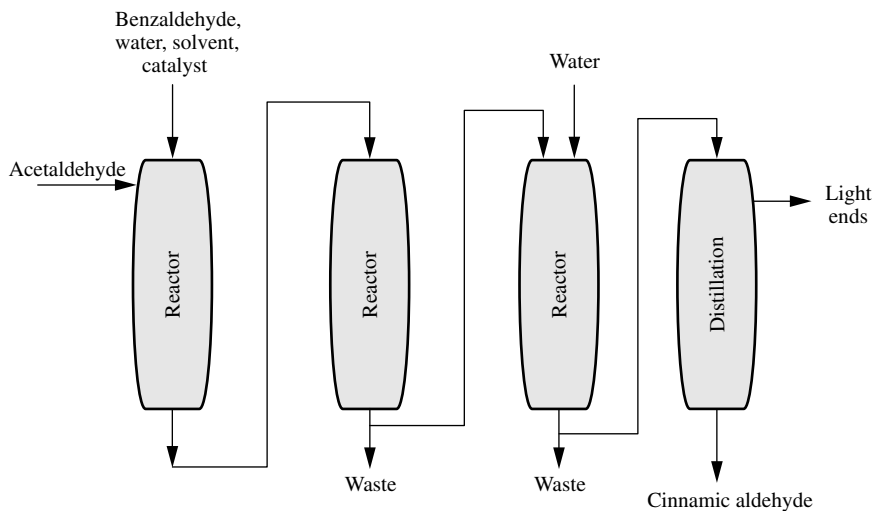
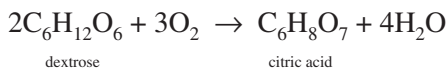
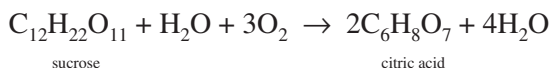


FIGURE 1 Manufacture of cinnamic aldehyde.

CITRIC ACID

Citric acid (melting point: 153°C, density: 1.665) is one of our most versatile organic acids and is used as an acidulant in carbonated beverages, jams, jellies, and other foodstuffs. Another large outlet is in the medicinal field, including the manufacture of citrates and effervescent salts. Industrially citric acid is used as an ion-sequestering agent buffer and in the form of acetyl tributyl citrate, as a plasticizer for vinyl resins.

Except for small amounts produced from citrus-fruit wastes, citric acid is manufactured by aerobic fermentation of crude sugar or corn sugar by a special strain of *Aspergillus niger*,



The submerged process for the manufacture of citric acid (Fig. 1) involves coordinated sequences of biochemical conversions with the aid of *A. niger* and various unit operations and chemical conversions.

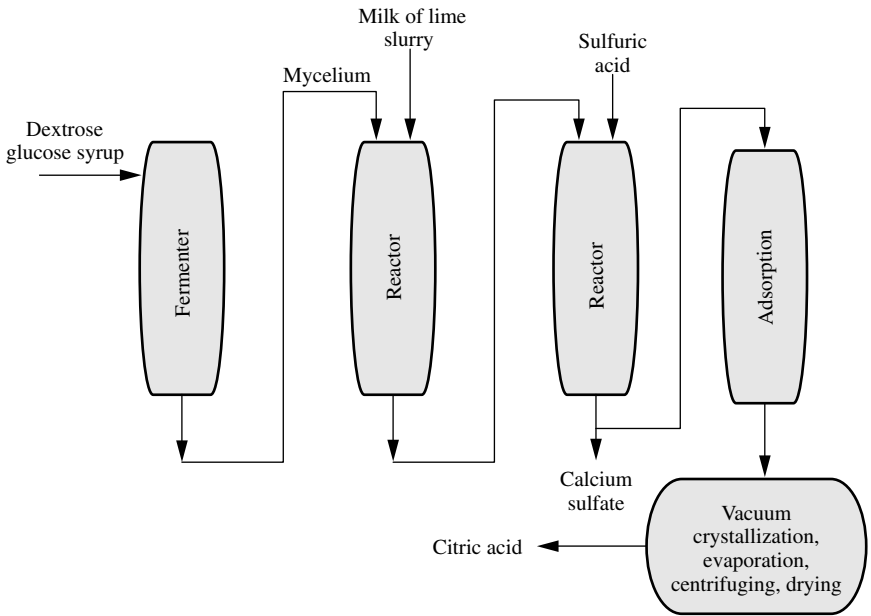


FIGURE 1 Manufacture of citric acid.

COAL CHEMICALS

Coal is an organic rock that can be converted by heat treatment into a variety of products (Fig. 1).

When coal is thermally pyrolyzed or distilled by heating without contact with air, it is converted into a variety of solid, liquid, and gaseous products. The nature and amount of each product depends upon the temperature used in the pyrolysis and the variety of the coal used. In general practice, coke-oven temperatures are maintained above 900°C but may range anywhere from 500 to 1000°C. The principal product by weight is coke.

If temperatures on the order of 450 to 700°C are employed, the process is termed *low-temperature carbonization*; with temperatures above 900°C, it is designated *high-temperature carbonization*. In the low-temperature carbonization process, the quantity of gaseous products is small and that of the liquid products is relatively large, whereas in high-temperature carbonization the yield of gaseous products is larger than the yield of liquid products, the production of tar being relatively low.

For the same coal, low-temperature liquids contain more tar acids and tar bases than high-temperature liquids. With high-temperature carbonization, the liquid products are water, tar, and crude light oil. The gaseous products are hydrogen, methane, ethylene, carbon monoxide, carbon dioxide, hydrogen sulfide, ammonia, and nitrogen. The products other than coke are collectively known as coal chemicals, or *by-products*.

The gas from the destructive distillation of the coal, together with entrained liquid particles, passes upward through a cast-iron gooseneck into a horizontal steel pipe, which is connected to a series of ovens. As the gas leaves the ovens, it is sprayed with weak ammonia water to condense some of the tar from the ammonia from the gas into the liquid. The liquids move through the main along with the gases until a settling tank is reached, where separation is effected according to density. Some of the ammonia liquor is pumped back into the pipes to help condensation; the rest goes to the ammonia still (Fig. 2), which releases the ammonia for subsequent chemical combination in the saturator. All the tar flows to storage tanks for tar distillers or for fuel.

Starting material	Initial products	Secondary products	Tertiary products
Coal	Gas	Fuel gas	
		Sulfur	
	Light oil	Naphtha	Cyclopentadiene
			Indene
		Benzol	Benzene
		Toluols	Toluene
		Xylols	<i>o</i> -xylene
			<i>m</i> -xylene
			<i>p</i> -xylene
	Coal tar	Pitch	
		Tar	Fluorene
			Diphenylene oxide
			Acenaphthene
			Methyl-naphthalenes
		Creosote	
		Tar acids	Phenol
			<i>o</i> -cresol
			<i>m</i> -cresol
			<i>p</i> -cresol
			3, 5-xyleneol
		Tar bases	Pyridine
			Alpha-picoline
			Beta-picoline
			Gamma-picoline
			2, 6-lutidine
			Quinoline
	Coke	Naphthalene	
		Crude anthracene	Anthracene
			Phenanthrene
			Carbazole
			Carbon

FIGURE 1 Selected chemicals from coal.

The tar separated from the collecting main and the tar extractors or electrostatic precipitators is settled from ammonia liquor, together with light oil. The tar is filtered and pumped through the reflux vapor-tar heat exchanger and economizer, pitch-tar heat exchanger into the top of the lower third of the distillation column and out at the bottom, to the circulating pumps and into the pipe still where the crude tar joins 4 to 5 volumes of the circulating pitch, and on finally to near the top of the distillation column.

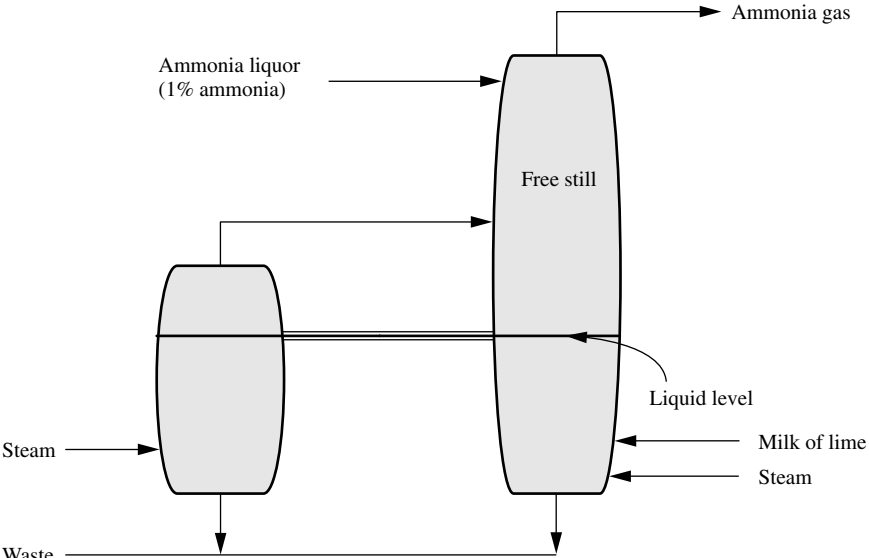


FIGURE 2 An ammonia still.

The vapors, steam distilled and superheated, pass overhead from the top of the tray-type distillation column, enter the bottom of the bubble-cap fractionating column, and are separated into four fractions and a residue, leaving the residue at the bottom of this fractionating column. The pitch cascades from the top of the distillation column down through the superheated steaming section to establish the desired pitch hardness and to strip this pitch of the higher-boiling volatile oils. It is then withdrawn from above the middle of the distillation column and conducted through the pitch-tar heat exchanger to storage. The products are:

Product	Boiling point, °C
Light oil	To 170
Carbolic oil	170–205
Naphthalene oil	205–240
Creosote or wash oil	240–280
Residue or anthracene	270–340
Residuum or pitch	325–400

The gaseous mixture leaving the oven is made up of permanent gases that form the final purified coke-oven coal gas for fuel, along with con-

densable water vapor, tar, and light oils, and solid particles of coal dust, heavy hydrocarbons, and complex carbon compounds. Significant products recoverable from the vapors include: benzene, toluene, xylenes, creosote oils, cresols, cresylic acid, naphthalene, phenols, xylols, pyridine, quinoline, and medium and hard pitches usable for electrode binders, road tar, or roofing pitch.

The gas is passed into the primary condenser and cooler at a temperature of about 75°C. Here the gases are cooled by water to 30°C. The gas is conducted to an exhauster, which serves to compress it. During the compression the temperature of the gas rises as high as 50°C. The gas is passed to a final tar extractor or an electrostatic precipitator. On leaving the tar extractor or precipitator, the gas carries three-fourths of the ammonia and 95 percent of the light oil originally present.

The gas is led to a saturator containing a solution of 5 to 10% sulfuric acid where the ammonia is absorbed, and crystalline ammonium sulfate is formed. The gas is fed into the saturator through a serrated distributor underneath the surface of the acid liquid. The acid concentration is maintained by the addition of sulfuric acid, and the temperature is kept at 60°C by the reheater and the heat of neutralization. The crystallized ammonium sulfate is removed from the bottom of the saturator by a compressed-air ejector, or a centrifugal pump, and drained on a table, from which the mother liquor is run back into the saturator.

The gas leaving the saturator is at about 60°C; it is taken to final coolers or condensers, where it is scrubbed with water until its temperature is 25°C. During this cooling, some naphthalene separates and is carried along with the wastewater and recovered. The gas is passed into a light oil or benzol scrubber, through which the absorbent medium, a heavy fraction of petroleum known as straw oil, or sometimes tar oil, is circulated at 25°C. The straw oil is sprayed into the top of the absorption tower while the gas flows upward through the tower. The straw oil is allowed to absorb about 2 to 3 percent of its weight of light oil, with a removal efficiency of about 95 percent of the light oil vapor in the gas.

The rich straw oil, after being warmed in heat exchangers by vapors from the light-oil still and then by light oil flowing out of the still, is passed to the stripping column where the straw oil, flowing downward, is brought into direct contact with live steam. The vapors of the light oil and steam pass off and upward from the still through the heat exchanger previously mentioned and into a condenser and water separator. The lean, or stripped, straw oil is returned through the heat exchanger to the scrubbers. The gas, after having been stripped of its ammonia and light oil, has the sulfur

removed in purifying boxes, which contain iron oxide on wood shavings, or by a solution of ethanolamine (Girbotol) in scrubbing towers (the best present-day practice).

An alternative procedure uses ammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) to absorb the ammonia to form more alkaline phosphates [$(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_3\text{PO}_4$] that are returned to the original form by steaming, thus releasing the ammonia (the Phosam process).

Coal tar is a mixture of many chemical compounds, mostly aromatic, which vary widely in composition and can be separated into various fractions by distillation.

1. Light oils usually comprise the cut up to 200°C . They are first crudely fractionated and agitated at a low temperature with concentrated sulfuric acid, neutralized with caustic soda, and redistilled, furnishing benzene, toluene, and homologs.
2. Middle oils, or creosote oils, generally are the fraction from 200 to 250°C , which contain naphthalene, phenol, and cresols. The naphthalene settles out on cooling, is separated by centrifuging, and is purified by sublimation. After the naphthalene is removed, phenol and other tar acids (phenol and its homologs) are obtained by extraction with 10% caustic soda solution and neutralization, or *springing* by carbon dioxide. These are fractionally distilled.
3. Heavy oil may represent the fraction from 250 to 300°C , or it may be split between the middle oil and the anthracene oil.
4. Anthracene oil is usually the fraction from 300 to 350°C . It is washed with various solvents to remove phenanthrene and carbazole; the remaining solid is anthracene.

A substantial fraction of the coal tar produced continues to be used as fuel as well as for road asphalt and roofing asphalt. For these purposes the tar is distilled up to the point where thermal decomposition starts. This *base tar* is then diluted with creosote oil to ensure satisfactory rapid drying. Similar tars are used to impregnate felt and paper for waterproofing materials.

Largely because of the present competition from aromatic chemicals produced from petroleum, interest in aromatics from coal is not as great as it used to be. At one time coal tar was the sole source of pyridine; however, synthetic processes using aldehyde and ammonia are now supplying the increased demand. This is also true of phenol.

COCAINE

Cocaine (melting point: 79°C) and similar alkaloids are extracted commercially by alkalizing the ground leaves of the coca plant with a 10% sodium carbonate solution and percolating countercurrently in large steel percolators, using kerosene or toluene. The total alkaloids are extracted from the kerosene or toluene by a process that blows them up with a 5% sulfuric acid solution in tanks. The extracted kerosene or toluene is returned to the percolators. From the sulfuric acid solution, the mixed alkaloids are precipitated by alkalizing with sodium carbonate. The precipitated crude alkaloids are slowly boiled in an 8% sulfuric acid solution for several days to split all the alkaloids to ecgonine. During the splitting, many of the organic acids, like benzoic, are partly volatilized from the kettle with the steam. Those acids that are still suspended and those that crystallize out on cooling are filtered off. The acid aqueous solution of ecgonine is neutralized with potassium carbonate and evaporated. The low-solubility potassium sulfate is filtered hot, and cooling causes the ecgonine to crystallize. After drying, it is methylated, using methanol and 92% sulfuric acid, filtered, and washed with alcohol. The methylecgonine sulfate is benzoylated to cocaine in a very vigorous reaction with benzoyl chloride in the presence of anhydrous granular potassium carbonate. The cocaine is extracted from the potassium salts with ether and removed from the ether by sulfuric acid extraction, precipitated with alkali, and crystallized from alcohol. To form the hydrochloride, an alcoholic solution is neutralized with *acid alcohol* (hydrogen chloride dissolved in absolute ethyl alcohol), and the cocaine hydrochloride is crystallized.

Because of decreased demand, cocaine is also obtained as a by-product in the preparation of a decocained extract of *Erythroxylon coca*, this being one of the principal flavors of cola beverages. The procedure is to alkalinize the *Erythroxylon coca* and extract *all* the alkaloids with toluene. The decocainized leaf is dried and extracted with sherry wine to give the flavoring extract.

CODEINE

Codeine (boiling point: 250°C at 22 mmHg, melting point: 157°C, density: 1.32) can be isolated from opium and morphine (also obtained from opium). To direct this alkylation to the phenolic hydroxyl and to reduce alkylation of the tertiary nitrogen, a quaternary nitrogen-alkylating agent, phenyltrimethylammonium hydroxide, is employed. This results in yields of 90 to 93 percent codeine and some recovery of unalkylated morphine. The alkylation is carried out with the morphine dissolved in absolute alcohol in the presence of potassium ethylate. The dimethyl aniline and solvents are recovered and reused.

COKE

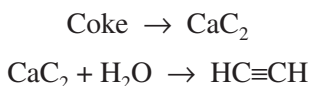
Coke is conventionally manufactured from coal by using the beehive process—a small batch process that tends to produce very large amounts of pollutants.

Coke is also produced from coal in the by-product ovens in which the coal charge is heated on both sides so that heat travels toward the center and thus produces shorter and more solid pieces of coke than are made in the beehive oven. Air is excluded so that no burning takes place within the oven, the heat being supplied completely from the flues on the sides. About 40 percent of the oven gas, after being stripped of its by-products, is returned and burned for the underfiring of the battery of ovens, and some is used for fuel gas locally.

Coke is also produced from petroleum, and it is the residue left by the destructive distillation of petroleum residua.

The composition of petroleum coke varies with the source of the crude oil, but in general, large amounts of high-molecular-weight complex hydrocarbons (rich in carbon but correspondingly poor in hydrogen) make up a high proportion. The solubility of petroleum coke in carbon disulfide has been reported to be as high as 50 to 80%, but this is in fact a misnomer, since the real coke is the insoluble, honeycomb material that is the end product of thermal processes.

Petroleum coke is employed for a number of purposes, but its chief use is in the manufacture of carbon electrodes for aluminum refining, which requires a high-purity carbon, low in ash and sulfur free; the volatile matter must be removed by calcining. In addition to its use as a metallurgical reducing agent, petroleum coke is employed in the manufacture of carbon brushes, silicon carbide abrasives, and structural carbon (e.g., pipes and Rashig rings), as well as calcium carbide manufacture from which acetylene is produced:



COPPER SULFATE

Copper sulfate (CuSO_4) is the most important compound of copper, and is commonly known as *blue vitriol*.

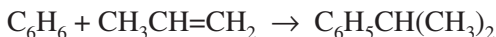
Copper sulfate is manufactured by the action of sulfuric acid on cupric oxide (CuO).

Because of its poisonous nature, copper sulfate is used in the fungicide Bordeaux mixture, which is formed upon mixing copper sulfate solution with milk of lime and is added to water reservoirs to kill algae. It is also employed in electroplating and used as a mordant, germicide, and agent in engraving.

CUMENE

Cumene (*iso*-propyl benzene, boiling point: 152.4°C, density: 0.8619, flash point: 44°C) is an important intermediate in the manufacture of phenol and acetone.

Cumene is manufactured by reacting benzene with propylene over a catalyst such as a phosphoric acid derivative at 175 to 250°C and 400 to 600 psi (Fig. 1). A refinery cut of mixed propylene-propane is frequently used instead of the more expensive pure propylene. Benzene is provided in substantial excess to avoid polyalkylation. The yield is near quantitative (in excess of 90 percent) based on propylene.



Excess benzene stops the reaction at the monoalkylated stage and prevents the polymerization of propylene. The cumene is separated by distillation, boiling point 153°C. Other catalysts that have been used are aluminum chloride and sulfuric acid.

Cumene is used to manufacture phenol, acetone, and α -methylstyrene

See Benzene.

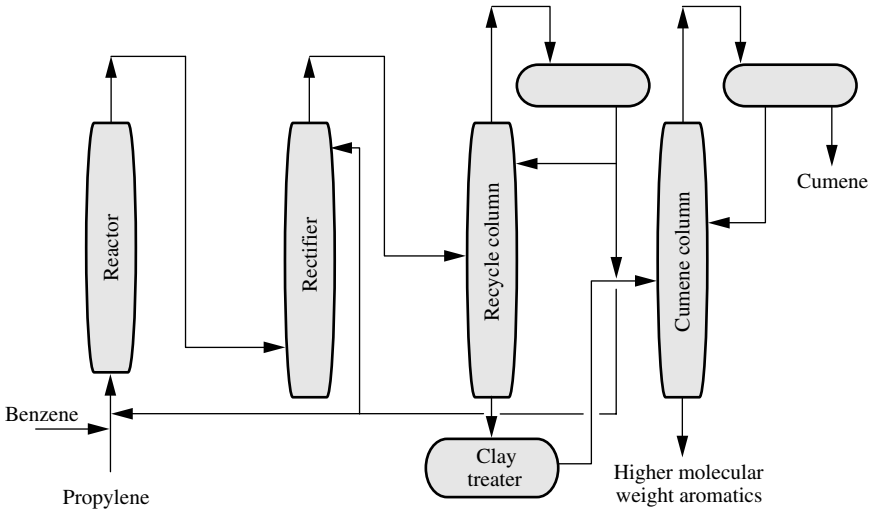
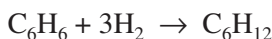


FIGURE 1 Manufacture of cumene.

CYCLOHEXANE

Cyclohexane (hexahydrobenzene, melting point: 6.5°C, boiling point: 81°C, density: 0.7791, flash point: -20°C) can be quantitatively produced from benzene by hydrogenation over either a nickel or a platinum catalyst at 210°C and 350 to 500 psi hydrogen (Fig. 1).



Several reactors may be used in series and the yield is over 99 percent.

Cyclohexane is used for the manufacture of adipic acid and caprolactam. Adipic acid is used to manufacture nylon 6,6, and caprolactam is the monomer for nylon 6.

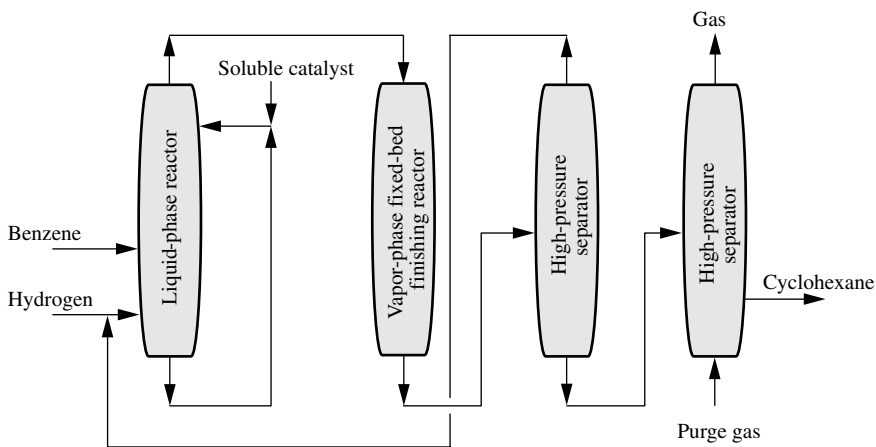


FIGURE 1 Manufacture of cyclohexane.

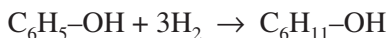
CYCLOHEXANOL

Cyclohexanol (melting point 25.2°C, boiling point: 161.1°C, density: 0.9493, flash point: 67.2°C) and cyclohexanone (melting point -47°C, boiling point: 156.7°C, density: 0.9478, flash point: 54°C) are made by the air oxidation of cyclohexane with a cobalt(II) naphthenate or acetate or benzoyl peroxide catalyst at 125 to 160°C (255 to 320 °F) and 50 to 250 psi.



The ratio of the cyclohexanol to cyclohexanone in the product mix is 3 to 1.

The hydrogenation of phenol at elevated temperatures and pressures, in either the liquid or vapor phase and with a nickel catalyst, is also used in the manufacture of cyclohexanol.



Cyclohexanol is used primarily in the production of adipic acid, which is further used as a raw material in nylon 6,6 production, and in methylcyclohexanol production.

CYCLOHEXANONE

See Cyclohexanol.