

# MAGNESIUM

Magnesium occurs in seawater and in ores such as dolomite ( $\text{CaCO}_3 \cdot \text{MgCO}_3$ ), magnesite ( $\text{MgCO}_3$ ), and carnallite ( $\text{MgCl}_2 \cdot \text{KCl} \cdot 6\text{H}_2\text{O}$ ).

Magnesium can be made by several methods (Fig. 1), but the most common method of manufacture is by the electrolytic process, as for example the electrolysis of magnesium chloride.

The magnesium chloride is obtained from saline solution, from brine, and from the reaction of magnesium hydroxide (from seawater or dolomite) with hydrochloric acid (Fig. 2). Electrolyzing magnesium chloride from seawater, using oyster shells for the lime needed is also an option. The oyster shells, which are almost pure calcium carbonate, are burned to lime, slaked, and mixed with the seawater, thus precipitating magnesium hydroxide. This magnesium hydroxide is filtered off and treated with hydrochloric acid prepared from the chlorine evolved by the cells to form magnesium chloride solution that is evaporated to solid magnesium chloride in direct-fired evaporators, followed by shelf drying. The chloride tends to decompose on drying and, after dehydrating, the magnesium chloride is fed to the electrolytic cells, where it is decomposed into the metal and chlorine gas. The internal parts of the cell act as the cathode, and 22 graphite anodes are suspended vertically from the top of the cell. The arrangement is very similar to the Downs sodium cell (Fig. 3).

Process	Source of chemical
Electrolysis of magnesium chloride	Magnesium oxide potash mining brine wells seawater
Ferrosilicon reduction process	Electric furnace blast furnace dolomite quarry

**FIGURE 1** Process for the production of magnesium.

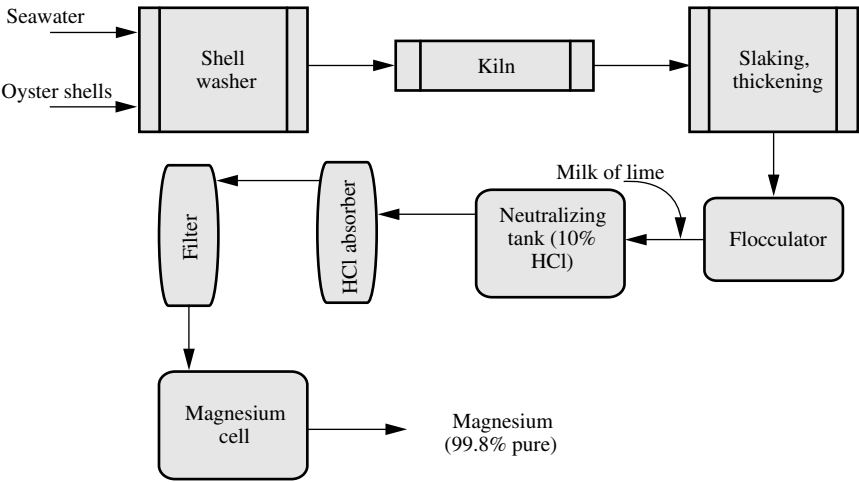


FIGURE 2 Production of magnesium from seawater.

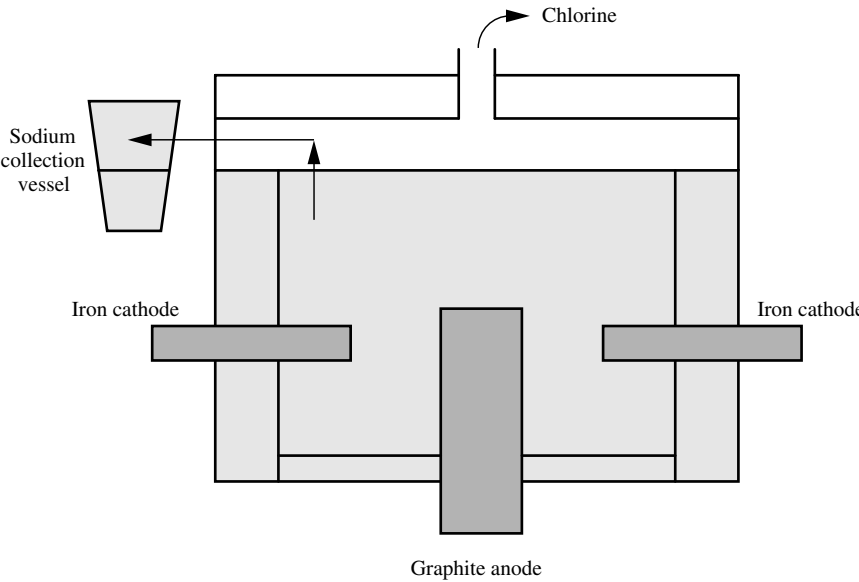
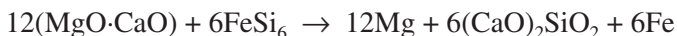


FIGURE 3 General schematic of the Downs cell.

Sodium chloride is added to the bath to lower the melting point and also increase the conductivity. The salts are kept molten by the electric current used to extract the magnesium plus external heat supplied by external gas-fired furnaces. The usual operating temperature is 710°C, which is sufficient to melt the magnesium (melting point 651°C). The molten magnesium is liberated at the cathode and rises to the bath surface, where troughs lead to the metal wells in front of the cell. The 99.9% pure magnesium metal is dipped out several times during the day, each dipperful containing enough metal to fill a 20-kg self-pelleting mold.

The silicothermic, or ferrosilicon, process involves mixing ground burned dolomite with ground ferrosilicon and fluorspar (eutectic) and pelletizing after which the pellets are charged into the furnace. High vacuum and heat (1170°C) are applied and the calcium oxide present in the burnt dolomite forms infusible calcium silicate that is removed from the retort.



*See Magnesium Compounds.*

# MAGNESIUM CARBONATE

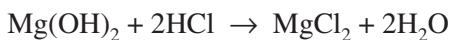
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Magnesium carbonate ( $\text{MgCO}_3$ ) varies from dense material used in magnesite bricks to the very low density hydrated mixed carbonate-hydroxides  $[\text{4MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 5\text{H}_2\text{O}]$  and  $[\text{3MgCO}_3 \cdot \text{Mg(OH)}_2 \cdot 3\text{H}_2\text{O}]$  once employed for insulation. There are also other basic carbonates on the market with variations in adsorptive index and apparent density. Many of these are employed as fillers in inks, paints, and varnishes.

# MAGNESIUM CHLORIDE

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Magnesium chloride is made from hydrochloric acid and magnesium hydroxide.

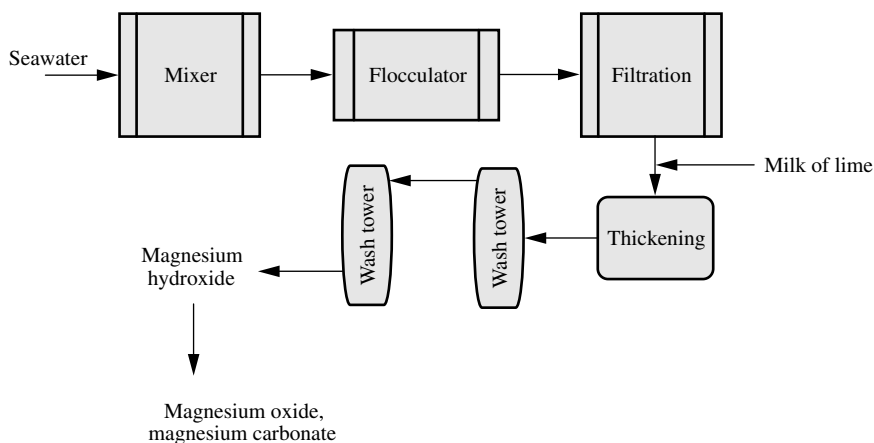


Magnesium chloride much resembles calcium chloride and has many of the same uses. In addition, it is used for production of magnesium, in ceramics, in the sizing of paper, and in the manufacture of oxychloride cement.

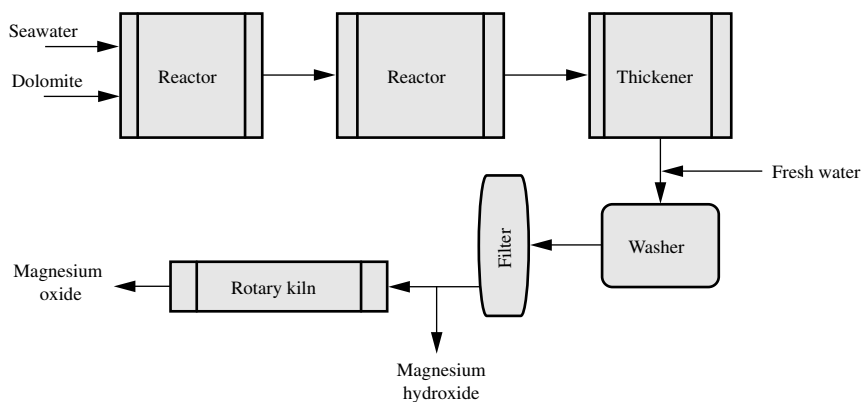
# MAGNESIUM COMPOUNDS

The production of magnesium compounds by separation from aqueous solutions may be divided into four processes:

1. Manufacture from seawater without evaporation, using seawater and lime as the principal raw materials (Fig. 1).
2. Manufacture from bitterns or mother liquors from the solar evaporation of seawater for salt.



**FIGURE 1** Production of magnesium compounds from seawater.



**FIGURE 2** Production of magnesium hydroxide from seawater and dolomite.

3. Manufacture from dolomite ( $\text{MgCO}_3$ ) and seawater (Fig. 2).

4. Manufacture from deep-well brines.

The production of magnesium compounds from seawater is made possible by the almost complete insolubility of magnesium hydroxide in water.

*See Magnesium.*

# MAGNESIUM HYDROXIDE

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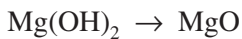
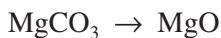
*See Magnesium Oxide.*



# MAGNESIUM OXIDE

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Heating magnesium carbonate ( $\text{MgCO}_3$ ) or magnesium hydroxide [ $\text{Mg}(\text{OH})_2$ ] produces magnesium oxide ( $\text{MgO}$ ).



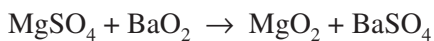
Magnesium oxide has many uses, e.g., in the vulcanization of rubber, as a material for making other magnesium compounds, as an insulating material, as a refractory material, and as an abrasive.

*See **Magnesium Compounds**.*

# MAGNESIUM PEROXIDE

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Magnesium peroxide is manufactured by the reaction of magnesium sulfate and barium peroxide.



It is employed as an antiseptic and a bleaching agent.

# MAGNESIUM SILICATE

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Magnesium silicate ( $\text{MgSiO}_3$  or  $\text{MgO} \cdot \text{SiO}_2$ ) exists in two predominant forms—*asbestos* and *talc*. *Asbestos* is a magnesium silicate mixed with varying quantities of silicates of calcium and iron.

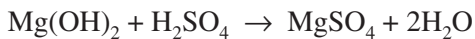
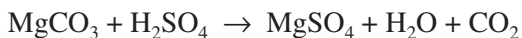
It is a fibrous noncombustible mineral and is used in the manufacture of many fireproof and insulating materials. Because of the cancer-causing characteristics of its fibers, government regulations have sharply reduced its use.

*Talc* is a pure magnesium silicate in the form of  $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ , found naturally in *soapstone*. It is employed as a filler in paper and plastics and in many cosmetic and toilet preparations.

# MAGNESIUM SULFATE

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Magnesium sulfate is prepared by the action of sulfuric acid on magnesium carbonate or hydroxide.



It is sold in many forms, one of which is the heptahydrate ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ), long known as *Epsom salts*. The less pure material is used extensively as sizing and as a fireproofing agent.

# MALATHION

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Malathion, also known by the generic name *carbophos* (*o,o*-dimethyl phosphorodithioate or diethyl mercaptosuccinate), is one of the very popular, short-lived broad-spectrum insecticides for application to nearly all fruits, vegetables, field crops, dairy livestock, and household insects.

*See Insecticides.*

# MALEIC ACID

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*See Liquefied Petroleum Gas.*

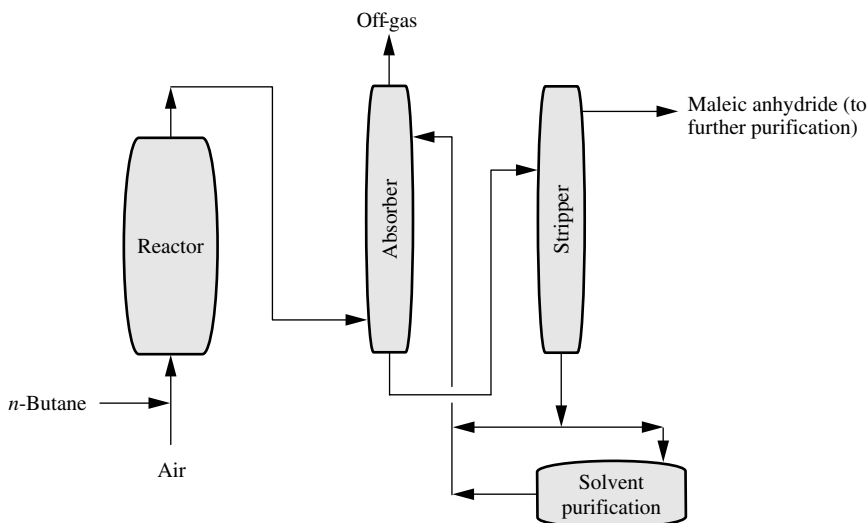
# MALEIC ANHYDRIDE

Maleic anhydride (melting point: 52.8°C, boiling point: 202°C, flash point: 110°C), formerly made from benzene, is now made from butane (Figs. 1 and 2) a switch in manufacturing method that was very rapid and complete.

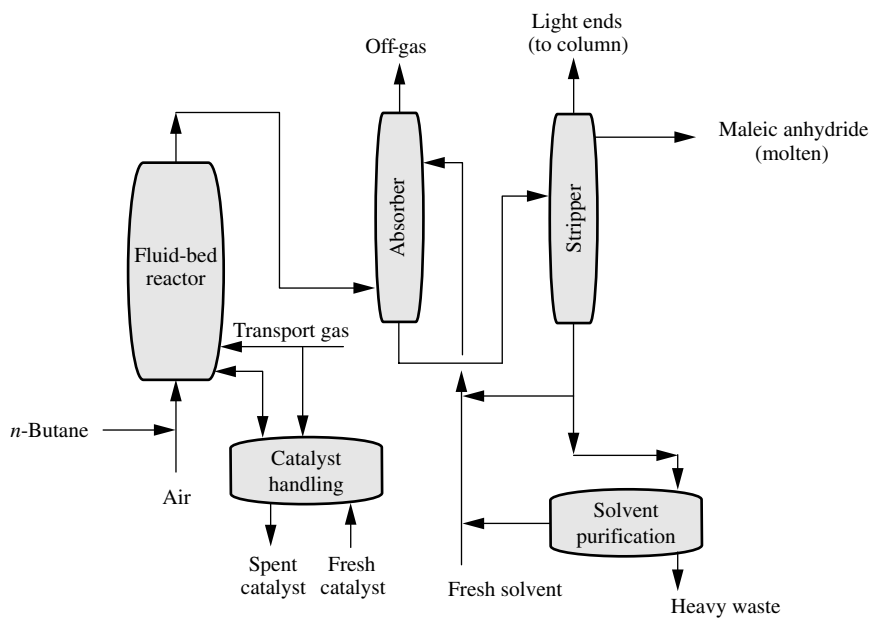
Maleic anhydride is used in the manufacture of unsaturated polyester resins, copolymers, food additives, agricultural chemicals, and lube oil additives. Agricultural chemicals made from maleic anhydride include daminozide (Alar<sup>®</sup>), a growth regulator for apples that in 1989 was found to be carcinogenic because of a breakdown product, unsymmetrical dimethylhydrazine (UDMH).



*See Liquefied Petroleum Gas.*



**FIGURE 1** Fixed-bed process for maleic anhydride manufacture.



**FIGURE 2** Fluid-bed process for maleic anhydride manufacture.



# MELAMINE RESINS (MELAMINE-FORMALDEHYDE POLYMERS)

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Melamine, having three amino groups and six labile hydrogen atoms, will also form thermoset resins with formaldehyde (melamine-formaldehyde polymers). The chemistry is similar to that for the urea resins.

*See Urea Resins.*

# MERCURY FULMINATE

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*See Explosives.*

# METALDEHYDE

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Metaldehyde, a cyclic tetramer of acetaldehyde, is formed at temperatures below 0°C in the presence of dry hydrogen chloride or pyridine-hydrogen bromide. The metaldehyde crystallizes from solution and is separated from the paraldehyde by filtration.

Metaldehyde melts in a sealed tube at 246.2°C and sublimes at 115°C with partial depolymerization.

# METHANE

Methane (CH<sub>4</sub>, marsh gas, fire damp, melting point: -182.6°C, boiling point: -161.4°C, density: 0.415 at -164°C) is a colorless, odorless that is only very slightly soluble in water and moderately soluble in alcohol or ether. When ignited, the gas burns when ignited in air with a pale, faintly luminous flame. It forms an explosive mixture with air between gas concentrations of 5 and 13%.

Methane occurs as the principal constituent of natural gas and is often produced by separation from the other constituents of natural gas.

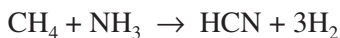
Alternatively, methane can be manufactured by the reaction of carbon monoxide and hydrogen in the presence of a nickel catalyst. Methane also is formed by reaction of magnesium methyl iodide (Grignard's reagent) in anhydrous ether with substances containing the hydroxyl group. Methyl iodide (bromide, chloride) is preferably made by reaction of methyl alcohol and phosphorus iodide (bromide, chloride).

Methane, as the major constituent of natural gas, is an extremely important raw material for numerous synthetic products. For most processes, it is not required to isolate and purify the methane, but the natural gas as received may be used.

Starting material	Reactant conditions	Product conditions	Reactant conditions	Product	Reactant	Product
Methane	Water heat	Synthesis gas	Water heat	Carbon dioxide, hydrogen	Nitrogen	Ammonia
		Synthesis gas	Catalyst heat	Methyl alcohol	Heat	Formaldehyde
				Methyl alcohol	i-butylene	MTBE
				Methyl alcohol	Terephthalic acid	Dimethyl terephthalate
				Methyl alcohol	Carbon monoxide	Acetic acid

FIGURE 1    Manufacture of chemicals from methane.

In addition to the preparation of synthesis gas, which is used so widely in various organic syntheses (Fig. 1), methane is reacted with ammonia in the presence of a platinum catalyst at a temperature of about 1250°C to form hydrogen cyanide:



Methane also is used in the production of olefins on a large scale. In a controlled-oxidation process, methane is used as a raw material in the production of acetylene.

*See Synthesis Gas.*

# METHYL ACETATE

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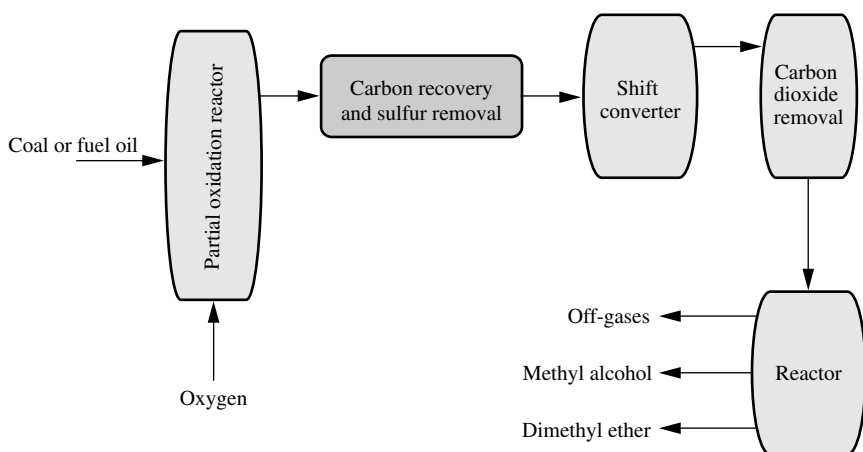
*See Acetic Acid.*

# METHYL ALCOHOL

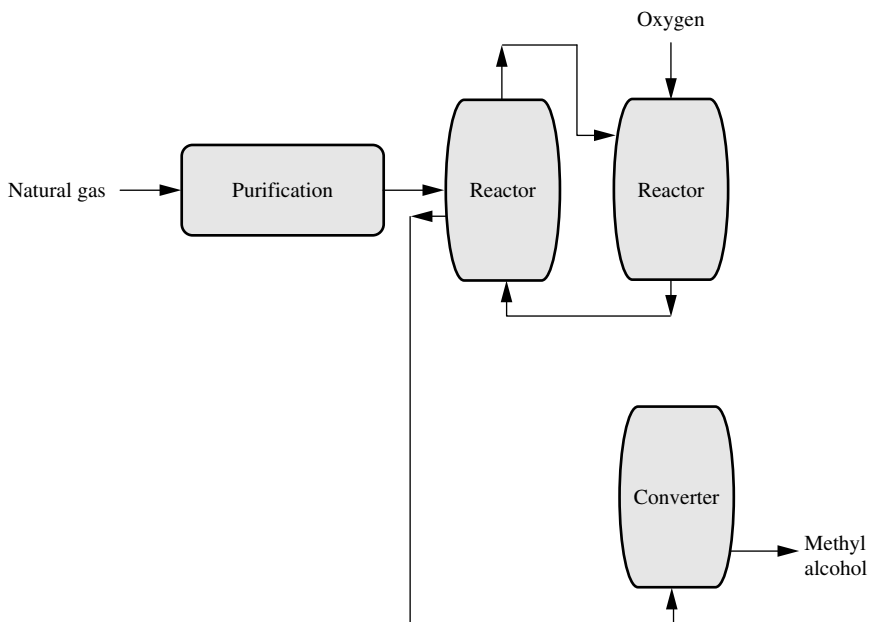
Methyl alcohol (methanol, wood alcohol,  $\text{CH}_3\text{OH}$ ; boiling point:  $64.7^\circ\text{C}$ , density: 0.7866, flash point:  $110^\circ\text{C}$ ) is a colorless, mobile liquid with a mild characteristic odor (and narcotic properties) that is miscible in all proportions with water, ethyl alcohol, or ether. When ignited, methyl alcohol burns in air with a pale blue, transparent flame, producing water and carbon dioxide. The vapor forms an explosive mixture with air. The upper explosive limit is 36.5% and the lower limit is 6.0% by volume in air.

Before 1926 all methyl alcohol was made by distillation of wood. Now methanol is produced by synthetic methods.

Methyl alcohol is obtained from synthesis gas under appropriate conditions (Fig. 1) or by the oxidation of methane (Fig. 2). This includes zinc, chromium, manganese, or aluminum oxides as catalysts,  $300^\circ\text{C}$ , 250 to

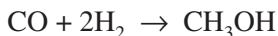


**FIGURE 1** Production of methyl alcohol from synthesis gas.



**FIGURE 2** Production of methyl alcohol from methane (natural gas).

300 atm (3000 to 5000 psi), and most importantly a 1:2 ratio of carbon monoxide (CO) to hydrogen ( $\text{H}_2$ ). Copper oxide catalysts require lower temperatures and pressures, usually 200 to 300°C and 50 to 100 atm (750 to 1500 psi). A 60 percent yield of methanol is realized.



The methanol can be condensed and purified by distillation. Unreacted synthesis gas is recycled. Other products include higher boiling alcohols and dimethyl ether ( $\text{CH}_3\text{OCH}_3$ ).

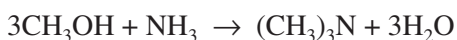
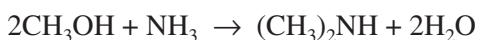
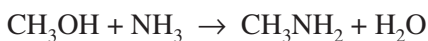
Methyl alcohol is also obtained by the oxidation of methane using natural gas as the feedstock (Fig. 2).

*See Synthesis Gas.*



# METHYLAMINES

Methylamine ( $\text{CH}_3\text{NH}_2$ , boiling point:  $-6.3^\circ\text{C}$ ), dimethylamine [ $(\text{CH}_3)_2\text{NH}$ , boiling point:  $7^\circ\text{C}$ ], and trimethylamine [ $(\text{CH}_3)_3\text{N}$ , boiling point:  $3^\circ\text{C}$ ] are manufactured by the reaction of methanol with ammonia (Fig. 1).



The ratios of the reactants can be adjusted to produce the desired product mix.

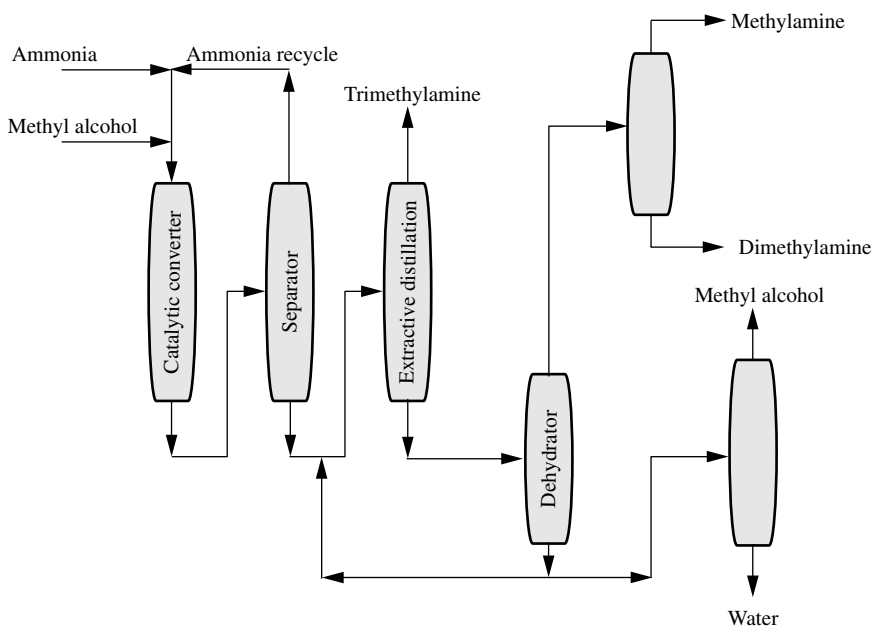
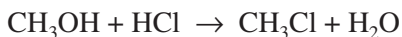


FIGURE 1 Manufacture of methylamines.

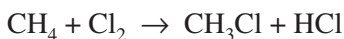
# METHYL CHLORIDE

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The major method for the production of methyl chloride (melting point:  $-97.1^{\circ}\text{C}$ , boiling point:  $-24.2^{\circ}\text{C}$ , density: 0.9159) is by the reaction of methanol and hydrogen chloride, with the aid of a catalyst, in either the vapor or liquid phase.



Methyl chloride is also manufactured by the chlorination of methane.

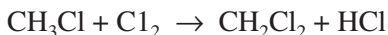
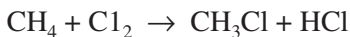


Methyl chloride is used for the production of silicones, agricultural chemicals, methylcellulose, and quaternary amines.

# METHYLENE CHLORIDE

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Methylene chloride (methylene dichloride, dichloromethane, melting point:  $-95.1^{\circ}\text{C}$ , boiling point:  $40^{\circ}\text{C}$ , density: 1.3266) is produced by the chlorination of methyl chloride, which in turn is made by the chlorination of methane.

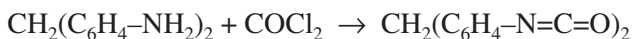
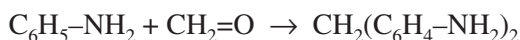


The main uses of methylene chloride are in paint remover, aerosols, chemical processing, urethane foam blowing agents, metal degreasing, and electronics.

# METHYLENE DIPHENYL DIISOCYANATE

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Methylene diphenyl diisocyanate (MDI) is produced by the condensation of aniline with formaldehyde followed by reaction with phosgene.

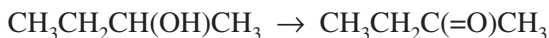
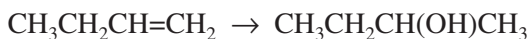


Methylene diphenyl diisocyanate is used to manufacture polyurethane foams for construction, refrigeration, and packaging.

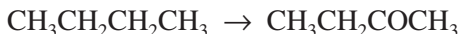
# METHYL ETHYL KETONE

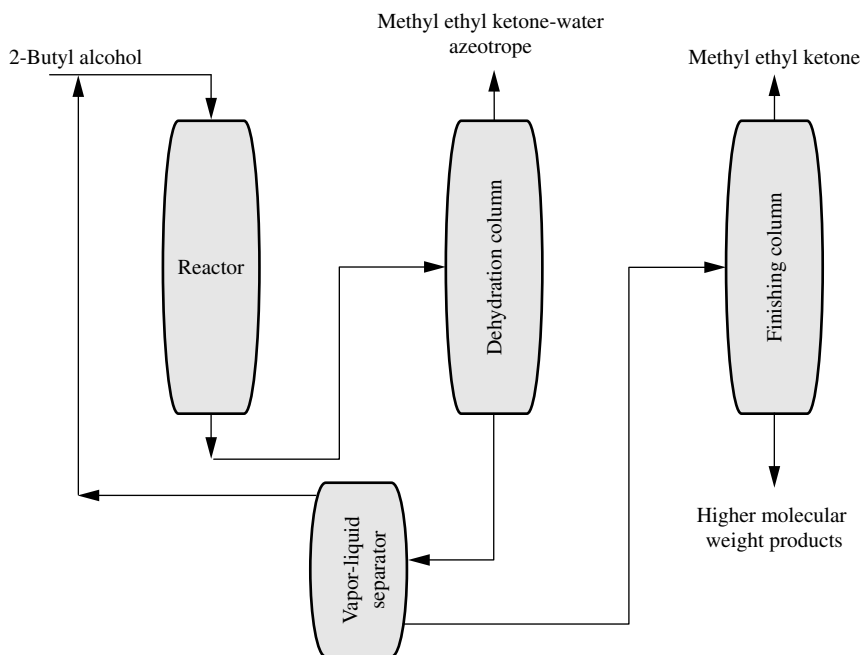
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Methyl ethyl ketone (MEK; boiling point: 76.6°C, density: 0.8062, flash point: -6°C) is an important coating solvent for many polymers and is made by the sulfation and hydration of 1 or 2-butene to *sec*-butyl alcohol, which is then dehydrogenated to the ketone (Fig. 1).



Butane oxidation is another route to methyl ethyl ketone.



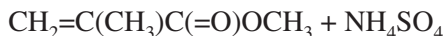
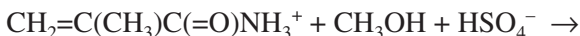
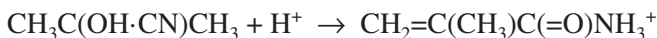


**FIGURE 1** Manufacture of methyl ethyl ketone.

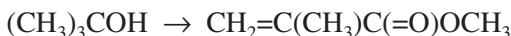
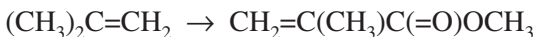
# METHYL METHACRYLATE

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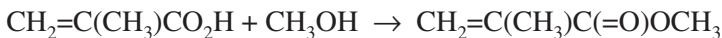
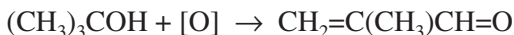
Methyl methacrylate (melting point:  $-48^{\circ}\text{C}$ , boiling point  $100^{\circ}\text{C}$ , density: 0.9394, flash point:  $9^{\circ}\text{C}$ ) is produced by the acetone cyanohydrin process in which the acetone cyanohydrin (from the reaction of acetone with hydrogen cyanide, *q.v.*) is reacted with sulfuric acid to yield methacrylamide sulfate, which is further hydrolyzed and esterified. The process is continuous.



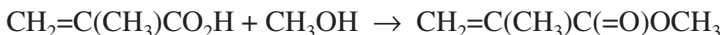
Methyl methacrylate is also manufactured by oxidation of *iso*-butene or *t*-butyl alcohol.



Other routes to methyl methacrylate include starting with *t*-butyl alcohol and ethylene:



or



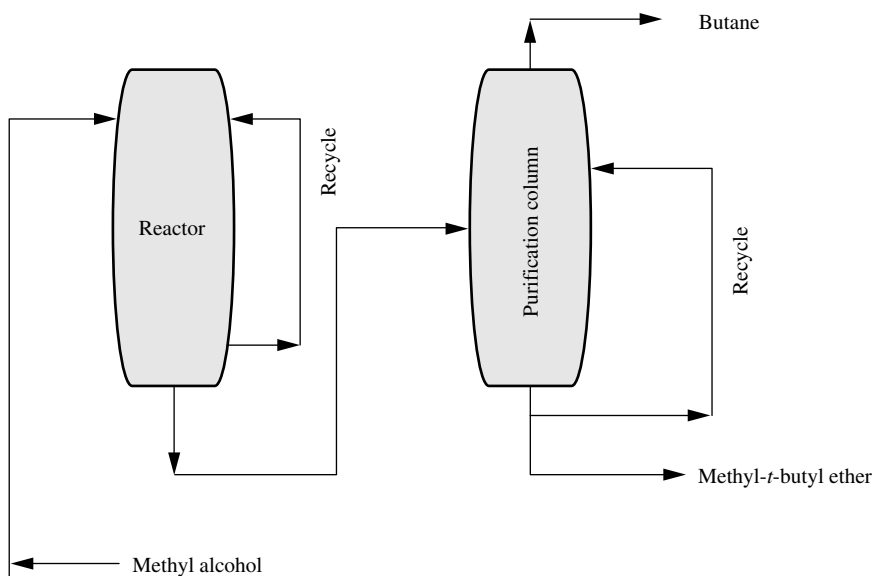
Methyl methacrylate is polymerized to poly(methyl methacrylate), which is used in cast and extruded sheet, molding powder and resins, surface coatings, impact modifiers, and emulsion polymers.

# METHYL TERTIARY BUTYL ETHER

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Methyl tertiary butyl ether (methyl-*t*-butyl ether, MTBE; boiling point: 55°C, flash point: -30°C) has excited considerable interest because it is a good octane enhancer for gasoline (it blends as if it had a research octane number of 115 to 135). It also offers a method of selectively removing *iso*-butylene from a mixed C<sub>4</sub> stream, thus enabling the recovery of high-purity butene-1. Furthermore, methyl tertiary butyl ether can be isolated, then cracked to yield highly pure *iso*-butylene and methanol.

The reaction for making methyl-*t*-butyl ether proceeds quickly and highly selectively by reacting a mixed butene-butane fraction with methyl alcohol in the liquid phase on a fixed bed of an acidic ion-exchange resin catalyst (Fig. 1).



**FIGURE 1** Manufacture of methyl-*t*-butyl ether.





Reactor effluent is distilled, giving methyl-*t*-butyl ether of 99% purity. A few percent of *iso*-butylene remains unchanged and can be scavenged by use of a second unit.

# METHYL VINYL ETHER

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*See Vinyl Ethers.*

# MOLYBDENUM COMPOUNDS

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Molybdenum occurs naturally as the mineral *molybdenite*, which, by roasting, produces molybdenum trioxide (up to 90% purity).

Molybdenum disulfide is dispersed in greases and oils for lubrication; in volatile carriers it is used to form dry coatings of lubricant. Sodium molybdate is an especially effective corrosion inhibitor on aluminum surfaces and is dissolved in cooling solutions to protect aluminum motor blocks in automobiles.

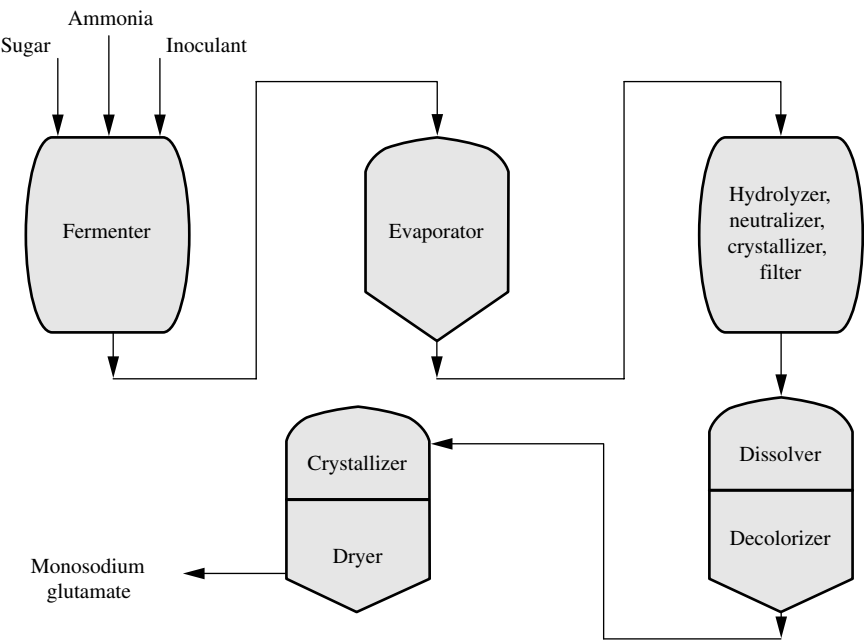
Molybdenum salts used as catalysts include cobalt molybdate for hydrogen treatment of petroleum stocks for desulfurization, and phosphomolybdates to promote oxidation. Compounds used for dyes are sodium, potassium, and ammonium molybdates. With basic dyes, phosphomolybdic acid is employed. The pigment known as *molybdenum orange* is a mixed crystal of lead chromate and lead molybdate. Sodium molybdate, or molybdic oxide, is added to fertilizers as a beneficial trace element. Zinc and calcium molybdate serve as inhibitory pigments in protective coatings and paint for metals subjected to a corrosive atmosphere. Compounds used to produce better adherence of enamels are molybdenum trioxide and ammonium, sodium, calcium, barium, and lead molybdates.

# MONOSODIUM GLUTAMATE

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Monosodium glutamate (MSG) is an important flavoring agent, yet has no flavor of its own but it does accentuate the flavors of food in which it is used. Glutamic acid exists in three forms, but only the monosodium salt of L-glutamic acid has a flavor-accentuating capacity. Glutamic acid is a constituent of all common proteins and is produced by a process in which the principal steps are (Fig. 1): (1) concentration and collection of the filtrate, (2) hydrolysis, usually with caustic soda, (3) neutralization and acidification of the hydrolysate, (4) partial removal of the inorganic salts, and (5) crystallization, separation, and purification of the glutamic acid.

L-Glutamic acid can be obtained directly from fermentation of carbohydrates with *Micrococcus glutarnicus* or *Brevihacterium divaricatum*.



**FIGURE 1** Manufacture of monosodium glutamate.

# MORPHINE

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Morphine ( $C_{17}H_{19}NO_3 \cdot xH_2O$ , melting point:  $253^{\circ}C$ ) is a white powder that is derived from opium which is the dried juice obtained from unripe capsules of the poppy plant (*Papaver somniferum*), cultivated in various regions of the world.

The opium poppy is an annual. When the petals drop from the white flowers, the capsules are cut. The juice exudes and hardens, forming a brownish mass that is crude opium. It contains a total of about 20 narcotics, including morphine.

Morphine (about 11%) and codeine (about 1%) are extracted, along with many of the other alkaloids occurring in opium, by mixing sliced opium balls or crushed dried opium with lime water and removing the alkaloids by countercurrent aqueous techniques. Other solvents are also used, for instance, acetone and acetic acid or acidulated water. The crude morphine alkaloid is precipitated with ammonium chloride, purified by crystallization of one of its inorganic salts from water, and centrifuged; crystallization is repeated if necessary. The purified sulfate or hydrochloride is converted into the alkaloid by ammonia precipitation. If a still further purified alkaloid is needed, it can be prepared by crystallization from alcohol. Otherwise the morphine alkaloid is dissolved in water with sulfuric acid and crystallized in large cakes from which the mother liquor is drained and then sucked off. The sulfate is dried and cut into convenient sizes for the manufacturing pharmacist to compound it, make it into tablets, or otherwise facilitate its use by physicians.

Morphine has been, and remains, an important drug even though codeine is used to a larger extent than morphine and, while its analgesic action is only one-sixth of morphine, it is employed for its antitussive effect, as a cough repressant.

The discovery of morphine's analgesic activity in 1806 started a long series of studies of the alkaloids from the opium poppy, including morphine's first correctly postulated structure in 1925 and its total synthesis in 1952. The depressant action of the morphine group is the most useful

property, resulting in an increased tolerance to pain, a sleepy feeling, a lessened perception to external stimuli, and a feeling of well being. Respiratory depression and addiction are its serious drawbacks.

The important structure-activity relationships that have been defined are: (1) a tertiary nitrogen, the group on the nitrogen being small; (2) a central carbon atom, of which none of the valences is connected to hydrogen; (3) a phenyl group connected to the central carbon; and (4) a two-carbon chain separating the central carbon from the nitrogen.

The *codeine* that occurs naturally in small amounts in opium is isolated from the aqueous morphine alkaloid mother liquors by immiscible extraction with a nonaqueous solvent. Dilute sulfuric acid is employed to extract the codeine sulfate from the nonaqueous solvent. This solution is evaporated, crystallized, and recrystallized. The alkaloid is precipitated from a sulfate solution by alkali and purified, if necessary, by alcoholic crystallization. It is converted into the phosphate by solution in phosphoric acid, evaporation, crystallization, centrifugation, and drying.

Codeine is the methyl ether of morphine and therefore is also prepared from morphine by methylating the phenolic hydroxyl group with diazomethane, dimethyl sulfate, or methyl iodide.

Since the source of the natural alkaloids is opium, all narcotics whose actions resemble those of morphine are sometimes referred to as *opiates*. Semisynthetic agents are usually made by altering the morphine molecule, and include such agents as ethylmorphine (Dionin), dihydromorphinone (Dilaudid), and methyldihydromorphinone (Metopon). Synthetic narcotics include agents with a wide variety of chemical structures. Some of the important synthetic agents are meperidine (piperidine-type), levorphanol (morphinian-type), methadone (aliphatic-type), phenaxocine (benzmorphinan-type), and their derivatives.

Heroin is diacetylmorphine (diamorphine hydrochloride) and is prepared by the action of acetic anhydride on morphine. It possesses four times the analgesic effect of morphine, but has considerably less depressant effect. Addiction is common, the drug being taken in the form of snuff, or by injection.