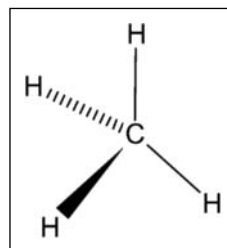


55. *L-Dopa*. See 33. Dopamine, L-Dopa

56. *Methane*

CHEMICAL NAME = methane
CAS NUMBER = 74-82-8
MOLECULAR FORMULA = CH₄
MOLAR MASS = 16.0 g/mol
COMPOSITION = C(74.87%) H(25.13%)
MELTING POINT = -182.6°C
BOILING POINT = -161.4°C
DENSITY = 0.71 g/L (vapor density = 0.55, air = 1)



Methane is a colorless, odorless, flammable hydrocarbon gas that is the simplest alkane. The root word, *met*, in methane is derived from the Greek root word *methe* meaning wine. Methylene was used in the early 19th century as the name for methanol, which is wood alcohol, CH₃OH. Methylene comes from *methe* + *hydē*, the latter being the Greek word for wood, so methylene would mean wine from wood. Methanol got the names methylene and wood alcohol because it was discovered by Robert Boyle (1627–1691) in the 17th century by the destructive distillation of wood. Destructive distillation involves heating in the absence of air. Methane is the first alkane and carries the suffix “ane” denoting an alkane, thus *methez* + *ane* = methane. The structure of methane, as shown in Figure 56.1, is tetrahedral. The carbon is at the center of the tetrahedron, which can be assumed to be an equilateral pyramid, with a hydrogen atom at each of the four corners of the tetrahedron. The bond angles are all 109.5 degrees.

Methane is the principal component of natural gas, with most sources containing at least 75% methane. Methane production occurs naturally through a process called methanogenesis. Methanogenesis involves anaerobic respiration by single-cell microbes collectively called methanogens. Methanogens belong to a class of organisms called archaeobacteria, which are prokaryote bacteria. Some classification systems differentiate archaeans from bacteria. The anaerobic digestion of dead plant matter under water produces methane and led to the common name of marsh gas for methane.

Methane has been used as a fossil fuel for thousands of years. The discovery of methane is attributed to the Italian physicist Alessandro Volta (1745–1827). Volta, known primarily

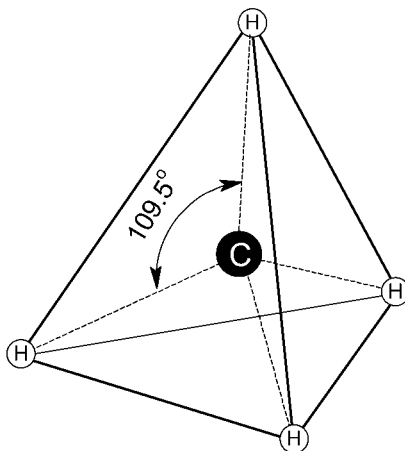
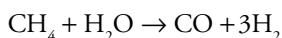
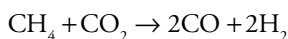
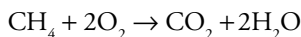


Figure 56.1 Structure of methane.

for his discoveries in electricity, investigated reports of a flammable gas found in marshes. In November 1776, Volta, while visiting the Lake Maggiore region of northern Italy, noticed that gas bubbles emanated from disturbed sediments in marshes. Volta collected the gas and began investigations on its nature. He discovered that the gas was highly flammable when mixed with air. He developed an instrument termed Volta's pistol (also called a spark eudiometer) that fired metal balls like a miniature cannon to conduct combustion experiments with methane. He also developed a lamp fueled by methane.

Methane is the principal gas found with coal and oil deposits and is a major fuel and chemical used in the petrochemical industry. Slightly less than 20% of the world's energy needs are supplied by natural gas. The United States get about 30% of its energy needs from natural gas. Methane can be synthesized industrially through several processes such as the Sabatier method, Fischer Tropsch process, and steam reforming. The Sabatier process, named for Frenchman Paul Sabatier (1854–1941), the 1912 Nobel Prize winner in chemistry from France, involves the reaction of carbon dioxide and hydrogen with a nickel or ruthenium metal catalyst: $\text{CO}_2 + 4\text{H}_2 \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$.

Methane is an important starting material for numerous other chemicals. The most important of these are ammonia, methanol, acetylene, synthesis gas, formaldehyde, chlorinated methanes, and chlorofluorocarbons. Methane is used in the petrochemical industry to produce synthesis gas or syn gas, which is then used as a feedstock in other reactions. Synthesis gas is a mixture of hydrogen and carbon monoxide. It is produced through steam-methane reforming by reacting methane with steam at approximately 900°C in the presence of a metal catalyst: $\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$. Alternately, methane is partially oxidized and the energy from its partial combustion is used to produce syn gas:



Hydrogen from syn gas reacts with nitrogen to produce ammonia: $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$. Carbon monoxide and hydrogen from syn gas can be combined to produce methanol: $\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH}$. Methanol is primarily used for the production of formaldehyde through

an oxidation process: $2\text{CH}_3\text{OH} + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$ or an oxidation-dehydrogenation process: $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$.

Chlorination of methane, in which chlorine is substituted for one to all four of the hydrogens in methane, produces methyl chloride (CH_3Cl), methylene chloride (CH_2Cl_2), chloroform (CHCl_3), and carbon tetrachloride (CCl_4). The substitution of chlorines and fluorines in methane results in chlorofluorocarbons (see Dichlorodifluoromethane).

Methane is a fossil fuel that acts as a greenhouse gas, making it a subject of widespread interest in global warming research. Methane is much more effective at absorbing infrared radiation than is carbon dioxide. Its global warming potential is 21, which means it is 21 times more effective than carbon dioxide at trapping heat. Like carbon dioxide, concentrations of methane accelerated at the start of the Industrial Revolution and have climbed steadily throughout the 20th century, although in the last decade methane increases have plateaued for unknown reasons. Concentrations determined from ice cores place atmospheric methane concentrations at approximately 700 parts per billion (ppb) by volume in 1750, with a 150% increase to current levels of 1,750 ppb. Both natural and human sources contribute to global atmospheric methane concentrations. Estimates of the contribution from difference sources are difficult to make and vary highly among countries and global regions. Approximate contributions from major sources are summarized in Table 56.1.

Values in Table 56.1 are expressed in teragrams per year. A teragram is equivalent to 10^{12} grams. Table 56.1 indicates that approximately two-thirds of methane comes from human sources, principally related to agriculture. Animal digestion (flatulence) is chiefly from livestock such as cattle. An adult cow emits 600 liters of methane each day. Fossil fuel sources include both combustion and processing of oil, natural gas, and coal. Landfills are the primary anthropogenic source of methane in the United States.

A global system of natural gas wells, processing plants, and pipelines has been established to make natural gas available to millions of people. Exploration for conventional sources continues, but one large potential source of methane is methane hydrate. Methane hydrate is a solid crystalline structure of methane molecules surrounded by a frozen cage of water molecules. Methane hydrates form under the conditions of low temperature and high pressure. They occur in the polar regions, in cold water off the continental shelf, in permafrost, and in deep ocean sediments. The U.S. Geological Survey conservatively estimates that the amount of natural gas trapped in hydrates is twice the existing known reserves of all other fossil fuels combined.

Table 56.1 Major Sources of Atmospheric Methane in Tg/yr

Natural		Human	
Wetlands	150	Animal digestion	100
Termites	20	Rice fields	80
Oceans	15	Fossil fuels	80
Hydrates	10	Biomass burning	45
		Landfills	40
		Sewage plants	30
Total	190		375