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Old Gas, New Gas

Roald Hoffmann

AT THE WELLHEAD, natural gas is 70 to 90 percent methane. The gas we use at home—expensive, this winter—is nearly pure methane. That simple, archetypical organic molecule, CH₄, methane, has a carbon bonded to four hydrogens at the corners of a tetrahedron. And methane's structure is the only simple thing about it.

Origins

In a hurry to get to methane hydrates, I began by writing, "Along with petroleum and coal, methane is a fossil fuel, of plant origin..."—at which point I got corrected by the president of Sigma Xi. When I changed what I wrote, geologists gave me more trouble. I had stumbled right into a nest of controversies. Or, an area of current research.

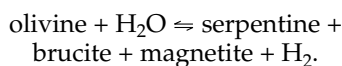
It appears that methane on Earth has not one source, but many. Most (but not all) of the commercial methane in natural gas is *thermogenic*—thought to derive from petroleum (originally from plants) that is heated and processed deep underground. It's old.

A great deal of additional methane, however, is sequestered in sediments, at sea bottom and in permafrost, in a remarkable set of structures I will soon describe. And its origins are controversial. Much (some think all) is made by archaeans—the neither-bacterial-nor-eukaryotic microorganisms that were only distinguished in recent decades.

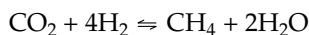
But there is an abiogenic source of sequestered methane too. Mantle rocks that contain the mineral olivine (which describes a range of minerals from Mg₂SiO₄ to Fe₂SiO₄) are often altered to serpentine ((Mg,Fe)₃Si₂O₅(OH)₄), a change that also produces brucite ((Mg,Fe)(OH)₂) and magnetite (Fe₃O₄). The chemistry of this "serpentinization" reaction is roughly

Methane—made and taken apart by microbes, in the Earth, by people

this (to balance the equation, we'd have to specify the olivine):



The important thing about this reaction is that the olivine is a source of electrons that convert the protons in water to H₂. Combining it with CO₂ results in methane, courtesy of the so-called Fischer-Tropsch reaction:



This reaction proceeds in geological strata at accessible temperatures and pressures in the presence of the necessary catalysts. Some geologists think that most methane is created this way.

But the reaction also runs (catalyzed by enzymes now) in microbes—methanogens—at temperatures hundreds of degrees lower. To return to the very different setting of thermogenic methane, geologist and chemist John M. Hayes of Woods Hole Oceanographic Institution suggests that even there microbes could have catalyzed thermogenic CH₄ formation.

I am staying tuned. But let's return to that underwater methane, wherever it comes from.

Methane Hydrates

Under pressure and low temperature, methane (which normally boils at -161 degrees Celsius) forms a thermodynamically stable association with water. These solids are called methane hydrates, examples of a broader class of structures, the clathrates.

What's stable at one temperature and pressure may not be at another. Under ambient conditions at sea level, methane is a gas, water a liquid. But in the permafrost and deep at sea, the weak hydrogen bonds between water molecules reinforce the still weaker forces between CH₄ and H₂O to create an aggregate made of a water cage around one or more methane molecules.

Methane hydrates are white solids, less dense than water. They remain on the seafloor only because they are agglomerated with rocks and mud. (There, opportunistic evolution has led a variety of species to use the methane *in situ*, as a carbon and energy source.) Under the weight of 1,000 meters of ocean, methane hydrate is stable to about 12 degrees, and because the seafloor is colder than that, the ice-like hydrates form spontaneously wherever methane is available. Brought up to the surface the hydrates fall apart to methane and water.

In a previous issue of *American Scientist* (May-June 2001), Robert L. Kleinberg and Peter G. Brewer looked at how gas hydrate deposits might be exploited. Current guesses of the quantity of methane contained in hydrates are around 10¹⁶ cubic meters—exceeding by a factor of 100, roughly, our estimates of "normal" natural gas resources. Could they be mined? Not easily. Much of that methane hydrate is tied up in inaccessible clays and pores. Moreover, one would have to get it out very carefully, as methane is a most effective greenhouse gas. The existing atmospheric burden of methane from natural-gas leaks, cows and termites is consequential enough.

(An aside: In 2003, as part of its adherence to the Kyoto protocol, the government of New Zealand proposed a flatulence tax on its 54 million sheep and cattle. New Zealand also has a population of approximately 4 million people, but belching and farting ruminants are responsible for roughly half of the country's greenhouse-gas burden. The

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proposal was withdrawn after strong opposition from farmers, but it still has supporters.)

One more lesson from the methane hydrates, part of my ongoing struggle against the seductive forces of simplicity: The structure at right, a dodecahedron of water molecules called 5^{12} (referring to its twelve pentagonal faces), is only one building block of the methane hydrates. The three most common hydrate structures contain repeating units of 46, 136 and 34 water molecules, some making up the 5^{12} cavities. But the common structures also incorporate polyhedra with four-membered and six-membered hydrogen-bonded water rings of substantially greater complexity, for instance $5^{12}6^8$ and $4^35^66^3$.

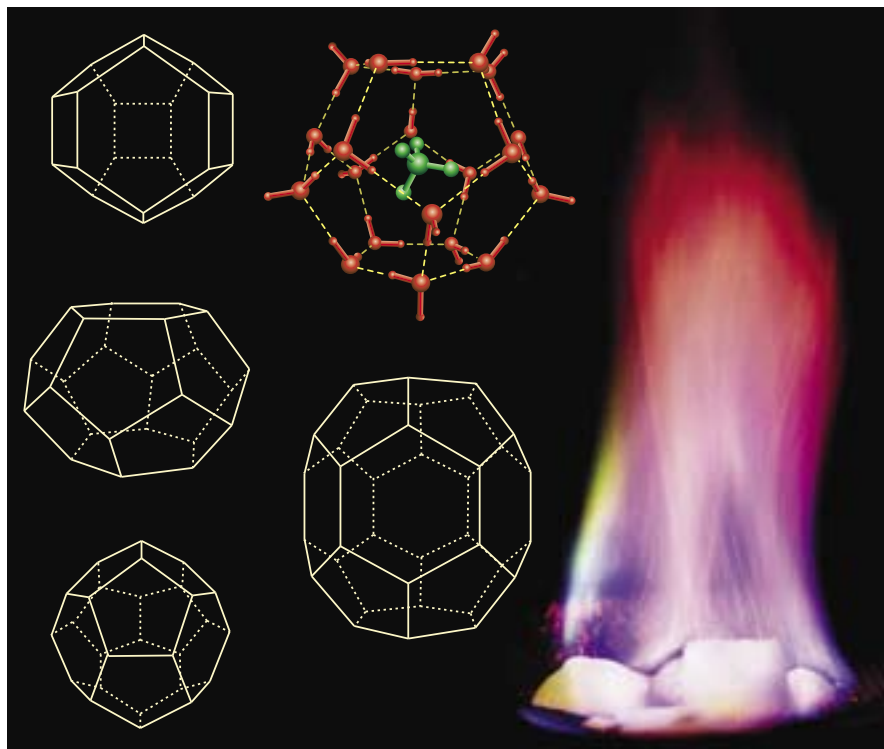
A Kiln on a Landfill

A few years ago, I spent some time at the Penland School for Crafts in the Blue Ridge country of North Carolina. There I met Jon Ellenbogen, a potter with a good background in technology. Jon showed me pictures of glass and ceramic kilns and of greenhouses on the site of the nearby Mitchell/Yancey county landfill. Once a smelly six-acre eyesore, the landfill now provides not only a home for artists and greenhouses, but also, importantly, the energy they consume. From methane.

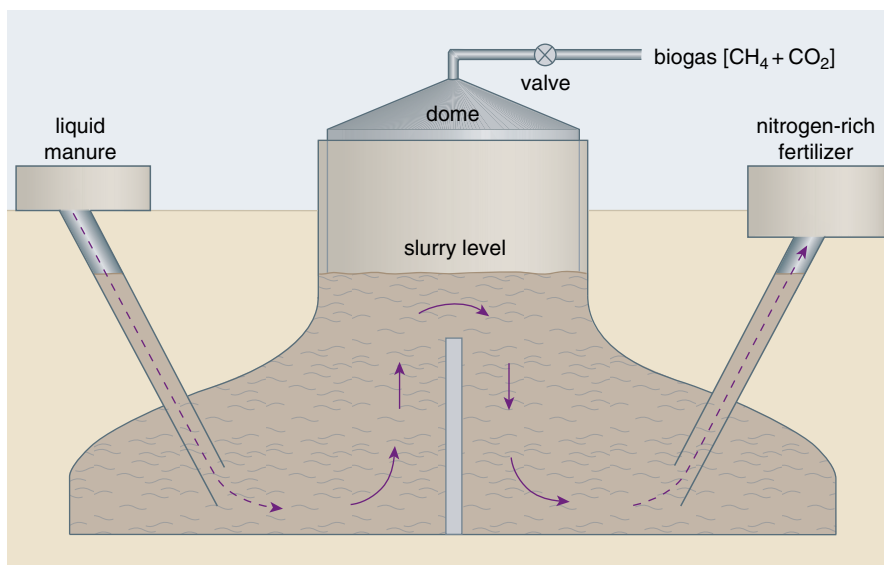
The U.S. Environmental Protection Agency estimates that 33 percent of methane released into the atmosphere by human activity comes from landfills. This production is the result of microbes (they're at it, around the globe) that decompose the buried waste. Landfill gas is roughly 50 percent methane, 45 percent CO_2 , and a few other gases. The total gas-generation potential of the Mitchell/Yancey landfill is 2 cubic feet of methane per pound of refuse buried. Figuring that each year the dump operated, it swallowed perhaps 10,000 tons of waste, there's lots of methane there. EnergyX-change, Ellenbogen's nonprofit organization, reasoned, why not use it? If only more landfills around the country did so!

Biogas may be generated from any organic waste, but animal manure is an especially good source. Large-scale animal productions of swine, poultry or cattle are natural places to site biogas digesters—dedicated residences for domesticated methanogens. And there are already millions of small ones, adapted for household use, installed around the world, especially in China and India.

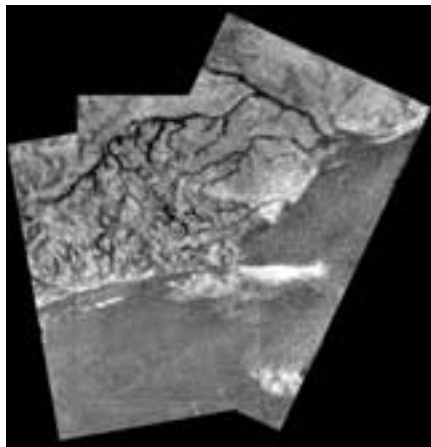
The Indian biodigesters work mainly with cow manure—it takes three good



Methane hydrates are stable only at high pressure and low temperature. The opaque, icy solid falls apart at the surface and will burn if ignited. The simplest structure for this clathrate is a regular dodecahedron (12 pentagonal sides, or 5^{12} , red) that encloses one methane molecule (green). However, the frozen-water cage around methane can also assume other shapes that incorporate four- or six-sided rings. (Photograph courtesy of Laura A. Stern and John C. Pinkston, Woods Hole Oceanographic Institution.)



Methanogenic microbes can digest animal or human waste and produce a useful stream of methane gas for cooking and light. Martin Fisher, a founder of the technology firm KickStart, describes the design of the biodigester found commonly in India: "It has a large underground domed circular (brick or concrete) tank with a smaller cylindrical opening on the top (between 6 and 15 feet in diameter for a household unit). Overall the tank is in the shape of a buried bell with the top cut off and the bottom sealed. Floating in the cylindrical top of the tank is a large metal gas drum of a slightly smaller diameter than the tank opening. This drum is like a large upside-down pot and it floats on top of the digesting sludge and captures the gas. The underground tank has a large inlet and outlet pipe for the waste material and fertilizer and the gas pipe comes out of the top of the floating drum. The big advantage of this design is that the gas is kept at constant pressure—controlled by adding weights to the floating drum."



In early 2005, the European Space Agency's Huygens spacecraft photographed these methane river channels emptying into a dry lake bed on Titan. The widest channel is about 50 meters across. (Photograph courtesy of ESA/NASA/JPL/University of Arizona.)

cows to provide a household with cooking gas and some lights. The Chinese digesters, a somewhat different design, use human nightsoil. In both designs, there is much useful digested manure left in the end.

Meanwhile, Back on Titan

Just about a year ago, on January 14, 2005, the European Space Agency's Huygens probe completed a one-way, 4-billion-kilometer journey to Saturn's largest moon, Titan. The temperature there on the surface is around -179 degrees, cold enough that methane is a liquid. If you look at some of the startling images sent back by Huygens you can see river-like channels that were probably carved by streams of the stuff. Why methane? After nitrogen, it's the most abundant component of Titan's atmosphere, and a heated sample of the Titan soil released a puff of it.

So where does Titan's methane come from? People think it's that serpentinization reaction mentioned earlier.

Activating Methane

The C-H bond in methane is very strong. But there are bacteria, methanotrophs, that have evolved to use methane as their carbon and energy source. To do so, they must break the C-H bond of CH_4 . This they accomplish with enzymatic finesse, using methane monooxygenases, which contain a core of one or more copper atoms.

We now use petroleum as a carbon source for fuel, plastics, fibers and pharmaceuticals. That resource will soon be exhausted. Methane will be around

longer. One idea is that we might farm those bacteria to give us carbon feedstocks from methane. But could we invent an efficient industrial process that breaks the strong C-H bond?

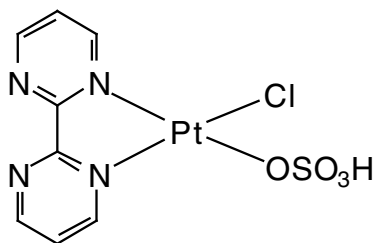
Perhaps the nitrogen fixation story provides a lesson here. While our biochemistry craves nitrogen atoms, we cannot fix abundant atmospheric nitrogen. Some bacteria can; biologically assimilable nitrogen also comes from minerals in the soil and naturally acid rain.

But the natural sources do not suffice. Fritz Haber and Carl Bosch devised (over ninety years ago) an industrial process to make ammonia from N_2 and H_2 . The chemistry is so successful, so economical, that today over half the nitrogen atoms in our bodies have seen the inside of a Haber-Bosch factory. If all those factories disappeared, there would be enough fixed N for only half the people on earth.

To put it another way: In providing us with a key element, N, cultural evolution (science and technology) competes effectively with nature.

Returning to methane: Of course, there is one reaction we all know—burning—which certainly activates methane. The problem is that it does it too well, taking CH_4 all the way to inert CO_2 . Along the way, inside hydrocarbon flames, are the partially oxidized "intermediates" that industry wants. But the process of burning is nonselective; it does not stop, for example, at methanol, CH_3OH , a molecule we could use.

In principle, several desirable reactions are feasible, such as the ones that lead methane to methanol or acetic acid, or produce, using methane, ammonia and hydrogen peroxide. Indeed, several commercial processes currently begin with methane and convert it to such molecules. The problem is that they require really high temperatures. For selective, low-temperature chemistry, a catalyst is needed.



This catalyst from Roy Periana's laboratory converts methane to methanol in good yield at reasonable temperature.

Alexander E. Shilov of the Russian Academy of Sciences came up with the first candidate in 1969. Using platinum salts, he saw hydrogen/deuterium exchange in alkanes (compounds of just C and H, such as methane) that had been mixed with deuterated water, D_2O . Therefore, some of the C-H bonds must have been broken and reformed—the first evidence that the C-H bond was not untouchable.

Passing over, unwillingly, much beautiful chemistry, we come to the exciting, recent work by Roy Periana and his coworkers at the University of Southern California, who have improved on Shilov-like chemistry to the stage that they can convert methane to methanol with a yield of better than 70 percent at 220 degrees. They can also convert methane directly to acetic acid at 180 degrees—much cooler than the >800 -degree conditions of other processes.

Periana thinks that within 10 years (I guess 50) we will have all the carbon-containing molecules we need—and many we haven't thought of—made from coal and methane sources. Good-bye petroleum.

Acknowledgments

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