The Story of Methane

Five Atoms that Changed the World

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ROYAL SOCIETY
OF **CHEMISTRY**

Print ISBN: 978-1-83767-101-4
PDF ISBN: 978-1-83767-175-5
EPUB ISBN: 978-1-83767-176-2

A catalogue record for this book is available from the British Library

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Printed in the United Kingdom by CPI Group (UK) Ltd, Croydon, CR0 4YY, UK

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How Much Do You Know About Methane?

This simple five-atom molecule is a cornerstone of the modern energy climate and has the potential to become the key to green renewable energy. Herein, *The Story of Methane* highlights the history as well as the current and future utilizations of methane gas, which include energy generation, heating, and conversion to other chemical feedstocks. The work illustrates some choice cutting-edge scientific developments in the world of methane in a digestible manner with an end goal of sharing enthusiasm and hope in the potential of the most basic hydrocarbon gas.

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In darkness deep, where microbes roam,
In marshy lands and ocean's foam,
There lies a gas, both friend and foe,
A molecule, methane, far below.

From cows that graze on verdant fields,
To swamps where silence never yields,
Methane rises, unseen yet strong,
Invisible threads that weave along.

It whispers tales of ancient times,
Locked in ice and in deep sea brines,
A relic of Earth's primordial dance,
A molecule with a mystic trance.

But heed its call with cautious ear,
For in the atmosphere, it does steer,
A potent force, the climate's game,
Its rise may kindle Earth's fierce flame.

Yet in its grasp may be energy's key,
A fuel for change, a pathway free,
To power homes and light our way,
If harnessed wisely, some might say.

So let us tread with mindful pace,
As the stewards of this wondrous space,
For in the tale of methane, we find,
A story of balance for humankind.

Jessica Ye, 2024.

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Dedication

To our partners, Linda and Ryan.

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Acknowledgements

This work would not be possible without the help of our families, friends, and colleagues who supported us along the way. Their untiring efforts, unending scientific creativity, and steadfast teamwork have been an inspiration while putting together this book. A special thank you must be given to Victoria Cincotta for her continuous support in both daily laboratory activities and for managing all the logistics of publishing.

Jessica would like to give named thanks to her family. To her mother and godmother, Doris and Amanda, for their continuous support from her birth to the present day. It was the blood, sweat, and tears of their labour and love which have granted her the opportunities to become who she is today. To her sister, Elizabeth, with whom she has shared many a laugh and whose presence she has and will always cherish. Finally, her cats, Artemis and Huhu, are always deserving of praise.

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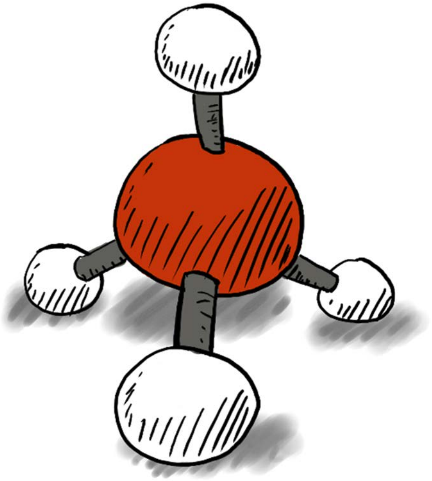
Preface



Have you ever wondered how just a few atoms have changed our world? Carbon and hydrogen together make up the backbone of life on Earth. In their simplest combined form, they form methane, a molecule merely five atoms in size that has immense potential for both good and bad. This simple molecule can impact us in ways that can either better human life or threaten its very existence.

The Story of Methane details the origins, uses, and possible futures of methane in a way that is hopefully understandable by anyone who picks up the book. Special care was taken to provide the reader with the necessary background to understand the topics discussed. Within, one can find answers to how the gas is extracted from deep beneath the earth, how it is made following centuries of human ingenuity, its mechanisms for warming the planet as a greenhouse gas more potent than carbon dioxide, and the different avenues available to it when we transform it into the various commodity chemicals of today.

Understanding what methane is and what it can do has become increasingly important for society as its rate of consumption steadily increases. Herein, we attempt to shine light on some of the latest research on the five-atom molecule. The topics covered range from its extraction from natural gas, artificial synthesis from carbon dioxide, and types of reactions which

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can occur to convert it into other industrially useful compounds. Methane, despite being largely derived from non-renewable fossil fuel, is also looked at under a new lens as the possible solution for the climate crisis. It burns cleaner than liquid or solid fuels. More important in the context of this book, it can also be stored and processed as a source of clean hydrogen gas. However, this is not to say these processes are easy to implement. Throughout and especially in the last chapter, we take care to detail the difficulties with implementing new methane utilization technologies.

The sheer number of *possibilities* surrounding methane is something to behold. As the story of methane continues to be inscribed alongside the history of mankind, we hope that readers of this work can share in the awe we have towards the simple five-atom molecule.

Geoffrey Ozin and Jessica Ye

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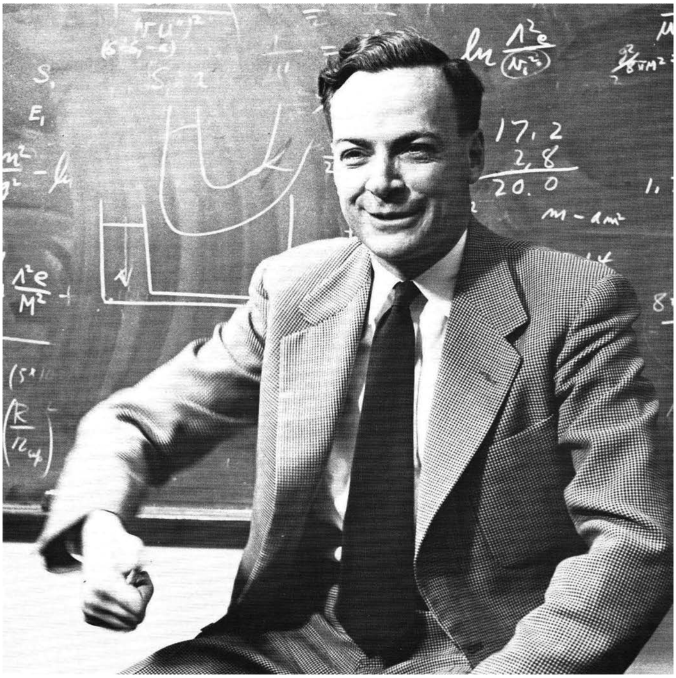
CHAPTER 1

Introducing Methane



Photograph in Public Domain

> What men are poets who can speak of Jupiter if he were a man, but if he is an immense spinning sphere of methane and ammonia must be silent?
>
> From *The Feynman Lectures on Physics Vol. 1*
> Richard P. Feynman

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1.1 Methane's Early History

Alessandro Giuseppe Antonio Anastasio Volta (1745–1827), an Italian physicist and inventor of the battery, is also credited with the discovery and isolation of methane between 1776–1778 during his studies of marsh gas from Lake Maggiore on the south side of the Italian alps.[1] Before Volta's work, natural gas was a mystery to humankind. In Iran prior to 2000 BCE, flames fuelled by natural gas leaking out of the ground, perhaps lit by lightning long ago, were perceived as "eternal fires" by the fire-worshiping religion of ancient Persians. Similar flames found rising from fissures in rock on Mount Parnassus around 1000 BCE were believed by Ancient Greeks to be of divine origin.[2] A temple at this site was occupied by a priestess known as the Oracle of Delphi, who forecast prophecies supposedly inspired by the flame.[3]

The practical potential of these natural gas flames emanating from the earth was discovered in China around 500 BCE to extract brine, prepare food, and to fuel lamps. Around 200 CE, the Chinese began methodical explorations for natural gas and invented how to transport discovered deposits through bamboo pipes over long distances to use sites.[4] Much later in America, by around 1821, natives living along the western side of the Appalachian Highlands observed fissures of natural gas in the ground and burned it for light.[5]

1.2 Only Natural

When we think about natural gas, our first thoughts are that: (1) it comes from deep in the earth, (2) it is a fossil fuel, (3) it originates from the decomposition of animal and plant matter buried under sedimentary rock. An illustration of natural gas's distribution underground shows that it is a bit more complicated.[6]

As seen in Figure 1.1, gas distributions vary widely depending on the geological make-up of the area. Moreover, natural gas is not pure methane. Instead, it is a mixture of low molecular weight alkanes, or saturated hydrocarbons with the chemical formula C_nH_{2n+2}, which have double plus two added hydrogens for every carbon added. Though the gas consists mostly of methane (CH_4, 94%), small but not insignificant amounts of ethane (C_2H_6@4%), propane (C_3H_8@0.2%), butane (C_4H_{10}@0.02%), pentane (C_5H_{12}@0.02%), and hexane (C_6H_{14}@0.01%) also exist.[7] Furthermore, carbon dioxide (CO_2; the "*di*" in front of "oxide" denoting two oxygens in the molecule) can be found in quantities ranging anywhere from 40–60% depending on the deposit.

What is not shown in the figure is that natural gas distributions are not found solely on land. Instead, the fossil fuel is distributed in a 70/30 ratio onshore *versus* underwater, with most of the oceans' methane being dissolved in seawater and confined in the seabed as biological oxygen-free sediments, in geological pools, and encapsulated in methane hydrate deposits. Unfortunately, from a climate change perspective, an increasing amount of methane is also being released into the atmosphere as a by-product of

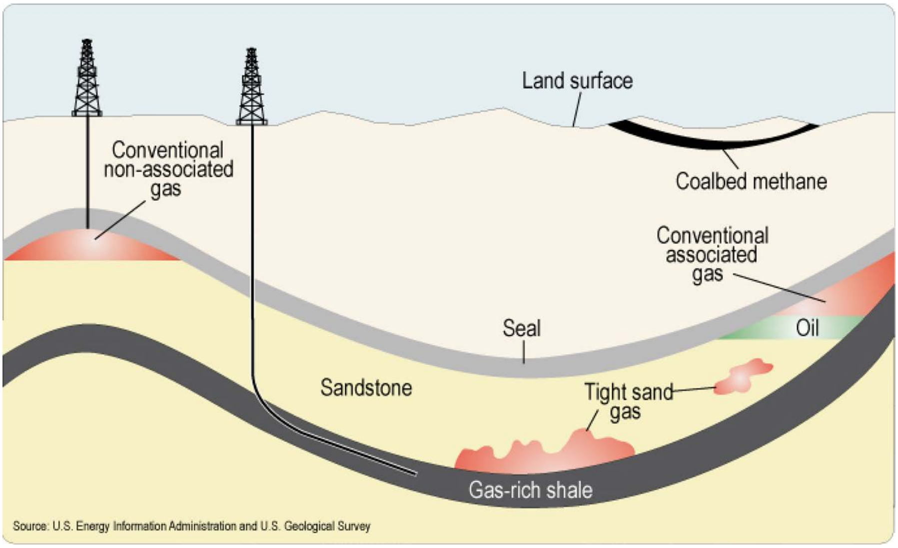

Figure 1.1 Locations in which natural gas deposits are found.[6] Source: U.S. Energy Information Administration and the U.S. Geological Survey. Figure in Public Domain.

human activity. This happens due to the decomposition of organic material in landfills, production of rice and livestock, the combustion of biomass, as well as leaks during the extraction, transportation, and use of fossil fuels.

Though we have been led to believe that natural gas is the most eco-friendly of the fossil fuels, it still produces about half of coal and oil's carbon emissions per unit of energy produced. Therefore, emissions from methane combustion remain a concern as it becomes an increasingly popular alternative to its dirtier burning cousins. Furthermore, anthropogenic methane is one of the most potent greenhouse gases. Making up 20% of the world's emissions, methane is 27–30 times more potent than carbon dioxide at warming the Earth. Though it possesses a relatively short atmospheric lifetime, degrading to carbon dioxide *via* chemical processes in the air over the course of a bit more than a decade, methane's concentration in the atmosphere has been steadily increasing since the industrial revolution. This situation is being taken very seriously by the Intergovernmental Panel on Climate Change (IPCC).[8]

In addition to its use as fuel for heat and electricity generation, lesser-known utilizations of methane involve its incorporation into a myriad of products. Methane-derived chemicals can be found everywhere, including as additives in antifreeze, fertilizer, and sanitation products. This poses a conundrum. While natural gas extraction and consumption are undoubtedly harmful to the fragile state of the planet, methane-sourced products have become the keystone of a multitude of industries ranging from polymers to pharmaceuticals.

1.3 The End of Natural Gas

With the eventual depletion of underground natural gas deposits in sight, the world will have to investigate alternative methane sources. This is where chemistry and chemical engineering solutions enter the picture. Scientists have been able to synthesize methane on an industrial scale from carbon dioxide *via* a reaction called the Sabatier process:

Sabatier process:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{1.1}$$

Though consuming carbon dioxide as a chemical feedstock to produce methane *via* the Sabatier reaction seems like an attractive proposition, there remain a few hiccups in the process. First, clean energy must be used to fuel the process, and second, an environmentally cheaper source of green hydrogen than conventional steam–methane reformation (a process where water and methane are heated up to extreme temperatures to produce hydrogen and carbon monoxide, or CO, gas), must be used. This is where another industrial reaction known as electrolysis comes into play:

Electrolysis of water:

$$2H_2O \rightarrow 2H_2 + O_2 \tag{1.2}$$

By running an electrical current through water, the water molecule can be forced to split into two parts hydrogen and one part oxygen. The hydrogen can then be separated using special filters for use in the Sabatier reaction described in eqn (1.1) to generate more methane.

Notably, methane can also be used to sequester carbon dioxide and convert it into useful feedstocks. Through a process called dry reforming, methane is combined with carbon dioxide to form two parts of industrially significant carbon monoxide and hydrogen gas.

Dry reforming:

$$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2 \tag{1.3}$$

Then, the hydrogen gas can be recovered to make more methane using the Sabatier reaction and recycled back into the process. Such a method would result in a net reaction that effectively converts carbon dioxide and hydrogen gas into useful carbon monoxide and water, where methane acts as a key intermediate.

Net reaction of Sabatier process and dry reforming:

$$CO_2 + H_2 \rightarrow CO + H_2O \tag{1.4}$$

Furthermore, a ready source of methane can be found from undesirable emission sources, such as landfills or anywhere else that decomposition takes place. These sites are the third largest source of anthropogenic methane and make up over an eighth of total human methane emissions in the United States. In essence, two greenhouse gases can be utilized in a sustainable process to produce viable feedstock chemicals. However, the impact of such a process on the global carbon footprint remains a hotly debated topic.

It becomes apparent that the depletion of buried methane does not spell the end of the chemical's usefulness in human history. Synthetic methane sourced from carbon dioxide and captured from fermentation remain viable sources long past the age of digging fossil fuels from the ground.

1.4 Methane Facts

The industrial revolution unlocked a new form of energy, fossil fuels, to power the machines which used to be driven by humans and animal muscle. Fossil energy has since proven to be the indisputable driver of technological, economic, and social development and continues to dominate global energy infrastructure. However, the emissions associated with their use are also the greatest contributor to the dangers of global warming and air pollution.

Since the industrial revolution, the scale and type of fossil fuel consumption has changed dramatically. A graph of global primary energy consumption with respect to fossil fuel source in terawatt hours is shown in Figure 1.3. After about 1950, a dramatic increase in consumption and a shift away from coal towards oil and gas can be seen.

The United States has overtaken Russia as the top natural gas producer in 2010. Qatar, Canada, and the United Kingdom, respectively, lag far behind in production. Despite these statistics, the largest consumer per capita of natural gas is Canada, followed by Russia, the United States, Singapore, South Korea, Germany, and Norway. For decades, natural gas as an energy source has lagged behind coal and oil but has recently become a cleaner and more attractive alternative for electricity and heat generation (Figure 1.2).

1.5 Alarm Bells

About 55 million years ago in the Paleocene-Eocene Thermal Maximum (PETM), a sudden increase in the level of atmospheric methane was thought to be responsible for a global warming event of 4–8 °C.[11] The rise in ocean and air temperatures was likely triggered by a massive volcanic eruption that released methane from methane hydrates, which are ice-like crystals of methane trapped in water, in the ocean bed. This temperature change resulted in global extinctions of terrestrial and marine ecosystems.

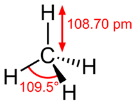

Figure 1.2 A representative illustration of a methane molecule.[9] Figure in Public Domain.

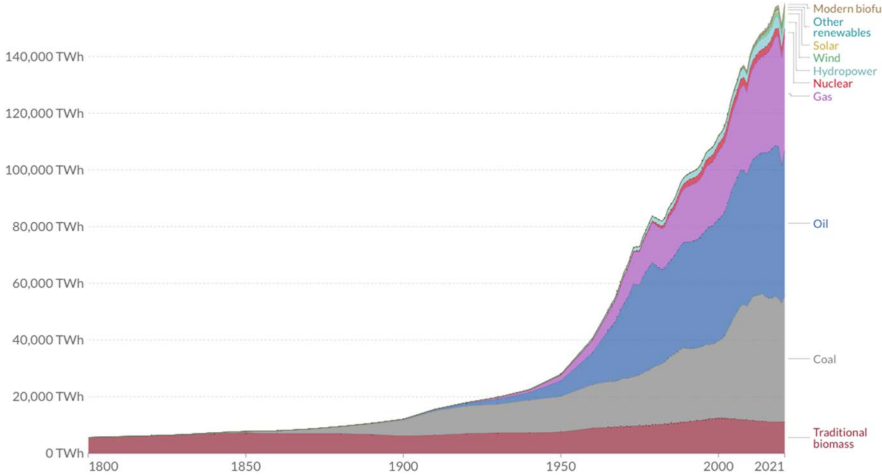

Figure 1.3 Global primary energy consumption by fuel source.[10] Reproduced from ref. 10, https://ourworldindata.org/global-energy-200-years, under the terms of the CC BY 4.0 license, https://creativecommons.org/licenses/by/4.0/.

It is uncertain how long and at what concentrations methane existed during the PETM. At very high concentrations, the residence time, or average lifetime, of atmospheric methane may be much longer than the decade that it exists for in today's atmosphere. During the Pleistocene ice age cycles, the concentration of methane varied between about 0.35–0.80 ppm before stabilizing around preindustrial levels of 0.70 ppm. This value remained constant until the start of the industrial revolution, where anthropogenic activity spiked the world's methane emissions. Today, atmospheric methane concentrations reach nearly 1.9 ppm.[12]

Though methane concentrations are about 200 times lower than the 421 ppm of atmospheric carbon dioxide, methane is estimated to be around 28 times more potent in its greenhouse gas warming potential. This means that one molecule of methane warms the Earth 28 times more effectively than one molecule of carbon dioxide. Furthermore, carbon dioxide and methane work on a feedback loop. Increasing the amount of carbon dioxide causes more methane to be released as a side effect of global warming induced climate change. Increased rainfall in wetlands has been shown to increase methane release from biomatter during anaerobic (without oxygen) decay. Meanwhile, defrosting permafrost in the northern hemisphere results in the release of large pockets of trapped methane gas underground.

The Global Carbon Project has conducted a comprehensive study of all methane emission sources and sinks, shown in Figure 1.4.[13] The chart reveals the contributions from anthropogenic (fossil fuels, agriculture, waste), natural (wetlands, inland waters, geological, oceans, termites, wild animals, permafrost, vegetation), and combined fluxes (biomass and biofuel

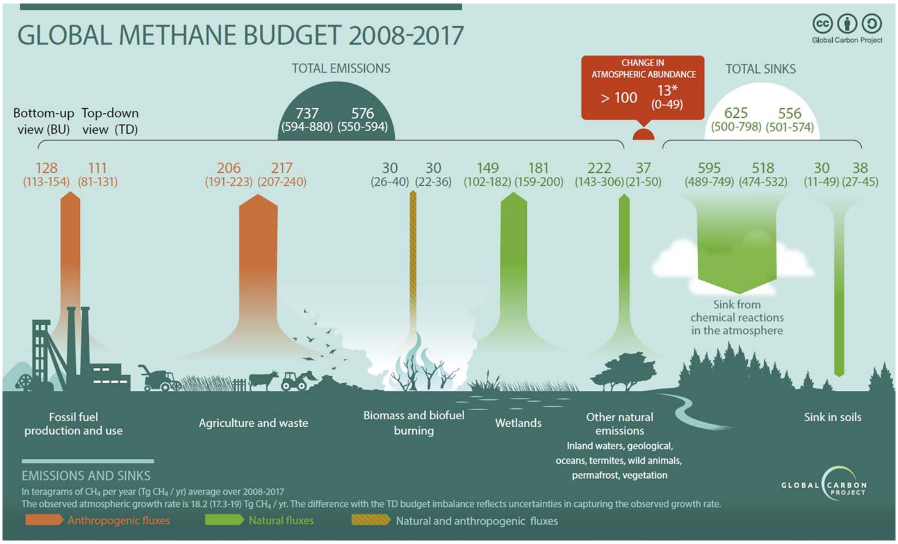

Figure 1.4 The Global Methane Budget, including all sources and sinks of methane in the environment.[13] Uncertainties are in the parentheses below the stated average values. Reproduced from ref. 13, https://www.globalcarbonproject.org/methanebudget/, under the terms of the CC BY 4.0 license, https://creativecommons.org/licenses/by/4.0/.

combustion). Roughly 60% of emissions can be traced to human activity and another third can be attributed to natural emissions from wetlands. These methane emissions are balanced by methane sinks found in the soil and atmospheric chemical reactions. Together, global methane emissions have a global warming effect roughly equal to 189 million additional automobiles.

1.6 Methane Maps

Satellites with an on-board scanning imaging absorption spectrometer enabled the first global-scale mapping of atmospheric methane concentrations. These satellites track methane concentrations by analyzing the spectra of infrared light reflected by the Earth's surface. Figure 1.5 shows the monthly average concentrations over land in ppb, recorded August 2004 by Frankenberg and colleagues.[14] These maps pinpoint the distribution of atmospheric methane around the world and reveal emission hot spots. The highest concentration of methane was found in the Sichuan Basin, a low elevation fertile area in southwestern China rich with natural gas, rice paddies, and livestock farms. The methane maps also identified major farming areas in the Indo-Gangetic plain, northern Thailand, and eastern China. In contrast, the arid Tibetan Plateau displayed very low levels of methane, while the swampy Sudd wetlands of southern Sudan in Africa and Uzbekistan's fertile Fergana Valley in central Asia showed high methane concentrations.

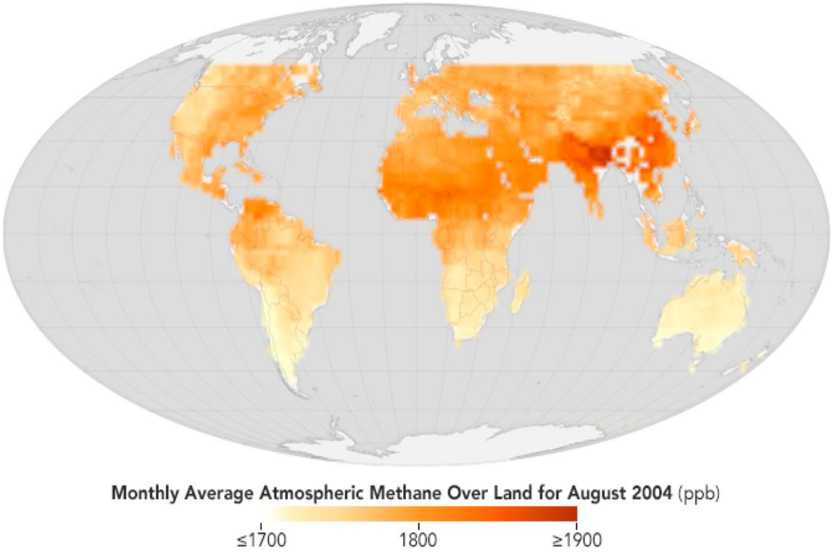

Figure 1.5 Monthly average atmospheric methane concentrations.[15] Reproduced from ref. 15 with permission from NASA Earth Observatory, Copyright 2021.

Methane mapping of the San Juan Basin in the Four Corners Region of the western United States, renowned for prolifically active gas, coal, and oil industries, revealed a methane cloud comparable in size to the state of Delaware, by far the dominant methane hot spot in North America. This spot alone was equivalent to the United Kingdom's annual methane emissions from the oil, gas, and coal industries.

1.7 Methane Isotopes

Atoms are made of a nucleus and electrons. Though negatively charged electrons make up the bread and butter of chemistry, the composition of the atomic nucleus, or more specifically the number of positively charged protons in it, is what determines the elemental identity of the atom. All carbon atoms have 6 protons in their nuclei. However, the number of neutrons, which mitigate the forces between these positive protons, may vary. Atoms with the same number of protons but a different number of neutrons are called isotopes. Chemicals made with different isotopes can provide useful insights into their reactions.

Two isotopes of methane can be found in the atmosphere: the more common variant with ^{12}C, or carbon with 6 protons and 6 neutrons, and the less common with ^{13}C, or carbon with 6 protons and 7 neutrons, denoted $^{12}CH_4$ and $^{13}CH_4$, respectively. ^{13}C is heavier than ^{12}C by a single neutron particle and has slightly stronger carbon–hydrogen bonds, which means $^{13}CH_4$

production or removal through abiotic or biotic chemical reactions is slower. This phenomenon is known as the kinetic isotope effect and is a standard tool for exploring the mechanistic details of chemical reactions.

The ratio of atmospheric $^{13}CH_4/^{12}CH_4$ can provide a diagnostic signature of the combined effects of methane emission and sink processes. This is because different methane sources and sinks have distinct $^{13}CH_4/^{12}CH_4$ signatures. Thus, measuring the isotope ratio can distinguish each factor's contribution over global length scales.

1.8 More than Fuel

Methane has also found use beyond energy utilizations. The simple five-atom molecule is also the feedstock for a range of commodity chemicals, polymers, pharmaceuticals, and materials. However, with the projected demise of natural gas around mid-century, its substitution by synthetic methane will grow in importance.

Methane synthesis typically proceeds *via* thermochemical heterogeneous catalysis, or the conversion of gas or liquid reactants to products on the surface of a solid material using heat energy. These solid materials, or catalysts, speed up chemical reactions. The Sabatier process, invented in 1912 by French chemist Paul Sabatier, uses a nickel catalyst to add hydrogen to carbon dioxide at 300–400 °C to produce methane. Alternatively, the Fischer–Tropsch process, developed in 1925 by German chemists Franz Fischer and Hans Tropsch, uses an iron or ruthenium catalyst to do the same with carbon monoxide at 150–300 °C to produce a range of low, medium, and high molecular weight alkanes, with methane being the lightest product. Here, carbon monoxide is often obtained by the reverse water–gas shift reaction which uses a palladium or platinum catalyst to convert carbon dioxide to carbon monoxide using hydrogen.

Methane can also yield value-added products by catalytic processes driven by heat, light, electricity, or even biologically using engineered bacteria or other species. Key products include hydrogen, carbon monoxide, methanol, ethylene, benzene, and various specialized forms of carbon, like nanotubes and nanosheets, which find uses as clean energy carriers, chemical feedstocks, and incorporated into super property materials for engineering applications. Their production will be touched upon in more depth in later chapters.

1.9 Methane Storage

Methane's prevalence as a fuel and as a feedstock necessitates the development of safe and efficient systems for its storage and transportation. Currently, the gas is stored using expensive and complex compression and liquefaction strategies which utilize high pressures (up to 250 bar) and low temperatures (77 K). High surface area microporous materials may be a viable alternative capable of impressive methane storage capacities under significantly milder conditions. In 2021, the goal set by the United States Department of Energy was to fit 263 cm^3 of gaseous methane into a space of 1 cm^3 at room temperature and 65 bar.

To achieve this, a library of microporous materials was investigated for suitable methane adsorption and desorption under practical pressures and temperatures. Potential candidates include zeolites, porous carbons, and metal organic frameworks, where the latter dominates the field.

It is worth mentioning that nature does have an example of solid-state storage of methane. However, it is also notorious for its instability. Methane hydrates are crystalline microporous solids built of hydrogen bonded water molecules that, at low temperatures, encapsulate methane molecules in their pores. Also known as clathrate ice, they exist in cold oceanic sediments and permafrost in arctic and subarctic regions. These clathrates are significant carbon sinks, having trapped methane from the decomposition of ancient life buried deep in the frozen ocean beds hundreds of thousands of years ago. With a warming planet, the threat of a "tipping point" looms on the horizon. Rising temperatures are expected to cause a sudden massive release of trillions of tonnes of methane into the atmosphere. Such an event would have the power to catastrophically expediate climate change.

1.10 Methane on Mars

Mars' atmosphere is primarily comprised of carbon dioxide (95.3%) with some nitrogen (2.6%) and argon (1.9%). Despite these harsh conditions, it is possible to use the Red Planet's unforgiving atmosphere to generate fuel and other useful compounds using a bit of chemistry knowledge.

It is known that there is enough water on Mars to form a 35-meter-deep pool when melted to cover the entirety of the planet's surface. This, combined with heat and electrical power from the sun *via* light concentrators and solar panels, can be used to generate oxygen, methane fuel used in space crafts, and carbon monoxide for other chemical reactions *via* our old friends: the electrolysis, Sabatier, and reverse water–gas shift reactions.

Electrolysis of water:

$$2H_2O \rightarrow 2H_2 + O_2 \tag{1.5}$$

Sabatier process:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O \tag{1.6}$$

Reverse water–gas shift:

$$CO_2 + H_2 \rightleftharpoons CO + 2H_2O \tag{1.7}$$

This is especially important because the payload of a space craft leaving Earth is extremely limited. Every extra pound of weight, be it in fuel or life-supporting food and supplies, requires an additional volume of fuel to propel it from the reaches of our planet's gravity. However, this additional fuel also must offset the energy sink attributed to propelling its own weight.

The above reactions generate life-giving oxygen, hydrogen, water, carbon monoxide (CO), and methane. By being able to generate these chemicals on Mars, it is no longer necessary to bring them with us should manned-space flights be conducted to the Red Planet. Electrolysis would give astronauts a steady source of oxygen, crucial for sustaining life from Earth. Hydrogen can be used for conversion of carbon dioxide to methane or as a chemical storage of electricity when used in fuel cells. Methane can be used as combustible fuel for any application, such as heat or for refuelling for return flights. Meanwhile, synthesis gas, or a combination of CO and H_2, is a feedstock for making commodity chemicals such as methanol, ethylene, and dimethyl ether, which have utilizations as fuels and in a myriad of chemical processes which may be crucial in space.

1.11 Methane Photochemistry in Space

Methane, with its simple structure, is the most abundant hydrocarbon in the known universe.[16] It co-exists with lesser amounts of heavier ethane, ethylene, and acetylene, which are believed to have originated from photochemical reactions of methane. Photochemical reactions occur when a molecule absorbs a photon, or a particle of light, which gives it the energy to react with other molecules to form new compounds. The compounds formed from methane are believed to be the progenitors of the even more complex organic molecules which started life on Earth.

Sunlight is comprised mostly of ultraviolet, visible, and near infrared light. The wavelengths that make up visible light, between 400–700 nm, have intensities over 100 times greater than that found in the far ultraviolet region between 100–200 nm. However, only ultraviolet light has sufficient energy to excite the electrons in methane and cause it to react. These high energy photons excite electrons in the C–H bond, causing the C–H bond to break. The resulting fragments, called radicals, can then react to form higher molecular weight hydrocarbons. However, this phenomenon is only well studied in gaseous methane. At the cryogenic temperatures of outer space, typically below −233 °C or −387 °F, methane exists as a solid. Thus, its photochemistry could be distinct because of the effects of restricted movement in its solid-state crystal lattice.

Cryogenic spectroscopy proved extremely useful for resolving any differences between the photochemistry of gaseous and solid methane. This technique visualizes the absorption spectra, or wavelengths of light absorbed, at cryogenic, or below-freezing, temperatures. Such spectra yield a series of troughs at wavelengths corresponding to the energy of certain vibrational or rotational movements in molecular bonds. It was found that the lowest energy—and thus longest—wavelength needed for producing the $^{\bullet}CH_3$ radical, an important intermediate for production of longer hydrocarbons, is 140 nm. The wavelengths required for production of C_2H_4, C_2H_6, and C_2H_2 were 140, 175 and 190 nm, respectively.

These types of laboratory studies are important for understanding methane in space environments. Understanding its absorption spectra also allows us to identify its existence on far-away bodies. At the cryogenic temperatures of Titan, Saturn's largest moon, the Cassini–Huygens spacecraft used infrared spectroscopy to identify primordial lakes of methane filled with frozen methane ice floats under a largely methane atmosphere.

Key Takeaways

- Methane was isolated in the 18th century by Alessandro Volta from marsh gas.
- Natural gas was a key part of ancient cultures.
- Natural gas, made mostly of methane and its main source, comes from decomposed organic matter and is distributed underground across land and under water. Most of the natural gas in the world is from the United States and Russia.
- Natural gas burns cleaner than other fossil fuels, but methane is a more potent greenhouse gas than carbon dioxide, contributing significantly to global warming.
- Methane can be made by synthetic means or captured from emission sites such as landfills.
- Fossil fuels have powered technological and economic development.
- Current atmospheric concentrations are much higher than preindustrial levels. Most emissions are centered around agricultural and industrial regions.
- Methane isotopes can be used in science to track where the methane comes from.
- Methane can be used to make other chemicals.
- Methane is stored largely *via* compression and liquefaction. Microporous materials are being developed for milder and more efficient storage methods.

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Key Takeaways

- Methane is the second most significant greenhouse gas after carbon dioxide.
- Preindustrial atmospheric methane concentration was about 680 ppb; today, it is around 1932 ppb, with levels continuing to rise. Preindustrial methane levels were stable due to a balance between methane sources and sinks. The industrial revolution disrupted this balance due to increased anthropogenic methane emissions.
- Major human sources of methane include rice and livestock farming, fossil fuel combustion, and natural gas drilling leaks.
- Increasing population and changes in methane emissions make it difficult to predict future atmospheric methane levels and climate change progression.
- Solar radiation is partly absorbed by Earth and converted to heat, while some is reflected back to space. The balance between absorbed and emitted energy is crucial for maintaining Earth's temperature. Greenhouse gases absorb and reradiate infrared radiation, trapping heat and causing global warming.
- Methane has a significantly higher global warming potential than carbon dioxide, especially over shorter time frames (84–87 times over 20 years, reducing to 27–30 times over 100 years due to its short atmospheric lifetime).

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- Catalysts speed up reactions by lowering the activation energy without being consumed. Catalysts can be activated by heat, electricity, or light.
- Methane is stable due to its strong, short C–H bonds. Thus, reacting it requires high temperatures and significant energy input.
- Catalysts are crucial for large-scale chemical industries, including methane conversion.
- Effective catalysts must be designed to maximize active sites and control product formation.

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Key Takeaways

- Methane can be produced from carbon dioxide and water, potentially reducing carbon emissions from burning and leaks. However, the synthesis of methane is energy-intensive and requires renewable energy to be viable. The Sabatier reaction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) is the primary method for methane synthesis, requiring high temperatures and pressures.
- Biocatalysts, such as methanogenic microorganisms, and electrolytic cells combining water splitting and CO_2 reduction offer an alternative method under milder conditions.
- High costs of renewable hydrogen and impurities in feedstock are significant challenges.
- Light can be combined with thermally, electrically, and biologically catalyzed reactions to speed them up or obtain better reaction conditions.
- Standardized testing and protocols for photocatalysts and photoreactors are essential.
- Identifying and mitigating degradation and failure mechanisms will ensure economic feasibility.
- Continued research could lead to practical technologies capable of replacing natural gas as a source of methane.

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Key Takeaways

- 82% of global primary annual energy demand comes from non-renewable fossil resources. Usage is expected to peak in 2025 and then decline, with renewables rising.
- Global growth in natural gas use is slowing, with an expected annual growth rate of 1.6% until 2026. However, predictions are affected by rapid changes in environmental, geopolitical, health, and conflict situations.
- Catalysis drives 90% of chemical processes and accounts for over a third of global gross domestic product.
- Methane is crucial for providing heat in industrial thermal catalysis. It is also used to produce key chemicals including pure carbons (graphene, carbon black), hydrocarbons (ethylene, jet fuel), alcohols (methanol, ethanol), and syngas.
- Real-world catalytic reactions often achieve lower conversions due to issues like catalyst sintering and coking. Developing highly active and selective catalysts to operate at lower temperatures could improve efficiency and reduce costs.
- New developments in valorizing methane include using water as an alternative oxidant, utilizing non-equilibrium thermodynamics and kinetics, electrochemical catalysis, and biochemical catalysis. Solar-driven photocatalysis can be combined with the aforementioned methods to increase their effectiveness.
- Methane separation from natural gas is an involved process. Natural gas contains significant quantities of water, oxygen, hydrogen, nitrogen, sulfur-containing and halogen-containing compounds, carbon dioxide, and other hydrocarbons. These contaminants dilute energy density and create harmful by-products when burned.
- Contaminants must be removed before methane valorization reactions to avoid catalyst poisoning, reactor damage, and costly by-products.
- Traditional cryogenic separation is effective but energetically expensive. Alternative room-temperature methods, like materials separating gases based on geometry, are under research.

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Though materials exist which have been shown to adsorb and desorb methane, namely zeolites doped with copper, iron, or other metals, their ability to do so with naturally found catalyst/materials and at the extremely low methane concentrations found in the atmosphere have yet to be proven.[19,26] Instead, perhaps it is more likely that future carbon dioxide DAC machines can be retrofitted to also capture methane to improve their greenhouse gas reduction efficiency.[24]

Key Takeaways

- Natural gas is favored among fossil fuels due to its cost-effectiveness, cleaner combustion, and availability. However, compression and liquefaction for storage and transport require significant energy and safety measures.
- Enhancing methane's storage solutions could make it a viable alternative fuel for transport vehicles. Some storage solutions include rigid or flexible adsorbent materials made from metal oxide frameworks or polymers.
- Methane capture from the air could significantly reduce global warming but requires high energy due to low atmospheric concentrations. Thus, direct air capture (DAC) for methane is complex and costly, but future integration with carbon dioxide DAC could enhance greenhouse gas reduction efficiency.

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integrated sensor networks and satellite data to improve leak detection. Global mapping and monitoring are essential for regulatory compliance and reducing methane emissions cost-effectively.

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is sourced from biogenic or recycled sources and energy is sourced from 100% renewable energy.[19] Olive Creek 1, the company's first facility located in Nebraska, currently generates 5 kilotonnes of hydrogen and 15 kilotonnes of carbon per year[20] with plans to expand in the future.

Key Takeaways

- Methane conversion offers an environmentally friendly alternative to coal and oil for producing commodity chemicals.
- Feedstock purity allows better control over chemical reactions.
- Methane has a higher hydrogen-to-carbon ratio, making it cost-effective and energy-dense for hydrogen extraction. Increasing demand for methane can reduce global methane emissions from fossil fuel processing.
- Global recoverable natural gas reserves are around 7300 trillion cubic feet.
- The costs of using methane include extraction, transport, and market fluctuations.
- Methane is currently mainly used for electricity generation and household purposes with limited use as chemical feedstock. Smaller portions are being used in hydrocyanic acid production, methane reforming to syngas, and ammonia and methanol production.
- Potential new uses include methane pyrolysis for hydrogen and carbon, oxidative coupling for hydrocarbons, and selective oxidation for aromatics. However, new processes must compete with established, cost-optimized methods.
- Transitioning to greener energy sources like electricity or light requires development of new reactors, which is costly and complex. Selection of reaction pathways, conditions, catalysts, and reactors is critical for cost-effective operations.
- Methane can be used to produce hydrogen. Current commercial endeavours from companies working on making more environmentally friendly hydrogen gas include the H2H Saltend Project in the United Kingdom, Hycamite's Carbomite Project in Finland, and Monolith's pyrolysis system in the United States.

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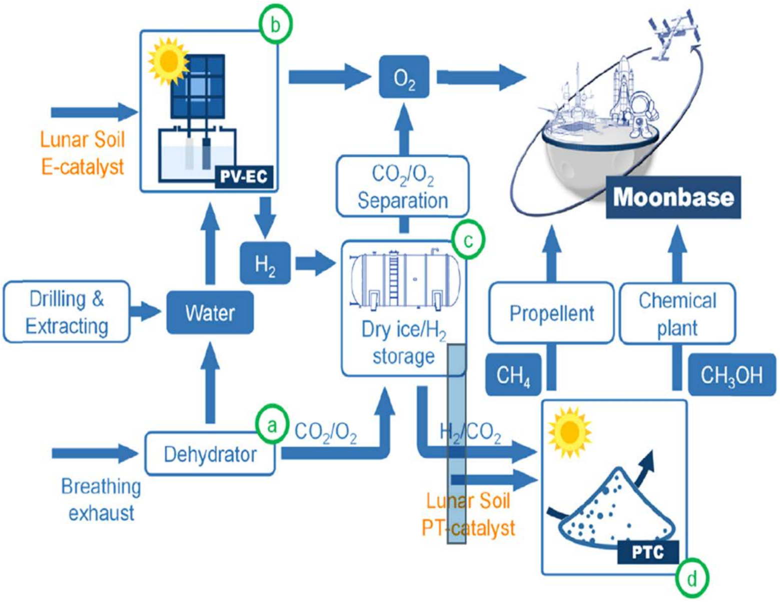

Figure 2 Illustration of a futuristic energy and chemical infrastructure to sustain a community of humans on the Moon.[4] Reproduced from ref. 4 with permission from Elsevier, Copyright 2022.

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