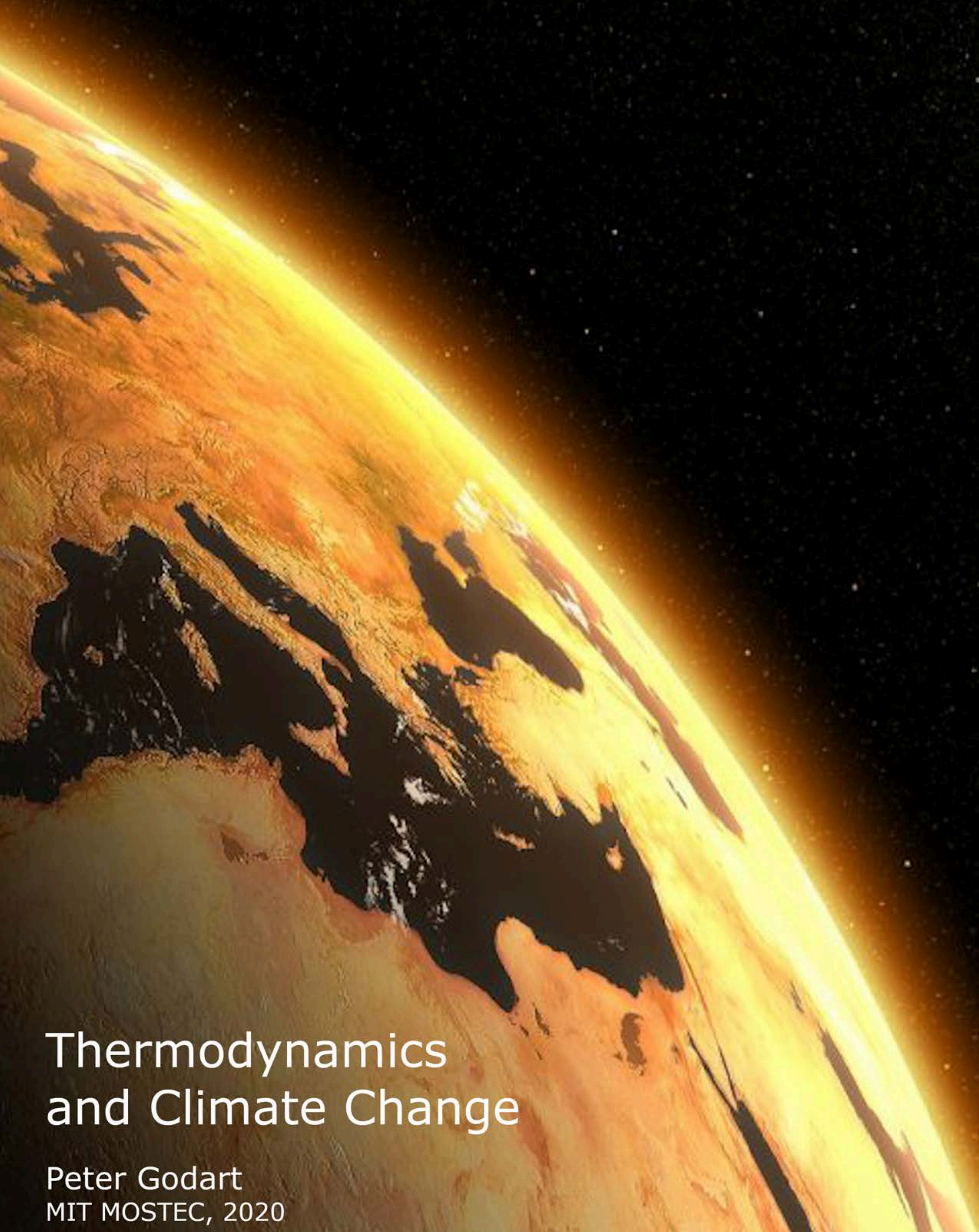

Thermodynamics and Climate Change

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MIT MOSTEC, 2020

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Course Description

From air-conditioners and electric vehicles to humans and photosynthesizing plants, every system that converts energy from one form to another is governed by the laws of thermodynamics. So fundamental are these laws that Einstein himself once said they comprise “the only physical theory of universal content, which I am convinced...will never be overthrown”. However, with great power comes great responsibility. Our understanding of thermodynamics enabled the industrial revolution and virtually every technological breakthrough since, but it has also led to the over-consumption of fossil fuels and associated global warming. Now we need to turn the problem on its head and use these theories to find a solution. In this course you will learn the three laws of thermodynamics, explore concepts like entropy and enthalpy, and investigate the causes and effects of global warming from a thermodynamics perspective. We will also apply these concepts to learning about state-of-the-art energy conversion and storage technologies like heat pumps, hydrogen fuel cells, metal-air batteries, artificial photosynthesis, molten salt storage, concentrated solar power, and many more. Weekly deliverables will include problem sets on fundamental topics, as well as interactive coding assignments to simulate and analyze various thermodynamic systems. As a final group project, you will pick one of these systems and provide an in-depth analysis and simulation to better understand its potential for reducing greenhouse gas emissions.

Prerequisites: Proficiency in single-variable calculus and experience with basic programming are required for this course. Classes taken in chemistry, physics, and biology are helpful but not required.

Contents

Preface

In this course we will learn the thermodynamics behind what is arguably humanity's greatest existential threat: anthropogenic climate change (also called anthropogenic global warming or just AGW). Simply stated, AGW is the unprecedented rapid elevation of the Earth's mean atmospheric temperature as a direct result of human activity, leading to the collapse of the many ecosystems upon which we rely. Together, we will not only explore the physics behind the technologies and practices that brought us to this precipice, but also the theoretical and computational tools we will need in order to back away.

To ground our understanding of thermodynamics, we will take a narrative approach, learning not only the science but also the story of climate change - starting all the way from the big bang, continuing through to present day, and finally imagining what our future may hold under several different mitigation scenarios. This approach is a nod to "Big History", which places human history in its maximally broad context (the Universe). While this approach can err towards trivializing our lived experiences, we will not be shying away from grappling with our humanity in this course. Instead, we will use the greater context provided by the persistent backdrop of the historical universe to uncover the ways in which we are living at odds with the fundamental physical laws and timescales that govern our very existence. Additionally, as Big History uses the results of scientific discovery to inform the study of history, we will be using a historical narrative to motivate the need to understand the physics. As we will see, scientific and technological advancement with disregard for its context, and thus for its far-reaching consequences, is a recipe for disaster.

As we will discover, the Laws of Thermodynamics are some of the most fundamental theories that govern how our Universe operates and have withstood hundreds of years of scientific scrutiny. While slight modifications are made over time as we improve our ability to probe physics at smaller length- and time-scales and at higher energy levels, they are at their core inviolable as far as we can tell. In this way, these laws exhibit the immutable - if sometimes opaque and mysterious - permanence of the Big History itself. Contrast this with climate science built many layers of abstraction above these fundamental theories. As computational power has largely followed the exponential growth described by *Moore's Law*, so too has climate scientists' ability to predict how the global climate will continue to evolve in response to human activity. Consequently, we may find even 5-10 years from now that the climate projections presented in this book will need serious revision; however, the *trends* are likely to remain largely the same. And so we will look to thermodynamics also to ground our understanding of climate change and the mechanisms that translate human "productivity" into a warming planet and its many impacts on various ecosystems, while attempting to avoid getting lost in the actual numerical details that are nearly guaranteed to change.

By teaching the course in this paradigm, it is my hope that we can develop our internal ethical frameworks alongside our scientific frameworks. Ethics cannot be applied retroactively and therefore must be baked into what, how, and why we learn. The story of climate change paints a bleak picture if we extrapolate the patterns of the past into the future, but there is a consensus among scientists that AGW is not irreversible. While the physics is still on our side - for the next 10-20 years as we will learn - we need a major shift in our motivations and definitions of "progress" to reverse course. As future scientists, engineers, teachers, or generally conscientious stewards of a healthy and sustainable global ecosystem, it is now more than ever imperative that you keep the bigger picture in mind as you continue to learn and apply the concepts presented here.

Learning Objectives

The primary aim of this course is to have students reach an undergraduate-level understanding of thermodynamics through the lens of climate change, paying special attention to placing fundamental concepts within a narrative that emphasizes both the benefits and dangers of technological progress. Throughout this course, students will:

1. Develop an understanding of the fundamental laws of thermodynamics and an intuition for how they relate to observed physical phenomena through concepts like energy, entropy, and enthalpy.

2. Apply these thermodynamic principles to illuminate the impact of human industrialization on the climate.

3. Think broadly about the greater context of climate change and the history of the Earth and Universe as a whole to better understand the competing timescales of human consumption and the carbon cycle.

4. Use Python to evaluate the performance and climatological impact of thermodynamic systems that are contributing to climate change and their proposed replacements.

5. Work together as teams to evaluate the efficacy of leading climate change mitigation strategies using the theory and computational tools learned throughout this course.

Course Organization

Thermodynamics and Climate Change is not organized according to the fundamental physics as is usually the case in texts on these subjects, but rather by the story of anthropogenic climate change itself. We will see the motivation to dig deeper into thermodynamics emerge organically from the narrative as we progress through the following units:

1. *Universal Beginnings*, where we will discuss at a high level the history of the Universe, including the formation of the Earth and the importance and ubiquity of solar energy. The origins of Thermodynamics as a field will be discussed as well.

2. *Energy, Climate, and the Carbon Cycle*, where we will learn how the Earth's climate was established, various forms of energy and First Law of Thermodynamics, the greenhouse effect, and the delicate balance between atmospheric composition and temperature that enables life to exist.

3. *Controlling Fire*, where we will take a look at the origins of thermodynamics and the physics of fire, heat, and combustion chemistry, as well as early human uses of fire and its effect on the climate.

4. *Entropy and a Move Towards Chaos*, where we extend our understanding of heat with the concept of entropy and its relationship to processes, cycles, and the Second Law of Thermodynamics.

5. *Engines, Power, and the Anthropocene*, in which we will develop an understanding of engines and other power machinery, as well as the climate change caused by human use of fossil fuels and industrialization.

6. *A Return to Renewables*, where we will look at carbon-neutral alternatives to fossil fuels, energy storage, and how the world could be powered sustainably by solar and geothermal energy.
7. *Mitigating the Climate Crisis*, where we will explore promising approaches to slowing and altogether stopping global warming, as well as how to evaluate these approaches on technical and ethical merit.
8. *Surviving the Anthropocene*, in which we grapple with the fact that the climate has *already* changed and learn the thermodynamics required for adapting to the Anthropocene.

Each chapter is paired with a Python Jupyter notebook that provides students a means to explore and gain an intuition for the various thermodynamic properties presented, as well as provide exposure to the computational tools necessary for analyzing various thermodynamic systems. Students are encouraged to complete both the qualitative concept-question style and quantitative computation exercises given in these notebooks after reading each chapter to solidify understanding. Thermodynamics is at times as confusing as it is rewarding, and students are encouraged to stick with it. Much effort was taken to ensure that the concepts are presented here from multiple perspectives and that the coding examples provide practical hands-on learning opportunities; however, only so much material can be covered in a reasonably compact textbook. Where possible, I provide links and references to excellent additional texts and resources that can provide yet another perspective on this subject matter.

Chapter 1

Universal Beginnings

1.1 The (Short) Big Story of Climate Change

The story of climate change, in particular *anthropogenic*[1] climate change, is the story of *energy*[2] in our Universe, and it is one of balance. A balance that, unlike the abstract constructions of human society and culture, is a requirement for existence. In fact, it is rigidly baked into the physics as the First Law of Thermodynamics, which states that within a closed system, energy cannot be created nor destroyed, only converted from one form to another[3]. So while we cannot remove energy from the closed system that is our Universe, we can absolutely control *how* and *when* we use it, and therefore the story of climate change is also one of competing timescales - exhausting resources faster than they are replenished can have dire results, as we will soon see.

1.1.1 The First 10 Billion Years

For some context, let us zoom out to the largest timescale we are aware of - the history of the universe itself - and start by looking at the energy we have to work with. Going back to the very beginning[4] of time itself, some astrophysicists believe that the *Big Bang* brought our Universe into existence

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[1] human-caused

[2] We will define *energy* in all of its many forms in detail later, but for now, your intuitive understanding will be sufficient.

[3] For those of you hip to astrophysics, you may know something about the accelerating expansion of the Universe and *dark energy*, but we will be ignoring this topic here, as it is highly complex and not universally agreed upon by the scientific community.

[4] Physicists largely take issue with referring to the origin of the universe as a “beginning”, as our conception of time and space breaks down at some point as we go farther back in time.

from nothing [1, 2, 3]. No energy, no mass, no heat - pure zero. From the nearly intractable void, all that we now know spontaneously flickered into existence. While this process is not well understood, one hypothesis attributes this flash of creation to a random quantum fluctuation, which in general allows "positive" energy to be created as long as it is paired with an equal amount of "negative" energy. Curiously, it can be shown that if we look around, the total energy does seem to equal zero roughly, though this result is still widely debated [4].

Setting aside the disputed ultimate origin story, what we do know pretty well is that just after the Big Bang, some 13.8 billion years ago [5], there existed a roughly equal balance between "positive" energy in the form of extremely hot matter and "negative" gravitational potential energy holding it together. As the Universe expanded and the dense, homogeneous matter soup began to cool, it condensed into subatomic particles called *quarks*, trading some energy for mass[5], which then coalesced further to form protons and neutrons. These composite *baryons* eventually combined to form elementary hydrogen and helium, the first *atoms* of our Universe, and shortly after, *electrons* were able to form and bind to those atoms, making them neutrally charged. Over millions of years, these single atoms were pulled into clusters under their own gravitational attraction, trading gravitational potential energy for kinetic energy and heat. As these clouds became more and more dense, their temperature and pressure eventually rose high enough to ignite *nuclear fusion*, a process in which atoms combine, losing a small amount of mass in return for a substantial amount of light and kinetic energy. With enough atoms fusing under these conditions, a chain reaction can initiate to create a massive fireball contained by the force of its own gravitational self-attraction - a *star*.

The early universe was - and still is - a constant cycle of birth and death for stars on timescales ranging from a few million years to many billions of years depending on how quickly they consume their nuclear fuel. The stars that burn hot and fast are of particular interest to our story of climate change, as they help explain the origin of the Earth itself. In general, if it were not for nuclear fusion in stars, we would be stuck with mostly hydrogen, helium, and some lithium [6], the first three elements on the periodic table containing 1, 2, and 3 protons respectively. With standard fusion, all stars are capable of turning these smaller atoms into larger ones, all the way up to nickel, containing 28 protons [7].

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[5] You may have learned about the conservation of mass as being a rigid fundamental physical law; however, while this tends to hold true for fluids and solids that we can measure at the macro scale, at the atomic scale, we can actually trade mass for energy directly. According to Einstein and rigorously validated by many experiments since, this mass energy is given as the famous $E = mc^2$, where c is the speed of light.

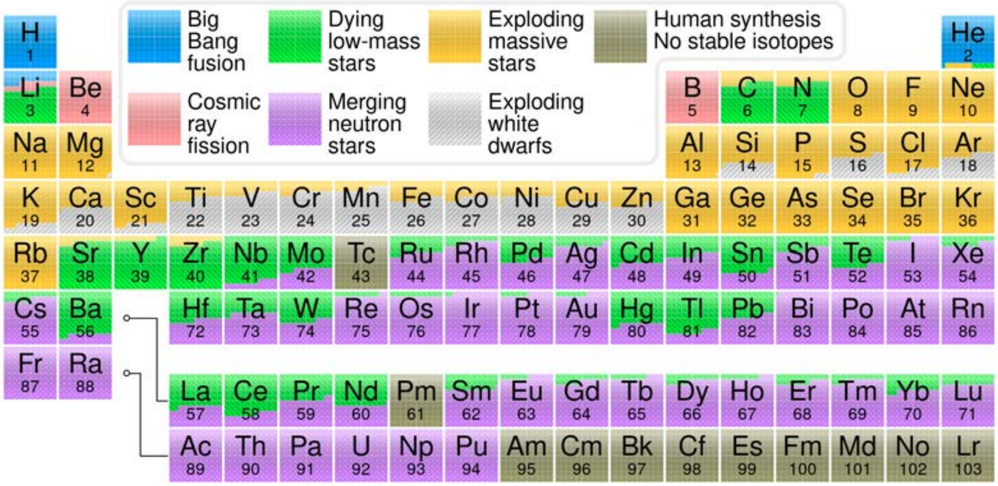

Figure 1.1: All known elements in our Universe and how they were created. Stellar nucleosynthesis is responsible for the creation of the elements Carbon through Plutonium. Image courtesy of cmglee on Wikipedia. License CC BY-SA. This content is excluded from our Creative Commons BY-NC-SA license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

To create even larger atoms, however, a still more explosive approach is required. One such process can occur at the end of a star's life, depending on its initial size and energy content. Instead of simply fizzling out, under the right conditions, a star can undergo a *supernova* in which it experiences a sudden collapse of its core, causing a shock wave that generates the temper-atures and pressures required for the fusing of even more neutrons than was previously possible, creating many of the other elements we naturally find in our Universe[8]. If the remnants of that same star are not massive enough to collapse into a black hole, they can condense into an incredibly dense *neutron star*, and the subsequent colliding of neutron stars is thought to be responsible for the synthesis of the remaining elements, up through Plutonium, as shown in Fig. 1.1.

So now that the Universe has traded some gravitational potential energy to create stars, and with them all of the elements that can conceivably be produced over their lifetime, we can talk about the emergence of *planets*, which are the stellar remnants that are too heavy for *exothermic*[6] fusion. Instead the inert stellar dust collapses to form a molten ball of dense elements that stays together under the pull of its own gravity. Roughly 4.5 billion years ago,

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[6] releases heat as opposed to *endothermic* which absorbs heat

one such dust cloud formed into what is now the Earth we inhabit. Given that at the same time, many other planets were forming in much the same way, this was not a tame or organized process. Indeed, for a long time, the Earth was bombarded with not just asteroids and meteors, but various other fledgling planets as well. As we can see now, only a few survived. One such collision near the end of the Earth's formation ripped enough material away from the young planet to form the Moon [9, 10]. Despite the destructive nature of this process, in a bit of dramatic irony, some of these collisions were with protoplanets rich in carbon, water, and nitrogen - the seeds of carbon-based life.

Eventually - roughly 4 Ga[7] - the "Late Heavy Bombardment", as it is referred to, slowed, giving rise to an environment in which life as we know it could spring forth and thrive. During that time, on the Earth's surface, volcanism was the norm, as the young planet was still essentially just a super hot ball of magma from its formation process. Frequent volcanic eruptions and the occasional extraterrestrial collision produced massive amounts of *greenhouse gasses* (carbon dioxide, hydrogen sulfide, methane, etc.), creating an early atmosphere that allowed the Earth to retain heat from incoming solar radiation. This development was incredibly important, because as the Earth cooled and water started coming in from collisions with icy asteroids and comets, the sun alone did not have the required power to keep that water in liquid form. Especially since in the Earth's formative years, the Sun was 30% dimmer than it is now, without this atmosphere acting like a thermally insulating blanket, all of this water would have likely been frozen in what scientists call a "Snowball Earth" scenario[8]. Instead, despite painting a hellish scene on land, the rampant volcanism actually enabled the formation of liquid water oceans, creating the necessary environmental conditions for life.

So to recap the Big History of the Universe up to this point, let us take stock of how the energy balance we started with has shifted. Ignoring the controversial exact beginning of the Universe's origin story (i.e. for $t < 10^{-11}$ seconds), we know pretty well that at some point, all measurable energy was contained as balance between hot matter in the form of subatomic particles called quarks and gravitational potential energy. As they cooled, quarks formed protons, which in turn formed various lightweight atoms that later combined with electrons to form the first several elements of the periodic table. From there, gravitational potential energy was cashed in repeatedly to form larger, hotter clumps of atoms, which eventually generated the temperatures and pressures

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[7] Ga = billion years ago

[8] see *Faint Young Sun Paradox*

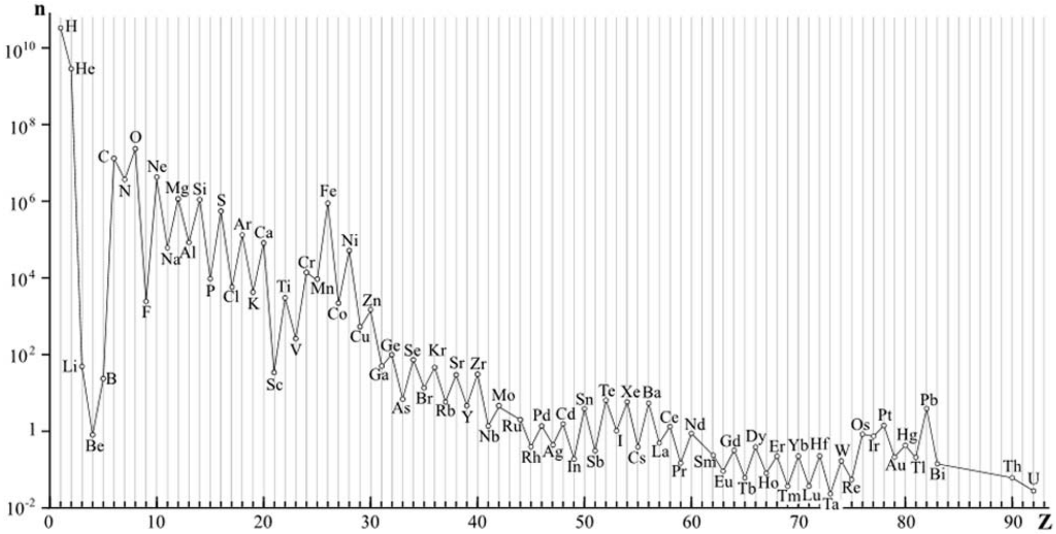

Figure 1.2: The abundance of all naturally occurring elements in the Universe [11]. This image is in the public domain.

to ignite fusion reactions that turned these dust clouds into stars. In nuclear fusion, rest mass energy (i.e. $E = mc^2$) is released as heat and light, which in turn promotes more fusion, creating a chain reaction that continually converts some rest mass of hydrogen and other lightweight elements into more heat and more light.

Depending on its size, a star can undergo a massive explosion at the end of its life that converts some thermal energy back into mass energy as most of the remaining elements that are naturally found in our universe are created, at the same time spreading them out into more massive dust clouds. Again under the pull of gravity, these clouds reform into more suns or planets now that we have some heavier elements to play with. In our solar system, this process formed the Earth, and the residual heat from the solar remnants powered the eruption of volcanoes on Earth to help create an early atmosphere. At this point, as the Earth slowly cooled, it also continued to receive an influx of energy as light from the Sun; however, this energy alone would not be sufficient for keeping the Earth's surface temperature above the freezing point of water. With an atmosphere, our planet began trapping some of this light as heat, keeping the conditions at just the right temperature and pressure for life to form - the first instance of climate change and a foreshadowing of what was to come.

1.1.2 The Inhabited Earth

Back to our story, a hasty several hundred million years into the life of planet Earth, the stage for life was set. The earliest fossilized records we have show the emergence of the first self-replicating biological structures happening somewhere between 4.3 and 3.8 Ga, with the earliest self-replicating *RNA molecules* deriving their energy for reproduction from hydrothermal vents powered by thermal energy from the Earth's core - a remnant of solar energy - and carbon monoxide. These early molecules used iron and nickel sulfides found inside the vents to catalyze the various chemical reactions required for building and sustaining proteins [12]. These free-floating *chemosynthetic* organisms eventually found homes within *liposomes*, small bubbles made from lipids that also spontaneously began to form in the primordial soup. These protocells, which from the outside very much resemble our own, could now travel somewhat farther from their sources of energy, but they still lacked most of the basic functionality our cells enjoy now. Eventually, about a hundred million years later (around 3.5 Ga), these cells evolved into the organism that would give rise to all life presently on Earth, our so-called *last universal ancestor*.

At this point, we are 10 billion years into the history of the Universe and 1 billion years into the history of Earth, and organisms have evolved another special ability - capturing the energy of sunlight directly to make their own food. To achieve this, our single-celled ancestors evolved the first "solar panels", internal structures called *chloroplasts* that enable the conversion of sunlight, water, and the highly abundant CO_2 in the atmosphere into oxygen (O_2) and sugars (e.g. glucose, $C_6H_{12}O_6$) that they could then consume for *metabolic* energy and structural material required for growth (i.e. cellulose). Very quickly the atmosphere filled with oxygen, which at first had many beneficial effects, the primary of which was that it started reacting under the intense sunlight to form *ozone* (O_3) in the upper atmosphere. This gas absorbed much of the harmful ultraviolet radiation produced by the Sun, allowing photosynthesizing organisms to be able to leave the oceans and cover the land without burning. Over the next billion or so years, however, as more and more oxygen was generated, its atmospheric concentration eventually rose to toxic levels. Additionally, more oxygen meant that more methane in the atmosphere could be converted to carbon dioxide, a much less potent greenhouse gas by comparison. Suddenly, the blanket covering the Earth became less effective, temperatures dropped to -50 °C, and the Earth was plunged into its first major ice age starting about 2.2 Ga.

Clearly, we can already see that the greenhouse effect is a) essential to maintaining conditions suitable for life, which would otherwise be impossible

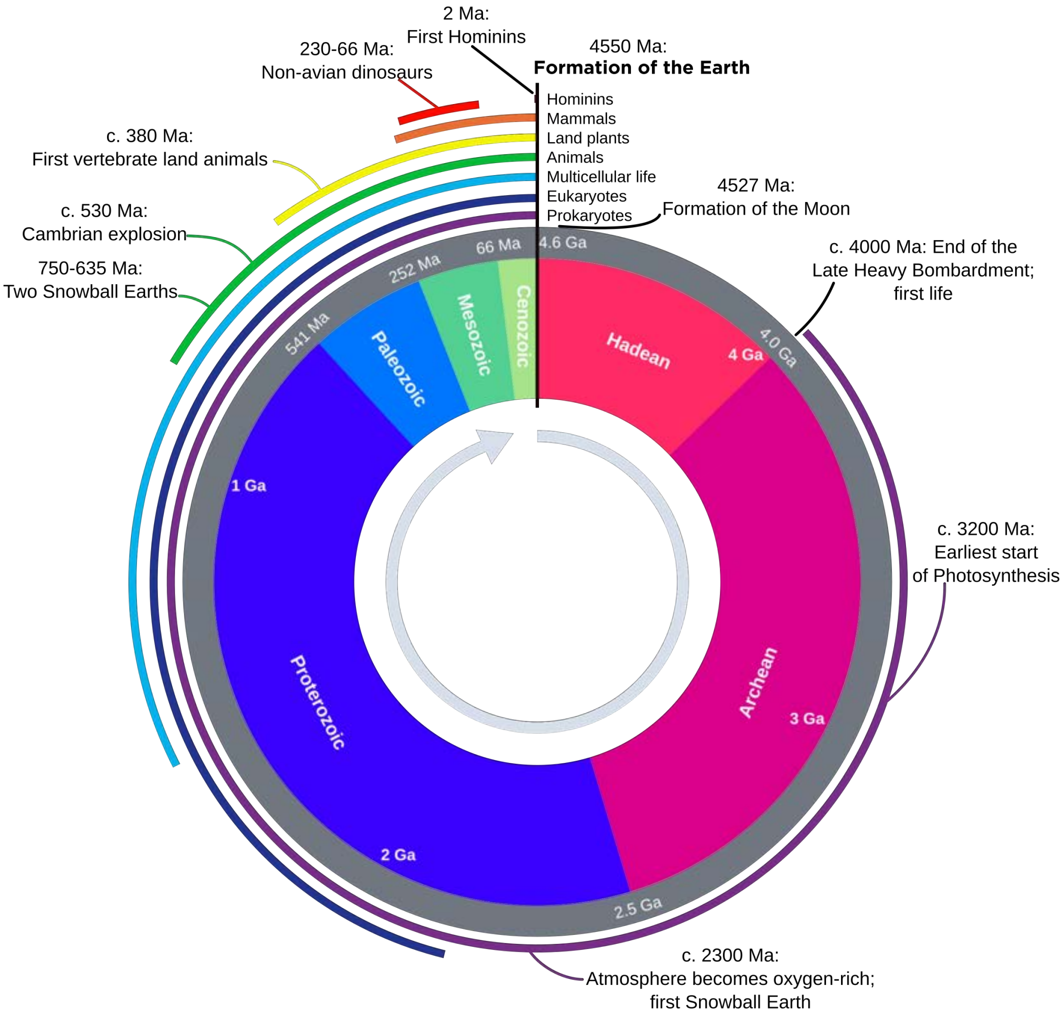

Figure 1.3: Geological history of the earth. This image is in the public domain.

given the insufficient solar power to heat the earth directly and b) highly sensitive to atmospheric compositions. When left alone, however, the climate is kept in check by the *carbon cycle*. In this process, as we have seen, carbon dioxide and other greenhouse gasses in the atmosphere trap solar energy as retained heat. Photosynthesizing organisms take carbon dioxide out of the air, and when these organisms die, their carbon is either released back into the atmosphere as methane or sinks to the bottom of the ocean, where under intense pressure it is turned into molecules made from long chains of carbon and hydrogen that we harvest today as oil. As we will see in detail later, the temperature of the atmosphere and oceans also play an important role in maintaining this balance, but at a certain point, this delicate balance can be permanently disrupted (see Venus). In the case of the Earth's first ice age, it is widely believed that volcanic activity boosted atmospheric carbon dioxide supply, once again wrapping the Earth in enough thermal insulation to bring the temperature back up above the freezing point of water[9].

Over the following 2 billion years (from 2.5 Ga to 0.5 Ga), life continued to slowly evolve, from single cell *prokaryotes* to *eukaryotes* as *DNA* migrated into a central cell *nucleus* and then to simple multicellular life. Major continents formed and moved around, and the Earth experienced several more ice ages as the carbon cycle kept getting pushed a bit too far and then recalibrated. With the end of the last major "Snowball Earth" event came the *Cambrian Explosion*, a brief 50 million year period starting around 542 Ma[10], in which the rate of evolution began to accelerate, producing molluscs, arthropods, vertebrates (including the direct ancestors of many modern fish), trilobites, and many more. With ozone now protecting land from harmful radiation, many of these species started moving farther onto land. This migration was helped by oxygen concentrations being brought down to safe levels by frequent fires and respiration, demonstrating another advantageous feedback loop within the carbon cycle. A few major extinction events occurred during this time, but soon after each, a new diversity of species would invariably spring up.

From a thermodynamics perspective, this development was also remarkable in that we began to see organisms that cannot make their own food via chemosynthesis or photosynthesis directly. Instead, these new creatures had to eat other organisms that could, in the process converting the sugars they contain into heat and metabolic energy, releasing carbon dioxide as a byproduct. Some animals start eating other animals, but as we get further from the source, it is important to remember that all life is still, and always will be, solar powered. The carbon cycle also gets more complex as a result of this development, since we now have both organisms that can remove net carbon dioxide from the air and organisms that eat this stored carbon and release it back. As before, when these organisms die, the carbon that comprises their bodies is released as methane or slowly gets compressed over millions of years as it sinks deeper into the Earth. Depending on the conditions, this carbon can turn into coal or oil stored deep in the crust, where it is effectively removed from the carbon cycle for millions of years.

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[9] The climate is also affected by the procession of the Earth's axis, but it is widely believed this can still be overpowered by the carbon cycle [13].

[10] Ma = million years ago

1.1.3 Humans and the Control of Fire

At this point, we are at 500 Ma in our story, 4 billion years into the formation of the Earth, and we are just seeing life that would be familiar to us today. The 500 million years connecting then until now were a blur compared to the rate of previous development. Plants and animals soon filled the oceans and covered the land. Several smaller ice ages repeatedly froze the early continents, with their melting leaving lasting impressions on the landscape, forming lakes and other terrain that helped to diversify life further. We saw mammals, birds, and dinosaurs spring into existence around 300 Ma. The dinosaurs in particular dominated the landscape until 66 Ma when a major extinction event - the *Cretaceous-Paleogene* event - occurred in large part due to a massive asteroid hitting the Earth, resulting in the elimination of 95% of all living species at the time. Among the survivors were the mammals, however, and they seized the opportunity to take over, quickly engendering a new diversity. 10 Ma we saw the first apes[11] and roughly 8 million years later we had our first direct *human* ancestors. All the while the smaller ice ages continued to help shape the landscape and guide the movement of animals on land, breeding further diversification.

Then there was a fundamental shift in how life uses energy around 2 Ma, when the early humans discovered they could control fire. With this new ability, they could begin to extract thermal energy from solar energy stored in the carbon chains of dead plant matter. Very much like organisms that consume sugars and fats, inhale oxygen, and exhale carbon dioxide, the fires set by early humans were quite similar, though less complex, chemical reactions that combined some flammable carbon source with oxygen to produce carbon dioxide, releasing tons of heat in the process. With that, thermodynamics, though we did not know it at the time, formally began, and a world of possibilities opened up. Now humans had a new tool to protect themselves against harsher environments, which among other things, meant they no longer needed to migrate with the seasons. Staying put gave rise to permanent societies that could use agriculture to sustain more and more people. The ability to cook food and boil water meant that humans could eat a wider variety of plants and animals and better stave off disease and infection, enabling them to grow larger, stimulate larger brain development, and live longer. Control of fire also gave humans control over time in some respect, as they could now make light at will and see in the darkness. From photosynthesis to eating plants to burning plants (on purpose), this discovery truly brought us into a new era of being.

It took another 2 million years for early humans to start settling en masse

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[11] *hominids*

in fertile regions, but before that, their new abilities to thrive and multiply in what were once hostile environments had a profound impact on other species. In fact, from about 130,000 BCE to 8,000 BCE, we saw the first major extinction at the hands of humans, the *Quaternary Extinction Event*, in which a significant number of animal species were wiped out due to over-hunting, in particular those in the *megafauna*[12][14] group. Their removal had long lasting repercussions that reverberated throughout the Earth's many ecosystems, fundamentally changing the makeup of life across the planet.

Conveniently in the wake of that mass extinction, which ended roughly 10,000 years ago, the first agrarian societies started cropping up. The first major civilization was established 5,000 years ago in Sumer in the Middle East, and with the advent of the first civilization also came the beginnings of anthropogenic climate change, again forewarning of the dangers of overconsumption. Studies have shown a spike in greenhouse gasses around this time, likely as a result of humans clearing forests and burning large swaths of land to make way for farms [15]. The carbon currency that kept the Earth's climate in a delicate balance (with the occasional imbalance leading to an ice age), was suddenly being expended at a rate that was greater than could be replenished by solar energy in the short term, a theme we will see persists until present day. With these early civilizations, however, this effect was minimal, as there simply were far too few humans using fire and repurposing land to make much of a difference. Early increases in carbon dioxide levels might have also been balanced by plants growing larger and more verdant during this time.

As civilizations developed, the human population began expanding both in terms of numbers and geographic area. As early as 3,500 BCE, Egyptians realized they could harness the power of the wind to propel boats to high speeds, greatly opening up the amount of territory that could be traversed, ushering in the age of rapid colonization. A quick aside, wind energy is the result of thermal gradients caused by, you guessed it, the Sun. So even wind energy is actually solar energy at its core (sensing a theme here?). The ability to now harness solar energy in three different forms, food, fire, and wind, led to the ever increasing ability of humans to manipulate their environment, other species, and later even members of their own to their own advantage, begetting more growth and more power.

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[12] Think large mammals like woolly mammoths.

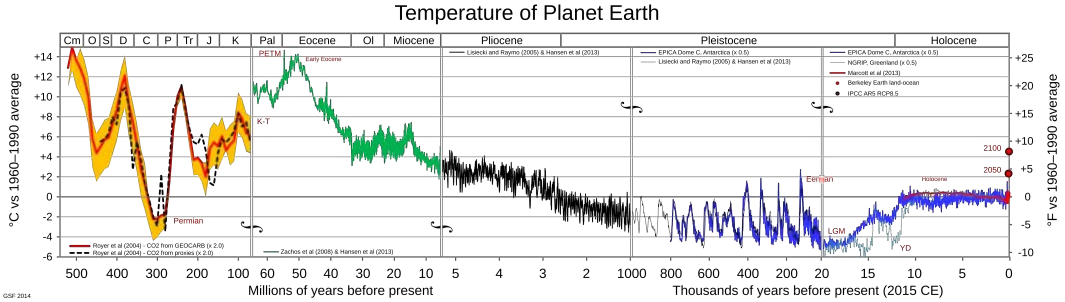

Figure 1.4: Historical global mean temperature. © GSF-USA. All rights reserved. This content is excluded from our Creative Commons BY-NC-SA license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

1.1.4 The Origin of Thermodynamics as a Tool

In the first century CE, another incredible thermodynamics development occurred, but like with fire, it took some time to catch on - people in Ptolemaic Egypt realized that heating water inside an enclosed vessel would generate "wind", hot vapor that could be ejected in such a way that caused the vessel to spin. Thus, the first engine, called an *Aeolipile*[13] was born, though when it was discovered, it was considered to be just a simple party trick. It would not be for another 1,500 years that someone had the idea of sticking this engine in a ship to power locomotion. Fast forward another thousand years, taking us to 900 CE, when the Chinese discovered a way to harness this "wind" to make weapons. They realized that powderized charcoal[14] could be mixed with sulfur and potassium nitrate to make it burn extremely rapidly and at high temperatures. By sticking this powder mixture into a tube that is closed on one end and has a projectile blocking the other, humans had their first guns. Suddenly what was once an advantage over other species, was now an advantage over other groups of humans. The same technology that could be used to warm, cure, and liberate could now be used to threaten, destroy, and enslave.

Human development[15] continued at an accelerating rate in centuries that followed as we kept discovering how to harness available energy in new and more effective ways. In 1500 CE, which is now extremely recent compared to the timescales we have been discussing, we saw the first design of a steam-driven ship, though wind-driven vessels were still the norm. Just 200 years

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[13] In Greek this translates to "ball of Aeolus", the god of air and wind.

[14] Charcoal is just wood that is heated in the absence of oxygen, leaving only the carbon behind and is itself highly flammable.

[15] from a Eurocentric perspective

later, steam engines were widely adopted for powering locomotion on land, around the same time electricity was discovered in the West. Then in the early to mid 1800's, the field of thermodynamics as we know it was starting to take shape as several key physical laws, which we will learn about in detail in later chapters, were discovered and formalized, providing engineers and technologists with powerful mathematical tools to design more efficient engines.

Around that same time, in the 1880s, humans started using coal to generate electricity, at which point we were not only burning plants that had died recently, but also now carbon from plants that died during the *Carboniferous* period - 300 Ma - that would have otherwise remained in the ground for millions of more years to come. Indeed, the adoption of coal as a widely used energy source marked a dangerous turning point in the story of climate change as our energy demands exceeded what could be readily supplied by the sun, instead causing humans to turn to stores of solar energy that had been accumulating for millions of years. Somewhat ironically, it was around this same time that scientists[16] discovered the greenhouse effect [16], with some even noting that the continued excess burning of fossil fuels would have a profound effect on the climate.

These warnings were largely overlooked, as the burning of fossil fuels also had a profound effect on technological and thus economic development via the *Industry Revolution*. Just 50 years later, in the early 1900's, vast stores of oil, which again are the liquefied carbonaceous remains of ancient sea creatures, were discovered underground, providing humanity with another energy-rich and carbon-intensive fuel source. Bolstered by numerous major wars and the rapid economic development in the West that followed, we saw the emergence of a seemingly runaway cycle of more energy consumption leading to net economic development leading to higher energy demands and so on. By the mid 1900's, now only 50 years ago and about the same time humans demonstrated their ability to escape the gravitational pull of Earth itself [17], the ever increasing carbon emissions began to leave their mark on the climate as the global mean temperature started to rise as a direct result of the pronounced greenhouse effect [17], proving many of the earliest climate scientists correct.

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[16] This discovery is often wrongly attributed to John Tyndall but was actually made by Eunice Foote several years earlier in 1856.

[17] see Sputnik and the Apollo Program

1.1.5 The Anthropocene

This brings us to today, where in 2020 the Earth has warmed a deceptively substantial 1 °C above pre-industrial temperatures. Looking back, in just the past 50 years, a span of time encompassing only 0.003% of the history of humans or 0.000001% of the history of the Earth or 0.000000... - you get the idea - the culmination of human achievement in science and technological development has brought about countless advancements[18] in medicine, agriculture, transportation, communications, computation, and the list goes on. As was meticulously outlined by the most recent IPCC special report [18], we are now seeing, however, that this progress has come at cost of the stability of our climate. The rate of development and the associated energy consumption has been at direct odds with the timescale on which the Earth's carbon cycle regulates the climate, which, works over millions of years. The stress on the system from just the past 150 years is finally catching up as we begin to see measurable sea level rise, more powerful and frequent severe weather events, and beginnings of mass extinctions. What is even more concerning is that, as Solomon[19] et al showed, even if we stopped emitting carbon dioxide today, these adverse effects are "locked" into the climate response for potentially hundreds of years [19].

So where do we go from here? The IPCC report also showed a consensus among the world's leading climate experts that a 2 °C global mean temperature rise above pre-industrial levels would cause a catastrophic and irrevocable disruption to nearly all of the of the Earth's many interwoven ecosystems upon which we rely. The best climate models developed to date indicate that to avoid a safer - but still potentially devastating - 1.5 °C temperature rise, the atmosphere must absorb no more than 316 Gt of carbon dioxide if we start counting from July 2020 onward; however, at current rates of consumption, this budget is set to run out by the end of 2027 [20], just 7 years from now. Needless to say, the race is on, and just as much as the manipulation of thermodynamic principles played a central role in the development of this impending crisis, these same principles - *in responsible and conscientious hands* - may be the keys to getting us out of it.

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[18] enjoyed by a small subset of humanity

[19] Susan Solomon is an MIT professor who is famous for her work that helped galvanize support around repairing the Earth's ozone layer

1.1.6 Thermodynamics - A Human History

At this point, you may be wondering just what is *thermodynamics* anyway? We have hinted in the previous section's Big Historical perspective that it has something to do with heat, engines, and carbon emissions but have left its definition intentionally vague up until now to avoid getting lost in the finer details. To start, thermodynamics is a branch of physics that investigates the relationship between energy in its various forms, in particular how *thermal* energy or *heat* interacts with matter to transform into mechanical energy and vice versa. For thousands of years, humans tried to formally understand the visceral sensation of heat, attributing it at first to mythological phenomena and eventually postulating that it was a unique physical "element" as tangible as water and earth. Ancient Greek philosophers wrote at length about the ability of heat to "flow", likening it to a fluid[20].

In fact, this fluidic theory of heat would persist for nearly another 2000 years, where by the 1700's the supposed fluid was given the name *caloric*. Around this same time, it was also postulated that all bodies had a different "volume" for this fluid, defined as the body's *heat capacity*, which despite being established using now outdated physics, is still a term we use today. It wasn't until 1798 that Count Rumford, a British physicist, undermined this theory by showing that heat could be generated via friction[21]. These observations were further supported by the research of Antoine Lavoisier and Joseph Black who concurrently were reporting that heat could be released or absorbed by chemical reactions or by freezing and thawing water, marking the end of heat being thought of as a distinct conservative quantity. This theory was instead replaced by the notion that heat is simply a different form of energy that can be traded and transformed just like kinetic or potential energy. James Joule would later show in 1843 that there was in fact an exact mechanical equivalence of heat[22].

Parallel to these developments, people were observing a peculiar relationship between heat and the motion of fluids. For example, it was also known for thousands of years that boiling water in a partially enclosed container would generate "wind" - hot gas that would exit the container with some velocity[23]. Later in the 1600's CE, scientists like Galileo were observing that a vacuum

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[20] see Heraclitus, 500 BCE

[21] In line with some of the sentiment of the Big Historical context presented here, it is unsurprising perhaps that he discovered this when he noticed that boring out chunks of iron to make cannons caused the metal to heat up substantially.

[22] Interestingly, nobody believed him at first because his experiments were *too* accurate.

[23] see *aeolipile*

chamber had the ability to draw in water from the environment, and soon after, Irish chemist Robert Boyle showed in 1656 that the pressure and volume of a gas were predictably correlated. These observations, however, were not connected until French chemist Joseph Louis Gay-Lussac laid the groundwork for the famous *ideal gas law*, which accurately relates the pressure of a gas to its temperature and density.

From there, another French physicist, Sadi Carnot, the "father of thermodynamics", united the more modern framework of heat and the thermomechanical properties of gasses in pistons into a unified field, which was later first called *thermodynamics* by Lord Kelvin. Rudolf Clausius formalized the concept of energy that is "wasted" to the environment as being proportional to the quantity of *entropy*, which was then rigorously related to the statistical thermodynamics of large groups of particles through the work of James Clerk Maxwell[24] and Ludwig Boltzmann in the late 1800's. Finally, Willard Gibbs defined the concept of *enthalpy* and *free energy* to quantify the amount of useful mechanical energy (*work*) that could be extracted from a system, and he finally formally stated the first two laws of thermodynamics in 1873. With these contributions, and the many that followed from countless other physicists, mathematicians, and engineers, the groundwork for the subject presented in this book was laid.

There is considerable overlap between thermodynamics and the fields of chemistry, biology, magnetism, and both classical and quantum mechanics, a testament to the ubiquity and importance of thermal energy conversion in a wide array of observed phenomena. For example, combustion - and all forms of *oxidation* for that matter - is described by various chemical reactions that release thermal energy as a result of breaking and reforming covalent atomic bonds. The heat released acts as a kind of currency that can be captured and converted into mechanical energy to turn a shaft, as is done in the internal combustion engines that power a majority of the world's cars. Thermodynamics provides us with tools to examine exactly how much heat is released in these chemical reactions, how much of that heat we can expect to convert in mechanical energy, and perhaps most importantly for our future discussion about climate change, how much is "lost" to the environment. These same physics govern the operation of power plants, refrigerators, jet engines, hot air balloons, batteries, air conditioners, and the list goes on.

While thermodynamics can help explain how we came to emit enough carbon dioxide to radically change our environment, it also lays the foundation for the physics underlying the behavior of our atmosphere and climate itself.

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[24] who revolutionized many fields over his career

In particular, thermodynamics dictate how clouds form from water vapor in the air and then turn into storms, as well as how thermal energy from the sun in part drives oceanic and atmospheric currents (i.e. wind)[25] and the greenhouse effect. The study of these phenomena provides an analytical basis for talking about climate change in general, and it even provides some insights into ways we might be able to manipulate certain feedback loops directly to undo some of the damage we have already done[26].

Finally, as an appeal to some sort of cosmic aesthetic beauty, it is incredible (and somewhat unsettling) to reflect on the predictive power of thermodynamics and realize that the fundamental laws, from which virtually everything we discuss here will be derived, are based solely on observation. Let that sink in. As far as we know, the three laws of thermodynamics hold true, but they have never been proven, nor is there a credible procedure for even going about proving them. Regardless, they have held up over the past two hundred or so years - through endless experimentation and theoretical development built on top of them. Even Einstein said of thermodynamics that they comprise “the only physical theory of universal content, which I am convinced...will never be overthrown”. Regardless of the context of its many applications, the theories presented in this subject are truly an achievement in human imagination and is worth appreciating as we move through this content.

1.2 Summary

The history of the Universe from the Big Bang to the present day spans nearly 14 billion years, the last 4.5 billion of which saw the development of our planet Earth. Just 500 million after the Earth was formed, the first living organisms appeared. Over the next 4 billion years, what were originally strands of free-floating RNA in the depths of the oceans, evolved to create the vast diversity of life we see today, all the while shaping the climate and the Earth itself along with it. These persistent cycles of change were not only common, but *necessary* for the diversification of life and its ability to survive over the incredible stretch of time it has - now almost a third of age of the Universe itself.

Something fundamental changed, however, once humans came on the scene a comparatively short 2 million years ago. Before this time, plants and animals used energy both directly and indirectly from the sun as it was provided to

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[25] In reality these phenomena are made much more complex by *coriolis* forces that arise from the fact that Earth is spinning and *tidal* forces from the moon, but thermal energy is still a major driver.

[26] see *geoengineering*

them, letting the natural rhythm of the seasons and the gradual oscillations of the climate guide their rates of consumption and therefore their evolution and development. With the emergence of humans and their ability to control fire soon after, this pace quickened, as life was no longer subject to the natural cycles of growth and decay. In the ability to liberate thermal energy stored in the bonds between carbon atoms that comprise organic matter - energy that originally came from sunlight - humans suddenly had vast stores of heat and light at their immediate disposal.

With the control of fire ultimately came the control of ecosystems, driving more development, expansion, and consumption, and once humans discovered the even more energy-dense deposits of solar energy stored in the remains of ancient plants and animals as coal and oil, this cycle accelerated. By the early 1700's CE, now just 300 years ago, the study of thermodynamics got its footing as scientists and engineers learned how to turn thermal energy into mechanical energy and then into electricity, opening the door for the invention and adoption of a seemingly limitless number of new technologies.

This progress has come at a cost, however, as the mass burning of carbon-based fuels results in the re-emission of carbon dioxide at rates greater than can be absorbed by natural means. Because carbon dioxide functions as the currency of the Carbon Cycle, its excess has put considerable strain on the climate's main feedback loop keeping temperatures within livable conditions. Coupled with the additional ecosystem destruction from over-development and pollution that further inhibits the natural uptake of carbon dioxide, the net effect of our energy consumption has been pushing the Earth towards an unprecedented warming scenario that threatens to destabilize our many necessary ecosystems.

The silver lining here is that the field of thermodynamics - which up until now has led us down this destructive path - has also provided us with many tools to work towards solutions that prevent a devastating additional 1-2 °C of warming if we so *decide* to use them in that way. The purpose of this text is to tell the story of climate change in greater detail, introducing the fundamental physics of thermodynamics and the analytical tools that use them along the way. As we continue this educational journey, be aware of the perspective you bring to this story and its impact on your motivations to learn the material. Without this greater context, we get the dangerous and unchecked push towards progress that got us here. Fortunately for all of us, the ending of this story is somewhat uncertain, and the proverbial publishers are still accepting submissions; however, we have little time to waste, as what we do in the next 10-50 years - just a veritable blip in the grand timeline - will likely seal this fate.

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Chapter 2

Energy, Climate, and the Carbon Cycle

The *field* of thermodynamics arose from observations made by humans in artificial settings over the last 10,000 years or so, but in reality, thermodynamics has been guiding the physics of the natural world since the formation of the Earth 4.5 billion years ago and its atmosphere and oceans - its climate - shortly thereafter. So let us begin there with a discussion of energy and its relationship to the Earth's climate systems[1]. To that end, in this chapter we will start off by defining some terminology to get on the same lexical page. Then we will introduce the First Law of Thermodynamics, develop a framework for analyzing systems through the lens of energy balances, and discuss the nature of thermal energy. From there, we will learn some additional important mathematical models necessary for understanding how the climate stores, transforms, and transports energy. Finally, remembering that we are ultimately telling the story of anthropogenic climate change, it will help to understand the physics at the root of this problem. We will therefore introduce the Carbon Cycle at a high level and show from a thermodynamics perspective how it regulates - and de-regulates when pushed too far - the climate.

2.1 Thermodynamic Systems

Despite the natural world's ability to operate just fine without our imposed frameworks for understanding, it will be helpful for us to define some terminology. A thermodynamic *system* simply refers to a well-defined region of

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[1] This course is primarily focused on thermodynamics, so we will unfortunately gloss over much of the climate science, which is itself a very rich field.

space called a *control volume*, that can be characterized by some quantities of interest and can either be thought of as being *open* or *closed*. In an open system, mass is allowed to traverse the system's *boundary*, adding or removing net mass and the energy associated with it over time. In a closed system, energy may be exchanged with its environment in various ways.

Just as important as it is to define physical boundaries that separates a system from its external *environment*, it is also important to understand the timescale over which a system is relevant. As we will see, many systems can be very well approximated as being closed if we restrict ourselves to very short timescales of interest. Conversely, in real systems, for example, we often see that if given enough time, even the best insulators will let heat out. Thus what might be a considered a closed system, might in reality be more of an open system the longer we wait.

And so there is also this warped perspective of time that emerges from breaking down physical systems in this way. Depending on for how long or short a period of time we observe some phenomenon, we can arrive at completely different conclusions about its behavior. With this in mind, it becomes useful to instead think of thermodynamic systems as undergoing changes of *state*, each of which is a discrete snapshot of the various quantities that characterize the system at a specific instance of time. The quantities that do not depend on the history of the system, like temperature, pressure, density, etc., are typically called *properties*, and they tell us how much energy and mass are present and in what forms. Properties can be either *intensive*, which do not depend on the size and mass of the system (e.g. temperature, pressure, and density), or *extensive*, which do (e.g. mass, volume, and internal energy).

Instead of considering the time-dependent internal physics of how a system evolves over time, which can be highly complex, we can then think about a system undergoing a series of state changes that in total comprise a *process*. A process whose final state is equivalent to its initial state is called a *cycle*, which we will see over and over again throughout this material. An important subtlety here is that in thermodynamics, we actually do not care what happens precisely in between states, as long as the states themselves are well defined. In this way, the *-dynamics* part of thermodynamics can be a bit of misnomer, as well-defined states typically require that the system be in *equilibrium*, that is after all of the messy time-dependent physics have settled, resulting in more-or-less *homogeneous* and *static* system properties. As we will see, however, it is usually possible to break up a system both physically and temporally in such a way that even highly dynamic processes like combustion can be approximated as being a series of *quasistatic* states.

That leaves one last important term to define - or rather we must hash out the opposite meaning of a term we have already defined. As discussed, a property is a quantity that does not depend on the history of the system, but what quantities do? It turns out that these *non-properties* are actually the key to making anything interesting happen in the Universe, as they consist of any quantity that characterizes the *transfer* of energy into or out of a system. Heat transfer or mechanical work, which we will define more rigorously later in Section 2.2, are the two primary non-properties we will learn about, and said another way, they represent the transitions from one state to the next. We can talk about energy *flux*, which is the rate of energy entering or exiting a system per unit area, but as is the case with properties, all we care about from a thermodynamics perspective is the total amount of energy transferred between two adjacent states.

2.1.1 Establishing a Control Volume for the Climate

Looking at the climate as an open thermodynamic system, we can begin to appreciate its complexity. First, it is possible to draw the system's boundaries in a number of ways, the simplest being a spherical shell that captures all of the gas molecules comprising the upper atmosphere down to the hot radioactive core of the Earth. Ignoring the gravitational pull of the Sun and Moon, the only energy in and out of the volume is thermal energy via *radiation*, both from the Sun into the system and from the various matter in the system to outer space[2]. If we zoom in, however, we quickly see that there is no one set of homogeneous properties that can completely define the state of our system given that within its boundaries we find many different *species*[3] in many different *phases*[4]. Defining any sort of process for this control volume would be a nightmare.

Instead, it tends to be more useful to break things up into domains that can be characterized by similar properties. For example, we might instead decide that two separate systems are required - one for the atmosphere and another for the oceans, each characterized by properties including temperature and pressure. With this added boundary, it is now important to carefully define how energy (and mass) are transferred back and forth between the two volumes, not just with the sun and outer space. Zooming in again, though, it is apparent that the atmospheric temperature, pressure, and composition in Cambridge, MA, for example, is rarely the same as somewhere over the

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[2] Radiation will be described in more detail later

[3] used in thermodynamics to mean substance comprised of single type of atom, molecule, etc.

[4] i.e. solid, liquid, gas, and even plasma

Sahara Desert, and thus further subdivisions by climate zone might be necessary. Indeed, this exercise can continue until we are left with billions of very small domains, each with uniform properties. In fact, computer models of the climate do exactly that, though with great effort and not always terrific accuracy.

We can take another approach at modeling the climate, though. Simulating this entire system in high fidelity to get accurate results is an extremely laborious task for computers and basically impossible for humans by hand; however, much can be learned by creating simplified models that are less accurate, but make the problem easier (or even possible) to solve. We can ask questions about how the climate would behave if the oceans were all one temperature or if the atmosphere had a uniform composition, and then compare the results to what we actually observe and see if we need more granularity. Or we can zoom in on a small region that actually does have easily characterizable properties and use the information we derive to make larger predictions about similar regions. Clearly, there is no correct procedure for delineating boundaries for the climate, let alone for any thermodynamic system, though depending on the quantities of interest, there are better or worse ways of going about it. As statistician George Box aptly put it, "All models are wrong, but some are useful." Throughout this text, we will be learning many of these useful models and when and how to apply them.

2.2 Energy and the First Law

That brings our discussion to the nature of *energy* itself, which as it turns out, is not just a single well-defined quantity. In fact, energy can take many forms. In classical mechanics, a system's kinetic energy is defined by its mass and velocity as $\frac{1}{2}mv^2$ and its gravitational potential energy on Earth by its mass, the acceleration due to gravity, and its height relative to some starting point as mgh[5]. Experience tells us that dropping a stone on Earth from some height above the surface will cause it to accelerate, continuously converting gravitational potential energy into kinetic energy. If we do this experiment in a vacuum such that there is no air resistance, we would find that the gain in

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[5] This is an approximation of the more general form for gravitational potential energy derived from Newton's Law of Gravitation: $\Delta U = -G\frac{mM}{R+h}$, where M and R are the mass and radius of the Earth respectively, and G is the gravitational constant, 6.67408x10^{-11} m^2/kg-s^2. For small h above the Earth's surface, a Taylor expansion about $h = 0$ gives us that $\Delta U = -G\frac{mM}{R^2}((R-h)-R) = mgh$, where $g = GM/R^2$ and is approximately 9.81 m/s^2 at the Earth's surface.

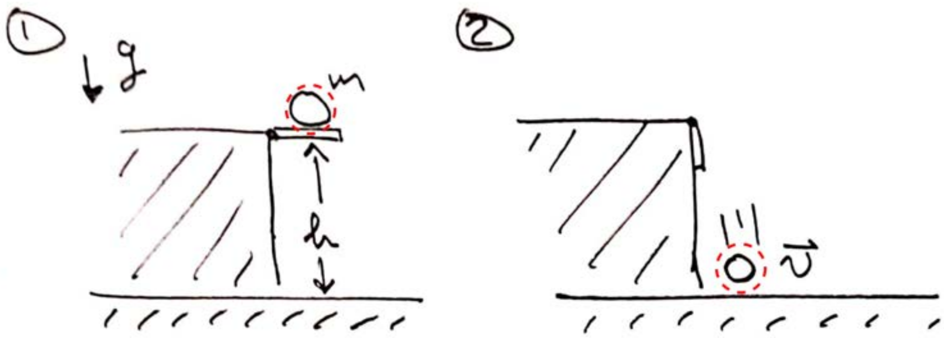

Figure 2.1: Two "thermodynamic" states for the stone drop example. Dashed red circle shows the control volume. Note that in the case of gravitational potential energy, technically the force of gravity and thus any potential difference requires 2 bodies. Here, the mass of the Earth is also implicitly contained within this control volume.

kinetic energy is exactly equal to the loss in potential energy:

$$\frac{1}{2}mv^2 = mgh \tag{2.1}$$

or that its velocity, if starting from rest, is equal to $\sqrt{2gh}$, after falling a distance h. That is to say, if you only told me the height from which you dropped the stone, I could tell how fast it will be traveling just before it hits the ground.

Taking a step back, we arrived at this prediction by looking at the problem from a thermodynamics perspective, and this example illustrates something subtle but profound about this approach. Notice that we did not say anything about what happened to the stone during its flight. We could have arrived at the same conclusion by saying the stone experiences a force due to gravity equal to mg, and from Newton's second law that it must therefore experience an acceleration of g:

$$F = ma \tag{2.2}$$

$$\cancel{m}g = \cancel{m}a \tag{2.3}$$

Then using calculus to equate this acceleration to the second derivative of position with respect to time as

$$a = \frac{d^2h}{dt^2} = g \tag{2.4}$$

and finally integrating once to get its velocity:

$$v = \int \frac{d^2h}{dt^2}dt = \int g\,dt = gt \tag{2.5}$$

Eq. 2.5 solves for the stone's velocity as a function of time, but to get an expression in terms of its initial height, we need to solve for how long it takes the stone to fall a height, h. As an exercise in calculus review, the rest is left to the reader, but the answer will also come out to $v = \sqrt{2gh}$. The point of this exercise, however, is that going down this time-dependent path can be much more convoluted than viewing the problem holistically and asking instead how the energy changes from one *state* to another, especially if all we care about is the velocity right before the stone hits the ground.

In the first thermodynamics-based approach (again a bit of a misnomer as we actually did not say anything about the *dynamics* of the system at all!), we described the stone as a closed system whose properties of interest were its height, mass, and velocity. In its initial state, the stone system was at some height h with zero velocity, and in its final state, the stone was just about to hit the ground with some velocity v. Because it is a closed system, the energy it started with was the energy it was left with, just in a different form. As we would expect, the units of both kinetic and gravitational potential energy are kg*m/s^2, or *Joules*, as they are equivalent quantities.

In fact, this equivalence and in general the observation that on the macro scale, energy is not created nor destroyed but rather sloshes around between its various forms, is the *First Law of Thermodynamics*. In other words, the *change* in energy of a well-defined system is equal to the net energy transferred between the system and its environment. Even in extreme conditions where classical mechanics breaks down like black holes or masses moving near the speed of light, everywhere we look, energy seems to be a *conservative* quantity[6], leaving little doubt as to the validity of the First Law despite its empirical origins. Our first job as thermodynamicists will therefore be keeping track of how energy moves into, out of, and within our systems, paying careful attention to how their boundaries are defined.

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[6] Things get more interesting at the quantum mechanics level, but this law still holds with some slight modifications.

2.2.1 Thermal Energy and Temperature

As introduced in Section 1.1.6, the idea that mechanical, or kinetic, energy is directly equivalent to thermal energy was a major breakthrough in thermodynamics. Before then, heat was thought of as its own conservative quantity[7] similar to energy but of its own origin. Eventually it came to be understood that via a mode of interaction called *friction*, a mass's kinetic energy can transform into thermal energy, which manifests itself as an increase in the mass's *temperature*, a property that quantifies how "hot" or "cold" it is. Experientially, we can confirm this is true by rubbing our hands together vigorously and observing that they do in fact heat up. This phenomenon was obviously not difficult to discover on a surface level of understanding, but Joule's experiments in 1843 were the first to precisely measure this equivalence.

The exact correspondence between the two forms of energy should be expected though, as it turns out that thermal energy *is* kinetic energy at the atomic scale. All matter - including the water in the oceans, the rocks in the mountains, and the gasses in the atmosphere - is comprised of atoms and molecules that are bound together in various ways by electromagnetic forces. These bonds, however, are not perfectly rigid, leaving the atoms some freedom to *vibrate*, *rotate*, and even *translate* depending on the matter's *phase*. That is to say, individual atoms typically have some finite, non-zero kinetic energy, even though at the macro scale, the matter they make up might appear to be at rest. This energy can be transferred to other particles by repeatedly bumping into them, explaining in part why our skin heats up when we go outside on a hot summer day. The fast-moving molecules in the air collide with molecules in our skin, losing some kinetic energy to our thermal energy in the process.

Going back to our discussion about picking useful system boundaries, keeping track of the energy of every atom or molecule in a system is often impractical[8]. Instead of modeling each individual particle, which would require a supercomputer for all but the smallest systems, we can define a highly useful aggregate property that captures the average kinetic energy of a large group of atoms. With gases, for example, particularly those that comprise the Earth's atmosphere, this problem is well defined, as individual atoms and molecules can be modeled with reasonable accuracy as being simple balls that collide perfectly *elastically*[9] with one another and external objects. From statistics, we find that the average kinetic energy, $\overline{E_{KE}}$, of a large number of these particles is given as:

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[7] called *caloric*

[8] As a point of reference, a single grain of sand contains roughly 10^{20} atoms!

[9] Kinetic energy going into the collision = kinetic energy going out

$$\overline{E_{KE}} = \frac{3}{2}RT \tag{2.6}$$

where R is the *Universal Gas Constant* (8.314 J/mol-K) and T is the *absolute temperature* of the gas in units of Kelvin (K)[10]. Rephrasing this statement, it is also equally valid to say that the temperature of a gas - or a substance in any phase for that matter - is proportional to the average kinetic energy of its constituent molecules. This relationship is more complicated for solids and liquids, but the general concept and proportionality is the same.

A corollary to Eq. 2.6 illuminates another important concept in thermodynamics - that a group of atoms will always have some average kinetic energy unless its collective temperature is 0, a point on the absolute Kelvin scale called *absolute zero*. Also since negative kinetic energies are not well defined, neither is a negative temperature on this scale. These are minor points, but important to note, especially if you are familiar with the units of Celsius or Fahrenheit [11]. Converting from Celsius to Kelvin requires that we simply add 273.15 to the value in Celsius[12].

Mechanical Work

It is important to make the distinction here between thermal energy and macroscopic mechanical energy. From classical mechanics, we know that exerting a constant net force, F, on a mass over some distance, d, results in an acceleration that changes the mass's kinetic by exactly Fd[13]. In general, this change in energy due to a forced displacement is called *work* expressed as

$$W = \int_0^d F\,dl \tag{2.7}$$

in its simplest 1D form for a variable force.

Thermal energy also manifests itself as changes in kinetic energy, but because we are typically interested in the aggregate effect of many particles, we treat it as a separate quantity to facilitate calculation for the many applications

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[10] see *kinetic theory of gases* for derivation

[11] In this course and text, we will altogether ignore Fahrenheit. There is some historical context for the once useful Fahrenheit, but it is no longer relevant and makes the math more difficult.

[12] Recall that 0 °C and 100 °C are the freezing and boiling points of water at atmospheric pressure respectively.

[13] $F = ma = m\frac{dv}{dt}$. For a constant force, integrating both sides with respect to dt yields $Ft = mv$. Multiply both sides by dv and integrate again to give us $Fd = \frac{1}{2}mv^2$. *QED.*

in which we do not really care what is happening with each individual atom or molecule. Consequently, the First Law of Thermodynamics is typically stated mathematically as

$$\Delta E_{CV} = Q - W \tag{2.8}$$

which states that the change in energy inside our control volume is equal to the net heat transfer into the system, Q, minus the net work done by the system on the environment, W. This minus sign comes from a convention that the work done *by* the system is positive.

2.2.2 Thermal Radiation

Before returning to our discussion of the climate, there is one more piece of physics that we need to cover - *radiation*, and more specifically, *thermal* radiation. If we zoom in on a single particle doing its thing above 0 K, we would now expect to see that it is moving around as a result of it having some sort of average positive kinetic energy. We would also find, however, that its kinetic energy is not constant but rather is fluctuating slightly due to its velocity not being constant, especially if it is simply oscillating back and forth in a matrix of other particles. These tiny fluctuations also cause perturbations in the net charge of the particles[14], and we know from electromagnetism - thanks again to Maxwell - that an accelerating charged particle generates an electromagnetic wave, also called *light* or radiation. If we then zoom out to a large collection of particles, we see that they are all doing the same thing, together emitting a concerted and continuous stream of radiation.

Given what we know about temperature and kinetic energy at the microscopic level, it should come as no surprise that the macroscopic *thermal* radiation we observe increases in intensity as temperature goes up, as the individual particles are moving and changing direction more rapidly as well. In fact, the radiative power emitted by a *black body*, which is an object that perfectly absorbs and emits light at all frequencies so as to appear black to our eyes, is given by the *Stefan-Boltzmann Law* as

$$P_{rad} = \sigma A T^4 \tag{2.9}$$

where σ is the Stefan-Boltzmann constant (5.67x10^{-8} W/m^2-K^4), A is the surface area of the body, and T is the temperature as previously defined.

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[14] Atoms have electronics and protons that can separate slightly, creating net regions of negative and positive charge.

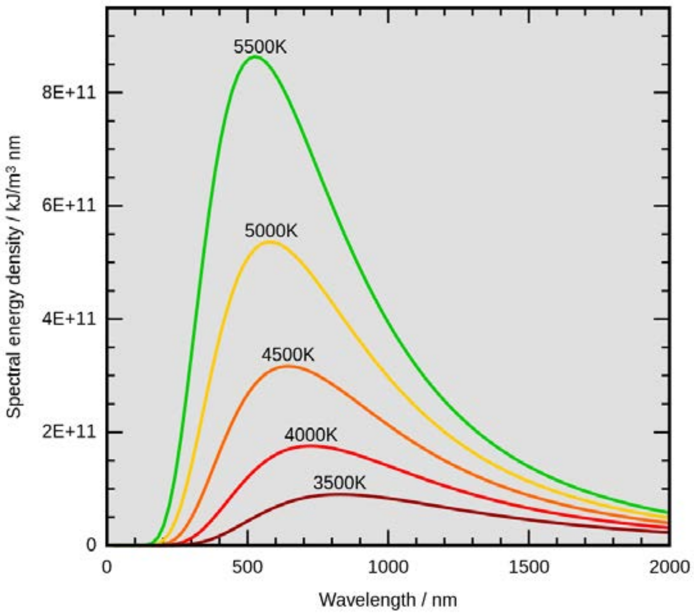

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Figure 2.2: Intensity of thermal radiation from bodies at different temperatures as functions of wavelength. Notice that the peak shifts in wavelength and thus color, explaining why cooler objects glow red and hotter objects glow white as their radiation incorporate all the other colors in between [source].

It is exactly this phenomenon that explains how light is emitted from the sun, as well as incandescent lightbulbs and anything hot enough to "glow" for that matter. The Sun in particular is constantly undergoing nuclear fusion in its core, which provides a constant source of high-intensity gamma rays[15]. These high frequency *photons* are absorbed by hydrogen and helium in the outer layers of the Sun, which then heat up and re-emit radiation at lower frequencies. As expected, we see that this process of thermal radiation works in reverse as well. Particles can absorb light, causing them to vibrate faster and therefore increasing the net temperature of the group they comprise. This phenomenon is the reason why objects are cooler in the shade than in direct sunlight.

Finally, there is one other critical aspect to thermal radiation as it relates to climate change, and that is the fact that particles emit a *spectrum* of radiation

---

[15] very high frequency radiation that our eyes cannot detect

across all wavelengths of light at varying intensities[16]. This intensity, I, is therefore a function of both wavelength, λ, and temperature given by *Planck's Law*[17] as

$$I(\lambda, T) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k_B T}} - 1} \tag{2.10}$$

where h is the Planck Constant (6.626x10^{-34} J-s), c is the speed of light in the medium[18], and k_B is the Boltzmann Constant (1.38x10^{-23} J/K), not to be confused with the Stefan-Boltzmann constant from earlier.

Fig. 2.2 shows Planck's Law in Eq. 2.10 plotted as a function of wavelength for different emitting temperatures. Notice that wavelength of the peak intensity changes as the temperature increases, a phenomenon called *Wien's Displacement Law*. These shifting peaks explain why extremely hot bodies like the sun emit light that appears white as its intensity peak covers a large swath of frequencies within the visible spectrum, but cooler bodies like the embers of a wood fire emit light that appears mostly red. This is important to climate change because as a result of this phenomenon, sunlight is comprised of light at different wavelengths, each of which interacts with the gases in the atmosphere in different ways. In reality, actual substances are not perfect black body emitters or absorbers, but instead favor specific ranges of wavelengths, which forms the basis of the *greenhouse effect*, discussed in detail later Section 2.3.3.

Light Absorption and Albedo

Just as objects can emit light at different wavelengths, all objects naturally absorb light preferentially over certain wavelengths. In fact, to our eyes, the *color* of an object gives a clear indication of which wavelengths in the visible spectrum[19] are *not* being absorbed[20]. Also in general, objects that appear darker absorb more light, with a perfect absorber appearing completely black as we discussed. Conversely an object that reflects all light equally will appear

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[16] Light can be thought of as a sum of individual waves, each at a single frequency. White light contains waves of all frequencies at equal power.

[17] This solved a very important issue with classical physics, called the *Ultraviolet Catastrophe*.

[18] There is a maximum value of 3x10^8 m/s in a vacuum but this can be substantially lower when traveling through a medium.

[19] 750-380 nm

[20] The story is a bit more complicated for gases. E.g. the sky appears blue because blue light is preferentially bounced around as a result of *Rayleigh Scattering*.

white[21]. In terms of energy transfer, the amount of radiative heat that can be absorbed by an object is proportional to how dark it appears, with darker objects absorbing more energy. The proportionality constant is called the *emissivity*, ε and appears in a simplified power equation as

$$P_{rad} = \varepsilon \sigma A T^4 \tag{2.11}$$

where ε can vary from 0 to 1. In reality, ε is a function of wavelength as well, but for now we will ignore this.

In our climate, the net reflectivity of the Earth is called its *albedo* and has a deeply important impact on climate change, as it controls how much of the Sun's light is reflected back into space. We are now witnessing an unfortunate *positive*[22] feedback loop, in which bright white ice at the poles melts, revealing dark blue water underneath. This process reduces the local albedo, allowing more radiation to be absorbed and thus more ice to melt. Clouds also have a significant impact on albedo. More white clouds means more reflective surfaces that help to shield the Earth from sunlight. The story with clouds, though, is made more complex in that they also contribute greatly to the greenhouse effect as we will see. Presently, the net effect of clouds on climate change is still a widely debated subject amongst climate scientists, but they all agree that clouds have the ability to tip the scales one way or the other on these global feedback loops.

2.3 The Thermodynamic Climate System

The Earth's climate system is the highly complex and interwoven network of many geological, atmospheric, oceanic, and biological ecosystems. Feedback loops across these many subsystems have shaped the sum total climate over billions of years, yielding a net stable equilibrium via an evolutionary process much like the one that created humans. The fact that all these components have worked so harmoniously for all this time is no accident, but rather a patient product of trial and error. Given the complexity of all that is considered to be the climate, much of these underlying physical processes are well out of the scope of this course, but this is an extremely well studied and developed field with many excellent resources that dive deeper.

For our purposes, we need to better understand the climate as it relates to the macroscopic thermodynamics driving global warming and climate change.

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[21] ignoring a discussion here on mirrors which rely on reducing *scattering*

[22] one in which the tendency is to spin out of control

To that end, we will explore a few additional properties of gases to better explain observations made about the atmosphere. We will also discuss in finer detail the ability of various substances to store thermal energy. Finally, we will discuss a key interaction between the surface of the Earth and the atmosphere that dictates their temperatures - the *greenhouse effect*.

2.3.1 The Atmosphere as an Ideal Gas

To a great level of accuracy, we can model the atmosphere as being an *ideal gas*, which simply means it can be modeled well using the *ideal gas law*:

$$PV = nRT \tag{2.12}$$

where P, V, and T are the pressure, volume, and temperature of the gas respectively, n is the number of *moles*[23] of the gas, and R is the universal gas constant from earlier. For the atmospheric system where it might be troublesome to think of its entire volume, we can rewrite Eq. 2.12 instead as

$$P = \rho\widetilde{R}T \tag{2.13}$$

where ρ is the local *density* of the gas in units of mass per volume and $\widetilde{R}$ is the species-specific gas constant equal to R/M - the universal gas constant divided by the gas's molar mass.

Stepping back, however, it is important to understand the nature of *pressure* itself, which is also a direct result of the kinetic theory of particles. If we think of particles as being balls that can bounce off each other and other objects such that the total kinetic energy is conserved, we can then zoom in closer on the collision itself. Let us look at the case in which we have some solid object sitting out in the air. Due to their random motion, air molecules are constantly colliding and bouncing off the surface of this object. Each of these particles has some velocity, $\vec{v}$, and mass, m, and therefore some *momentum*, $\vec{p}$, equal to

$$\vec{p} = m\vec{v} \tag{2.14}$$

At each collision, the particle changes directions, and therefore since momentum is *vector quantity*[24], this results in a change in momentum up to $2mv$. We know from classical mechanics that a change in momentum over a given time requires a force whose magnitude is given by

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[23] One mole of a substance is defined to contain 6.022x10^{23} (*Avogadro's Number*) particles.

[24] one where both direction and magnitude are important

$$F = \frac{\mid \Delta\vec{p} \mid}{\Delta t} \tag{2.15}$$

Looking at the statistics of N particles randomly impacting our object over one of its faces with area A, we find that the force on just that face is on average equal to

$$\overline{F} = \frac{1}{3} A N \rho \overline{v^2} \tag{2.16}$$

and recalling that pressure is simply force divided by area, we can rewrite this in terms of pressure as

$$P = \frac{\overline{F}}{A} = \frac{1}{3} N \rho \overline{v^2} \tag{2.17}$$

where the right-hand side is conveniently equal to 2/3 the average kinetic energy per unit volume.

Pausing here, we find that pressure is simply the force due to random collisions of molecules with our object per unit area. Oddly, in this way, the notion of pressure actually requires the existence of an object boundary off of which those molecules can bounce. An ideal cloud of gas in the middle of outer space with nothing interacting with it has no intrinsic pressure. In our atmosphere, pressure is well defined at the surface of Earth or the air-ocean interface, but it is less well defined in the upper atmosphere until we provide something else for the gas to interact with other than itself. In this way, pressure is unlike temperature, which describes the inherent kinetic energy of the gas itself and is always valid, even when there is nothing there to feel its effects.

It is also interesting to observe how pressure and temperature are intrinsically related through these particle interactions. From our previous discussion on the relationship between temperature and average kinetic energy, we know that the square of the average thermal velocity for a particle is given by

$$\overline{v^2} = \frac{3 k_B T}{m} \tag{2.18}$$

Plugging Eq. 2.18 into Eq. 2.17 yields

$$P = \frac{1}{3} N \rho \left(\frac{3 k_B T}{m} \right) = \rho \left(\frac{k_B N}{m} \right) T \tag{2.19}$$

noting that $\frac{k_B N}{m}$ is exactly equal to $\widetilde{R}$, we get the ideal gas law in Eq. 2.13 back[25]! So in short, what we have shown is that we can derive the ideal gas law by just knowing something about the kinetic energy of individual particles. Pressure and temperature are really two sides of the same phenomenon, with temperature alone describing the embodied energy of a substance and pressure emerging from the interaction between that substance and its environment.

Finally, because gases have the ability to exert forces via pressure, they also have the ability to do mechanical work. Combining Eq. 2.7 with the facts that pressure is simply F/A and volume is equal to Ad, we find that the work done by or on a gas is given as

$$W = \int_{d_0}^{d} (PA)\, dl = \int_{V_0}^{V} P\, dV' \tag{2.20}$$

where the pressure can vary over the expansion or compression of the gas. If pressure is not known but the temperature and quantity of the gas are, the ideal gas law can be substituted into this equation for P as

$$W = \int_{V_0}^{V} \frac{nRT}{V}\, dV' \tag{2.21}$$

A similar substitution can be made to eliminate volume instead to get an expression in terms of P and T[26]. Finally, sometimes we care only about a small change in the work done by the system, dW, which yields the very commonly used relation,

$$dW = P\, dV \tag{2.22}$$

which comes from taking the derivative of Eq. 2.20.

Atmospheric Pressure

Again, pressure in general is the average force per unit area that a fluid exerts on an object as a result of many microscopic collisions. This is true for the high pressures at the bottom of the oceans, and it is true for the low pressures in the upper atmosphere. On a macroscopic scale, pressure is also affected by gravity, in that all fluids[27] have mass and therefore experience the pull of

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[25] For a more detailed derivation of this, see Maxwell-Boltzmann distribution

[26] Interestingly, we actually only need to know two properties of the gas to say something substantial about its interaction with energy. The reason for this will become clear later.

[27] We use *fluid* in this text to mean either a liquid and a gas, as is commonly done in this field.

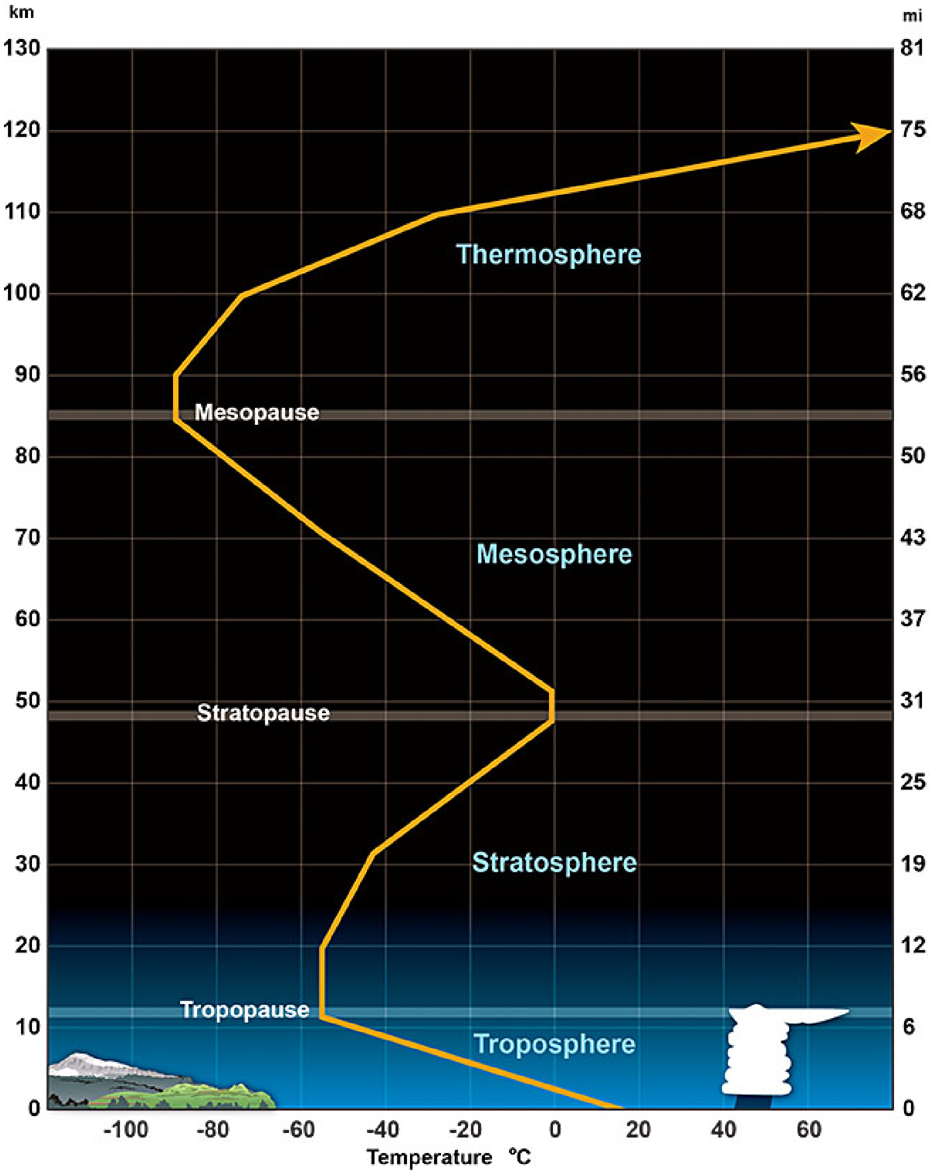

Figure 2.3: Average temperature profile of the Earth's atmosphere [NWS].

Image courtesy of US Dept. of Commerce.

the Earth's gravity well. The pressure at the bottom of the ocean is higher than near the surface simply because there is more water on top to weigh it down. In fact, for near-*incompressible* fluids like water, the pressure felt is exactly equal to the sum of the atmospheric pressure at the surface, P_a, and the weight of the water column above it per unit area:

$$P_{hydrostatic} = P_a + \rho g h \tag{2.23}$$

Though it might be less apparent, on land, we are also always experiencing the weight of all the air above us. If we knew the density, temperature, and composition of the gases in the air, we could compute the pressure by the ideal gas law, but what if we wanted a similar equation that predicts the pressure as a function of altitude? Unfortunately, the answer is a bit too complex to go into detail here, as the temperature can vary nearly 100 °C over the entire height of the atmosphere as shown in Fig. 2.3. In reality, the pressure decays exponentially with altitude, mostly due to the decreasing density.

The last point that is necessary to make here about the pressure of a gas is that in our ideal gas model, particles do not interact with each other - aside from the very occasional collision with another particle - and take up a minimal amount of volume individually. Consequently, if we have multiple different gas *species* occupying the same space, it is as if they are almost completely unaware of each others' existence. Therefore, as far as pressure is concerned, we can actually treat these gases completely separately and sum their various contributions to get an accurate total. This consequence is called *Dalton's Law of Partial Pressures*, which manifests itself mathematically as

$$P_{total} = \sum_{i=1}^{n} P_i \tag{2.24}$$

for n different gas species. Written a different way,

$$P_i = x_i P_{total} \tag{2.25}$$

where x_i is the *mole fraction* of gas species i in our mixture. The nature of heat transfer ensures that the temperatures of all of the gas species will eventually be equal, even though pressures will not. In fact, the reason the pressures will not be equal is ensured by the constraint the temperatures be equal.

In our atmosphere, we find mostly nitrogen (78%), oxygen (21%), argon (0.93%), carbon dioxide (0.04%), water vapor (0.4-1%), and trace amounts of helium, neon, methane, krypton, and hydrogen. While the climate cannot be perfectly modeled as an ideal gas under all conditions, it is interesting to note that even though gases like carbon dioxide, water vapor, and methane make up a small portion of the gases in our atmosphere and therefore contribute little to macroscopic effects like pressure, they still have a significant impact on global warming, as we will soon see.

2.3.2 Energy Storage

At this point it should be clear that materials can store energy in a variety of manners. We have established that on the atomic scale, particles above absolute zero have some finite kinetic energy, and the collective kinetic energy of a group of particles - its thermal energy or *heat content* - is characterized by its temperature. Because of this relationship, all materials that have mass have the ability to store thermal energy; however, the correlation between temperature and stored energy varies between different substances, and even between different phases of the same substance.

Solids and Liquids

For example, if we take a piece of limestone[28], and somehow transfer a known amount of heat into it, Q, we find that its temperature will increase by some amount, ΔT. In our experiment, we can continue inputting more and more heat, and plot its temperature as a function of the total heat transfer up to a given point, which will look something like the curve in Fig. 2.4. If we do the same thing for quartz[29], the resultant plot will look different.

In short, what our simple experiment shows us is that every substance requires a different amount of thermal energy to raise its temperature by some ΔT. Mathematically, this is stated as

$$Q = C\Delta T \tag{2.26}$$

where C is the substance's *heat capacity* in units of J/K. We can actually compute C for different materials from first principles using quantum mechanics[30], but in practice, the Q-T curve is measured experimentally with the heat capacity given as the curve's *slope*:

$$C = \frac{dQ}{dT} \tag{2.27}$$

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[28] calcium carbonate ($CaCO_3$)

[29] silicon dioxide (SiO_2)

[30] Potentially covered later in this course.

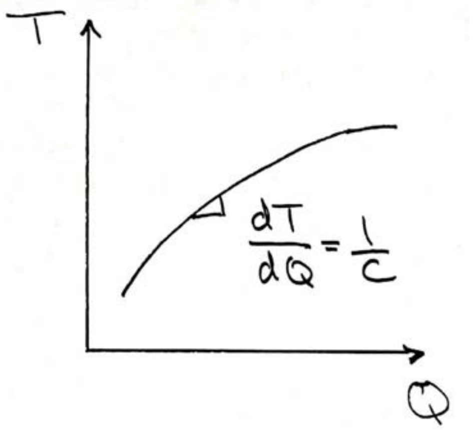

Figure 2.4: T-Q diagram for solids and liquids.

which itself is usually a function of temperature. Fig. 2.4 shows this relationship.

To illustrate the capability of masses to store heat, let us take a look at a quick example. Fig. 2.5 shows a block of mass m sliding across an insulating surface with some friction. The block initially has a velocity v and a temperature of T_1 in state one. If take our control volume as just the block, highlighted in the figure by the dashed red box, its energy in state 1 is given as

$$E_1 = \frac{1}{2}mv^2 + mcT_1 \tag{2.28}$$

and in state 2 after it has come to rest as

$$E_2 = mcT_2 \tag{2.29}$$

where in both Eqs. 2.28 and 2.29, c is the *specific heat* equal to C/m. Using the First Law, we find that

$$\Delta E = E_2 - E_1 = \cancel{Q} - \cancel{W} \tag{2.30}$$

where Q is equal to 0 if we take the surface on which the block slides to be perfectly insulating and ignore any ambient gases, and W is equal to zero since the volume of our control volume does not change throughout this process[31].

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[31] For the block to do work under this framework, the boundary must deform under some force.

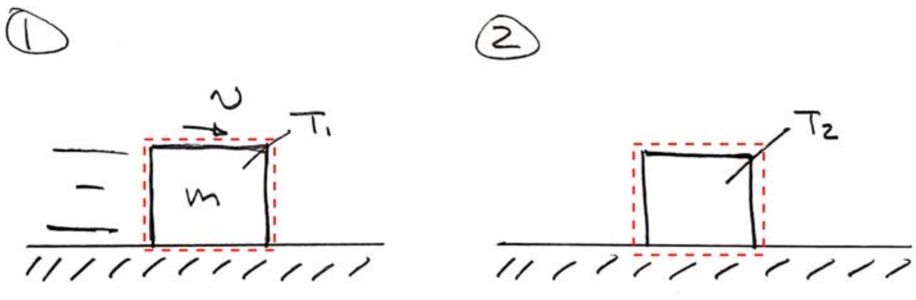

Figure 2.5: Two states for mass sliding on a surface with friction and ultimately coming to a stop.

After combining these equations and doing some rearranging, we can solve for T_2 as

$$T_2 = T_1 + \frac{v^2}{2c} \tag{2.31}$$

which tells us that pure macroscopic kinetic energy transforms into thermal energy via friction.

In our thermodynamic climate system, thermal energy can be stored in this way in both the Earth's landmasses and its many bodies of water. In the real system, this heat comes from a variety of places, including direct solar radiation, thermal energy in the Earth's core left over from its formation, and warming from the atmosphere itself. As Fig. 2.6 shows, the heat content of the Earth's oceans has been steadily rising since the early 1990's, and likely well before then, due to human activity and the greenhouse effect that we will discuss later in Section 2.3.3. This has an impact not just on the climate, but on the weather as well, as energy stored in the ocean supplies power to major storms like hurricanes and typhoons. More energy means storms that are more powerful as well.

Gases

Now while this relationship is straightforward for solids and liquids, gases complicate things. If we do the same experiment we did for limestone but instead used nitrogen gas, the primary component of our atmosphere, for example, the plot of Q vs. T will actually look different depending on whether we keep the volume constant during our experiment or the pressure constant instead. We know from the ideal gas law that a change in temperature must also company a change in either or both its pressure and volume. In the constant volume

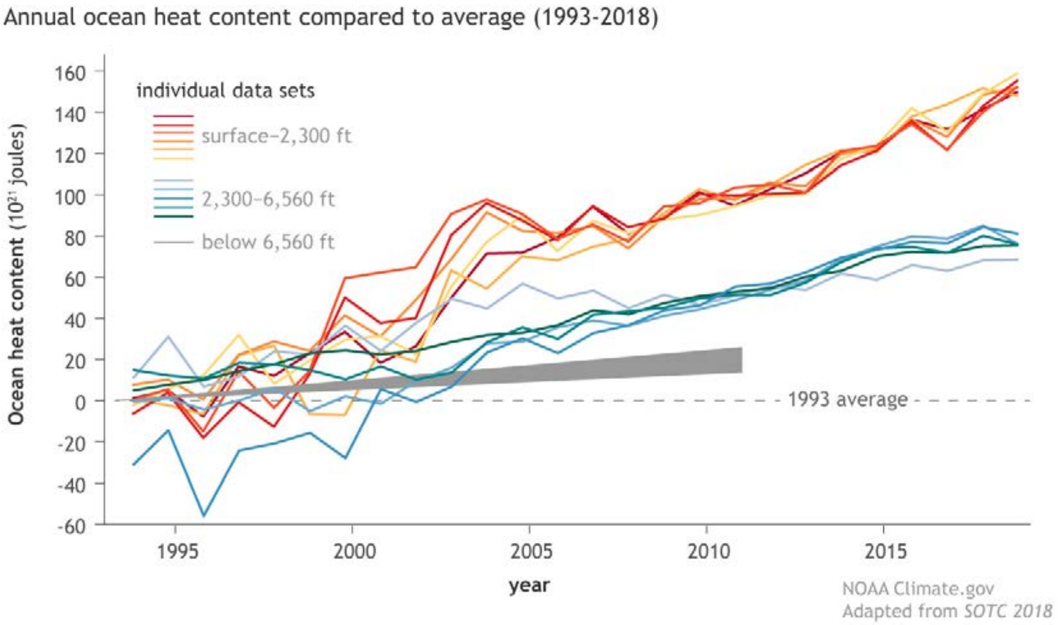

Figure 2.6: Plot of the ocean heat content showing it steadily rising as a result of human activity [NOAA]. Image courtesy of NOAA.

case, all of thermal energy added to the system goes into changing its internal energy and thus its temperature, similar to the solid case. We find that

$$dQ = C_v\, dT \tag{2.32}$$

For the constant pressure case, however, as is described by the ideal gas law, as you increase the temperature of a gas, it will expand if not contained and will do work on its surroundings by Eq. 2.20. Therefore by the First Law, only some of the heat transferred to the system goes into raising the gas's temperature, and the rest goes into mechanical work. For this case

$$dQ = C_p\, dT \tag{2.33}$$

and as we would expect, C_p is always *greater* than C_v since we need more thermal energy to change the gas's temperature by the same amount as compared to the constant volume case. This effect is captured in Fig. 2.7.

We can actually relate C_v to C_p precisely by first considering the constant volume process. Writing the First Law for an incremental change in the state of the gas, we get

$$dU = dQ - dW = dQ - \cancel{P\, dV} \tag{2.34}$$

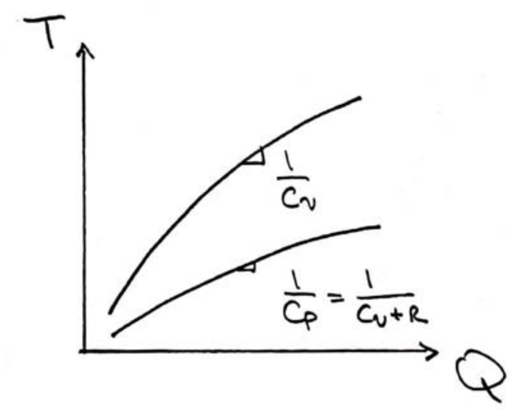

Figure 2.7: T-Q diagram for gas in constant volume (top curve) and constant pressure process.

since there is no change in volume. Here dU is the incremental change in the gas's internal energy. Then substituting the constant volume heat capacity relationship in Eq. 2.32 for dQ yields

$$dU = C_v \, dT \tag{2.35}$$

A subtle but very important point about this equation is that because temperature and internal energy are both state properties (i.e. they do not tell us anything about the history of the substance), this relationship is always valid, regardless of how the gas got to this state. As long as we know its temperature, we know its internal energy. This allows us to write the First Law for the constant *pressure* case as

$$dU = dQ - P \, dV \tag{2.36}$$

and substitute both Eq. 2.35 for dU and Eq. 2.33 for dQ, giving us

$$C_v \, dT = C_p \, dT - P \, dV \tag{2.37}$$

Combining terms and substituting the ideal gas law to eliminate $P \, dV$, we get

$$(C_p - C_v) \cancel{dT} = m\widetilde{R} \cancel{dT} \tag{2.38}$$

giving us the final relationship that

$$\boxed{c_p = c_v + \widetilde{R}} \tag{2.39}$$

where it is important to note that c_p and c_v are the gas's *specific* heats in units of J/kg-K[32], and in practice they are measured experimentally. Also, because it often shows up in calculations, it is useful to define the ratio of specific heats for a gas and give it its own variable, γ, as

$$\gamma \equiv \frac{c_p}{c_v} \tag{2.40}$$

Adiabatic Expansion and Compression

What about processes where both the pressure and volume of the gas change? The First Law still holds of course, but you need to be careful about keeping track of both the heat and work exchanged with the environment during the process. One common case is where a gas expands or contracts without exchanging any heat with the environment in what is called an *adiabatic process*. To model this, we can again start with the First Law:

$$dU = \cancel{dQ} - dW \tag{2.41}$$

since there is no heat transfer. From there, we can substitute our expressions for small changes in internal energy and work, giving us

$$C_v \, dT = -P \, dV \tag{2.42}$$

Substituting in the ideal gas law for dT, applying chain rule, and performing some algebra to rewrite things in terms of γ yields

$$C_v \, d\left(\frac{PV}{mR}\right) = -P \, dV \tag{2.43}$$

$$\frac{c_v}{R}(P \, dV + V \, dP) = -P \, dV \tag{2.44}$$

$$\frac{1}{\gamma - 1}(P \, dV + (\gamma - 1)P \, dV + V \, dP) = 0 \tag{2.45}$$

$$\gamma P \, dV + V \, dP = 0 \tag{2.46}$$

Finally, we divide both sides by PV, separate variables, and integrate:

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[32] $C_p = mc_p$ and $C_v = mc_v$

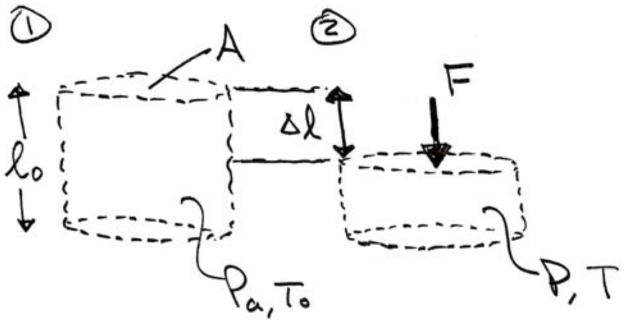

Figure 2.8: Example adiabatic compression problem. Gas is constrained to move in the vertical axis.

$$\gamma \int \frac{dV}{V} = \int -\frac{dP}{P} \tag{2.47}$$

$$\boxed{PV^{\gamma} = const.} \tag{2.48}$$

which means in practice that between two states, 1 and 2,

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \tag{2.49}$$

The ideal gas law can again be used to show that Eq. 2.48 is equivalent to

$$P^{1-\gamma} T^{\gamma} = const. \tag{2.50}$$

and

$$TV^{\gamma-1} = const. \tag{2.51}$$

For this adiabatic expression case, let us pretend for a moment that we can constrain the motion of the gas to one axis with a cross sectional area, A. Starting from atmospheric pressure, P_a, and compressing the gas by some length Δl, we can rewrite Eq. 2.48 replacing P with F/A to yield

$$F = AP_a \left(\frac{l_0}{l_0 - \Delta L} \right)^{\gamma} = AP_a l_0^{\gamma} \left(l_0 - \Delta l \right)^{-\gamma} \tag{2.52}$$

which appears to be a non-linear spring with a spring constant of $AP_a l_0^{\gamma}$. This is important, because where you have springs, you have the capacity for potential energy storage. Indeed, given that no heat is lost to the environment in this adiabatic process, the potential energy stored is simply related to the

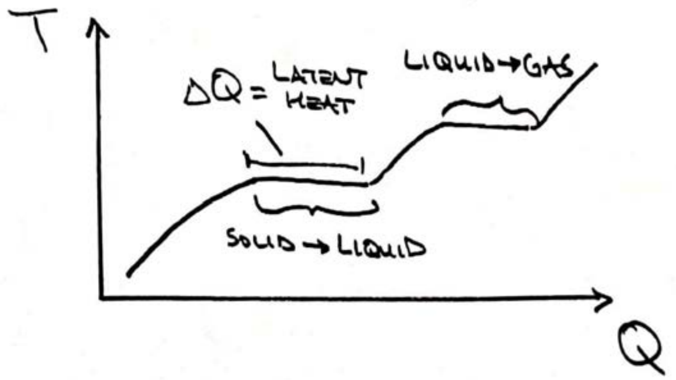

Figure 2.9: T-Q diagram for substance undergoing phase changes. During each phase change, the temperature remains constant.

change in temperature over the compression. We can solve for temperature assuming that it started at T_0 using Eq. 2.51

$$T = T_0 \left(\frac{V_0}{V}\right)^{\gamma-1} = T_0 \left(\frac{l_0}{l_0 - \Delta l}\right)^{\gamma-1} \tag{2.53}$$

giving us a total change in energy via Eq. 2.35 as

$$\Delta U = C_v(T - T_0) = C_v T_0 \left[\left(\frac{l_0}{l_0 - \Delta l}\right)^{\gamma-1} - 1\right] \tag{2.54}$$

So it is now apparent that the gases in the Earth's atmosphere can store energy as thermal energy in multiple ways - via either heat transfer or by physical compression. It turns out, for example, that the expansion of certain gases as they rise in the atmosphere can be roughly modeled as an adiabatic process, giving some predictive power to these equations. Things get more complicated, however, once we start looking at phase changes of substances in our climate system.

Latent Heat

If we take a solid, for example, and continue adding thermal energy to it, we find that its temperature continues to rise until something strange starts happening - its temperature levels off and remains constant as the solid melts into a liquid. Then once as a liquid, the temperature continues to increase again. If we then heat the liquid until it becomes a gas, we find the same thing happening over that transition as well. Fig. 2.9 shows the now familiar Q-T plot for a substance undergoing two *phase changes*, first from solid to liquid and then from liquid to gas.

Interestingly, during each phase change, we can continue to add heat, but the temperature remains constant. This seems to violate the relationships we established previously that relate T to Q via a heat capacity. Indeed, in these regimes, those equations do not hold since heat is being absorbed or released as a result of chemical bonds being formed or broken. This extra energy storage mechanism is extremely important in nature and in the operation of many every-day devices and is called *latent heat* - typically denoted as Δh for reasons that will become clear in later chapters - and is notably different than the *sensible heat* we learned about in the previous section.

At a high level, this mechanism is responsible for one of the major atmospheric temperature feedback loops that helps regulate the Earth's temperature - the Water Cycle. For instance, trees soak up water from the ground through their roots and transport it to their leaves, where it is converted from a liquid to gas via solar-powered *evaporation* and enters the atmosphere. As we see in Fig. 2.9, this process requires that extra heat be taken from the environment, effectively cooling the leaves and their surroundings. This stored heat is then brought up into the atmosphere where the heat is dissipated and the vapor turns back into a liquid to form clouds. Without this cycle transporting heat to the atmosphere where much of it can be dissipated via radiation to outer space, the Earth would be considerably warmer. On Earth, this facet of the cycle is predominantly driven by tropical rainforests, which is one of the many reasons why deforestation, particularly in this region, has such a devastating effect on the climate.

The latent heat of the Earth's many bodies of ice also plays an important role in regulating both atmospheric and oceanic temperatures. Because of the relationship between heat transfer and temperature shown in Fig. 2.9 during a phase change, as more thermal energy is trapped on Earth, as these bodies of ice begin to melt, they help to keep the temperatures in their vicinity roughly constant at their melting point near 0 °C, providing a buffer against short-term excess heating. This is the same principle that drives using ice packs to keep food from spoiling by holding a constant temperature while they melt. Of course, once a majority of the ice melts and turns into liquid water, the temperature will start increasing rapidly again. Currently, we still have a bit of a buffer in the Earth's polar ice caps, but once these are completely melted, coupled with the change in albedo that was previously discussed, temperatures will likely rise much more rapidly than they currently are, further accelerating climate change.

Gravitational Potential Energy

The final form of energy storage we will discuss here briefly, though this list is certainly not exhaustive, comes from the interaction between gravity and substances on Earth - water in particular. Recall that gravitational potential energy on Earth takes the simplified form of

$$U_{gravitational} = mgz \tag{2.55}$$

for small z compared to the radius of the Earth[33]. Here m is some mass, g is the acceleration due to gravity (9.81 m/s^2), and z is the altitude of that mass relative to some reference point. If we look at clouds, for example, the average cumulus cloud can weigh up to 500,000 kg and hovers about 2,000 m above sea level, which gives it nearly 10 *gigajoules* (10^9) of potential energy. For reference, this is 3,000 times the energy deposited by full sunlight in square meter on the Earth's surface over an hour, or 300,000 average cell phone batteries[34].

This water eventually falls back to the Earth as rain, converting its potential energy into kinetic energy then into some thermal energy as it strikes the ground. Rainwater is ultimately transported through the soil and underground aquifers, and the cycle repeats. This process is fundamentally behind all power systems that extract energy from streams or rivers[35]. The water cycle naturally replenishes the stores of potential energy which trickle back out as flowing water.

Finally, a major source of potential energy on Earth, though we will not go into detail about it, is *tidal* energy that results from the orbit of the Moon around the Earth, as well as the Earth around the Sun. As the Moon and Sun "pass over" large bodies of water like the oceans, their gravitational attraction pulls up on that water, literally lifting it up slightly, raising its gravitational potential energy. The immediately observable effect from this phenomenon of course is that water recedes from the shorelines to create the "tides". The release of this water drops its average height, and it flows back towards the shores. While the tides do not move water very quickly, it moves *a lot* of it, and therefore its total kinetic energy can still be very high[36].

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[33] 6,378 km

[34] Electrical potential energy is outside the scope of this text but is very important for modern technologies that help mitigate climate change.

[35] e.g. hydropower dams

[36] In total tides produce about 1 TW of power, compared to the current average human

2.3.3 The Greenhouse Effect

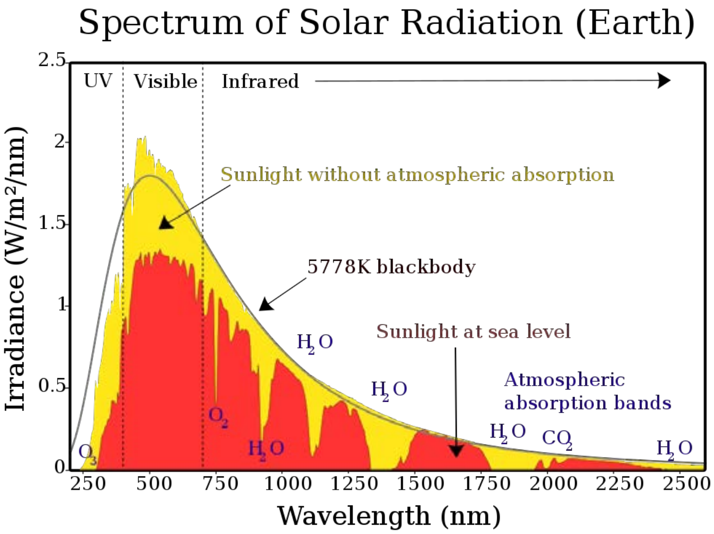

Figure 2.10: The absorption of sunlight by various molecules in the atmosphere. Image courtesy of Robert A. Rohde on Wikimedia. License: CC BY-SA. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

If we take as our thermodynamic system an ideal absorbing and emitting material with some finite mass, the First Law tells us that in *steady state*, the rate of energy coming in must equal the rate of energy going out, otherwise the stored energy would increase indefinitely, which is physically impossible. If we leave a piece of metal painted black out in the sun, indeed we see that its temperature, which is proportional to its internal energy, levels out at some point. Thus

$$\frac{d}{dt}E_{in} = \frac{d}{dt}E_{out} \propto T^4 \tag{2.56}$$

where the time rate of change - $\frac{d}{dt}$ - of energy is called *power* and in the case of thermal radiation is proportional to T^4. In fact, the temperature of our piece of metal will adjust itself to make that statement true given that a higher temperature means more power can be dissipated via radiation as in Eq. 2.9. The Sun bombards the metal with radiation, and as the metal increases in

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consumption of nearly 13 TW.

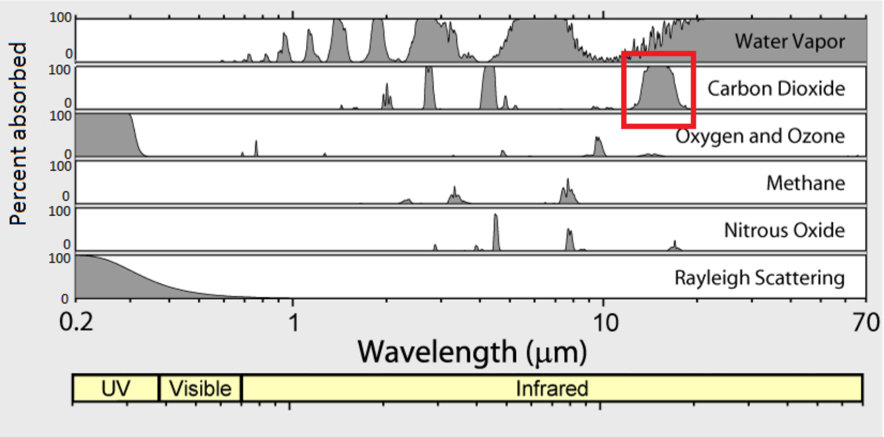

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Figure 2.11: Absorption spectrum of different molecules in atmosphere.

temperature, it releases more and more intense radiation until the outgoing power equals the incoming power.

If we ignore the atmosphere and think of the Earth as being that piece of metal, we can perform this calculation exactly to figure out what the temperature of the surface would need to be to balance the incoming radiation from the Sun. Working through the math, we find that the surface would on average be about -18 °C, far below the actual value of roughly 14 °C and even well below the freezing point of water! Clearly, the atmosphere is doing a lot to keep the planet warm. As we see here, on its own, the Earth is actually very effective at getting rid of this thermal energy.

Indeed, the primary reason that the Earth on average is not a ball of ice, with a couple historical exceptions, is that its atmosphere makes it more difficult for the Earth to reject heat via radiation. Water vapor, carbon dioxide, and methane in particular absorb radiation extremely well in roughly the *infrared* range that the Earth emits it. These gases then radiate some of this heat to space and the rest back to the Earth's surface. At the same time, light coming from the Sun, which is mostly in the *ultraviolet* and *visible* ranges, can pass through these gases mostly unimpeded, as shown in Figs. 2.10 and 2.11. Together these two phenomenon create a joint effect that allows sunlight to enter our control volume very easily but traps the resultant thermal radiation trying to escape. Consequently, going back to Eq. 2.56, the temperature of the system must increase further in order to be able to compensate.

This is fundamentally the driving principle behind anthropogenic climate

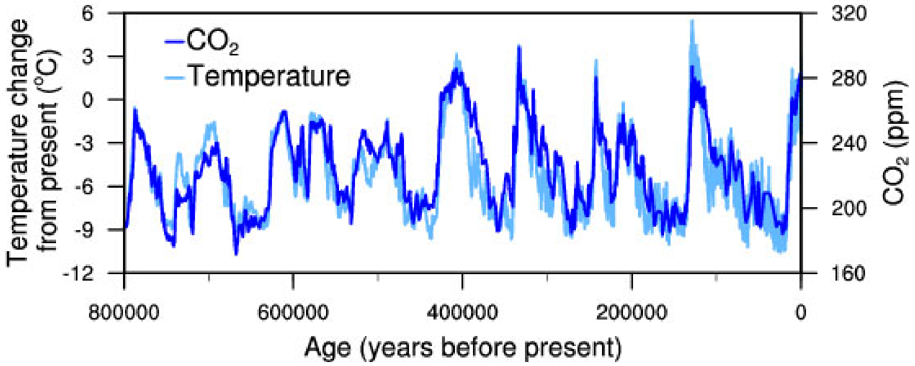

Figure 2.12: Historical carbon dioxide concentration and mean Earth surface temperature. Image courtesy of NOAA.

change. As the concentration of carbon dioxide and methane in the atmosphere increases, the temperature of the entire system must increase as well to balance out the incoming solar radiation. There are many natural feedback loops that help to regulate the amount of carbon dioxide in particular, but when it comes down to it, more carbon dioxide means higher temperatures. For proof of this, Fig. 2.12 shows historically the strong correlation between temperature and carbon dioxide concentrations. As we see from the physics though, they are not just correlated, but increasing CO_2 actually *causes* global warming.

2.4 The Carbon Cycle

So it is that maintaining just the right level of carbon dioxide in our atmosphere is essential for stabilizing the Earth's temperature and therefore its climate - too much and the planet heats up and triggers the many feedback loops that disrupt ecosystems (e.g. albedo reduction from ice melting), but too little and the Earth freezes. The fact that the Earth's climate has been more or less stable over the last *4.5 billion years* is not just luck, though. A stable interplay between the planet's many carbon sources and sinks has kept carbon dioxide concentrations in check all this time. This feedback loop, which itself is regulated in part by atmospheric and oceanic temperatures, is called the *Carbon Cycle*.

In short, carbon is constantly being added to the atmosphere as both carbon dioxide and methane (CH_4) by a variety of *sources*, and at the same time, it is constantly being absorbed by the Earth's many *sinks*. Fig. 2.13 shows the major climate sources and sinks. Recall from Chapter 1 that the Earth's

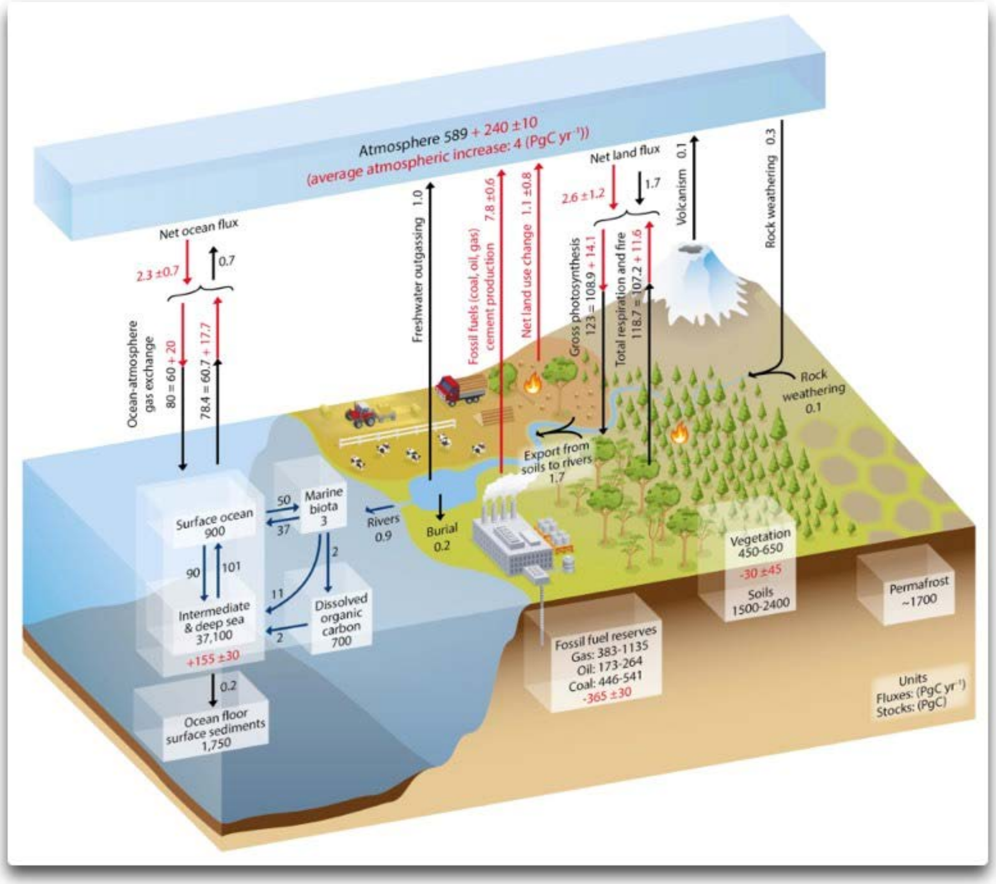

Figure 2.13: Graphical depiction of the carbon cycle [1].

atmosphere started with very high concentrations of CO_2. Over the years as photosynthesizing life developed, this gas was slowly taken out of the air and replaced with oxygen. As these organisms - and later animals that consumed them - died, their carboniferous remains were split between being remitted back to the atmosphere or being buried deep in the Earth over time, where they are much later remitted in volcanic eruptions.

A significant amount of CO_2 is also taken up by the *weathering* of rocks like limestone ($CaCO_3$). CO_2dissolves into water to form carbonic acid (H_2CO_3), which then reacts with dissolved calcium in the water from the weathering process to form more $CaCO_3$ that sinks to the bottom of the ocean. There it is used in the shells of crustaceans or gets slowly subducted into the seafloor, where it is stored. This process in particular is sensitive to temperature - higher temperatures accelerate these weathering reactions, creating a negative feedback loop that helps to take excess carbon out of the atmosphere and regulate its temperature.

Now in the anthropocene, humans are adding CO_2 from the fossilized or liquefied remains of previously living organisms back into the atmosphere at rates that are greater than what would have naturally occurred via volcanism or forest fires. Add the same time, human expansion has been removing forests and other ecosystems that take in CO_2, the net result of which is that on average, more CO_2 is being emitted than can be removed, driving climate change[37].

2.4.1 Warnings From the Past

The natural Carbon Cycle is not perfect of course, and we have geological records of many instances throughout the Earth's history of things getting a bit out of control. For example, in the early stages of life, a significant amount of carbon dioxide was removed and replaced with oxygen, which also resulted in the destruction of atmospheric methane, which has a much higher *global warming potential (GWP)*[38]. Consequently, the Earth cooled significantly, causing much of its water to freeze. It is believed that increased volcanic activity over thousands of years ultimately helped to replenish carbon dioxide levels, restoring livable conditions. So while the Carbon Cycle to date has been robust enough to maintain at least some life over billions of years, its natural feedback cycles can take thousands to millions of years to operate, which certainly puts the present rapid climate change in perspective.

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[37] For more information on the Carbon Cycle see here

[38] a measure of a gas's impact on greenhouse effect relative to CO_2. Methane has a value of about 30, meaning that is 30 times more potent than CO_2.

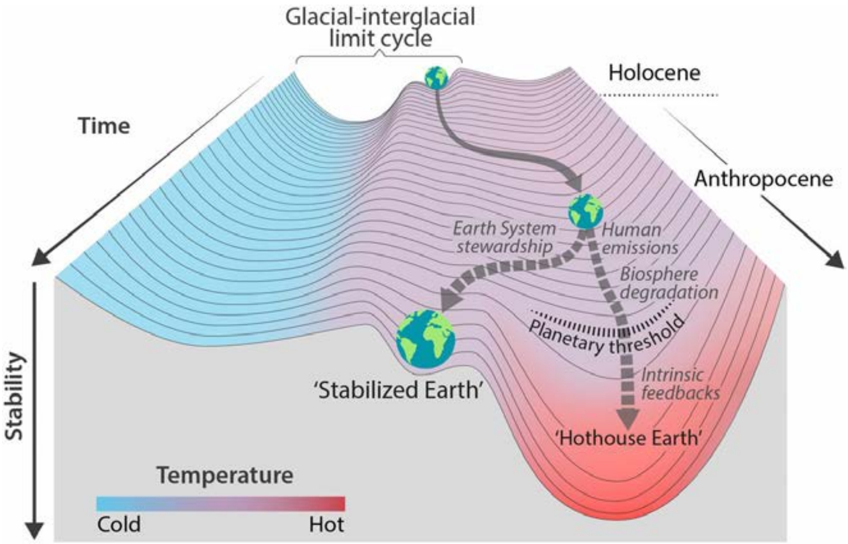

Figure 2.14: Possible states for the Earth's climate, showing the very stable glacial and "hothouse" scenarios [2]. **Image courtesy of Will Steffen, Johan Rockström, et al. "Trajectories of the Earth System in the Anthropocene."** ***PNAS*****. August 6, 2018. 115 (33) 8252–8259.**

Human colonization and development has had dramatic effects on the climate via the Carbon Cycle, and present-day global us is hardy the first time. Thousands of years ago when humans first shifted to massive agrarian societies, the clearing of forests and natural growth to make way for the early farms is thought to have resulted in a slight warming of the Earth due to the atmospheric CO_2 balance being shifted slightly towards excess[3]. In the late 1400's CE, Spanish colonization actually had the opposite effect. As soon as Christopher Columbus arrived in the Americas and began the genocide of the indigenous populations living there, land that had been reserved for farming was left to regenerate, causing more CO_2 to be pulled from the atmosphere, creating a net climate *cooling* effect[4]. This reduction in temperature was to be short-lived, however, as colonization boosted economies in Europe, giving rise to the industrialization that is presently driving climate change.

As a final word of warning, we can also look to other planets in our solar system which we believe at one point had similar environments as the Earth but are now completely uninhabitable - namely, Mars and Venus. Despite it being extremely cold and mostly barren today, Mars once had an atmosphere that likely supported vast amounts of liquid water. Over time however, due to an insufficient rate of CO_2 being added back to the atmosphere and a diminishing magnetic field unable to shield against *solar wind* that strips away particles from the upper atmosphere, the greenhouse effect eventually was

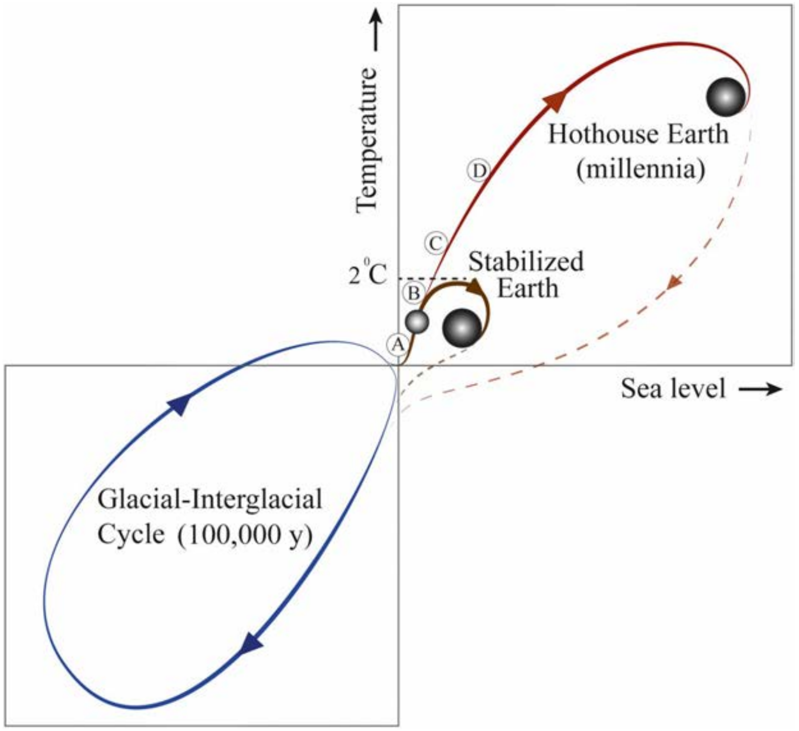

Figure 2.15: Possible trajectories for Earth's climate illustrating the long timescales for the glacial cycles and "hothouse Earth" scenario.

not powerful enough to sustain a habitable environment. On the other end of the spectrum, Venus had the opposite scenario happen, where a runaway greenhouse effect turned its once liquid oceans in water vapor, resulting in temperatures that can reach 462 °C and an atmospheric pressure over 90 times greater than on Earth [5]. It is important to note that the Earth, being in between Venus and Mars in terms of distance from the Sun, may receive a more suitable level of radiation than either of these planets for life in particular, but both planets' fates are indeed still a possibility here.

Scientists have hypothesized, in fact, that the Earth's current climate stability may be in such a precarious position now. As Figs. 2.14 and 2.15, a "hothouse Earth" scenario can occur in which a climatological tipping point is passed, creating a runaway greenhouse effect much like what happened on Venus. This possible scenario is incredibly stable, meaning that feedback loops we previously discussed all support the temperature increasing. As a result, it would take thousands of years to regulate naturally and return to cooler conditions [2]. Up to this point, this scenario has largely been avoided, and thus we are inching closer to an unprecedented global warming event.

2.5 Summary

The First Law of Thermodynamics describes the balance of energy in a system, precisely relating incoming and outgoing energy to the change in the stored energy within. For our thermodynamics climate system, this law tells us very plainly that the energy coming in from the Sun via radiation must eventually exit as radiation or else the amount of energy stored within - and thus the temperature - must increase. As we saw with thermal radiation, the higher a body's temperature, the more heat it can dissipate in this way, thus allowing some stable equilibrium temperature to be reached. Over billions of years the First Law has worked in concert with Earth's Carbon Cycle to maintain atmospheric and oceanic temperatures that are suitable for life. Energy is constantly being stored, transformed, and transported via many different modes, but the net effect is a stable balance on average. Disrupting these natural cycles, which took millions of years to establish, can have disastrous results on the climate, possibly leading the planet to similar conditions as the hothouse Venus or cold and barren Mars. With the burning of fossil fuels and destruction of natural carbon cycles, we are currently testing these limits - we will soon see just how we got to this point and the thermodynamics behind that as well.

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Chapter 3

Controlling Fire

Up until this point in our story, we have been primarily concerned with the "natural" world - a world situated within a universe whose underlying physics appear to obey the First Law of Thermodynamics. In Chapter 2 we learned about how this law applies to the Earth's climatological system via a number of *constitutive* relationships between the system's various properties (e.g. ideal gas law), and how over millions of years, these relationships guided the evolution of the many ecosystems that comprise the climate in a delicate balance between incoming solar energy and internal energy - and thus global temperature.

One key constraint of this "natural" world, whose timeline spans the majority of the Earth's 4.5 billion year history, has been that organisms only consume the energy that is immediately available to them. Chemosynthetic organisms derive their energy from hydrothermal vents, photosynthetic organisms from the sun, herbivores from these organisms, and the food chain continues up through the *apex predators* at the top. Looking back down the chain from the perspective of one of these top predators like a megalodon or velociraptor, as far removed as we seem from the initial source of energy, we are truly not far removed from the source *temporally*. Indeed, the time between when some phytoplankton first used solar energy to convert CO_2 into sugar and when the thing eats the thing that ate the thing that ate the thing...that ate the phytoplankton is on the order of months to years - instantaneous compared to the rate of the Carbon Cycle, which operates over millions of years.

As a result of these extremely disparate timescales, the Earth's natural feedback loops were able to drive not just the evolution of the climate as it pertains to temperature, atmospheric compositions, etc., but even life as well. For instance, when early photosynthetic life began to explode in numbers, it quickly and dramatically altered the composition of the atmosphere, leading to a climate cooling event that resulted in major glaciation, freezing much of the oceans and slowing the expansion of life. The balance swung back and forth between rapid growth and swift climatological resistance, each time getting less severe as ecosystems became more diverse and therefore more robust to change. Over billions of years, this rhythm, whose tempo was set largely by the constant influx of solar radiation, shaped the Earth. More importantly, this harmonious relationship between energy and growth prevented the system from going too far in either direction, as had happened with Venus for instance.

This leads us to the advent of the "unnatural" world almost 2 million years ago when humans discover they can control fire. At this precise moment, life became no longer bound to using energy that arrived at the Earth via sunlight over just the previous month or year. Instead, burning branches from a felled tree releases tremendous amounts of solar energy stored over hundreds to potentially thousands of years. Burning coal left over from the Carboniferous period in the Paleozoic era 300 million years ago or oil from the Mesozoic Era 100 million years ago releases solar energy stored over millions of years - now comparable to the rate of Carbon Cycle itself. With the control over fire - and later ambivalence to natural signals that something was awry - came the relinquishing of control over the natural tempo that had reliably guided the planet's development up to that point[1].

Just as thermodynamics explains the goings on of the "natural" world, it also governs the physics of the "unnatural" world, which should be the case since the only difference between the two is of sociological and cultural construction. The physics is exactly the same. As such, we will spend this chapter delving into the thermodynamics of fire and some of the consequences of heat transfer to various substances. We will learn about the chemistry of combustion, including concepts like enthalpy, heating values, and adiabatic flame temperature. Finally, will we conclude this chapter with a few related concepts and some of the early uses of fire to relate the concepts back to climate change and foreshadow what is to come.

3.1 Combustion

As before, it will help us to define a few terms. First, *fire* and *combustion* refer to the same phenomenon - a rapid and *exothermic* chemical process that releases heat via *oxidation*. An oxidation reaction is simply one in which an element or molecule loses electrons and has nothing intrinsically to do with

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[1] see Bill McKibbon's *End of Nature* for a now slightly outdated but still insightful discussion of this concept

oxygen, other than the fact that oxygen is a very common *oxidizer*. Water, for instance, is also a strong oxidizer that is responsible for rusting, another type of oxidation reaction.

Combustion, however, mainly refers to hydrocarbons or metals reacting exothermically with oxygen. For example, plain elemental carbon[2] will react with oxygen via the following reaction:

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)} \tag{3.1}$$

releasing a significant amount of heat in the process. This reaction in particular, releases roughly 33 megajoules of heat per kg of carbon. Notice that the carbon here is just a single atom - it has no chemical bonds to break to release that energy; however, the CO_2 product has less energy in its bonds than the oxygen has in its own, giving the pure carbon a potential energy of sorts. The reason for this will become evident later.

The reaction in Eq. 3.1 is typical of hydrocarbon combustion in general and as a quick aside about chemical equation notation, reads "one mole of carbon reacts with one mole of oxygen to produce one mole of carbon dioxide"[3]. We call this type of reaction *complete* hydrocarbon combustion in which all of the carbon in the *reactants* ends up in carbon dioxide in the *products*. CO_2 is *fully oxidized*, meaning that no more energy can be extracted from it. In fact if want to break those bonds, we must put energy back into it. This is exactly what happens in photosynthesis, with the energy coming from the Sun.

Hydrocarbons can also undergo partial or *incomplete* combustion where instead of producing CO_2, the reaction produces the intermediate, carbon monoxide (CO). With our pure carbon example, this looks like

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)} \tag{3.2}$$

and is also exothermic, but does not release as much heat as the reaction in Eq. 3.1 since CO has a slightly higher *energy state* than CO_2. We can subsequently combust CO via

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)} \tag{3.3}$$

to release the additional heat. If we measure and sum the heat released in Eqs. 3.2 and 3.3 it will exactly equal that released in Eq. 3.1.

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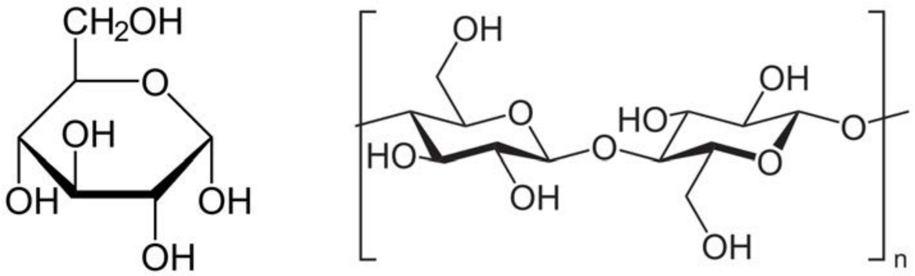
[2] graphite or coal

[3] In the majority of the chemical equations we look at in this text, mass is conserved. Therefore we must have the same number of moles of each element on either side of the arrow.



Glucose Cellulose

Figure 3.1: Molecular structure of glucose ($C_6H_{12}O_6$) and cellulose ($C_6H_{10}O_5$).

And so this notion of potential energy again arises in which a substance gives us the ability to create an exothermic reaction with a widely available oxidizer, releasing net energy in the form of heat. This becomes additionally evident if we look at where pure carbon or coal comes from on Earth. Let's start with a molecule of CO_2 in the air, which is happily floating around in its lowest possible energy state - it will remain as is if left untouched[4]. Chloroplasts in photosynthesizing organisms take this CO_2 and react it with water to produce a long chain of carbon, hydrogen, and oxygen called *glucose* via the following reaction:

$$6\,CO_{2(g)} + 6\,H_2O_{(l)} \longrightarrow C_6\,H_{12}\,O_{6(aq)} + 6\,O_{2(g)} \tag{3.4}$$

where because glucose ($C_6H_{12}O_6$) is in a higher energy state, this reaction requires energy be added, in this case via solar radiation.

Some of this sugar is consumed (oxidized) by the plant for its own energy needs, releasing some carbon back out as CO_2, while the rest is stored in molecules like cellulose, a complex *organic*[5] compound with repeating base units of $C_6H_{10}O_5$. After this organism dies and begins to decompose, over time, some of the carbon contained in these molecules turns into methane gas (CH_4)[6] and CO_2, and under the right conditions, the remainder gets pushed deep underground. Over millions of years, the heat and pressure underground provides additional energy to these molecules, slowly breaking more and more bonds until just pure carbon is left. So to recap from an energy perspective, CO_2 in a low energy state was brought to progressively higher potential energy states, first via input energy from the sun and then from geothermal energy

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[4] ignoring quantum effects for now

[5] any molecule comprised of some combination of carbon, hydrogen, and oxygen.

[6] see the end of the chapter for more about this process

deep in the Earth's crust. One can imagine the final carbon product as a ball pushed up a hill, waiting for oxygen to come along and knock it back down, converting that potential energy back into heat. From a time perspective, what took millions of years to process is undone in an instant via combustion.

In all of these combustion reactions, there is some *activation energy* required for the combustion to begin. In the ball on the hill example, there is a slight bump in that keeps the ball from easily rolling back down. In combustion, the energy required to overcome this bump typically comes from thermal energy, and the hotter the environment, the more likely individual particles have enough thermal (microscopic kinetic) energy to kick off a chain reaction. Most substances therefore have an *autoignition temperature* above which the reaction is likely to spontaneously ignite. Dry wood for example will nearly immediately ignite above 427 °C.

3.1.1 Combustion Stoichiometry

In nature, the majority of combustion that occurs - including the early fires set by humans - involves the reaction of a hydrocarbon with air. Oxygen is the oxidizer in these reactions but only comprises about 21% of air by mass. The primary component is nitrogen, comprising 78% of air by mass, with the rest made up of trace amounts of several other gases. A good model for combustion is to lump these other gases together with nitrogen, giving us the general *ideal* hydrocarbon combustion stoichiometric equation:

$$\mathrm{C}_x\mathrm{H}_y + z\,(\mathrm{O}_2 + 3.77\,\mathrm{N}_2) \longrightarrow x\,\mathrm{CO}_2 + \frac{y}{2}\mathrm{H}_2\mathrm{O} + 3.77\,z\,\mathrm{N}_2 \tag{3.5}$$

whose coefficients ensure that mass is conserved across the reaction. As a result, z, for this ideal case can be solved for explicitly as

$$z = x + \frac{y}{4} \tag{3.6}$$

Similarly, for alcohols or carbohydrates, which contain complex molecules of carbon, hydrogen, and oxygen, the ideal general combustion equation is given by:

$$\mathrm{C}_x\mathrm{H}_y\mathrm{O}_z + \beta(\mathrm{O}_2 + 3.77\,\mathrm{N}_2) \longrightarrow x\,\mathrm{CO}_2 + \frac{y}{2}\mathrm{H}_2\mathrm{O} + 3.77\,\beta\,\mathrm{N}_2 \tag{3.7}$$

where

$$\beta = x + \frac{y}{4} - \frac{z}{2} \tag{3.8}$$

Metal oxidation reactions are typically much simpler and involve a pure, *reduced* metal and oxygen reacting to form that metal's oxide. For example, aluminum and air react to form aluminum oxide by the following reaction:

$$2\,\mathrm{Al} + 3\,(\mathrm{O_2} + 3.77\,\mathrm{N_2}) \longrightarrow 2\,\mathrm{Al_2O_3} + 11.31\,\mathrm{N_2} \tag{3.9}$$

While these examples show ideal combustion stoichiometry, in reality there are many other molecules that can be made with carbon, hydrogen, and oxygen, for example, than just CO_2 and H_2O. Specifically in hydrocarbon or alcohol combustion, the reaction products also typically include carbon monoxide (CO) and hydrogen (H_2) as well. Thus, in pure oxygen, for example, the actual reaction equation might look like

$$\mathrm{C}_x\mathrm{H}_y + zO_2 \longrightarrow a\,\mathrm{CO_2} + b\,\mathrm{CO} + c\,\mathrm{H_2O} + d\,\mathrm{H_2} \tag{3.10}$$

where we can relate the stoichiometric coefficients a, b, and c to x and y by applying conservation of mass to the carbon, hydrogen, and oxygen respectively to find

$$a + b = x \tag{3.11}$$

$$2c + 2d = y \tag{3.12}$$

$$2a + b + c = 2z \tag{3.13}$$

Notice here that given $x, y,$ and z we have 3 equations but 4 unknowns: a, b, c, d. We can gain additional information from knowing that some CO will react with additional oxygen or with water vapor to form carbon dioxide and hydrogen, but will need some additional chemistry knowledge to determine the proportions.

3.1.2 Chemical Kinetics

Most chemical reactions can go both ways under the right conditions, and in fact, many naturally occurring chemical reactions do. In general, such a reaction can take the form

$$a\,\mathrm{A} + b\,\mathrm{B} \rightleftharpoons c\,\mathrm{C} + d\,\mathrm{D} \tag{3.14}$$

where the double arrows indicate that A and B can react for form C and D and vice versa. If we were to zoom in on the molecules during this reaction, we would find that both the *forward* reaction, where C and D are the products, and the *backward* reaction, where A and B are the products, are actually happening at the same time. From chemistry, though, we know that depending on the compounds and the temperature and pressure of the reaction, one of these reaction is happening more often than the other, skewing the concentrations[7] accordingly.

For the forward reaction in this general case, we observe that the time derivative of the concentration of the products is proportional to some constant, k_f - which is a function of temperature - multiplied by the concentration of both the reactants such that:

$$\frac{d[\mathrm{C}]_f}{dt} = ck_f(T)[\mathrm{A}]^a[\mathrm{B}]^b \tag{3.15}$$

and similarly for the backward reaction:

$$\frac{d[\mathrm{C}]_b}{dt} = -ck_b(T)[\mathrm{C}]^c[\mathrm{D}]^d \tag{3.16}$$

where the exponents come from the fact that a moles of A, for example, means we need to multiple the concentration of A by itself a times.

Because the forward and backward reactions are happening simultaneously, the net rate of change of [C] is the sum of these two rates, equal to

$$\frac{1}{c}\frac{d[\mathrm{C}]}{dt} = k_f(T)[\mathrm{A}]^a[\mathrm{B}]^b - k_b(T)[\mathrm{C}]^c[\mathrm{D}]^d \tag{3.17}$$

We also know that mass must be conserved, and by the stoichiometry, if this rate changes by some factor, λ, so too must the rate of change of the other species, each scaled by their stoichiometric coefficient. Expressed mathematically,

$$\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = \frac{1}{b}\frac{d[\mathrm{B}]}{dt} = -\frac{1}{c}\frac{d[\mathrm{C}]}{dt} = -\frac{1}{d}\frac{d[\mathrm{D}]}{dt} \tag{3.18}$$

In thermodynamics, however, we mainly care about what happens in equilibrium - when the time derivatives of all the individual species' concentrations go to zero. Thus, in equilibrium we can set the left-hand side of Eq. 3.17 to zero and rearrange to find that

$$\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = \frac{k_f(T)}{k_b(T)} \tag{3.19}$$

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[7] as used here, *concentration* has units of mass per volume

It is important to note that we could have started with the time derivative of any of the species' concentrations per Eq. 3.18 and gotten the same expression.

If all of our reaction species are ideal gases, which is often the case in combustion reactions, we can relate the concentration of species i to its mole fraction, X_i, which is the number of moles of the species divided by the total number of moles, in the solution by the following:

$$[i] = \frac{n}{V} X_i = \frac{P}{RT} X_i \tag{3.20}$$

where the second equality is derived by substituting in the ideal gas law. Using this relationship, we can rewrite Eq. 3.19 as

$$\frac{X_{\mathrm{C}}^c X_{\mathrm{D}}^d}{X_{\mathrm{A}}^a X_{\mathrm{B}}^b} \left(\frac{P}{RT}\right)^{(c+d)-(a+b)} = \frac{k_f(T)}{k_b(T)} \tag{3.21}$$

and divide both sides by $(\frac{P_0}{RT})^{(c+d)-(a+b)}$ to get

$$\frac{X_{\mathrm{C}}^c X_{\mathrm{D}}^d}{X_{\mathrm{A}}^a X_{\mathrm{B}}^b} \left(\frac{P}{P_0}\right)^{(c+d)-(a+b)} = \left(\frac{RT}{P_0}\right)^{(c+d)-(a+b)} \frac{k_f(T)}{k_b(T)} \tag{3.22}$$

where the right hand side of this is defined as the temperature-dependent *equilibrium constant*:

$$k_p(T) \equiv \left(\frac{RT}{P_0}\right)^{(c+d)-(a+b)} \frac{k_f(T)}{k_b(T)} \tag{3.23}$$

giving us our final relationship:

$$\boxed{\frac{X_{\mathrm{C}}^c X_{\mathrm{D}}^d}{X_{\mathrm{A}}^a X_{\mathrm{B}}^b} \left(\frac{P}{P_0}\right)^{(c+d)-(a+b)} = k_p(T)} \tag{3.24}$$

or in the general case:

$$\frac{\prod_{i=1}^{n_p} X_i^{\nu_i}}{\prod_{i=1}^{n_r} X_i^{\nu_i}} \left(\frac{P}{P_0}\right)^{\left(\sum_{i=1}^{n_p} \nu_i - \sum_{i=1}^{n_r} \nu_i\right)} = k_p(T) \tag{3.25}$$

where ν_i is the stoichiometric coefficient for species i, n_p is the number of product species, and n_r is the number of reactant species.

This principle that the environmental conditions can shift the balance of concentrations in a chemical reaction is known as *Le Chatelier's Principle*. It is highly useful because if we know the equilibrium constant, the pressure at which it was calculated, P_0, and the pressure that reaction occurs at, we have another expression that relates the equilibrium concentrations for this reaction. Combined with our earlier combustion example, this gives us the final equation we need in an addition to the mass conservation equations to solve our problem, as we will soon see.

In practice, the equilibrium constant $k_p(T)$ is a function of temperature derived from experimental data and is specific to every reaction. Because there are too many chemical reactions that *can* occur, instead of tabulating this value for each reaction, it is instead computed from species-specific constants tabulated for every commonly used substance such that

$$\log_{10} k_p(T) = \sum_{i=1}^{n_p} \nu_i \log_{10} k_{p,i}(T) - \sum_{i=1}^{n_r} \nu_i \log_{10} k_{p,i}(T) \tag{3.26}$$

which is written in this form as the equilibrium constants for each species are typically tabulated as $\log_{10} k_{p,i}(T)$. These values can also be found in NASA or JANAF data.

Going back to our incomplete combustion example, recall that we needed an additional equation to determine the concentrations of the products. Again, the reaction in question is

$$\mathrm{C}_x\mathrm{H}_y + zO_2 \longrightarrow a\,\mathrm{CO}_2 + b\,\mathrm{CO} + c\,\mathrm{H_2O} + d\,\mathrm{H}_2 \tag{3.27}$$

but we know that CO, H_2O, CO_2, and H_2 can undergo an additional two-way reaction called the *water-gas shift reaction* such that

$$\mathrm{CO} + \mathrm{H_2O} \rightleftharpoons \mathrm{CO}_2 + \mathrm{H}_2 \tag{3.28}$$

Using our equilibrium constant equation for Eq. 3.28, we get the final equation needed to solve for the concentrations of the products in Eq. 3.27. If we have $n_p = a + b + c + d$ total moles, the mole fraction for each species is simply the stoichiometric coefficient for that species in Eq. 3.27 divided by n_p. Plugging this into Eq. 3.25 and noting that n_p will cancel out in the numerator and denominator, we get

$$\frac{cd}{ab}\cancel{\left(\frac{P}{P_0}\right)^{(1+1)-(1+1)}} = \frac{cd}{ab} = k_p(T) \tag{3.29}$$

where k_p is computed from the individual given species equilibrium constants using Eq. 3.26.

3.2 Enthalpy

To help us quantify the amount of heat released in these combustion reactions, it is helpful to define a quantity called the *enthalpy* of a substance. Enthalpy, H, is defined simply as

$$H \equiv U + PV \tag{3.30}$$

and while this definition may seem arbitrary, we can work it into our differential First Law equation to see its utility. Writing the law and then adding $d(PV)$ to both sides:

$$dU = dQ - dW \tag{3.31}$$

$$d(U + PV) = dQ - P\,dV + d(PV) \tag{3.32}$$

noting that $U + PV$ is our enthalpy, H, as defined in Eq. 3.30. This gives us

$$dH = dQ - \cancel{P\,dV} + \cancel{P\,dV} - V\,dP \tag{3.33}$$

If we look at just constant pressure processes - of which many combustion processes are - for the time being, we find can also set dP to zero giving us the final relationship that

$$dH = dQ \tag{3.34}$$

Therefore, for a constant pressure process the change in enthalpy tells us directly how much heat is absorbed or released. Enthalpy in fact has units of energy. Substituting Eq. 2.33 into Eq. 3.34 for dQ gives yields

$$dH = C_p\,dT \tag{3.35}$$

where C_p is the heat capacity at constant pressure.

3.2.1 Enthalpy of Formation

As we saw with the carbon combustion example, some net potential energy is transformed into thermal energy in the formation of CO_2. This heat is given by Eq. 3.34 as the change in enthalpy between the products and the reactants:

$$Q = \Delta H_{reaction} = H_{products} - H_{reactants} \tag{3.36}$$

which for this example is equal to -393.5 kJ/mol carbon at 300K. The negative sign here means that heat is *released* (i.e. the reaction is exothermic). In general, the change in enthalpy for reactions like this one that produce a single species is called the *enthalpy of formation* or *heat of formation*, denoted as ΔH_f, and in reality is a function of temperature since C_p is a function of temperature as we learned in Chapter 2. If the reaction occurs at 298.15 K, we refer to it as the *standard* enthalpy of formation, ΔH_f°.

An important point to make here is that enthalpy is a state variable and property, but because it also represents a *transfer* of heat, it is a *relative* quantity. That is, it is defined in relation to some reference value that we all agree on, usually specified at 298.15 K. This allows us to measure and tabulate the changes in enthalpies of commonly used substances as functions of temperature. Also to make the math easier, these enthalpies are defined such that single elements or molecules with multiple of the same element - C, O_2, N_2, etc. - have an enthalpy of exactly 0 J/mol at 298.15 K. If we take care to reference all species in our reactions at the same temperature, these will cancel out on both sides. For reactions that incur a temperature change, however, this cancellation cannot be made.

To illustrate this, let us look at a more complex reaction - the combustion of methane, which occurred naturally in the early Earth atmosphere when photosynthesizing plants came on the scene and began releasing massive amounts of oxygen and is thought to have caused the first major ice age. This reaction occurs as follows:

$$\mathrm{CH_4 + 2\,O_2 \longrightarrow 2\,H_2O + CO_2} \tag{3.37}$$

where now because we are combusting a *hydro*carbon, we also get water as a byproduct. For this reaction, we can write the change in enthalpy for this reaction accounting for the reference values as

$$\Delta H_{reaction} = (2\Delta H_f^{H_2O}(T_2) + \Delta H_f^{CO_2}(T_2)) - (\Delta H_f^{CH_4}(T_1) + 2\Delta H_f^{O_2}(T_1)) \tag{3.38}$$

where T_1 and T_2 are the temperatures of the reactants and products respectively and may not be equal. The factors of 2 in Eq. 3.38 come from applying the *stoichiometric* coefficients in Eq. 3.37[8]. For each of the enthalpies of formation for those compounds, which again are all functions of temperature. To compute ΔH_f, we can look to literature to find equations that model each individual enthalpy of formation for these various compounds. NASA, for

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[8] We did the same thing with the carbon reaction equation, but the coefficients were all 1.

example, has polynomial fits for the majority of elements and combustible compounds [1]. If we work out these numbers, we find that the combustion of one mole of methane at 300 K releases 890 kJ. Note that this reaction releases more than double the heat of the carbon reaction and produces the same amount of CO_2.

It is also important to emphasize that because c_p is a function of temperature, enthalpy is also a function of temperature, and sometimes only the enthalpy of formation at standard temperature and pressure is provided from experimental data. If we also know the heat capacity at constant pressure, however, we can compute the enthalpy at the new temperature via

$$H = \sum_i n_i \left[\Delta h^\circ_{f,i} + \int_{T_0}^{T} c_{p,i}(T) dT \right] \tag{3.39}$$

where the lowercase variables indicate a *specific*[9] quantity. Notice that this comes directly from integrating Eq. 3.35 with the appropriate initial conditions. Note that the same can be done for internal energy, yielding:

$$U = \sum_i n_i \left[\Delta u^\circ_{f,i} + \int_{T_0}^{T} c_{v,i}(T) dT \right] \tag{3.40}$$

which is required for characterizing combustion at constant volume instead. For these processes, the heat of reaction is the change in internal energy as was previously shown in Chapter 2.

3.2.2 Enthalpy of Phase Change

Because combustion often involves the phase change of some substance - typically from liquid to gas - it is important to understand how thermal energy is transferred as *latent heat* during this process. Because phase change is a *constant pressure* process in many cases, especially the ones that concern our work in this course, the latent heat can be often characterized using enthalpy. Just as before, the heat transfer is represented by a difference in enthalpy between the final state and initial state, though this time the states represent different phases of matter. From liquid to gas, for which we will use the subscripts f and g respectively as is common practice, this latent heat is given as

$$\Delta h_{fg} = h_g - h_f \tag{3.41}$$

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[9] per mass

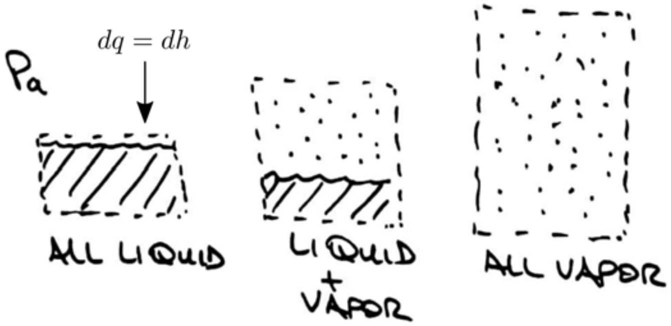

Figure 3.2: A vaporization process at constant pressure. As heat is added, the control volume expands to encapsulate the vapor such that the total system remains at constant pressure P_a.

which is typically called the *latent heat of vaporization*. The *latent heat of fusion* from solid to liquid is similarly given as

$$\Delta h_{sf} = h_s - h_f \tag{3.42}$$

As before, these are all quantities that are measured experimentally and given as functions of temperature. For some substances, this latent heat can be substantial, resulting in a significant energy transfer throughout the process and must therefore be carefully included in analyses. For example, the latent heat of vaporization for water at 100 °C is 2.3 MJ/kg, while its latent heat of fusion at 0 °C is only 334 kJ/kg. This is one of the many reasons why an atmosphere like Venus is so stable - it requires a lot of energy to condense water vapor, but not nearly as much energy to melt ice.

3.2.3 Liquid-Vapor Equilibrium

With the discovery of fire and the subsequent control of *heat*, early humans now had the ability to turn ice into liquid water and liquid water into steam. The latter involves the incredibly important phenomena of *evaporation* and *boiling*, which are both fundamentally *vaporization* - turning liquid into gas. The opposite process of turning gas into liquid is called *condensation*. As discussed previously, at the molecular level, if enough heat is absorbed by molecules at the surface of a liquid, they can be liberated from the bonds that are holding them together in liquid phase, which in the case of water molecules are *hydrogen bonds*. Conversely, gas molecules near the surface of a liquid of the same species can reject heat, reducing their kinetic energy to where they

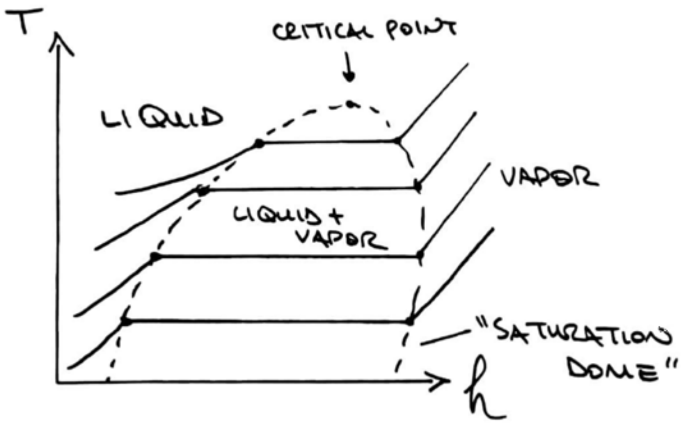

Figure 3.3: Multiple evaporation curves at different constant pressures are plotted on a T-h plot, showing that the points at which liquid begins to turn into vapor lie on the left side of the dotted curve, called the *saturation* or *vapor dome*. Under the dome, both liquid and vapor can exist, and to the right of the dome, only vapor can exist. The width of the dome at a particular pressure is exactly h_{fg}, the latent heat of vaporization.

can join the liquid phase. In reality, both processes are happening simultaneously, and there are several factors that determine whether net vaporization or condensation is occurring.

First, if we look at a constant pressure vaporization process, as we incrementally add heat dq - the heat per unit mass of substance - to a pure liquid, as we would expect, the liquid at first will increase in temperature until at some point the temperature remains constant and the phase change starts to take place. As the change from liquid to gas phase continues, the temperature and pressure remain constant[10] as more molecules are liberated from the liquid surface until finally all of the liquid is turned to gas and the temperature continues to rise. We discussed this process in Chapter 2 as a means of storing heat and showed in Fig. 2.9 the progression of the temperature of the system as a function of the heat added. Since for a constant pressure process, $dq = dh$ as we showed here, this plot is equivalent to same process plotted on T-h axes, as shown in Fig. 3.3.

We can go one step further and plot the constant-pressure temperature-enthalpy curves for vaporization occurring at different pressures, also shown in Fig. 3.3 as the solid curves. As we can see, both the points at which the

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[10] We assume here that this process happens slowly such that the temperature and pressure are always uniform throughout the control volume.

vaporization starts to occur and finishes changes as the pressure increases. If we connect these points with a curve, we get what is called the *vapor* or *saturation dome*, shown in this figure as the dashed curve. In this *phase diagram*, to the left of the dome, the substance only exists in liquid phase, under the dome the substance exists in both liquid and vapor phase, and to the right of the dome, only vapor phase can occur. Above the highest point of the dome, which is called the *critical point*, the substance exists as a *supercritical fluid* for which all of the properties - density, specific enthalpy, internal energy, etc. - of both the liquid and vapor phases are identical and thus cannot be told apart. From our definition of the latent heat, h_{fg}, we can see directly from this plot that the width of the dome at a particular constant pressure curve[11] is exactly $h_g - h_f = h_{fg}$.

During the vaporization process, under the saturation dome there can exist both liquid and vapor phases in equilibrium, which can make analysis of this process a bit more difficult. To characterize how much of the substance has been vaporized in a particular state, we define the *vapor quality*, x, defined as

$$x \equiv \frac{m_{vapor}}{m_{vapor} + m_{liquid}} \tag{3.43}$$

which is the ratio between the mass of the substance in vapor phase to the total mass of the substance across both phases. This allows us compute the total enthalpy - and all other state properties - at a given point under the dome as

$$h = xh_g + (1-x)h_f \tag{3.44}$$

If we look at the change in enthalpy between where the substance is pure vapor ($x = 1$) and pure liquid ($x = 0$), we get

$$\begin{aligned} \Delta h &= [1 * h_g + \cancelto{0}{(1-1)} * h_f] - [0 * h_g + (1-0) * h_f] && (3.45) \\ &= h_g - h_f && (3.46) \\ &= h_{fg} && (3.47) \end{aligned}$$

which is to be expected. Similarly, the total *specific volume*[12], v, is given as the quality-weighted sum of the specific volumes of the substance in gas and liquid phases - v_g and v_g respectively - as

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[11] called an *isobar* which we will explore in detail later

[12] volume per mass equal to $1/\rho$

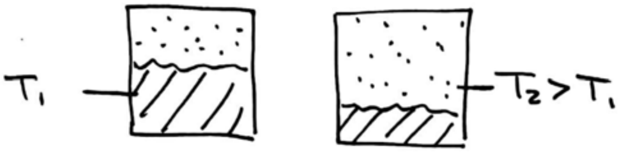

Figure 3.4: A constant volume vaporization process where both the temperature and pressure increase as more liquid is vaporized. Note that at every state, the vapor and liquid phases must be in equilibrium with one another.

$$v = xv_g + (1 - x)v_f \tag{3.48}$$

If we know the total volume and the values for v_g and v_f at a given temperature, we can solve for the quality.

Finally, we can look at vaporization at constant volume to get a sense for the relationship between the temperature and pressure in the two phase region, represented on the T-h plot in Fig. 3.3 under the saturation dome and on the T-P plot in Fig. 3.5 as the *saturation curve*. It can be shown that the relationship between temperature and pressure in this regime - T_{sat} and P_{sat} respectively - obeys the following expression:

$$\frac{dP_{sat}}{dT_{sat}} = \frac{h_{fg}}{T_{sat}(v_g - v_f)} \tag{3.49}$$

which is called the *Clausius-Clapeyron* relation. Typically the density of the vapor phase of a substance at temperatures and pressures reasonably below the critical point is much less than the density of the liquid phase density at those same conditions. Thus, in that case, $v_f << v_g$, and Eq. 3.49 can be simplified as:

$$\begin{aligned} \frac{dP_{sat}}{dT_{sat}} &\approx \frac{h_{fg}}{T_{sat}v_g} && (3.50)\\ &\approx \frac{h_{fg}}{T_{sat}\left(\frac{RT_{sat}}{P_{sat}}\right)} && (3.51)\\ &\approx \frac{h_{fg}P}{T_{sat}^2 R} && (3.52) \end{aligned}$$

or

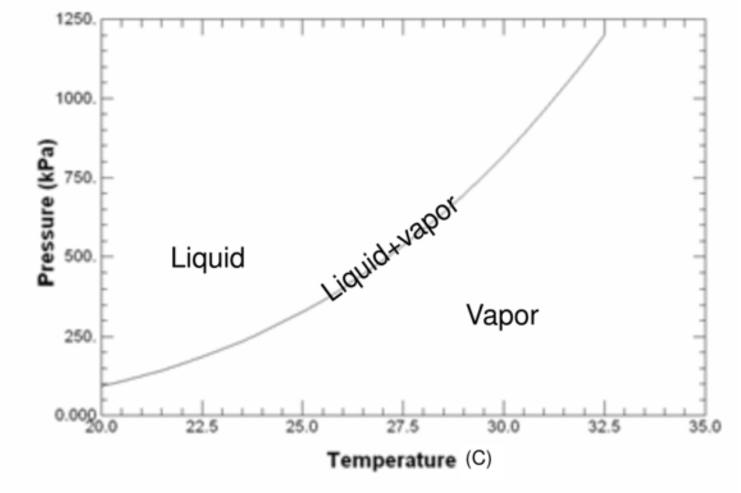

Figure 3.5: Pressure-temperature phase diagram for water. The curve represents the line on which both liquid and vapor can coexist and is typically called the *saturation curve*.

$$\frac{dP_{sat}}{P_{sat}} \approx \frac{h_{fg}}{R}\frac{dT_{sat}}{T_{sat}^2} \tag{3.53}$$

$$\int \frac{dP_{sat}}{P_{sat}} \approx \int \frac{h_{fg}}{R}\frac{dT_{sat}}{T_{sat}^2} \tag{3.54}$$

$$\ln P_{sat} \approx -\frac{h_{fg}}{RT_{sat}} + C \tag{3.55}$$

$$\Rightarrow P_{sat} \approx e^{-\frac{h_{fg}}{RT_{sat}}+C} \tag{3.56}$$

where C is some integration constant. This equation is often modeled from experimental data as the following:

$$\log_{10} P_{sat} = A - \frac{B}{C + T_{sat}} \tag{3.57}$$

where A, B, and C are tabulated for different substances in different temperature ranges. This expression is called the *Antoine Equation*. Fig. 3.5 shows an example of this curve plotted for water.

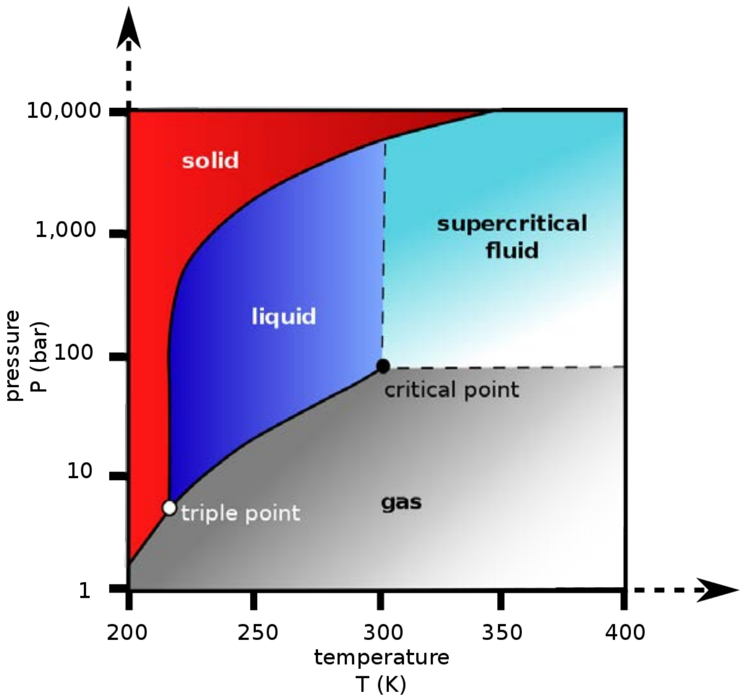

Figure 3.6: Generalized phase diagram for a pure substance.

Raoult's Law

These equations were all derived for a *pure* substance containing only one species. For a mixture, however, we have the simple expression - which closely mirrors Dalton's Law - that relates the total vapor pressure, $P_{sat,total}$, to the individual vapor pressures as

$$P_{sat,total} = \sum_i P_{sat,i} \tag{3.58}$$

where $P_{sat,i}$ is the vapor pressure of of species i in the mixture and is given as

$$P_{sat,i} = X_i P^{\circ}_{sat,i} \tag{3.59}$$

where X_i is the mole fraction of species i and $P^{\circ}_{sat,i}$ is the vapor pressure of the pure species. Note that an *ideal mixture* is one in which this law is obeyed, but that is not always necessarily the case.

3.2.4 Gibbs Phase Rule

Stepping back and looking at the two-phase equilibrium conceptually, these expressions for the saturation pressure and temperature tell us that for a closed volume containing both liquid and vapor phases of a substance, the temperature alone can tell us the pressure in the volume and vice versa. Recall that for an ideal gas, in order to nail down the total state, we need to know two of the state properties: (v, P, T). But if both liquid and gas are present, the state collapses to a single P-T curve. The number of variables required to fully describe a thermodynamic state is called the *degrees of freedom*, and is given by the *Gibbs Phase Rule* as

$$F = (\#\text{ Species}) - (\#\text{ Phases}) + 2 \tag{3.60}$$

where F is the number of degrees of freedom of the system.

So for an ideal gas with one species, we have $F = 1 - 1 + 2 = 2$ as we know. For our two phase equilibrium, $F = 1 - 2 + 2 = 1$, which again is to be expected. For an ideal gas mixture, we know that the total pressure is given by the sum of the individual partial pressures and so would expect we need an additional variable, the mole fraction, to fully describe the system. Indeed, for this case, $F = 2 - 1 + 2 = 3$. In general, the number of phases present can be determined by the phase diagram for a species. A generalized phase diagram is shown, for example, in Fig. 3.6.

3.3 Fuels

With this basic understanding of fire and combustion and how heat is released from combustion reactions and can interact with other surrounding substances, we can begin talking about combustible materials - wood, coal, oil, etc. - as *fuels*. Fuels have a several properties that facilitate calculations involving the energy they contain and, more importantly, their impact on climate change.

3.3.1 Heating Value

Now that we can compute the concentrations of combustion products for even incomplete combustion reactions where not all of the carbon in the reactants goes into CO_2, we can figure out precisely how much heat is released in the reaction using what we learned earlier about taking the difference in enthalpies of products and the reactants. As should be familiar by now, this *heating value* is also a function of whether the combustion is constant volume or constant pressure and the phases of the products. Also, by definition, the heating values presented as follows are given for ideal stoichiometric combustion reactions, though a non-ideal reaction heat release can be computed in the same way.

First, in Section 3.2.1, we showed that for constant pressure processes, the change in enthalpy is equivalent to the heat released in the reaction. This heat release is called the heating value at constant pressure and per unit mass is given by

$$q_p(T) = -\left[\sum_i (n_i \Delta h_{f,i}(T))_P - \sum_i (n_i \Delta h_{f,i}(T))_R\right] \tag{3.61}$$

where the negative sign ensures that q_p is positive for exothermic reactions. For constant volume processes, the heating value at constant volume per unit mass is given by

$$q_v(T) = -\left[\sum_i (n_i \Delta u_{f,i}(T))_P - \sum_i (n_i \Delta u_{f,i}(T))_R\right] \tag{3.62}$$

In nature, forest fires burning in the open or the combustion of methane in the atmosphere, for instance, are well-described as constant pressure processes.

Additionally, any combustion reaction that produces water - which includes all hydrocarbon, carbohydrate, and alcohol combustion reactions - has what are called a *lower heating value* (LHV) and *higher heating value* (HHV), which depend on the phase of the produced water. The LHV is the value that assumes all of the water generated is in vapor form, and thus the sensible heat released is lower as a significant amount of heat is contained within that phase change. Conversely, the HHV assumes that water produced is in liquid form, resulting in a greater quantity of sensible heat. As we saw earlier, the latent heat of water can be substantial and thus these values differ by a non-negligible amount. Methane, for example, at constant pressure has a LHV of 50.1 MJ/kg and a HHV of 55.6 MJ/kg. In reality, the actual heating value for the combustion of methane will fall between these values. In general, constant pressure combustion tends to be closer to the lower heating value as the conditions are not suitable to maintain liquid water.

3.3.2 Adiabatic Flame Temperature

As discussed in detail in Chapter 2, there is a fundamental difference between heat and temperature - though they are closely related. In the previous section, we learned about the heat associated with fire and combustion, but how can

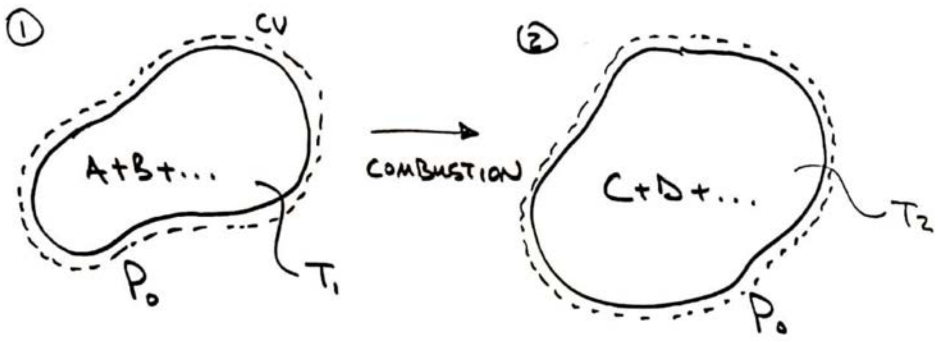

Figure 3.7: Constant pressure adiabatic flame temperature. No heat is transferred from the control volume but the control volume may do some work on the environment.

we define the temperature of such a reaction? The answer as we would expect is complex and depends precisely on the ambient conditions of the reaction, in particular how much other "stuff" is present to absorb the thermal energy. That said, we can compute an upper bound for the temperature if we assume all of the heat is contained within the reaction products themselves.

Because no heat is transferred in our idealized combustion reaction, we call this maximum temperature that can be achieved the *adiabatic flame temperature*. To compute this first for the constant pressure case, whose CV is given in Fig. 3.7, we start with the First Law:

$$\Delta U_{CV} = \cancel{Q} - W \tag{3.63}$$

where we are given that $Q = 0$. Substituting our definition for enthalpy as before, we find that

$$\Delta H_{CV} = H_2 - H_1 = 0 \tag{3.64}$$

and thus that

$$\sum_i (n_i h_i(T_2))_P = \sum_i (n_i h_i(T_1))_R \tag{3.65}$$

which says that the enthalpy of the products must equal that of the reactants across the reaction. Because the products are different species than the reactants and therefore have different individual enthalpies, T_2 - the adiabatic flame temperature - must increase to satisfy Eq. 3.65. This is represented graphically on the H-T plot in Fig. 3.8. Typically, this problem must be solved numerically with a computer as the functions for h can be highly non-linear.

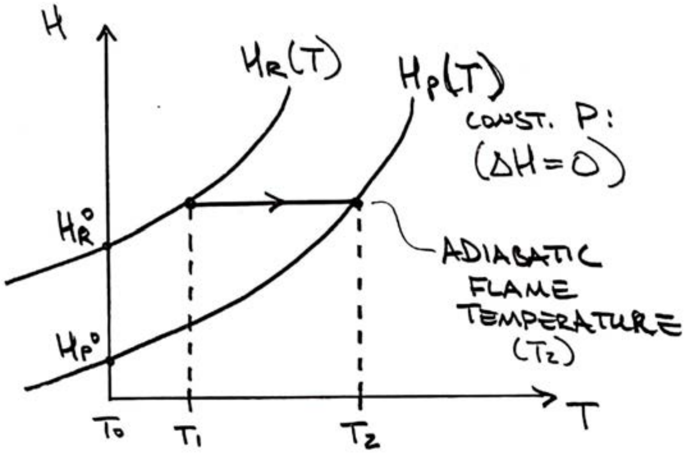

Figure 3.8: Adiabatic flame temperature (T_2 here) for constant pressure combustion.

Similarly, for the constant volume combustion case, we can start with the First Law, noting this time that because the volume of the control volume does not change over this process, there is no work done.

$$\Delta U_{CV} = \cancel{Q} - \cancel{W} \tag{3.66}$$

and thus that

$$\Delta U_{CV} = U_2 - U_1 = 0 \tag{3.67}$$

$$\sum_i (n_i u_i(T_2))_P = \sum_i (n_i u_i(T_1))_R \tag{3.68}$$

from which we can solve for T_2 numerically if we have functions for the internal energy of the products and reactants as functions of temperature. Fortunately, these values and values for $h_i(T)$ are typically available for most common species involved in combustion [13]. As with the constant pressure case, the constant volume combustion process can be represented graphically on a U-T plot as shown in Fig. 3.9.

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[13] There are so many data on combustion reactions due to the work of NASA and the US Air Force in trying to figure out rocket propellants and jet fuel.

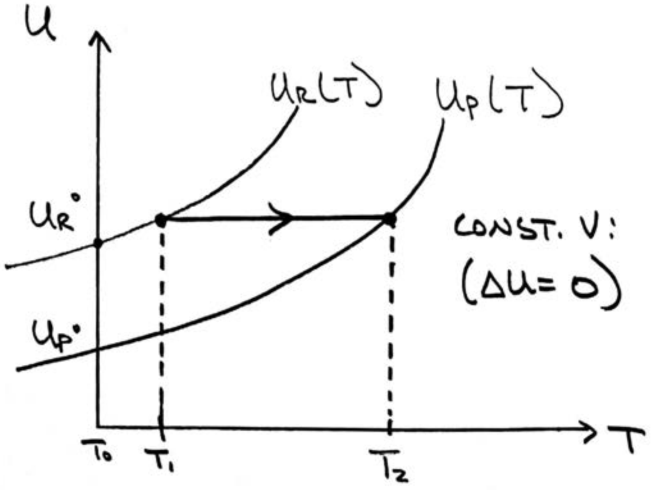

Figure 3.9: Adiabatic flame temperature (T_2 here) for constant volume combustion.

3.3.3 Carbon Intensity

The control of fire has come at the cost of a climate destabilized by the associated carbon emissions. We can quantify the carbon footprint of various fuels using the notion of *carbon intensity*[14]. While this value can be defined in several ways, we will define here as the mass of carbon dioxide produced per unit of thermal energy released. As an upper bound, the carbon intensity, $I_{\mathrm{CO_2e}}$, is approximately

$$I_{\mathrm{CO_2}} = \frac{m_{\mathrm{CO_2}}}{q_{p \text{ or } v}} \tag{3.69}$$

and in general is bounded by

$$\frac{m_{\mathrm{CO_2}}}{\mathrm{HHV}} < I_{\mathrm{CO_2}} < \frac{m_{\mathrm{CO_2}}}{\mathrm{LHV}} \tag{3.70}$$

where $m_{\mathrm{CO_2}}$ is the mass of carbon dioxide emitted per unit mass of fuel.

Looking at ethanol[15] combustion at constant pressure, for example, it will react ideally with oxygen by the following:

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[14] also called *emission intensity*

[15] a naturally occurring alcohol produced in the *fermentation* of corn and other starchy vegetables

Table 3.1: Carbon intensities of common fuels

Fuel	Carbon intensity [$gCO_2/MJ_{thermal}$]
Wood	115
Peat	106-110
Coal	88-94
Oil	73
Ethanol	63-70
Methane (natural gas)	51-68

$$C_2H_5OH + 3\,O_2 \longrightarrow 2\,CO_2 + 3\,H_2O + \Delta H_f(T) \tag{3.71}$$

From this equation, we see that 2 moles of CO_2 are produced per mole of ethanol combusted, which is equivalent to 1.87 gCO_2/g ethanol. Working out the enthalpies for each of the products and reactants yields a LHV of 26.8 kJ/g and a HHV of 29.8 kJ/g, giving us an ideal carbon intensity between 63-70 gCO_2/MJ. For comparison, some common carbon intensities are given in Table 3.1.

3.4 Related Concepts

While "combustion" involves the breakdown of organic molecules using an oxidation reaction, there are other similar processes that either differ in the direction of heat transfer or in the usage of oxygen in the reaction. We will briefly discuss a few of the most common related concepts here.

3.4.1 Anaerobic Digestion

The combustion of an organic molecule requires that oxygen be used to break it apart - however, it is often possible break the same molecule down in the absence of oxygen. Glucose, for example, can be decomposed *anaerobically*[16] via:

$$C_6H_{12}O_6 \longrightarrow 3\,CO_2 + 3\,CH_4 \tag{3.72}$$

which occurs in specially evolved bacteria called *methanogens*. This reaction is exothermic, which you can verify experientially by noticing that compost -

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[16] in the absence of oxygen

decaying plants and vegetables - is warm to the touch. Instead of being full broken down, however, considerable potential energy remains in the methane product of this reaction, as it can later be oxidized further by oxygen.

This reaction happens extremely frequently in nature due to the ubiquity of these bacteria. For example, this process occurs in the digestive tract of termites, which are capable of breaking down complex sugars in wood. In fact, termites alone are responsible for 1-3% of global methane emissions. In reality, they produce much more than this initially, but much of this methane gets oxidized to CO_2 inside the termite mounds before being released into the atmosphere [2]. Cows and other mammals that eat cellulose-rich plants as the majority of their diet also emit significant amounts of methane from their digestive processes. Consequently, global meat consumption has a significant impact on the climate, accounting for nearly 40% of human-activity-related methane emissions [3].

3.4.2 Hydrolysis

Hydrolysis is another anaerobic process capable of breaking down carbohydrates and even metals. Such a process is simply defined as an oxidation reaction that uses water as an oxidizer. In nature, this reaction is also extremely common and is often a precursor to digestion that occurs in living organisms. For example, many plants naturally produce sucrose ($C_{12}H_{22}O_{11}$), a *disaccharide* molecule containing both glucose and fructose and what is commonly referred to as table sugar. In order for other organisms to metabolize this sucrose into the more readily usable glucose, this molecule must first be split apart. This process occurs in digestion via hydrolysis.

The reaction of metals with water to produce hydrogen and a hydrated metal oxide - a process colloquially referred to as *rusting* or *corrosion* - is another example of hydrolysis. In general, this reaction can be carried out via:

$$2\,\mathrm{M}_{(s)} + 2\,\mathrm{H_2O}_{(l)} \longrightarrow 2\,\mathrm{M}^{+}_{(aq)} + 2\,\mathrm{OH}^{-}_{(aq)} + \mathrm{H}_{2(g)} \tag{3.73}$$

where M represents a generic alkali metal. Aluminum will also react with water via

$$2\,\mathrm{Al}_{(s)} + 4\,\mathrm{H_2O}_{(l)} \longrightarrow 3\,\mathrm{H}_{2(g)} + 2\,\mathrm{AlO(OH)}_{(aq)} \tag{3.74}$$

which is highly exothermic. Given the high abundance of aluminum on earth and its high energy density, it is potentially ideal energy storage mechanism[17] [4].

3.4.3 Pyrolysis

Many organic compounds when heated in the absence of oxygen will decompose in a process called *pyrolysis* whereby all volatile compounds like water are driven off and hydrogen and oxygen atoms are liberated, repeatedly breaking long carbon chains into smaller ones. This process is responsible in nature for turning dead plant matter into coal. In fact, most of the coal used today was formed over millions of years from plants that were once alive during the carboniferous period. As the plants decayed and their sugars were pushed deep underground, the high pressures and temperatures in the Earth's crust over time degraded these carbohydrates into nearly pure carbon.

3.4.4 Liquefaction

Liquefaction or *hydrothermal liquefaction* is a process that functions like pyrolysis but in reverse. Instead of converting complex organic molecules into charcoal, biomass is instead turned into even longer hydrocarbon chains under high pressure and temperature conditions. In nature, the crude oil and its derivatives that humanity has been burning for a couple centuries now, was formed as decaying biomass - mainly from algae and zooplankton that lived millions of years ago - got buried deeper and deeper in sediment at the bottom of large bodies of water. Under the intense pressure and in the presence of water, the carbonaceous remains of these critters reacted with water to form long chains of carbon, hydrogen, and oxygen. This added thermal and pressure work greatly increases the energy content of the original fuel [18].

3.4.5 Gassification

The final related concept to look at here briefly is *gassification*, which utilizes the reaction of elemental carbon with carbon dioxide to produce carbon monoxide by the following equation:

$$\mathrm{C} + \mathrm{CO_2} \longrightarrow 2\,\mathrm{CO} \tag{3.75}$$

---

[17] though current carbon emissions associated with its reduction process currently limit its utility as a carbon-neutral storage mechanism.

[18] for more information see *catagenesis*

which can then be reacted with water to recover the carbon dioxide and produce hydrogen gas via the previously discussed water-gas shift reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{3.76}$$

It is important to note here that not all of the carbon monoxide can be converted to carbon dioxide here, and thus this is not nearly a carbon-neutral process in practice. Also, if we look at the change in enthalpy across reaction 3.75, we find that this process is endothermic, requiring an input of heat equal to 173 kJ/mol carbon at 600 K. Typically, the heat required for this reaction comes from the burning of additional coal.

3.5 Early Uses for Fire

In our story of climate change, the discovery of fire - or more accurately, the ability to set fires - marked a new era of energy usage for life on Earth. Despite the long-term consequences of consuming stored solar energy in organic matter faster than it could be replenished, fire provided great utility to early hominids. First, fire simply provided warmth, allowing humans to greatly expand their reach into territories that were previously too cold to survive in. This also allowed permanent settlement to be established as they no longer had to migrate with the seasons. Additionally, fire could be used to ward off predators that previously created too hostile of an environment for survival.

In these early settlements, fire was also used to prepare land for what was to eventually become organized agriculture. The early humans likely found that burning large swaths of forests and other areas of dense growth was a convenient way to clear the land for farming. With farming came additional breakthroughs in diet and food preparation. The ability to cook food and purify water in particular reduced risks of infection and disease, and it also allowed for food to be stored for greater periods of time. The once hunter-gatherers were transitioning into farmers, and the control of fire played a significant role in that shift.

3.6 Summary

In this chapter we looked at the chemistry and thermodynamics behind fire - one of the key tools used by early humans to transform their evolution, expansion, and ultimately their world and climate. Fire (*combustion*) describes a wide variety of reactions between organic molecules or even metals and oxygen.

The heat produced in these reactions at constant pressure can be expressed as the change in enthalpy between the products and reactants. More generally, the enthalpy is an important thermodynamic properties derived from the sum of the more fundamental internal energy and the product of the substance's pressure and volume. Similarly, for constant volume combustion, the change in internal energy can be used to quantify the heat released.

We then looked at the stoichiometry of common combustion processes, including how various hydrocarbons can be oxidized to varying degrees of completion. To that end, we also learned about reaction equilibria to give us the tools necessary to determine the equilibrium concentrations of the products, allowing us to accurately determine the heats of reaction under different environmental conditions.

With an understanding of the basic chemistry underlying combustion, it is then possible to discuss substances as potential fuel sources[19]. We saw how these substances could be characterized by their heating value and carbon intensity - how much thermal energy is released relative to the quantity of carbon dioxide produced in the process. In this way, we can begin to quantify the impact of human development on the climate in terms of their production of greenhouse gases. As we will soon see, burning these fuels can be used to power mechanical work with the advent of the engine, providing additional motivation to keep producing such gases.

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[19] The desire to look around and ask which of these things can be used as fuel is eminently human.

Fiorenzo Piccioli Cappelli, Edward H. Cabezas-Garcia, Johanna Vilkki, Cesar Pinares-Patino, Kateřina O. Fliegerová, Jakub Mrázek, Hana Sechovcová, Jan Kopečný, Aurélie Bonin, Frédéric Boyer, Pierre Taberlet, Fotini Kokou, Eran Halperin, John L. Williams, Kevin J. Shingfield, and Itzhak Mizrahi. A heritable subset of the core rumen microbiome dictates dairy cow productivity and emissions. *Science Advances*, 5(7):8391–8394, 7 2019.

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Chapter 4

Entropy and a Move Towards Chaos

In the timeline of our Big History, the age of humans spans an incredibly short stretch of time - just 2 million years. And within that time period - which is bookended on one side by the discovery of fire and on the other with the present day - the age of industrialization and the ensuing *anthropocene* spans only the past 200 years, whose brevity in the greater context is almost unimaginable. Yet the impact of industrialization, for all its seeming transience, has left its permanent mark on the Earth's climate. In what might have otherwise been a natural cooling cycle for the planet driven by the slight precession of Earth's axis of rotation [1], we instead find the average global temperature continually increasing as a result of increasing carbon dioxide concentrations in the atmosphere. We know now for certain that this bolstering of the greenhouse effect is directly caused by human activity, but how did we get here?

In this chapter, we will begin to answer this question by diving deeper into the thermodynamics of the "unnatural" world - in particular, the physics underlying the breakthroughs that have enabled virtually everything wonderful and terrible in our modern societies. We will first develop an understanding of the conversion between thermal energy and mechanical work and the limitations therein posed by the Second Law of Thermodynamics. Next we will introduce the concept of *entropy*, a fundamental physical quantity crucial to understanding engines and all other types of thermodynamic cycles that represents a move towards not just chaos and disorder, but to equilibrium as well. As we will see, the move towards a more chaotic equilibrium is one that is difficult or impossible to undo under certain conditions. Finally, we will begin to discuss the relationship between this increase in entropy and the work required to undo it to help explain both the quantity of anthropogenic greenhouse gas emissions and why it is so difficult to remove them from the atmosphere, further compounding the issue.

4.1 Coupled Thermodynamic Systems

We have spent the better part of this book up to this point discussing energy and the many ways it can be converted from one form to another. While the delineations between certain forms of energy arise from fundamental differences in physical phenomena - for example gravitation potential energy vs. chemical potential energy - others represent only a difference in perspective and scale. In particular, we have shown that what we consider to be thermal energy is really the average kinetic energy of an ensemble of particles, and the reason for differentiating between the two is mainly for practical purposes. We simply cannot measure the kinetic energy of 10^{23} or so particles, but we can rather easily measure their *temperature*. Similarly, at the macro scale, momentum transfer from individual kinetic particles to the some external object results in net energy transfer via mechanical work. Again, instead of keeping track of the momentum exchange of the individual particles, we can define the emergent property of *pressure* to better facilitate our understanding and analysis.

To expand upon this relationship, we can make a further distinction between the ways in which thermal energy and mechanical work can be exchanged. First, an *uncoupled* thermodynamic system is one in which mechanical energy can be converted into thermal energy but not vice versa. For example, a block sliding on a horizontal (i.e. normal to gravity) surface with friction will slow down, and its temperature will increase as a result. This *dissipative* process cannot happen in reverse, however - no matter how much heat we add or remove from the block, we cannot change its macroscopic kinetic energy. In this case, the block and surface together form an *uncoupled* system in which heat transfer alone cannot be used to apply external mechanical work.

Gases on the other hand can expand predictably when heated as we know from the ideal gas law. In this way, the addition of thermal energy to our gas system can directly result in mechanical work as done by the integral of $P\,dV$, depending on the mechanical constraints of the system. Conversely, if we do work to compress a gas *adiabatically* - no heat transfer to its surroundings - for example, its temperature will increase. We call such a system a *coupled* thermodynamic system, as mechanical and thermal energy can just as easily transform from one to the other in either direction. In reality, all substances change in volume when heated, but for solids and liquids, this effect is often minimal enough for the work done in the expansion or contraction to be

Figure 4.1: An aeolipile, which is considered to be the first engineered coupled thermodynamic system that converts thermal to mechanical energy. Virtruvius first described this device in the first century BCE. **This image is in the public domain**.

ignored, especially compared to that of a gas for the equivalent heat transfer. To provide some context for our story of climate change, the discovery and subsequent engineering of coupled systems by humans dates back two thousands years to ancient Egypt, where as discussed in Chapter 1, it was discovered that heating water in a partially enclosed container creates high-velocity water vapor at its opening that can be directed in such a way as to cause the container to rotate. Fig. 4.1 shows an illustration of this early device - called an aeolipile - which was primarily used as a parlor trick in its early conception. In this coupled system, the fluid that enables this coupling - in this case the water vapor - is called the *working fluid*. It was not for another 1500 or so years that this concept would be formalized as a *heat engine* and applied for the purpose of generating power.

4.2 Processes and Cycles

Before diving into specifics about heat engines and their many related devices, we need to first reiterate a few concepts and terms, as well as define several more to frame our understanding. First, recall that a thermodynamic *process* represents some transfer or series of transfers (e.g. heat or work) that takes

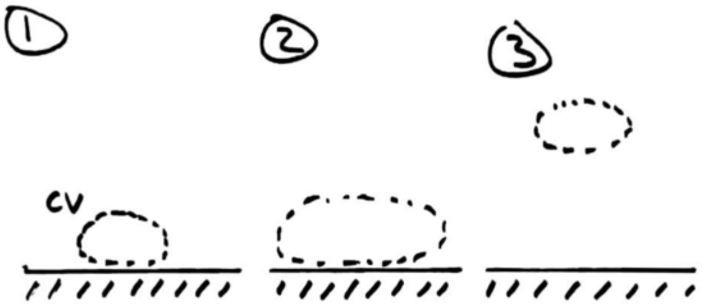

Figure 4.2: Example process of parcel of air being heated by Earth's surface, expanding, rising, and cooling.

a thermodynamic *system* through a series of *states*. We can characterize the system at each state using *state properties* that do not depend on the history of the system (e.g. temperature, enthalpy, internal energy, pressure, etc.).

For example, if we look at a 1 kg parcel of air at T_0 near the Earth's surface, which is at some elevated temperature $T_s > T_0$ due to solar radiation, the air will expand, rise, cool, and contract, as shown in Fig. 4.2. At any given time, the state of this parcel can be given by properties like temperature, pressure, volume, density, enthalpy, and internal energy. We can pick two of these properties and plot the process as a function of those properties. For this example, Fig. 4.3 is a sketched *property plot* that shows this process on T-V axes. States 1, 2, and 3 are represented as points on this plot and the transitions between them as curves with arrows indicating process directions. As indicated here, those transitions are driven by heat and work transfer to and from the environment. In reality, if we zoom in on the lines, we would actually find an infinite number of points representing individual states; however, if we know the constitutive relationship between the state variables for each leg of the process, we can abstract away those points as members of a known curve. This abstraction allows us to focus on the states that are perhaps more relevant to our system or at least easier to nail down (e.g. the initial or final states).

In our air parcel example, because we know that our state transition curves are actually made up of infinitely many individual states, even though the gas is expanding and moving, we can think of it as being *quasistatic*. That is to say, in between adjacent states on the plot, the system reaches internal *equilibrium* briefly before moving onto the next state. For an ideal gas, this means at every instance, the properties are *homogeneous* (uniform) throughout

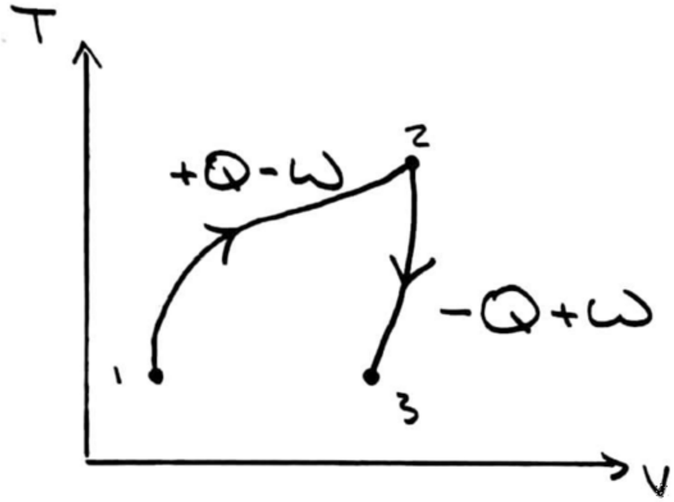

Figure 4.3: Example thermodynamic process for air parcel system plotted as Temperature-Volume curve. Note states and 3 do not necessarily have the same temperature and these curves are drawn arbitrarily for some unknown process.

the control volume. This assumption is valid typically if the internal dynamics of the system are much faster than the macro-level state changes. For instance, for all fluids, pressure equilibrates at the speed of sound, which for air is about 343 m/s. In many cases, this is much faster than the gas is moving on a macro-level[1]. For our air parcel example, this is certainly the case.

4.2.1 Reversibility

As we have hinted at thus far, the degree to which a transfer between thermal and mechanical energy can be undone is extremely important to our understanding of thermodynamic systems. Though a process may be quasistatic, it is not necessarily *reversible*. In this context, reversibility is achieved when the system is not just at internal equilibrium within itself - which is the requirement for quasistatic - but also with the environment in all states and sub-states. We can illuminate this concept with a few examples of *irreversible* processes. Again, consider a block sliding across a surface with some friction. We know that in this process, kinetic energy will be converted to thermal energy, raising the temperature of the block. As we previously discussed, there is no way that process can happen in reverse in such a way that restores the

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[1] When you move particles faster than the speed of sound, you get a *shock wave*.

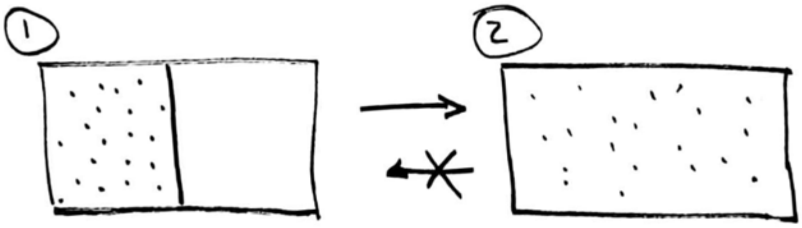

Figure 4.4: Irreversible gas diffusion process.

system to some previous state where it was cooler and had more kinetic energy. Friction and other *dissipative* processes can only generate heat and are thus irreversible.

Next consider heat transfer between a hot and cold object. We know experientially that heat moves from the hotter object to the colder object as long as there is a difference in temperature between the two. Microscopically, this is due to the simple fact that heat is transferred by vibrating, translating, or rotating particles exchanging kinetic energy with one another. On average, particles in the hot block will have more kinetic energy than those in the colder block, and therefore intuitively, the net exchange in kinetic energy will tend to go in one direction - hot to cold. In much the same way as our sliding block example, there is no way to undo this process. The transfer of heat, as long as there is a difference in temperature, can only go one way. A slower moving object colliding with a faster moving object will never result in the faster object leaving the collision with more kinetic energy than it started with. Thus, in general, heat transfer over a finite temperature difference - where adjacent particles have different average kinetic energies - is irreversible.

Finally, consider a container that is initially partitioned such that there is some gas on one side and a vacuum on the other as shown in Fig. 4.4. If we remove the partition all of a sudden (such that we do not do any work or transfer any heat), the gas will move to equilibrate and will eventually fill the entire container. In order to undo this, each particle would need to migrate on its own back to the left side of the container, and while this is theoretically possible, the statistics make it so unlikely that we can safely expect this to not happen in a reasonable time frame. Therefore, this process of *diffusion* is also irreversible for all practical purposes.

So in general, an irreversible process is one in which the physics or the statistics prohibit the system going back to an earlier state without needing to reverse time itself. Conversely, a reversible process *can* be restored to a previous state via heat or work transfer, which requires that the system always be in equilibrium with its environment and that no dissipation occurs. This *mutual equilibrium* requires that there never be a temperature or pressure difference across the system boundaries, which ensures that any heat transfer happens across zero temperature difference and any work transfer would occur slowly and smoothly with no dissipation. In our previous gas diffusion example, if we instead moved the partition to the right extremely slowly until the gas filled the container, we could reverse this, by moving the partition back to the left. This is a subtle difference, but because we are changing the state in infinitesimally small increments and can always characterize the state using the temperature and density of the gas, we can actually return to the prior equivalent states via the reverse of this process. We will explore this difference analytically later in this chapter, but for now it is important to understand this distinction intuitively.

In reality, no process perfectly reversible. There will always be some dissipation and heat transfer to the environment across some temperature difference. In some cases, the assumption of reversibility is a good one, but it is not always the case. As it turns out, however, this does not prohibit us from analyzing most thermodynamic systems of interest. In fact quantifying this level of irreversibility is extremely important in characterizing systems that convert energy from one form to another and is where we are heading.

4.2.2 Common Processes

In this chapter and going forward, it will be helpful to classify processes by the assumptions we make about them. Specifically, we will talk about processes in which one state variable is held constant throughout or in which an assumption is made about an interaction (or lack thereof) between the system and its environment. For example, we have already learned about *adiabatic* processes in which no heat is transferred between the system and its environment. In reality, no such process is truly adiabatic, but for systems that undergo very rapid changes compared to the timescale of heat loss to the environment, this is often a good approximation.

For changes in state that hold one particular state variable constant, we will use the following nomenclature:

1. *Isochoric* = Constant volume[2]

2. *Isobaric* = Constant pressure

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[2] From our definition of work, W, this ensures that $dW = 0$.

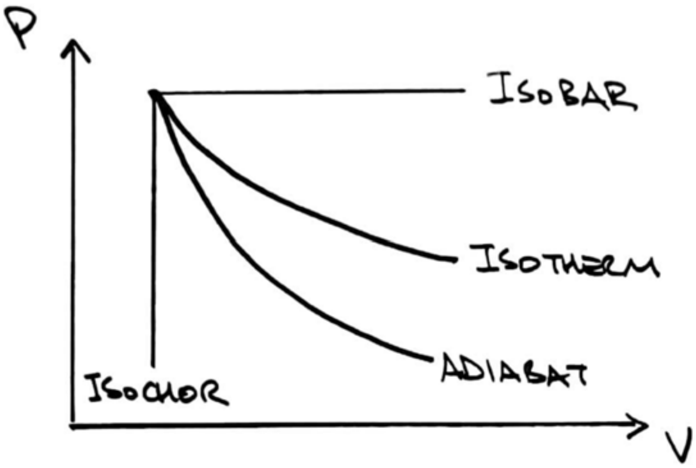

Figure 4.5: Types of processes plotted on a P-V diagram for the same initial pressure.

3. *Isothermal* = Constant temperature

More generally, we can also define a process to be *polytropic* in which the state can be described by:

$$PV^n = \text{constant} \tag{4.1}$$

which for an ideal gas, has the following equivalencies to our defined terms:

1. $n = 0$ for isobaric process ($PV^0 = P = \text{constant}$)
2. $n = 1$ for isothermal process ($PV = nRT = \text{constant}$)
3. $n = \gamma$ for reversible adiabatic process
4. n very large for isochoric process

On our property plots, we can represent these various types of processes as straight or curved lines. These curved lines are typically called *isotherms*, *adiabats*, *isobars*, and *isochors*, and examples of each are shown here in Fig. 4.5 on a P-V diagram.

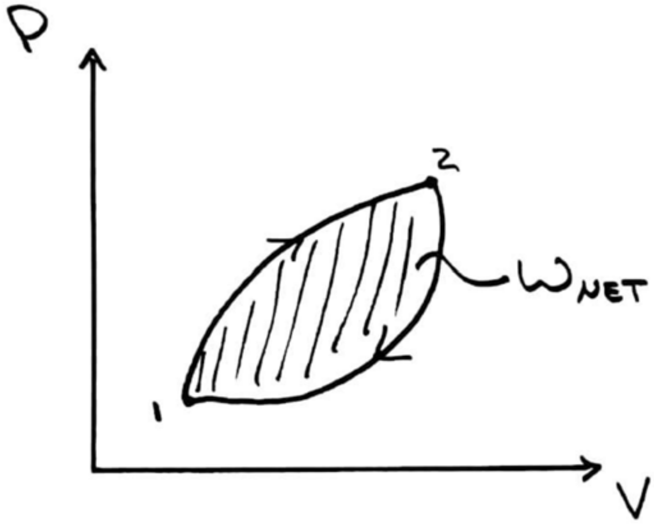

Figure 4.6: Thermodynamic cycle example with final and initial states being equivalent. Here the volume contained within the curve is the net work done by the system, $\oint P\,dV$.

4.2.3 Cycles

A process or series of processes where the initial and final states are equivalent is called a *cycle* and is the foundation for the modern human applications of thermodynamics. Cycles can be open or closed with mass potentially entering or exiting the control volume, but the important requirement is that the starting and end points share an *equivalent* state, meaning they have identical state properties even though the system may contain a different set of particles.

Fig. 4.6 shows the P-V diagram for an arbitrary cycle that goes between two states. Because work is given as

$$W = \int P\,dV \tag{4.2}$$

the area inside a closed curve on P-V plot tells us exactly the net work, W_{net}, done by the system over a single cycle. Expressed mathematically,

$$W_{net} = \oint P\,dV \tag{4.3}$$

and specifically for the example in Fig. 4.6,

$$W_{net} = \oint P\,dV = \int_1^2 P\,dV + \int_2^1 P\,dV \tag{4.4}$$

For a general cycle that can be represented by a closed contour, we can apply the first law over the entire cycle. Because the final and initial states are equivalent for this case, the change in internal energy, ΔU, (and all other state properties) over the whole cycle must be 0, as

$$\Delta U = U_{final} - U_{initial} = 0 \tag{4.5}$$

applying the first law for our system therefore yields

$$\cancel{\Delta U} = Q_{net} - W_{net} = \oint dQ - \oint dW \tag{4.6}$$

and thus

$$\oint dQ = \oint dW \tag{4.7}$$

which means that the sum of all work transfers in and out of the system must equal the sum of all heat transfers in and out of the system over one complete cycle.

Carnot Cycle

Cycles can also be classified by their degree of irreversibility. A perfectly *reversible* cycle is one in which each process is carried out reversibly - with no dissipation and the system in constant thermal and mechanical equilibrium with its environment. One such reversible cycle is called the *Carnot Cycle*, which is shown plotted on a P-V diagram in Fig. 4.7. The ideal closed Carnot Cycle, as shown in Fig. 4.8, operates between two *thermal reservoirs*[3], at temperatures T_H and T_L, and is carried out as follows:

1. From states 1 → 2, thermal energy is transferred to a gas *isothermally* at T_H in such a way that the temperature difference between the heat *source* and the system is always zero. To maintain constant temperature, the gas must expand and do some work.

2. From states 2 → 3, the gas expands *adiabatically*, bringing its temperature down to T_L.

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[3] a body with a theoretically infinite heat capacity

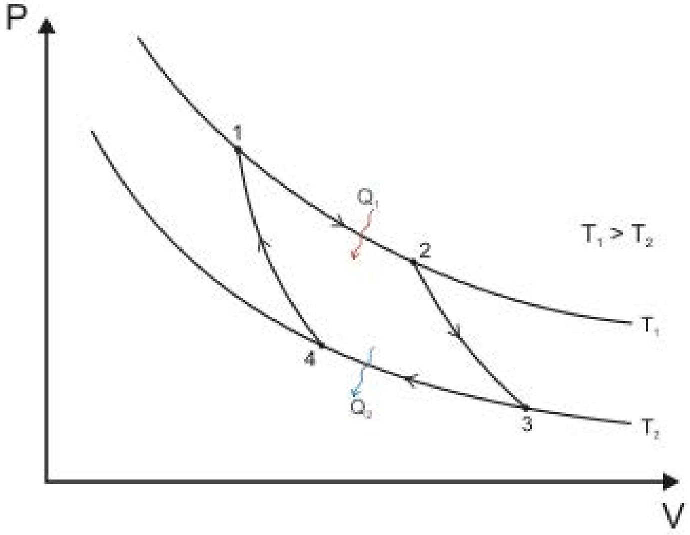

Figure 4.7: Carnot Cycle plotted on P-V diagram. Processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are carried out isothermally, while $2 \rightarrow 3$ and $4 \rightarrow 1$ are carried out adiabatically [source]. This image is in the public domain.

3. At its maximum volume at state 3, thermal energy is transferred *isothermally* at T_L from the gas to the heat *sink* in much the same way as step 1, bringing the gas to state 4.

4. Finally, from states $4 \rightarrow 1$, the gas is compressed back to its initial state at T_H *adiabatically*.

In the ideal case, each of these processes is carried out infinitely slowly to ensure no dissipation occurs and that at no point there is heat transfer across a temperature difference. When the temperature of the gas does change, it does so adiabatically. Consequently, this cycle would not be practical as it would take an inordinate amount of time to complete a single loop; however, it serves an important purpose as the theoretical upper limit of how much work can be extracted from an input of thermal energy to a cyclical process.

What has been implicit but not stated in our discussion thus far is that thermodynamic cycles provide the opportunity to continuously convert thermal energy to mechanical work and vice versa. It therefore makes sense to ask, how much energy do we get back compared to how much we put in? To

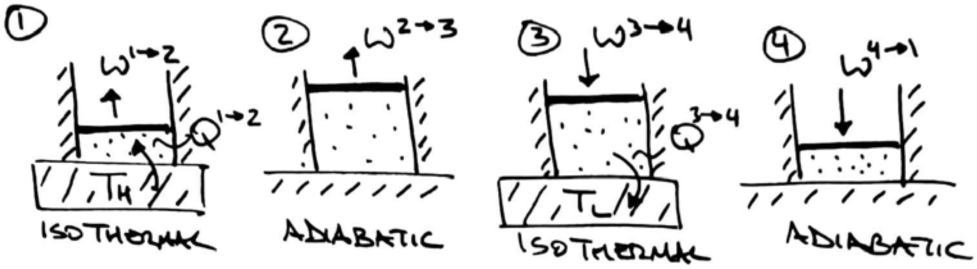

Figure 4.8: Carnot Cycle diagram. Ideal gas is in thermal communication with two different thermal reservoirs at T_H and T_L respectively.

answer this for the Carnot Cycle, we can start by writing the First Law for the cycle:

$$\cancel{\Delta U_{cycle}} = Q_{net} - W_{net} = 0 \tag{4.8}$$

where $\Delta U_{cycle} = 0$ since the initial and final states are equivalent. The net heat transfer Q_{net} and work transfer W_{net} are given as

$$Q_{net} = \oint dQ = Q_{in} - Q_{out} \tag{4.9}$$

$$= Q^{1\to 2} - Q^{3\to 4} \tag{4.10}$$

$$W_{net} = \oint dW = W_{out} - W_{in} \tag{4.11}$$

$$= W^{1\to 2} + W^{2\to 3} - W^{3\to 4} - W^{4\to 1} \tag{4.12}$$

We can define the *efficiency*, η, of the cycle as the ratio of the net work output to the heat added to the cycle, which in this case is just $Q^{1\to 2}$. From Eq. 4.8, we see that

$$W_{net} = Q_{net} = Q^{1\to 2} - Q^{3\to 4} \tag{4.13}$$

and thus the efficiency is given as

$$\eta_{Carnot} = \frac{W_{net}}{Q_{in}} \tag{4.14}$$

$$= \frac{W_{net}}{Q^{1\to 2}} \tag{4.15}$$

$$= \frac{Q^{1\to 2} - Q^{3\to 4}}{Q^{1\to 2}} \tag{4.16}$$

$$= 1 - \frac{Q^{3\to 4}}{Q^{1\to 2}} \tag{4.17}$$

To get this expression in terms of the temperatures of the thermal reservoirs, T_H and T_L, let us use what we have learned up to this point. Namely, we can solve for $Q^{1\to 2}$ and $Q^{3\to 4}$ using the First Law and the Ideal Gas Law. First, to compute, $Q^{1\to 2}$, we can use the fact that between states 1 and 2, the heat transfer occurs isothermally. Writing the First Law for this process, we have

$$\Delta U^{1\to 2} = Q^{1\to 2} - W^{1\to 2} \tag{4.18}$$

however, we know for an ideal gas, $U = C_v T$, and thus for an isothermal process, $\Delta U = C_v \Delta T = 0$. This gives us:

$$Q^{1\to 2} = W^{1\to 2} \tag{4.19}$$

where the work for an isothermal expansion of an ideal gas in our Carnot Cycle can be computed as

$$W^{1\to 2} = \int_{V_1}^{V_2} P\, dV \tag{4.20}$$

$$= \int_{V_1}^{V_2} \frac{m\widetilde{R}T_H}{V}\, dV \tag{4.21}$$

$$= m\widetilde{R}T_H \ln\frac{V_2}{V_1} \tag{4.22}$$

and thus

$$Q^{1\to 2} = m\widetilde{R}T_H \ln\frac{V_2}{V_1} \tag{4.23}$$

By this same reasoning, $Q^{3\to 4}$, is given by

$$Q^{3\to4} = -m\widetilde{R}T_L \ln \frac{V_4}{V_3} \tag{4.24}$$

where the negative sign is applied to be consistent with our definition that $Q^{3\to4}$ is the positive heat transfer out of the system. The relationship between V_1 and V_4, as well as V_2 and V_3, can be directly related to T_H and T_L via the expression we derived in Chapter 2 for adiabatic expansion of an ideal gas (Eq. 2.51):

$$T_H V_2^{\gamma-1} = T_L V_3^{\gamma-1} \tag{4.25}$$

and

$$T_H V_1^{\gamma-1} = T_L V_4^{\gamma-1} \tag{4.26}$$

Combining Eqs. 4.25 and 4.26 via T_H/T_L gives us:

$$\frac{T_H}{T_L} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} = \left(\frac{V_4}{V_1}\right)^{\gamma-1} \tag{4.27}$$

or

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \tag{4.28}$$

$$\Rightarrow \frac{V_2}{V_1} = \frac{V_4}{V_3} \tag{4.29}$$

which conveniently lets us cancel out the logarithm terms by dividing Eq. 4.23 by Eq. 4.24. Putting it all together, we find that the Carnot efficiency is simply:

$$\boxed{\eta_{Carnot} = 1 - \frac{T_L}{T_H}} \tag{4.30}$$

or

$$W_{net} = \eta_{Carnot} Q_{in} = \left(1 - \frac{T_L}{T_H}\right) Q_{in} \tag{4.31}$$

This expression is truly a profound statement, as it tells us the fraction of mechanical work we can extract from a given heat input using a reversible cycle with with two thermal reservoirs is related only a function of the temperatures

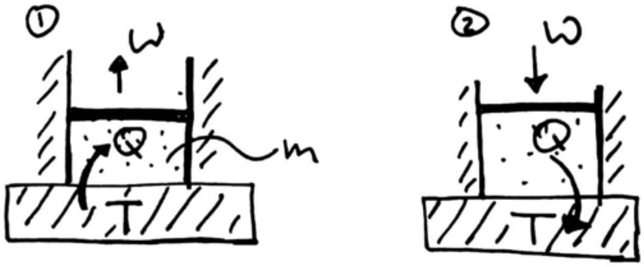

Figure 4.9: Reversible isothermal cycle with zero net work. Gas and thermal reservoir remain at temperature T throughout the whole cycle.

at which heat is input and extracted from the system. In nature, T_L/T_H will always be some finite, non-zero value, since in practice, extremely high and low temperatures are difficult to achieve and sustain. On Earth, for example, a Carnot Cycle operating between $T_H = 1000$ K, which is easily achievable via combustion, and $T_L = 300$ K would have an efficiency of

$$\eta = 1 - \frac{300}{1000} = 0.7 \tag{4.32}$$

which means that in the absolutely ideal case, we can on average only extract 70% of the thermal energy we put in to the cycle back out as work. A machine that does so continuously is called a *heat engine.* What this also tells us that thermal energy at higher temperatures relative to our cold reservoir is more valuable from a useful work perspective than the same thermal energy at lower temperatures. High-temperature or *high grade* thermal energy allows an engine to operate at higher efficiencies. This should make sense intuitively, as we know that even though the Earth's soil and the air surrounding us have massive amounts of thermal energy stored as mcT, we cannot do anything with that energy as our efficiency would essentially be 0, unless we could find a comparatively colder thermal reservoir. This distinction between energy at different temperatures will become important later in the discussion about renewable energy.

Interestingly, we can run such a cycle in reverse, inputting net work to move heat from a cold thermal reservoir to a hotter one. Because the Carnot Cycle is reversible, it runs the same backwards as it does forwards, allowing us to rearrange Eq. 4.31 as

$$W_{net} = \left(\frac{T_H - T_L}{T_H}\right) Q_{out} \tag{4.33}$$

$$\Rightarrow Q_{out} = \left(\frac{T_H}{T_H - T_L}\right) W_{net} \tag{4.34}$$

where Q_{out} is now the heat rejected to the hot thermal reservoir and is equal to Q_{in} added from the hot thermal reservoir in the forward cycle case. Observe here that the coefficient in front of W_{net} is greater than 1 for $T_H > T_L$, and thus more heat can be transferred than net work is input into the system. This is exactly the reciprocal statement of our observation that for the forward case, less work can be extracted than the amount of heat added. This is logically consistent again due to the reversibility of this cycle, though it may be counter intuitive. Remember that in both cases, heat is both being added *and* rejected in each cycle, though they are not equal in magnitude as long as $T_H \neq T_L$. Such a device that operates in this manner is generally called a *heat pump* and forms the basis for not just refrigerators and air conditioners, but certain atmospheric cooling cycles as well.

Now there is one more important distinction to make between cycles and processes and that has to do with why we even care about cycles to begin with. For a single reversible process, it is indeed possible to convert 100% of some thermal energy input to work. For example, consider a gas with total mass m in thermal communication with a heat reservoir at temperature T. The gas undergoes reversible isothermal expansion as shown in Fig. 4.9. In order to maintain constant temperature throughout this process, the gas must expand and do work as thermal energy is transferred to it. Writing the First Law from states 1 to 2, we have

$$\Delta U^{1\to 2} = Q^{1\to 2} - W^{1\to 2} \tag{4.35}$$

$$\cancel{mc_v(T - T)} = Q^{1\to 2} - W^{1\to 2} \tag{4.36}$$

$$\Rightarrow W^{1\to 2} = Q^{1\to 2} \tag{4.37}$$

so clearly we are getting 100% of the heat transferred to the gas back out as work. From a practical perspective, however, once this process is complete, the system can do no more work until we reset the gas to its original volume by inputting work back in. Thus, we need a *cycle* to continually convert heat to work.

For this reversible isothermal cycle in particular, we can then compress the gas isothermally at the same temperature T, which by the same logic as for the expansion process would require

$$W^{2\to 1} = Q^{2\to 1} \tag{4.38}$$

Writing the first law for the cycle, we have

$$\cancel{\Delta U_{cycle}} = Q_{net} - W_{net} \tag{4.39}$$
$$\Rightarrow W_{net} = Q_{net} \tag{4.40}$$
$$\oint dW = \oint dQ \tag{4.41}$$

If we plot this cycle on a P-V diagram as shown in Fig. 4.10, we can clearly see that because both processes traverse the same isotherm at temperature T, if $W^{1\to 2}$ is given by

$$W^{1\to 2} = \int_1^2 P\,dV \tag{4.42}$$

then

$$W^{2\to 1} = \int_2^1 P\,dV = -\int_1^2 P\,dV \tag{4.43}$$

and thus, W_{net} is

$$W_{net} = \oint dW = \int_1^2 P\,dV - \int_1^2 P\,dV = 0 \tag{4.44}$$

and by Eqs. 4.38 and 4.39,

$$Q^{1\to 2} = -Q^{2\to 1} \tag{4.45}$$

Consequently, the efficiency for this isothermal cycle, η, is simply

$$\eta = \frac{W_{net}}{Q_{in}} = 0 \tag{4.46}$$

which means that using this system, we cannot convert any thermal energy to work without putting the same amount of work back in on average, even though this cycle is perfectly reversible. Graphically, we can see this represented by the fact that the area contained within the curve in Fig. 4.10 is zero. As illustrated by this example, cycles are required for continuous net transfer of heat to work and vice versa, and as we are about to see, this poses some additional universal constraints.

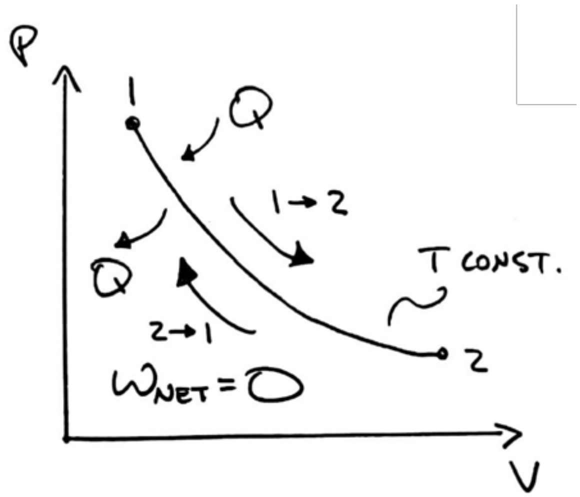

Figure 4.10: P-V diagram for isothermal cycle in Fig. 4.9

4.3 The Second Law of Thermodynamics

The First Law of Thermodynamics is based on the observation that you cannot extract energy from a system without depleting its stored internal energy by the equivalent amount - that is, energy cannot be created from nothing nor can it be destroyed, only transferred. In thermodynamics, this is the "what". We now have the tools, though, to talk about the "how". Specifically, as we just discussed, in order to continuously transfer heat to work and vice versa, we need to construct a cycle using a coupled system. Though it can take many specific forms, the *Second Law of Thermodynamics* is fundamentally the observation that the amount of net energy you can extract from such a cycle is limited. In fact, the best efficiency you can achieve is that of the Carnot Cycle[4].

Stated another way, the Second Law tells us that the maximum net conversion of thermal energy to work can only be achieved using a cycle comprised of all reversible processes. You can extract less work - and in nature this is virtually guaranteed as there is no such thing as a perfectly reversible process - but never more. Therefore, the Second Law is different from the First Law in that it is expressed as an *inequality* telling us about a *maximum* quantity. For a cycle operating in thermal communication with *one* thermal reservoir, as we previously showed, the net work is at most zero, which is written mathematically as

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[4] See Fermi *Thermodynamics* Chapter 3 for a excellent proof of this [2].

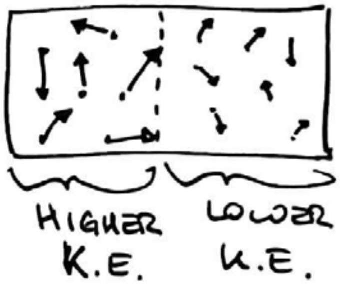

Figure 4.11: Graphical depiction of thermal energy diffusion. On average, because particles on the left are moving faster than those on the right, more particles will move from the left to the right than vice versa until average kinetic energy is equal throughout whole volume.

$$\oint dW \leq 0 \tag{4.47}$$

We can certainly put in more work than we extract - which again is nearly guaranteed to be the case in practice - but never the other way around[5].

For a system in thermal communication with *two* thermal reservoirs, the maximum efficiency you can achieve is via the Carnot Cycle. This notion, called *Carnot's Theorem*, can be expressed similarly as

$$\oint dW \leq \eta_{Carnot} Q_{in} \tag{4.48}$$

$$\leq \left(1 - \frac{T_L}{T_H}\right) Q_{in} \tag{4.49}$$

from which arises the corollary that without a temperature difference, no net work can be extracted from a thermodynamic cycle. Additionally, it can be shown that for both of these cases and in general, all perfectly reversible cycles operating between the same number of thermal reservoirs are equivalent[6]. Thus, this is a universal constraint on *how* energy is converted between these forms.

An important equivalent statement of the Second Law that arises from this observation is that **the net transfer of heat from a body at some temperature T_L to a body at some higher temperature $T_H > T_L$ is**

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[5] This is typically referred to as the *Kelvin Postulate* of the Second Law.

[6] See Fermi *Thermodynamics* Chapter 3 for a proof of this.

impossible without doing net work[7]. While we understand this from an intuitive perspective, the Second Law poses this as a universal truth. If we think about what heat transfer is at the molecular level, we can see the profundity of this statement. Because thermal energy is equivalent to kinetic energy, *conductive* heat transfer is simply a *diffusive* process driven by the statistics that on average, a body with particles of higher average kinetic will transfer that kinetic energy to nearby bodies with lower kinetic energy and not the other way around as we previously discussed.

For example, as Fig. 4.11 shows, if we have an enclosed volume that initially has gas particles with higher average kinetic energy on one side, over time, more particles will move from the "hot" side to the "cold" side. Statistically, this will happen until equilibrium is reached and the average kinetic energy is the same throughout the volume. In this example, the gas experiences an *irreversible* run down to equilibrium in which the system naturally goes from a state with more *order* to the equilibrium state with the maximum amount of *disorder*. Indeed, the Second Law arises from the observation that the opposite case is impossible, and that in general, **on average, irreversible processes will always result in an irreversible move from order to disorder**. At best, the degree of order in the system will stay exactly the same for a reversible cycle.

Since there are no truly reversible processes in our actual[8] Universe, we can equivalently say that all systems are ultimately heading towards maximum disorder, and once complete, the *information* about any previous states cannot be recovered. Indeed, in our gas diffusion example, if we were to only observe the final equilibrium state in which the entire volume had a uniform average kinetic energy, we can say nothing about how the system was initially ordered. The same exact thing is happening on a Universal scale, indicating that eventually, all energy in all of the forms we can currently observe will eventually be distributed equally throughout[9]. It is fascinating to note that because of this fact alone, *time* itself has an directionality to it. Most other physical laws are indifferent to whether time moves forward or backwards, but the Second Law of Thermodynamics can only go in one direction - the direction of time in which the disorder increases on average[10]. We will now see just how this disorder can be quantified.

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[7] This is typically referred to as the *Clausius Postulate* of the Second Law and its equivalence to the Kelvin Postulate is proven nicely again in Fermi *Thermodynamics* Chapter 3.

[8] as opposed to theoretical

[9] This is often referred to as the *Heat Death* of the Universe.

[10] see the *Arrow of Time*

4.4 Entropy

So we have learned that the Second Law of Thermodynamics places constraints on how much work can be extracted from a thermodynamic cycle as well as the degree to which a system can retain a sense of "order" under reversible and irreversible processes. This latter constraint in particular manifests itself as the fact that dissipative processes like thermal conduction cannot be undone. To quantify the degree to which a system is irreversible, we introduce the concept of *entropy*, which fundamentally represents how "disordered" a system is. As is the case with temperature and pressure being emergent macroscopic properties from microscopic phenomena, the same is true for entropy. This measure of system's "disorder" is fundamentally a measure of the number of possible configurations or *microstates* - position and momentum - of its constituent particles that equate to the same *macrostate* - temperature and pressure. Two moles of a gas at temperature T and pressure P will have double the number of possible microstates as one mole, all else held constant. The relationship between entropy, S, and the number of microstates, Ω, is not linear, but rather is given by

$$S = k_B \ln \Omega \tag{4.50}$$

where k_B is the familiar Boltzmann constant. This *Boltzmann Entropy* tells us fundamentally that entropy increases when there are more microstates.

Like enthalpy, we find that we often care more about the *change* in entropy for a process or cycle. So to define this quantity, it makes sense to relate it to a process we know is irreversible and therefore increases the degree of disorder - heat transfer across a temperature difference. If we return to our Carnot Cycle example, we observe that the ratio of the heat transfer from the thermal reservoir at T_H, Q_H, and the heat transfer to the thermal reservoir at T_L, Q_L, is given by Eq. 4.23 divided by Eq. 4.24 as

$$\frac{Q_H}{Q_L} = \frac{T_H}{T_L} \tag{4.51}$$

or equivalently:

$$\frac{Q_H}{T_H} - \frac{Q_L}{T_L} = 0 \tag{4.52}$$

More generally, it can be shown that for any reversible cycle with i discrete heat transfers,

$$\sum_i \frac{Q_i}{T_i} = 0 \tag{4.53}$$

or

$$\oint \frac{dQ}{T} = 0 \tag{4.54}$$

Looking at the arbitrary example cycle shown in Fig. 4.6 with discrete states 1 and 2, if this cycle is reversible, we consequently have that

$$\oint \frac{dQ}{T} = \left(\int_1^2 \frac{dQ}{T}\right)_I + \left(\int_2^1 \frac{dQ}{T}\right)_{II} = 0 \tag{4.55}$$

where I and II represent the two different process paths that comprise this cycle. By rearranging terms and flipping the limits of integration, we find that this expression is equivalent to

$$\left(\int_1^2 \frac{dQ}{T}\right)_I = -\left(\int_2^1 \frac{dQ}{T}\right)_{II} = \left(\int_1^2 \frac{dQ}{T}\right)_{II} \tag{4.56}$$

What this relationship tells us is that this quantity contained within the parentheses is not a function of the path taken between two points of a cycle, as long as those paths are reversible. In other words, under this condition, this quantity is a *state property*, just as enthalpy or internal energy. This is what we call *entropy*, S, whose change between states 1 and 2 via a reversible process is defined as

$$\Delta S \equiv S_2 - S_1 = \left(\int_1^2 \frac{dQ}{T}\right)_{reversible} \tag{4.57}$$

where S as defined here is typically called the *classical entropy*[11]. In differential form, a small change in entropy, dS, is given by

$$dS = \frac{dQ}{T} \tag{4.58}$$

which under certain conditions is equivalent to the Boltzmann entropy in Eq. 4.50[12].

For any cycle, including irreversible ones, in accordance with the Second Law, it follows directly that

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[11] In contrast with the *statistical entropy* we will later see.

[12] Showing this is the case is beyond the scope of this text, but any good statistical mechanics book will cover this in detail.

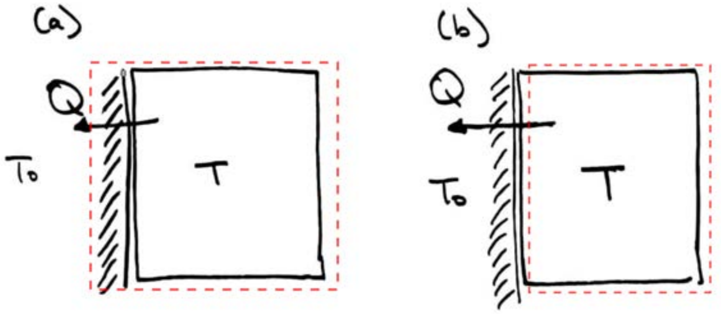

Figure 4.12: Two ways to draw a control volume (red) for the same heat transfer problem involving a transfer Q between a mass at temperature T and a thermal reservoir at T_0. (a) has a CV boundary inside the thermal reservoir and (b) just inside the mass. Assuming a discontinuous temperature change at the mass-reservoir interface, these heat transfers effectively occur at T_0 and T respectively.

$$\boxed{\Delta S_{cycle} = \oint \frac{dQ}{T} \geq 0} \tag{4.59}$$

which is in fact an equivalent statement of the Second Law. Because working with inequalities makes practical applications of this law more challenging, this expression is often restated for a general process as

$$\Delta S = S_2 - S_1 = \int_1^2 \frac{dQ}{T} + \Delta S_{gen} \tag{4.60}$$

where $\Delta S_{gen} > 0$ for irreversible processes and exactly $\Delta S_{gen} = 0$ for reversible ones. ΔS_{gen} is the entropy generated due to irreversibility and represents the information lost due to dissipative and diffusive processes. Note that the units of entropy are energy per temperature, J/K in SI units.

Like with enthalpy of formation, entropy is always defined relative to some reference value. Here, this must be the case as it is defined by the integral over some state interval. In practice, for all substances, we pick a standard state - some temperature and pressure - where the entropy is defined to be zero, and we compute the entropy at different conditions relative to that point. Thus, the entropy at some state A is really

$$S_A = \int_0^A \frac{dQ}{T} = S_A - \cancelto{0}{S_0} \tag{4.61}$$

and thus the change in entropy over a process has these implicit reference values as well, but they cancel out. For example,

$$\Delta S = (S_2 - \cancel{S_0}) - (S_1 - \cancel{S_0}) = S_2 - S_1 \tag{4.62}$$

which is what we have in Eq. 4.60 as we should expect. Because we will primarily deal with changes in entropy here, we do not need to define this reference state, as it will always cancel out[13].

One sticky point with entropy as we have defined it here is a question of what temperature is used in Eq. 4.60. We have learned that conductive heat transfer across a temperature difference is irreversible as heat can not flow back from one object to a hotter one, but then the natural question arises: which temperature do we use for this equation? The answer, as unsatisfying as it may be, is that it depends. As Fig. 4.12 shows, the temperature at the boundary of the control volume can change depending on where it is drawn. In reality, temperature is continuous and smoothly changes in space, so you end up with a *region of entropy generation* in the volume over which temperature changes. When looking at ideal systems, however, the temperature we use is the value directly at the boundary of the system, and thus it depends on how the control volume is defined.

4.4.1 The Entropy of Things

Now that we understand the basic form of entropy, we can start to look at how the entropy of various substances in their different phases changes with changes in state.

Solids and Incompressible Fluids

For solids and incompressible fluids, we can recall from Chapter 2 that a small reversible transfer of heat, dQ, to a control volume containing such a substance will correspond to a temperature increase, dT, such that

$$\frac{dQ}{dT} = mc(T) \tag{4.63}$$

where m is the mass of the substance and c is its specific heat, which may be a function of temperature. Solving for dQ and plugging into our definition for entropy in differential form in Eq. 4.58, we get

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[13] We will see later with the *Third Law of Thermodynamics* what this absolute reference state actually is.

$$dS = \frac{dQ}{T} = \frac{mc(T)dT}{T} \tag{4.64}$$

Integrating both sides between states 1 and 2, we get

$$\int_1^2 dS = S_2 - S_1 = \int_1^2 \frac{mc(T)dT}{T} \tag{4.65}$$

in its most general form, where c(T) can be any function. In reality, the specific heat for many solids and liquids is relatively constant over large temperature ranges and thus we can say $c(T) = c$, allowing us to solve Eq. 4.65 explicitly as

$$\Delta S = mc \int_1^2 \frac{dT}{T} \tag{4.66}$$

$$S_2 - S_1 = mc \ln \frac{T_2}{T_1} \tag{4.67}$$

What is important to note here is that even though we got to this result by applying a reversible heat transfer, because entropy is a *state function*, the path between two states is actually irrelevant. It is does not matter how we got there but just that we did. So for any solid or incompressible liquid at temperature T, its entropy relative to some zero reference point, S_0, is given by

$$S(T) = mc \ln T \tag{4.68}$$

or

$$s(T) = c \ln T \tag{4.69}$$

where s is the specific entropy in units of energy per temperature per mass, J/kg-K in SI units.

Ideal Gases

For gases, the relationship between entropy and the various other state properties becomes more complex due to the coupling between thermal energy and mechanical work as we know well know. For an ideal gas, with mass m, we can start by writing the differential form of the First Law:

$$dU = mc_v\, dT = dQ - P\, dV \tag{4.70}$$

and then the Second Law as

$$dS = \frac{dQ}{T} \tag{4.71}$$

Combining Eq. 4.70 and 4.71 and substituting the ideal gas law to get P as in terms of T and V,

$$\begin{aligned} dS &= \frac{mc_v\, dT + P\, dV}{T} \tag{4.72}\\ &= \frac{mc_v\, dT}{T} + \frac{m\widetilde{R}T\, dV}{TV} \tag{4.73}\end{aligned}$$

Dividing both sides by m to get the specific entropy and integrating from state 1 to 2:

$$s_2 - s_1 = \int_1^2 \frac{c_v(T)}{T}\, dT + \widetilde{R}\int_1^2 \frac{dV}{V} \tag{4.74}$$

where again the specific heat is a function of temperature. For a *perfect* gas, $c_v(T) = c_v$, and thus because it does not depend on temperature, this integral can be solved explicitly as

$$\Delta s = s_2 - s_1 = c_v \ln\frac{T_2}{T_1} + \widetilde{R}\ln\frac{V_2}{V_1} \tag{4.75}$$

from which we can obtain the alternate equivalent forms by substituting in the ideal gas for different variables:

$$\begin{aligned} s_2 - s_1 &= c_p \ln\frac{T_2}{T_1} - \widetilde{R}\ln\frac{P_2}{P_1} \tag{4.76}\\ &= c_p \ln\frac{V_2}{V_1} + c_v \ln\frac{P_2}{P_1} \tag{4.77}\end{aligned}$$

All of these forms are equivalent and can be used depending on the which state properties can be measured. Remember though, for real gases, c_p and c_v are functions of temperature and thus must be included in the above integrals. For many common substances, entropy values are approximated by functions much like the case for enthalpy, and can be computed directly.

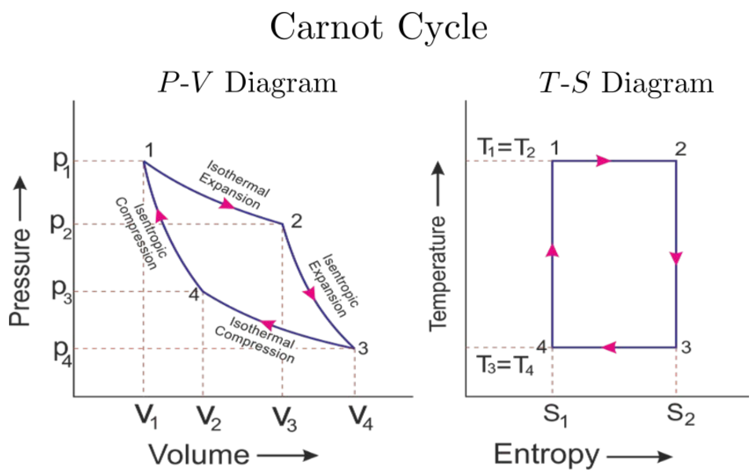

Figure 4.13: Property plots for the Carnot Cycle. Reversible adiabatic processes are *isentropic* and are given by vertical lines on a T-S diagram.

4.4.2 Cycle Entropy

Like temperature, pressure, and volume, for example, entropy is a state property, which means that we can track the system entropy on a property plot, much like on a P-V diagram. Typically entropy is plotted against temperature, forming a T-S diagram, for which isothermal and isentropic (reversible adiabatic) process show up as horizontal and vertical lines respectively. For example, we plot the Carnot Cycle on both a P-V and T-S diagram side by side for this cycle as shown in Fig. 4.13 to help illuminate what is going on. As we can see here, the reversible cycle operating between two thermal reservoirs at $T_1 = T_H$ and $T_3 = T_L$ is characterized by a rectangle on the T-S diagram with the horizontal lines representing the two isothermal heat transfers and the vertical lines the adiabatic expansion and compression. Because of our definition of entropy, we can clearly see that the area contained within a closed curve on this plot is the net heat transfer to the system over the cycle, Q_{net}, since

$$Q_{net} = \oint dQ = \oint T\, dS \tag{4.78}$$

which again comes right from our definition of entropy. This only holds, however, for *reversible* cycles.

This plot also highlights that the change in entropy of the system is always zero for a complete cycle, as by definition, a cycle has the same initial and final states. Because entropy is a state variable, that means the system must have the same entropy at the end of the cycle that it started with. For irreversible cycles, however, while this is still true, the plot does not tell us everything about how much irreversible entropy was generated at the boundary or within our system over the cycle. From the Second Law, we have that

$$dS = \frac{dQ}{T} + T\,dS_{gen} \tag{4.79}$$

and therefore that

$$dQ = T\,dS - T\,dS_{gen} \tag{4.80}$$

$$\Rightarrow \oint dQ = \underbrace{\oint T\,dS}_{\text{Area within curve}} - \oint T\,dS_{gen} \tag{4.81}$$

Consequently, because for an irreversible process, we have

$$\oint T\,dS_{gen} > 0 \tag{4.82}$$

by the Second Law, the net heat transfer will be *less* than the area contained within the enclosed curve. It is therefore essential that all assumptions for the analysis are well stated at the outset of defining the cycle. The net work done by the system over a cycle is still the area within a closed curve on the P-V diagram; however, the irreversibility will lower the cycle efficiency as Q_{in} will likely need to be higher for the same work production. In practice, we cannot measure the entropy generated directly, but we can often measure temperature and heat transfer and compute it from that.

A natural question that arises from this discussion is about *where* the entropy for the cycle goes. We can see graphically and by definition that the entropy of our control volume at the end of a cycle is the same as it had at the beginning. Thus, whether or not the cycle is reversible,

$$\Delta S_{cycle} = \oint dS = 0 \tag{4.83}$$

For an irreversible cycle then, we see that though the entropy of the control volume remains the same on average, entropy must still be generated by the Second Law *somewhere*. Some heat must have been transferred from a hot entity to a cooler one or some sort of dissipation must have occurred somewhere along the way, and if this associated entropy is not being generated in the control volume, then where? The vague philosophical answer to this question is that entropy is being generated in the *the Universe* in such a way that system's ability to do work over a cycle is reduced. In short, the entropy generated represents the difference in work that could have been done for the same heat input using a fully reversible cycle.

While there seems to be a tautology here since this is basically just a restatement of the Second Law, this is consistent if we remember that we defined ΔS_{gen} to serve exactly this purpose. For a cycle in thermal communication with only one thermal reservoir at T, we can write the First and Second Laws, and combine them to yield:

$$\cancel{\Delta U_{cycle}} = Q_{net} - W_{net} \tag{4.84}$$

$$0 = (T\cancel{\Delta S_{cycle}} - T\Delta S_{gen}) - W_{net} \tag{4.85}$$

$$\Rightarrow W_{net} = -T\Delta S_{gen} \tag{4.86}$$

which tells us we need to *add* net work in the quantity $T\Delta S_{gen}$ to keep our cycle going. In the best case scenario, we can do 0 net work for our cycle, which is what we already established with the Second Law. For a cycle with two thermal reservoirs, the math becomes a bit more complex but this same process can be applied to yield an expression of the form,

$$W_{net} = W_{net,rev} - W_{net,irr} \tag{4.87}$$

$$= \eta_{Carnot} Q_{in} - W_{net,irr} \tag{4.88}$$

where $W_{net,irr}$ is proportional to ΔS_{gen} and represents the extra work that could not be done as a result of whatever irreversibility occurred over the cycle.

4.4.3 Entropy of Phase Change

In Chapter 3, enthalpy as it relates to phase changes was discussed. We can easily see how entropy and enthalpy are related under the conditions we explored - namely constant pressure phase change - by writing the First Law for a substance undergoing such a process and immediately substituting the Second Law in for dQ:

$$du = T\,ds - P\,dV \tag{4.89}$$

which is another very commonly used expression. Adding $d(PV)$ to both sides as we have done previously to get enthalpy ($h = u + PV$):

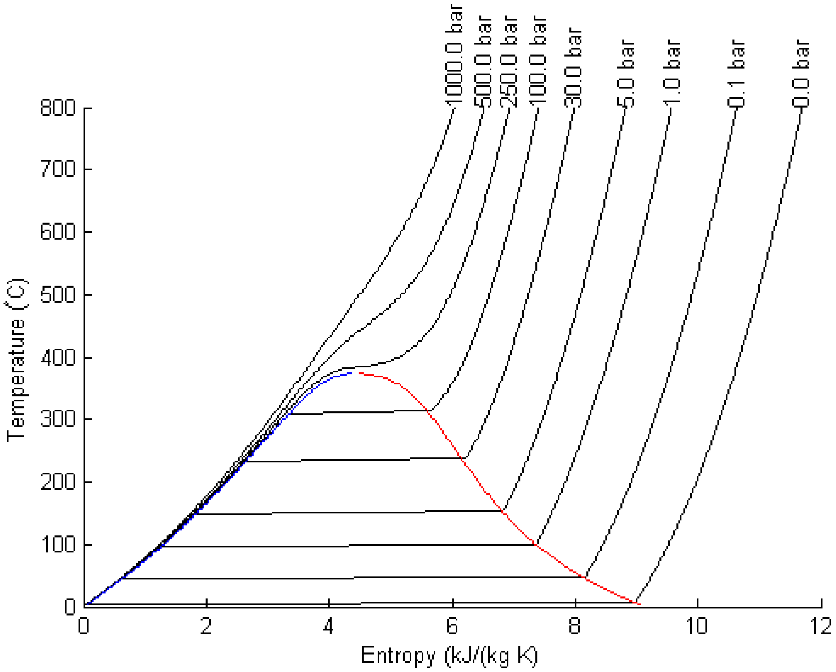

Figure 4.14: Saturation or vapor dome plotted for a substance on a T-s diagram. The black lines represent isobars on this plot, showing constant pressure phase change processes.

$$du + d(PV) = T\,ds - P\,dV - d(PV) \tag{4.90}$$

$$d(u + PV) = T\,ds - \cancel{P\,dV} - (\cancel{P\,dV} + \cancelto{0}{V\,dP}) \tag{4.91}$$

$$\Rightarrow dh = T\,ds \tag{4.92}$$

We could have also arrived at this expression by noting that for a substance undergoing constant pressure reversible heat transfer, the change in enthalpy equal to the heat transferred, Q, which is also equal to $T\,ds$ by the second law. In either case, the change in enthalpy across a phase change is

$$s_{fg} = s_g - s_f = \frac{h_{fg}}{T} \tag{4.93}$$

where f and g represent the liquid and gas phases of the substance respectfully. The same expression holds for any phase change at constant pressure.

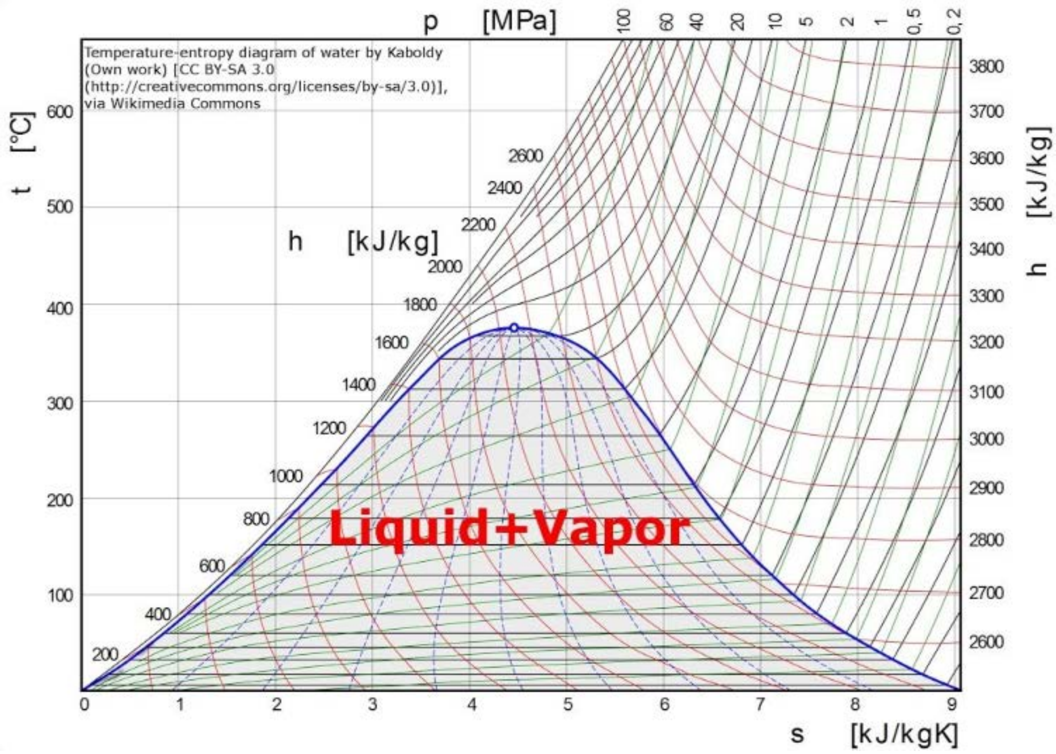

Figure 4.15: Vapor dome of water plotted on a T-s diagram showing lines of constant pressure and enthalpy.

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Note that the single-species, isothermal phase change we have introduced here is a reversible process if all heat transfer that occurs is at a single temperature and no dissipation occurs. In nature, these constraints are not typically adhered to and thus real phase changes will result in some entropy generation. Additionally, some polymers and other complex molecules require the breaking of additional hydrogen bonds to allow the phase change to occur which can generate some irreversible entropy in the process.

As we did previously with the enthalpy of phase changes, it is also highly useful to plot the temperature of phase change process on a property plot as a function of entropy. From the definition of entropy, we know that the area under a curve on a T-S diagram is exactly equal to the net heat transfer for a reversible process. Fig. 4.14 shows an example of such a diagram with multiple isobars indicating constant pressure phase change processes. As with the T-h diagram in Fig.3.3, a vapor dome also emerges on this type of plot, such that to the left of the dome the substances exists as pure liquid, to the right as pure vapor, under the dome as both liquid and vapor, and above as a supercritical

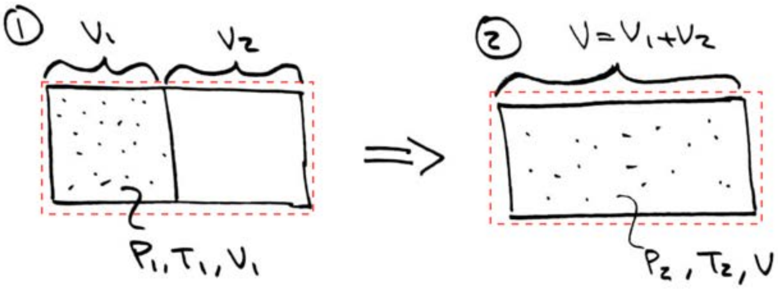

Figure 4.16: A perfect gas occupying part of a volume, V, in state 1. In between states 1 and 2, the barrier is removed and the gas can move to fill the remaining volume, coming to equilibrium at state 2. Control volume is shown in red.

fluid. The rectangular area under the portion of the curve contained within the vapor dome is exactly equal to the latent heat of vaporization per unit mass at that given pressure, as

$$\text{Area} = T(s_g - s_f) \tag{4.94}$$
$$= h_{fg} \tag{4.95}$$

where s_g and s_f are the entropy values where the isobar intersects the right and left sides of the vapor dome respectively.

Putting all of these concepts together, it is also useful to plot the temperature, pressure, enthalpy, and entropy for a substance near this saturation condition all at once. Fig. 4.15 shows how this is done in practice. Here the dome is plotted on standard T-s axes but with both lines of constant pressure and enthalpy drawn as well.

4.4.4 Entropy of Mixing

Entropy can also be generated in the mixing of two different gases. Let us first take a simplified example where, as shown in Fig. 4.16, we have a perfect gas with mass m in state 1 occupying only part of an enclosed insulated container with total volume V. If we immediately remove the partition holding the gas in place, it will expand via diffusion to fill the total volume, coming to equilibrium in state 2. Writing the first law for the control volume marked in red between states 1 and 2, we find that if there is no work or heat transfer with environment and thus

$$\Delta U = \cancel{Q} - \cancel{W} \tag{4.96}$$
$$mc_v(T_2 - T_1) = 0 \tag{4.97}$$
$$\Rightarrow T_2 = T_1 \tag{4.98}$$

and from the Second Law that

$$\Delta S = \cancel{\int_1^2 \frac{dQ}{T}} + \Delta S_{gen} \tag{4.99}$$
$$\Rightarrow \Delta S_{gen} = \Delta S = S_2 - S_1 \tag{4.100}$$
$$= \cancelto{0}{mc_v \ln \frac{T_2}{T_1}} + m\widetilde{R} \ln \frac{V}{V_1} \tag{4.101}$$
$$= m\widetilde{R} \ln \frac{V}{V_1} \tag{4.102}$$

which tells us that entropy generated for this process is positive as long as $V > V_1$. Therefore, by definition, this process is irreversible.

A natural question that arises is what happens instead if we move the partition slowly and reversibly to the expand the gas into the total volume? How are are these scenarios fundamentally different? Mathematically, this controlled expansion scenario is just our familiar adiabatic expansion, which gives us a relationship between T and V by Eq. 2.51 as

$$T_1 V_1^{\gamma-1} = T_2 V^{\gamma-1} \tag{4.103}$$
$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V}\right)^{\gamma-1} \tag{4.104}$$

and if we plug this relationship into our Second Law formula for a perfect gas to eliminate T, we find that

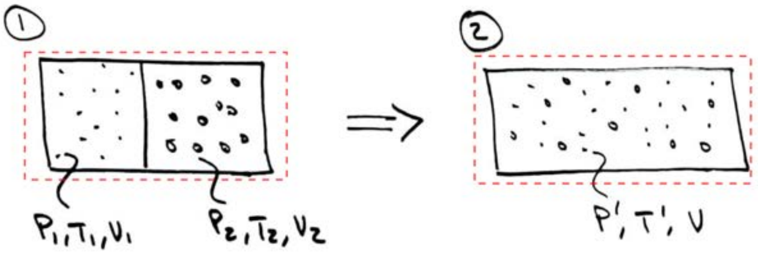

Figure 4.17: Two perfect gases of different species occupying separate parts of a volume, V, in state 1. In between states 1 and 2, the barrier is removed and the gases can move to fill the remaining volume, coming to equilibrium at state 2. Control volume is shown in red.

$$\Delta S = \cancel{\int_1^2 \frac{dQ}{T}} + \Delta S_{gen} \tag{4.105}$$

$$\Rightarrow \Delta S_{gen} = \Delta S = S_2 - S_1 \tag{4.106}$$

$$= m c_v \ln \left(\frac{V_1}{V}\right)^{\gamma-1} + m\widetilde{R}\ln\frac{V}{V_1} \tag{4.107}$$

$$= m\left[c_v(1-\gamma)\ln\frac{V}{V_1} + \widetilde{R}\ln\frac{V}{V_1}\right] \tag{4.108}$$

$$= m\left[\cancel{-\widetilde{R}\ln\frac{V}{V_1}} + \cancel{\widetilde{R}\ln\frac{V}{V_1}}\right] \tag{4.109}$$

$$= 0 \tag{4.110}$$

which confirms that our reversible adiabatic expansion is indeed reversible, as it generates no entropy.

The key difference in how we formulated these two similar problems is actually in how we defined our control volume and the work we had to add to the process in the second case. In the irreversible case, we took a static control volume that exchanged 0 work and heat with its environment, and therefore its temperature remained constant throughout the process. In the reversible case, we had to apply some work to ensure that no dissipation occurred and that the process was in perpetual equilibrium from states 1 to 2.

The irreversible single gas expansion case we outlined here is just one half of a gas mixing problem. Consider the same volume as before, but now on the right side, we have a different gas species with a different mass and starting state as shown in Fig. 4.17. At some time after the system has reached equilibrium in state 1, the partition is removed and the gases are free to mix, each filling up the total volume, reaching equilibrium in state 2. In state 1, we can use the ideal gas law to obtain the following expressions for the masses of each each gas:

$$m_1 = \frac{P_1V_1}{\widetilde{R}T_1} = Xm \tag{4.111}$$

and

$$m_2 = \frac{P_2V_2}{\widetilde{R}T_2} = (1-X)m \tag{4.112}$$

where m is the total mass and X is the mass fraction of gas 1.

As before, we define our control volume to be the total volume and write the First Law:

$$\begin{aligned} \Delta U = U_2 - U_1 = \cancel{Q} - \cancel{W} = 0 && (4.113)\\ \Rightarrow U_2 = U_1 && (4.114)\\ m(Xc_{v,1} + (1-X)c_{v,2})T' = m(Xc_{v,1}T_1 + (1-X)c_{v,2}T_2) && (4.115) \end{aligned}$$

where if $T_1 = T_2 = T$, then

$$\begin{aligned} \cancel{m(Xc_{v,1} + (1-X)c_{v,2})}T' = \cancel{m(Xc_{v,1} + (1-X)c_{v,2})}T && (4.116)\\ \Rightarrow T' = T && (4.117) \end{aligned}$$

which we see is exactly equivalent to our previous single gas case. This makes sense considering that a perfect gas does not interact with itself or other gases. In essence, we can therefore superimpose two separate single gas scenarios if the initial temperatures are equal. This allows us to skip directly to the equation for the entropy generated by linearly adding the results of each single gas case, given by Eq. 4.102. Because entropy is an *extensive property*, we must scale the results by the mass of each gas as:

$$\begin{aligned} \Delta S_{gen} &= m_1\widetilde{R}\ln\frac{V}{V_1} + m_2\widetilde{R}\ln\frac{V}{V_2} && (4.118)\\ &= m\widetilde{R}\left[X\ln\frac{V}{V_1} + (1-X)\ln\frac{V}{V_2}\right] && (4.119) \end{aligned}$$

Solving for V_1 and V_2 gives us

$$V_1 = \frac{m_1\widetilde{R}T}{P_1} = \frac{Xm\widetilde{R}T}{P_1} \tag{4.120}$$

$$V_2 = \frac{m_2\widetilde{R}T}{P_2} = \frac{(1-X)m\widetilde{R}T}{P_2} \tag{4.121}$$

where if the gases have the same initial pressure, P, we can further simplify Eq. 4.118 using the fact that

$$\begin{aligned} V &= V_1 + V_2 && (4.122)\\ &= \frac{(1-X)m\widetilde{R}T}{P} + \frac{(1-X)m\widetilde{R}T}{P} && (4.123)\\ &= \frac{m\widetilde{R}T}{P} && (4.124) \end{aligned}$$

to obtain:

$$\Delta S_{gen} = -m\widetilde{R}\left[X \ln X + (1-X)\ln(1-X)\right] \tag{4.125}$$

We call this quantity in Eq. 4.125 the entropy of mixing for a *binary* mixture and is very commonly used, as in many systems of interest, gases at the same temperature and pressure are being mixed. For i species, this can be generalized to

$$\Delta S_{gen} = -m\widetilde{R}\sum_i X_i \ln X_i \tag{4.126}$$

where it is important that this expression is only valid for isothermal and isobaric mixing, and under different conditions this value will change[14].

4.4.5 Minimum Work of Separation

Returning to our discussion of anthropogenic climate change, a crucial consequence arises from this notion that the mixing of gases irreversibly generates entropy. Specifically, we can clearly see that carbon emissions generated via combustion of hydrocarbons generate entropy as they rise and mix with air in

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[14] For a fascinating thought experiment that illuminates some of the intricacies of the definition of entropy from a microscopic perspective, see *Gibbs' Paradox*.

the atmosphere. Where this becomes important is in computing the energy required to separate that carbon dioxide back out. Intuitively, we might expect that even though no energy was required to mix the gases, because it was done so irreversibly, it will require some minimum amount of energy to separate them, especially since the units of entropy have units energy embedded.

To figure out how much energy is required for separation in the best case scenario, we can start with the combined First and Second Law statement:

$$\Delta U = T(\Delta S + \Delta S_{gen}) - W \tag{4.127}$$

where $\Delta U = 0$ if this process happens isothermally at temperature T, and $\Delta S_{gen} = 0$ if we can carry out this process reversibly. Simplifying, we have under these assumptions that

$$W_{min} = T\Delta S \tag{4.128}$$

where we know from our previous exploration of mixing perfect gases that this change in entropy in separating gases must exactly equal the entropy generated in the mixing process to begin with. Consequently, plugging in Eq. 4.126 into our expression for W_{min} yields

$$W_{min} = -m\widetilde{R}T \sum_i X_i \ln X_i \tag{4.129}$$

Eq. 4.129 tells us the total minimum work required to separate a gas into its constituent species, but it is often useful to know how much work is required per mole of individual species i. To find this, we convert to our molar ideal gas law and divide Eq. 4.129 by $X_i n$, where n is the total number of moles of our mixture. For a binary mixture, or any process where we want to separate a single gas species, we have

$$\hat{w}_{min,i} = -\widetilde{R}T \left[\ln \frac{X_i}{1 - X_i} + \frac{\ln(1 - X_i)}{X_i} \right] \tag{4.130}$$

Fig. 4.18 shows $\hat{w}_{min,i}$ plotted as a function of X_i, showing that for vanishingly small mole fractions of gas, the minimum work required approaches infinity asymptotically. For carbon dioxide in our atmosphere, the mole fraction is about 0.0004 and thus the minimum amount of energy required to remove the carbon dioxide we are emitting is enormous. Indeed, it is not a simple matter to just take the carbon dioxide back out of the air, further compounding the issues we are seeing today with the causes and effects of climate change. We will see later how carbon capture is performed in practice and some promising

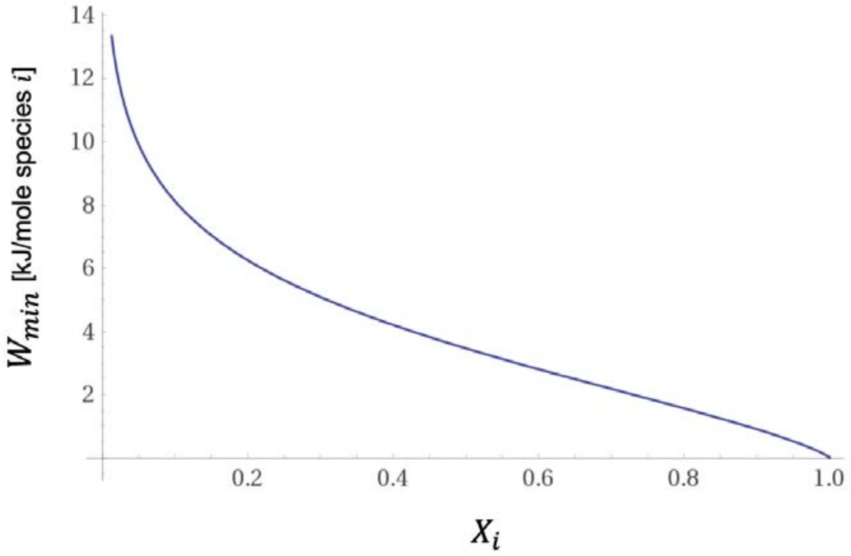

Figure 4.18: Minimum work of separation of gas species i in a mixture per mole of that gas.

new ideas for improving this process; however, the thermodynamics tell us that we must pay a minimum energy price for this separation.

4.5 Summary

This chapter presents the key limitations placed on the conversion between thermal energy and mechanical work as expressed by the Second Law of Thermodynamics, which states that the maximum work that can be extracted from a cycle is done so via all reversible processes. In this sense, irreversibility is defined as a mathematical representation of the work that is "lost" or unextracted due to dissipation, heat transfer at a finite temperature difference, or some other irreversible process. We showed we can quantify this irreversibility using the concept of entropy, which represents the degree of order within a system. For an irreversible process, the entropy of the Universe must increase, though the entropy of a particular gas or solid, for example, within the control volume of interest may decrease. Finally, we further illuminated the relationship between entropy generation and work by looking at an irreversible gas mixing process and showed that some minimum work is required to separate out a single gas species from the mixture. Relating back to our story of climate change, this means that there is a mandatory work penalty incurred when trying to separate CO_2 from the atmosphere, making the task of undoing anthropogenic greenhouse gas emissions extremely difficult.

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Chapter 5

Engines, Power, and the Anthropocene

Through the control of fire, early humans gained control over their *local* environments - clearing land, warding off predators, and providing warmth to survive the colder seasons. It took almost 2 million more years to discover how to turn that thermal energy released on demand via combustion into mechanical *power*, kicking off a seemingly unstoppable cycle of human expansion and increasing energy consumption. Indeed, since the advent and widespread adoption of the *heat engine*, there has been an accelerating influx of new applications to justify using more energy ranging from manufacturing and transportation to computation and space exploration - all largely driven by global politics and economics. Now we are seeing that what began as a dominance over our local environments has perhaps unsurprisingly resulted in the loss of control over our global environment, for which humans have had such a hand in shaping that it warrants its own geological age - the Anthropocene.

In the previous chapter, we showed that undoing carbon emissions by directly separating out CO_2 molecules from the air requires a substantial amount of energy, and while possible, this process would need to be carried out using entirely renewable sources to avoid exacerbating the energy usage to carbon emission feedback loop. While this process, called *Direct Air Capture (DAC)*, will need to be a prominent component of climate change mitigation - especially as humanity draws every closer to several dangerous climatological tipping points triggered by rising CO_2 concentrations - it is also essential that greenhouse gas emissions be curtailed and ultimately stopped at the source. To begin to understand the magnitude of these human-generated emissions, we will now look at the thermodynamics behind one of the largest collective carbon emitters of the “unnatural” world - engines.

Using what we have already learned, in this chapter, we will look at engines, heat pumps, and the various invented systems that drive the production and use of *power* today. We will discuss various combustion-based engine architectures and their ideal efficiencies, as well as systems that generate power continuously by manipulating the state of a continuous stream. For these continuous flow power systems, we will additionally define a Second Law efficiency to relate the actual and maximum performance for the various components that comprise them. In this context, we will then define the concept of the Gibbs Free Energy and how it relates to the maximum work that can be extracted from a stream. Finally, we will look at how all of the development that has resulted from these systems has pushed the global climate to the brink of crisis, and some of the reasons why it is such a challenging but necessary problem to solve as soon as possible.

5.1 Engines

An *engine* is simply a device that uses a thermodynamic cycle to continuously convert thermal energy - historically from the burning of wood or fossil fuels - into mechanical work. We have already seen an example of an engine in our discussion of the forward Carnot Cycle. A *Carnot Engine* is the device that uses the Carnot Cycle to produce mechanical *power* by transferring thermal energy from a hot thermal reservoir to a colder one, extracting energy as work in the process. As used here, power in the thermodynamic context is the rate of energy conversion in units of energy per time - J/s or Watts (W) in SI units. As we discussed, the Carnot Engine has the theoretical maximum efficiency $(1-T_L/T_H)$ for any engine operating between two thermal reservoirs, which is a statement of the Second Law of Thermodynamics. Recall that an equivalent statement for the Second Law is that a device operating in communication with only one thermal reservoir at best can produce no net work over a cycle, and thus that we need two thermal reservoirs to produce any net positive mechanical power.

So to extract continuous power, we can easily construct a coupled system in communication with (at least) two thermal reservoirs in such a way that net work is done. The primary questions for engines then becomes 1) how can we minimize T_L/T_H and 2) how do we efficiently transfer thermal energy between the thermal reservoirs and the working fluid? The answer to the former since the 1700's has largely been the combustion of fossil fuels but more recently has begun to include concentrated solar energy to achieve extremely high temperatures using massive mirror arrays, which we will explore in later chapters.

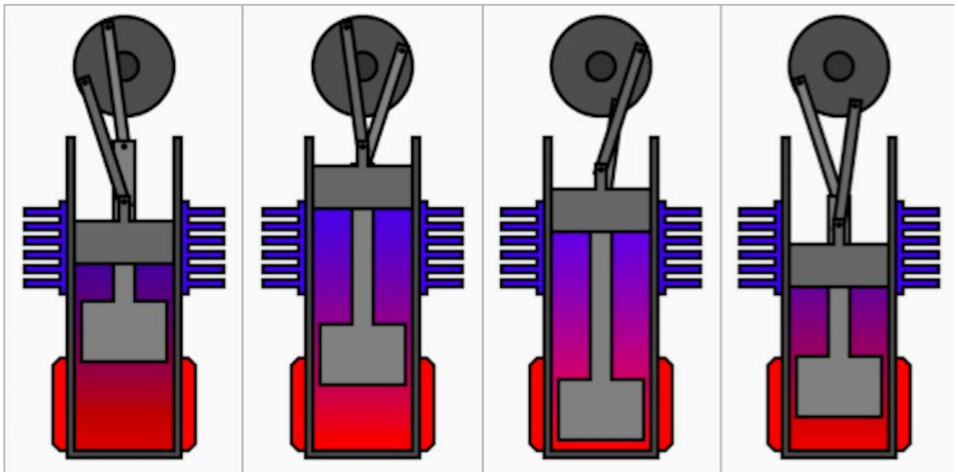

Figure 5.1: Four main stages of a Stirling Cycle. First the displacer forces the gas to be in contact with the hot reservoir, causing the gas to expand and do work via the top piston. The flywheel attached to both the piston and displacer then forces the displacer down, pushing the gas to the top part of the cylinder in communication with the cold reservoir. This cools the gas, causing it to contract and pull the piston down to reset the cycle.

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5.1.1 External Combustion Engines

For combustion-based power cycles, any device for which the heat is released externally and transferred to and from the working fluid indirectly is called an *external combustion engine*. The Carnot Engine we looked at fits this description as there is an external thermal reservoir from which heat is transferred to the working fluid. Early steam engines also operated in this way, and we will dive deeper into the thermodynamics of steam or Rankine Cycles shortly. We will now look at the most common engine architectures used in practice:

Stirling Engine

Another canonical external combustion engine is the *Stirling Engine*, which is shown in Fig. 5.1 and is characterized by the property plots in Fig. 5.2. As shown here, the engine works by displacing the working fluid back and forth between a hot and cold side of a single cylinder. As labeled in these property plots, from state 1 to 2, the working fluid is cooled by the cold thermal reservoir and is compressed by the piston isothermally. The coupled

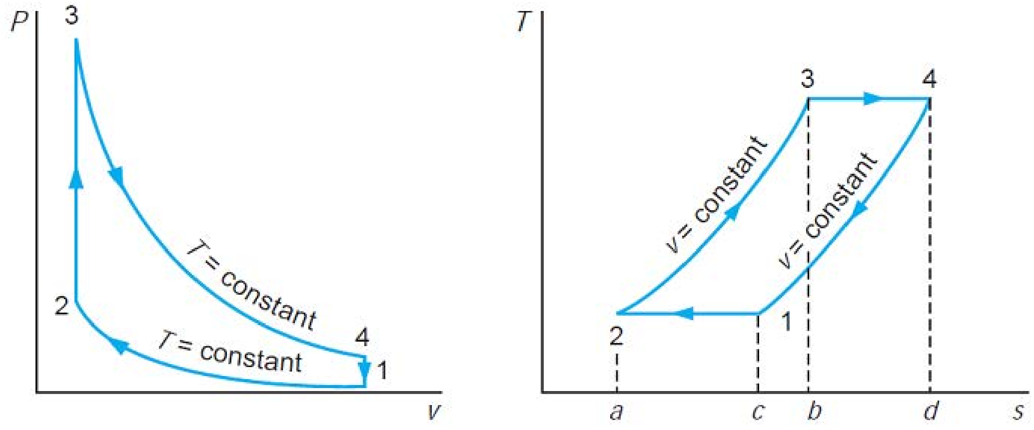

Figure 5.2: P-V and T-S diagrams for a Stirling Cycle. Note the key difference between this and an Otto cycle is that the expansion and compression happen isothermally instead of isentropically.

motion of the displacer pushes the gas to the hot side of the cylinder where thermal energy is transferred at constant volume between states 2 and 3. The piston then expands isothermally to do work from states 3 to 4 and finally heat is rejected to the cold reservoir at constant volume to bring the system back to its initial state.

To determine the efficiency for this system, we can start by looking at the heat added, Q_{in}, over the course of a cycle. Here, heat is transferred to the gas from states $2 \rightarrow 3$ and $3 \rightarrow 4$ and can be expressed mathematically by writing the First Law for each process as

$$\begin{aligned}
\Delta U^{2\to3} &= Q^{2\to3} - \cancel{W^{2\to3}} && (5.1)\\
U_3 - U_2 &= Q^{2\to3} && (5.2)\\
\Rightarrow Q^{2\to3} &= U_3 - U_2 && (5.3)\\
&= mc_v(T_H - T_L) && (5.4)
\end{aligned}$$

and

$$\begin{aligned}
\Delta U^{3\rightarrow4} &= Q^{3\rightarrow4} - W^{3\rightarrow4} \qquad (5.5)\\
mc_v \cancelto{0}{(T_H - T_H)} &= Q^{3\rightarrow4} - W^{3\rightarrow4} \qquad (5.6)\\
\Rightarrow Q^{3\rightarrow4} &= W^{3\rightarrow4} \qquad (5.7)\\
&= \int_3^4 P\,dV \qquad (5.8)\\
&= m\widetilde{R}T_H \int_{V_3}^{V_4} \frac{dV}{V} \qquad (5.9)\\
&= m\widetilde{R}T_H \ln\frac{V_4}{V_3} \qquad (5.10)
\end{aligned}$$

It is important to note here that the heat added from states 2 to 3 and 4 to 1 are equal and opposite in magnitude by this same logic. Typically, we call this the *regenerated heat* as this can be supplied by the thermal mass of the cylinder itself. That is to say from states 4 to 1, heat with a magnitude of $mc_v(T_H - T_L)$ is rejected to the cylinder walls, which is then completely reabsorbed by the gas - or regenerated - from states 2 to 3. Thus the total extra heat that we need to keep the engine running is just

$$Q_{in} = Q^{3\rightarrow4} = m\widetilde{R}T_H \ln\frac{V_4}{V_3} \tag{5.11}$$

The net work, W_{net}, is computed by similar logic as

$$\begin{aligned}
W_{net} &= W^{3\rightarrow4} + W^{1\rightarrow2} \qquad (5.12)\\
&= m\widetilde{R}\left[T_H \ln\frac{V_4}{V_3} + T_L \ln\frac{V_2}{V_1}\right] \qquad (5.13)
\end{aligned}$$

but since $V_1 = V_4$ and $V_2 = V_3$,

$$W_{net} = m\widetilde{R}(T_H - T_L)\ln\frac{V_4}{V_3} \tag{5.14}$$

Putting this all together, we can solve for the efficiency of the ideal Stirling cycle as

$$\eta_{Stirling} = \frac{W_{net}}{Q_{in}} \tag{5.15}$$

$$= \frac{m\widetilde{R}(T_H - T_L)\ln\frac{V_4}{V_3}}{m\widetilde{R}T_H \ln\frac{V_4}{V_3}} \tag{5.16}$$

$$= \frac{T_H - T_L}{T_H} \tag{5.17}$$

$$= 1 - \frac{T_L}{T_H} \tag{5.18}$$

$$= \eta_{Carnot} \tag{5.19}$$

which is exactly equal to the Carnot efficiency! Now we did not say anything about the reversibility of this cycle up until now, but looking carefully at each process, as long as the work is carried out infinitely slowly and all heat is transferred across zero temperature difference, this cycle is indeed reversible. For the regeneration step in particular to be reversible, the cylinder walls must always be the same temperature as the gas locally. The fact that we can recover the Carnot efficiency from this analysis of a completely different reversible cycle operating between two thermal reservoirs further supports the validity of the Second Law of Thermodynamics.

In reality, a Stirling engine will not exactly follow the cycle diagrams in Fig. 5.2 but instead will be closer to the bold curve shown in Fig. 5.3. This actual cycle will not be perfectly reversible and will therefore have an efficiency lower than η_{Carnot}, which again is consistent with the Second Law. In practice, Stirling engines can be made with extremely high efficiencies but typically do not scale well for many applications. Interestingly, because this cycle is reversible, we can run it backwards to get extremely efficient cooling via the heat pump effect previously discussed. This type of device - called a Stirling Cooler - is used in laboratories to achieve extremely cold temperatures down to 10 K or so.

5.1.2 Internal Combustion Engines

Another extremely common engine archetype is the *internal combustion engine* for which the heat driving the cycle is released in such a way that it makes direct contact with the working fluid or is released by the working fluid itself. This type of engine is most commonly used with the combustion of hydrocarbon fuels like gasoline and diesel and is used to power everything from cars to airplanes. While there are many different implementations of this architecture

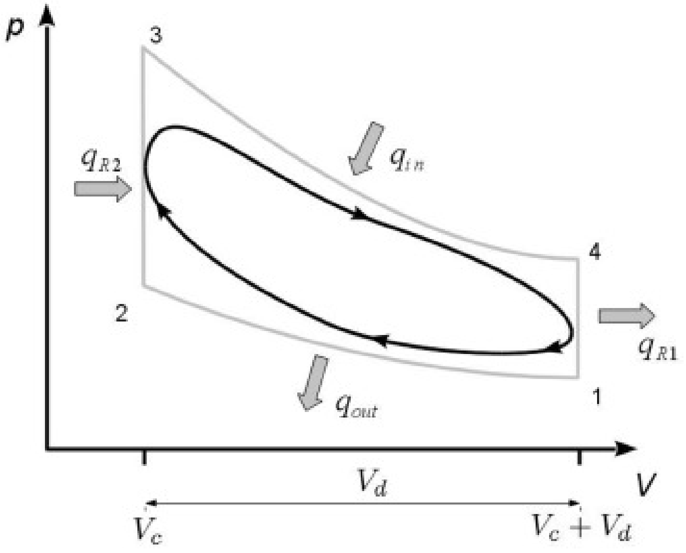

Figure 5.3: *P*-*V* diagram showing the path of an actual non-ideal Stirling Cycle in bold. In reality, it takes finite time to transfer heat to the working fluid and thus the heating does not happen isochorically.

with a plethora of compatible fuels, we will only look at a few of the most common here.

Otto Cycle

The *Otto Engine* - which operates on the *Otto Cycle* - powers virtually every internal combustion engine-based vehicle in the world. In this type of engine, vaporized liquid hydrocarbons and air are drawn into a piston, compressed, and ignited adiabatically using a spark plug to release thermal energy via a combustion reaction. The heat release causes the piston to expand isentropically[1] to do work, and the various combustion products are exhausted. Thus, this cycle is for an open system, so even though the exact molecules of gas are different from loop to loop, the cycle is still valid as long as the new reactants are brought in at the same thermodynamic state. Additionally, the idealized version of this cycle is shown in Fig. 5.4 and is theoretically reversible, though unlike with the Stirling and Carnot Cycles, there is a less clear notion of what the thermal reservoirs are.

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[1] Requires no friction and no heat transfer. The latter requirement can be achieved in practice if the time required for the piston stroke is sufficiently short. This tends to cause dissipation, however.

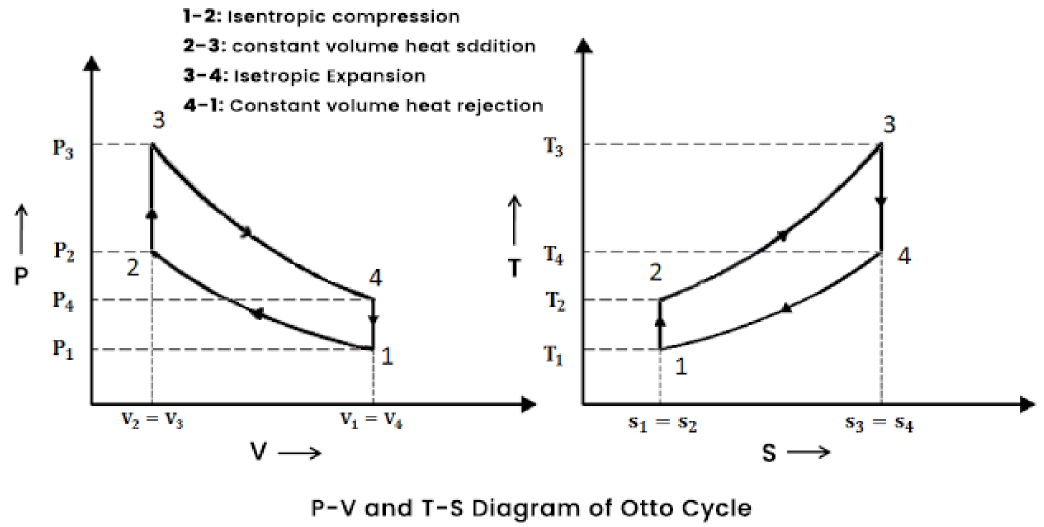

Figure 5.4: P-V and T-S diagrams for the Otto cycle used in many gasoline-powered internal combustion engines.

To determine the maximum efficiency of an Otto Engine, we can start by identifying the effective thermal energy input, Q_{in}, and net work W_{net}. Using the states as labeled in Fig. 5.4, we see that heating release occurs as a result of the combustion reaction between states 2 and 3. Writing the First Law for this process, we can immediately see that the work done is 0 as the combustion happens at constant volume:

$$U_3 - U_2 = Q^{2\to3} - \cancelto{0}{W^{2\to3}} \tag{5.20}$$

$$\Rightarrow Q^{2\to3} = U_3 - U_2 = Q_{in} \tag{5.21}$$

where U_3 is the internal energy of the products at T_3 and U_2 is the internal energy of the reactants at T_2. We will hold off for now saying anything else about their values, as keeping track of the different species is tricky.

Similarly, we can write the heat rejected between states 4 and 1 as

$$Q^{4\to1} = U_4 - U_1 \tag{5.22}$$

Next, noting that processes $1 \to 2$ and $3 \to 4$ are isentropic (reversible adiabatic) we can express the net work by writing the First Law for the cycle:

$$
\begin{aligned}
\cancelto{0}{\Delta U_{cycle}} &= Q_{net} - W_{net} && (5.23)\\
\Rightarrow W_{net} &= Q^{2\rightarrow 3} + Q^{4\rightarrow 1} && (5.24)
\end{aligned}
$$

and substitute in our expressions for $Q^{2\rightarrow 3}$ and $Q^{4\rightarrow 1}$ to yield

$$W_{net} = (U_3 - U_2) + (U_4 - U_1) \qquad (5.25)$$

The efficiency can therefore be written as

$$
\begin{aligned}
\eta_{Otto} &= \frac{W_{net}}{Q_{in}} && (5.26)\\
&= \frac{(U_3 - U_2) + (U_4 - U_1)}{U_3 - U_2} && (5.27)\\
&= 1 - \frac{U_4 - U_1}{U_3 - U_2} && (5.28)
\end{aligned}
$$

where assuming that the products and reactants have the same non-temperature-dependent specific heats, we can write:

$$
\begin{aligned}
\eta_{Otto} &= 1 - \frac{mc_v(T_4 - T_1)}{mc_v(T_3 - T_2)} && (5.29)\\
&= 1 - \frac{T_4 - T_1}{T_3 - T_2} && (5.30)\\
&= 1 - \left(\frac{T_1}{T_2}\right)\frac{T_4/T_1 - 1}{T_3/T_2 - 1} && (5.31)
\end{aligned}
$$

As we did with the Carnot Cycle analysis earlier, we can use the adiabatic expansion and compression relationships to show that

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} \qquad (5.32)$$

and thus

$$\eta_{Otto} = 1 - \frac{T_1}{T_2} \qquad (5.33)$$

which has a similar form as the Carnot Efficiency but represents a physically different phenomena.

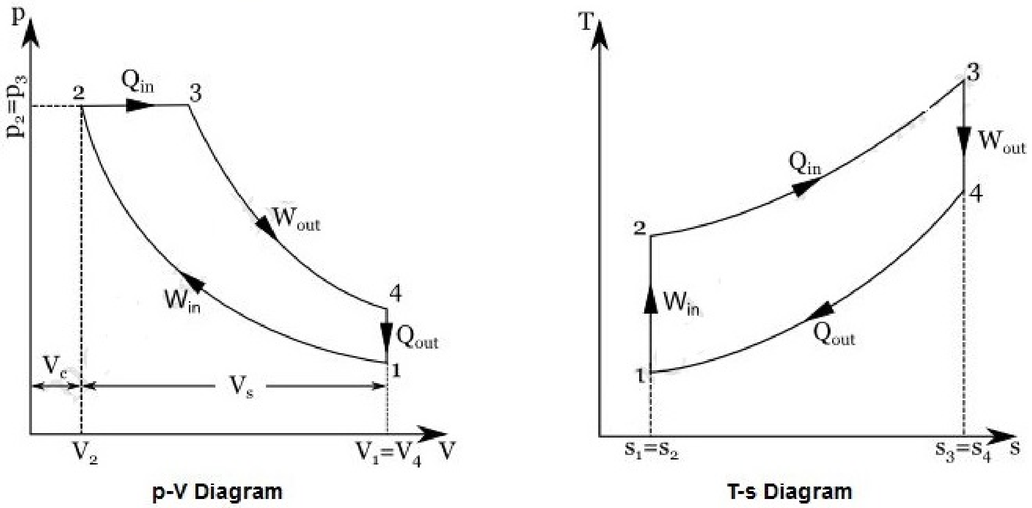

Figure 5.5: P-V and T-S diagrams for the Diesel cycle used in many diesel-powered internal combustion engines. The key difference between this and the Otto cycle is that combustion happens isobarically in the Diesel cycle and isochorically in the Otto cycle.

Finally, with Otto Engines, we typically know the minimum and maximum volumes of the piston well, so we will now get an expression for the efficiency in terms of those volumes, V_1 and V_2. To do this, we can easily relate T_1/T_2 to V_1/V_2 again via the adiabatic compression relationship:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \tag{5.34}$$

and thus

$$\eta_{Otto} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r^{(\gamma-1)}} \tag{5.35}$$

where r is the *compression ratio* equal to V_1/V_2. This is the maximum efficiency that an actual Otto Engine can achieve, and in reality heat loss to the environment and other irreversibility caused by friction and mixing of gases will detract from this efficiency.

Diesel Cycle

A similar process to the Otto Cycle is the *Diesel Cycle*, which differs from the Otto Cycle in that combustion happens at constant pressure instead of constant volume. Fig. 5.5 shows the property plots for the ideal reversible Diesel Cycle which look very similar to that of the Otto Cycle in Fig. 5.4, except for process 2 → 3. The efficiency can be derived in a similar manner, though it is made more complex by the fact that the system does work during the combustion process. We will not derive that here, but it can be shown that the efficiency of this cycle is given by

$$\eta_{Diesel} = 1 - \frac{1}{r^{(\gamma-1)}}\left(\frac{\alpha^{\gamma}-1}{\gamma(\alpha-1)}\right) \tag{5.36}$$

where $\alpha = V_3/V_2$ and $r = V_1/V_2$.

We can see directly from Eq. 5.36 that the efficiency of the theoretical Diesel Engine is less than that of the equivalent Otto Cycle, though in practice, diesel engines are often more efficient for a variety of reason we will not go into detail about here. One of the main reasons, however, is that in an internal combustion engine, a high compression ratio will cause the fuel to ignite before the piston reaches its minimum volume, wasting significant energy in the process. Diesel engines can achieve much higher compression ratios due to the fact that the combustion occurs at constant pressure and thus there is much more room to increase the pressure during the compression. In fact, because of this fact, diesel engines do not require a spark plug as the compression itself is what ignites the fuel.

Note that in internal combustion engines (and many external combustion engines as well), this cycle is occurring in several different piston simultaneously, each operating out of phase from one another. This helps to ensure that the engine is balanced and that power is more or less being continuously produced over time. Additionally, engines and the devices that use them rely on the inertia of the engine itself to smooth out the operation. This can be accomplished with a heavy spinning mass called a *flywheel*, which helps to ensure that any other moving parts coupled to the engine - like the displacer in the Stirling Engine - continue to operate in between the power strokes of the engine. In some machines - cars, for example - the inertia of the machine itself helps to smooth things out. For this reason, most combustion engines cannot simply start self start; instead, they need a small electric motor to start the engine spinning in order to build up enough inertia to sustain the cycle[2].

---

[2] This is why you cannot start a gasoline-powered car, for example, when the battery is dead.

5.2 Continuous Flow Power Systems

Up until this point, we have been primarily discussing closed systems and their associated cycles with discrete *temporally sequential* processes. For example, a gas in a piston undergoes expansion or compression but at any given time, our control volume has a homogeneous state throughout and moves throughout the cycle sequentially one step at a time. While most combustion engines operate with multiple pistons running out of phase from one another, we still treat each piston as a separate cycle with a homogeneous internal state. Also even though internal combustion engines, for example, exhaust the working fluid at the end of the cycle and replace the fuel and oxidizer before beginning again, we are still able to analyze the cycle as if the same gas remained inside the whole time.

In contrast to these closed temporally sequential cycles, *continuous flow* or *continuous power* cycles are comprised of a flowing working fluid whose state changes continuously throughout the system. The cycle is happening such that states are better represented *spatially* in the system than temporally as is the case with the discrete closed systems we previously looked at. We just as easily represent these cycles on property plots as we can imagine tracking a small homogeneous packet of working fluid as it flows from one device to the next, even though in reality, all states in the cycle exist at the same time but separated in space. This concept will be made clear by looking at some example devices and cycles.

5.2.1 Open Systems

Before we begin describing systems, we need to first establish a framework for analyzing *open systems*, which unlike *closed* systems, allow mass to enter and exist the control volume. Just like with closed systems, however, we can track the energy of the *streams* in and out and relate those fluxes to the change in internal energy using the First Law. As shown in Fig. 5.6 a generalized control volume for such a system has mass flowing in and out with its own internal energy, useful work done continuously via *shear* stresses of the liquid, useful work done by the *normal* stresses (i.e. $\int P\,dV$), and heat transfer in and out. Because these systems are operating continuously, we replace our Δ operators for $\frac{d}{dt}$ operators in order to analyze how the system changes continuously with time. For energy contained within the control volume, E_{CV}, we have for example

$$\Delta E_{CV} \rightarrow \frac{d}{dt}(E_{CV}) \equiv \dot{E}_{CV} \tag{5.37}$$

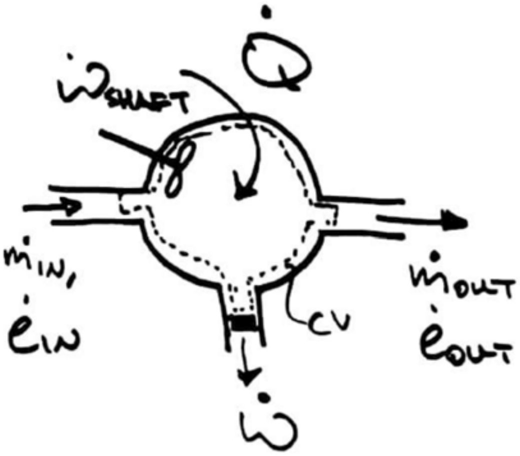

Figure 5.6: Generalized control volume for continuous flow open systems.

where $\dot{E}_{CV}$ has units of energy per time or Watts in SI units.

Conservation of Mass

For the open systems we will look at in this text, mass is conserved, which can be expressed mathematically as

$$\frac{d}{dt}m_{CV} = \dot{m}_{in} - \dot{m}_{out} \tag{5.38}$$

which simply states that the rate of change of mass inside the control volume is equal to the difference in mass flow rates between the entering and exiting mass streams. Note that in steady state, $\frac{d}{dt}m_{CV} = 0$. Here $\dot{m}$ is a *mass flow rate* in units of mass per time. Because there can be many streams coming in and leaving our system, Eq. 5.38 can be generalized to

$$\frac{d}{dt}m_{CV} = \left(\sum_i \dot{m}_i\right)_{in} - \left(\sum_i \dot{m}_i\right)_{out} \tag{5.39}$$

First Law

We can similarly write the First Law for open systems as

$$\dot{E}_{CV} = \left(\sum_i \dot{m}_i e_i\right)_{in} - \left(\sum_i \dot{m}_i e_i\right)_{out} + \dot{Q}_{net} - \dot{W}_{net} \tag{5.40}$$

where e_i is the specific internal energy of stream i and can include kinetic energy, gravitational potential energy, etc. For fluids flowing in and out of the system, it is important to note that at the boundaries of our control volume, the fluid stream itself is doing mechanical work of the form $\int P\,dV$ as it will have some pressure acting over a volumetric displacement. By definition, we differentiate this work from any other work done by the *deformation* of the control volume or mechanical work done by a shaft that is stuck into the fluid[3]. The reason for this differentiation is that we can directly lump together the internal energy of the stream, u_i, and this *PV flow* work done by stream at the boundary as the *enthalpy* of the stream:

$$h_i = u_i + (Pv)_i \tag{5.41}$$

where v is the specific volume in units of volume per mass.

Thus, it is often common to write the first law as

$$\begin{aligned}\dot{E}_{CV} = \left[\sum \dot{m}(h + \frac{1}{2}w^2 + gz + ...)\right]_{in} - \left[\sum \dot{m}(h + \frac{1}{2}w^2 + gz + ...)\right]_{in} \\ + \dot{Q}_{net} - \dot{W}_{net}\end{aligned} \tag{5.42}$$

where h is the specific enthalpy of the stream, $1/2w^2$ the specific kinetic energy, gz the specific gravitational potential energy, and the ellipsis represents all other forms of energy relevant to the particular problem.

Second Law

Similarly, we can write the Second Law for our open system as

$$\dot{S}_{CV} = \left(\sum_i \dot{m}_i s_i\right)_{in} - \left(\sum_i \dot{m}_i s_i\right)_{in} + \sum \frac{Q_i}{T_i} + \dot{S}_{gen} \tag{5.43}$$

where for irreversible cycles, $\dot{S}_{gen} > 0$, and for reversible cycles, $\dot{S}_{gen} = 0$.

Examples

Let us look at two simple examples to illustrate how to use these principles in practice for open systems. Perhaps the simplest open system is an adiabatic

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[3] We differentiate *shaft work* typically from PV work as shaft work requires that a shear stress be applied to some surface to spin a propeller for example vs PV work which requires that a normal stress be applied to a deforming boundary.

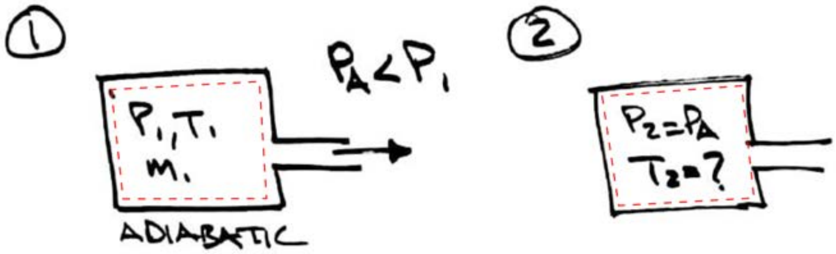

Figure 5.7: Example problem where a gas in an adiabatic container initially at some pressure $P_1 > P_a$ expands and exits the container.

container that is initially at some pressure, P_1, that is greater than ambient pressure. Intuitively if open the container, the gas contained within it will rush out. The question is, what is the final temperature of the gas that remains within the control volume, as shown in Fig. 5.7? There are two ways to solve this problem. First, how we would have approached this previously would be by working backwards and only encompassing the gas that remains in the container at the end of the process in our control volume. We could then track these particles back to state 1 and realize that this gas is simply undergoing adiabatic expansion and then apply the appropriate relationships between P and T for an ideal gas. Because we are tracking the same particles of gas throughout the process and morphing our control volume continuously, we are actually treating this control volume as a closed system. This allows us to directly write

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{5.44}$$

Using our new understanding of open systems, we can also approach this problem by maintaining a fixed control volume as shown in Fig. 5.7 and keeping track of the gas that leaves the control volume between states 1 and 2. Writing the open system form of the First Law, we have

$$\dot{E}_{CV} = \cancelto{0}{(\dot{m}h)_{in}} - (\dot{m}h)_{out} + \cancelto{0}{\dot{Q}_{net}} - \cancelto{0}{\dot{W}_{net}} \tag{5.45}$$

where we can immediately cancel out terms due to the system being adiabatic and the fact that no work is being done other than by the stream itself exiting the container, which as we saw, is captured in the enthalpy term of the outgoing stream. Note we assume here that the macroscopic kinetic energy of the gas leaving is negligible. Recalling that $h = c_pT$ and $u = c_vT$ for an ideal gas, we can rewrite this expression as

$$\frac{d}{dt}(mc_vT) = -\dot{m}_{out}c_pT \tag{5.46}$$

where m is mass in the control volume at some time t. By conservation of mass we know that $\dot{m} = -\dot{m}_{out}$, and thus

$$\begin{aligned}
\frac{d}{dt}(mc_vT) &= -\dot{m}_{out}c_pT & (5.47)\\
\dot{m}c_vT + mc_v\dot{T} &= \dot{m}c_pT & (5.48)\\
\Rightarrow mc_v\dot{T} &= \dot{m}(c_p - c_v)T & (5.49)\\
\Rightarrow \frac{\dot{T}}{T} &= \frac{c_p - c_v}{c_v}\frac{\dot{m}}{m} & (5.50)\\
&= (\gamma - 1)\frac{\dot{m}}{m} & (5.51)
\end{aligned}$$

Switching the limits of integration from time to state variables of T and m and integrating both sides, we have

$$\begin{aligned}
\int_{T_1}^{T_2} \frac{dT}{T} &= (\gamma - 1)\int_{m_1}^{m_2} \frac{dm}{m} & (5.52)\\
\Rightarrow \frac{T_2}{T_1} &= \left(\frac{m_2}{m_1}\right)^{\gamma-1} & (5.53)
\end{aligned}$$

and finally using the ideal gas law to replace m with $\frac{PV}{RT}$, we get

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{5.54}$$

which is exactly what would have gotten using our first approach. While for this example, this open system approach was more convoluted, for many systems, we cannot easily track the motion of the individual particles and instead must use a fixed control volume.

Recall that this is the same result we obtained for a perfectly reversible adiabatic expansion process, and thus if we compute the entropy for our control volume over this process, we would indeed find that it is exactly 0. Intuitively, however, we would not expect the process of gas rushing out of a container into the surrounding air to be a reversible process. In reality it is not, but in

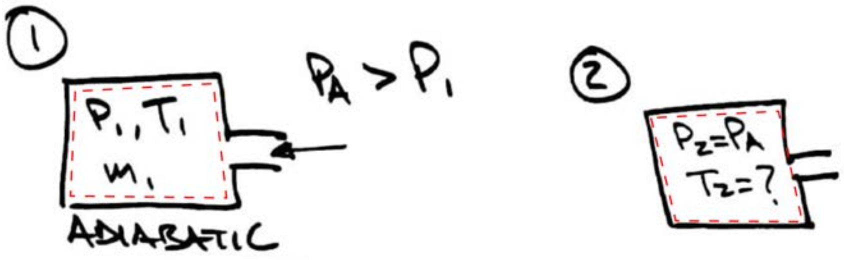

Figure 5.8: Example where an adiabatic container is initially at some pressure $P_1 < P_a$ and then opens to allow ambient air to rush in.

the way we defined our control volume, all irreversibility occurs *outside* the container and outside our control volume. This makes the math much easier.

We can also look at the opposite of this process, where instead we have the initial pressure inside the container less than ambient pressure such that when the container is opened, gas rushes in. We will take the same fixed control volume as in the previous example and as shown in Fig. 5.8. Clearly there will be irreversibility generated inside our control volume in this process due to mixing and dissipation; however, we can still write the First and Second Laws for this process. Starting with the First Law, again ignoring the macroscopic kinetic energy of the gas coming in, we have that

$$\dot{E}_{CV} = (\dot{m}h)_{in} - \cancelto{0}{(\dot{m}h)_{out}} + \cancelto{0}{\dot{Q}_{net}} - \cancelto{0}{\dot{W}_{net}} \tag{5.55}$$

As before, we can substitute our expressions for internal energy and enthalpy to yield

$$\frac{d}{dt}(mc_vT) = \dot{m}c_pT_a \tag{5.56}$$

where T_a is the ambient temperature of the entering gas - the temperature at the boundary where we are tracking the enthalpy. Using the ideal gas law and the relationship that $R = c_v/(\gamma - 1)$, this expression is equivalent to

$$\frac{d}{dt}\left(\frac{PV}{\gamma - 1}\right) = \dot{m}c_pT_a \tag{5.57}$$

Switching the limits of integration and integrating:

$$\frac{V}{\gamma - 1}\int_{P_1}^{P_2} dP = c_p T_a \int_{m_1}^{m_2} dm \tag{5.58}$$

$$\Rightarrow \frac{(P_2 - P_1)V}{\gamma - 1} = (m_2 - m_1)c_p T_a \tag{5.59}$$

$$= \left(\frac{P_2 V}{\widetilde{R}T_2} - \frac{P_1 V}{\widetilde{R}T_1}\right) c_p T_a \tag{5.60}$$

For $P_1 = 0$, this simplifies to the expression:

$$T_2 = \gamma T_a \tag{5.61}$$

We can write the Second Law for this example to characterize the irreversibility generated by this process as

$$\dot{S}_{CV} = (\dot{m}s)_{in} - \cancel{(\dot{m}s)_{out}} + \cancel{\sum_i \frac{Q_i}{T_i}} + \dot{S}_{gen} \tag{5.62}$$

Because entropy as used here is a relative quantity, we must choose some reference against which to measure the change in entropy throughout the process. If we choose the reference state to be (T_a, P_a), then we conveniently find that

$$s_{in} - s_0 = c_p \ln\frac{T_a}{T_a} - \widetilde{R}\ln\frac{P_a}{P_a} = 0 \tag{5.63}$$

and after integrating Eq. 5.62 and taking $P_1 = 0$,

$$\Delta S_{gen} = m_2(s_2 - s_0) - \cancel{m_1(s_1 - s_0)} \tag{5.64}$$

$$= m_2\left(c_p \ln\frac{T_2}{T_a} - \cancel{\widetilde{R}\ln\frac{P_a}{P_a}}\right) \tag{5.65}$$

$$= m_2 c_p \ln\frac{\gamma T_a}{T_a} \tag{5.66}$$

$$= m_2 c_p \ln\gamma \tag{5.67}$$

For gases, $\gamma > 1$, and thus the $\Delta S_{gen} > 0$ as we would expect for this irreversible process. Note that in the above analysis, we assumed that the system inside the control volume started as a perfect vacuum with zero mass, and therefore $S_1 = 0$. In this process, the irreversibility comes from the diffusion of the gas entering the container and the ensuing dissipation that drives an increase in the temperature of the gas.

5.2.2 Power Conversion Devices

With an understanding of how the First and Second Laws are formulated for open and continuous flow systems, we can now take a high level look at a class of devices that are used in the various processes of power cycles. These so-called *power conversion devices* are used to manipulate the thermodynamic state of a stream, extracting or supply net work or net heat to the stream in the process. On our cycle diagrams, each one of these devices typically represents a single process taking the system from one well-defined state to the next. For each of the following devices, we are interested in characterizing the subsystem at *steady-state* - where total internal energy and mass within the control volume at any given time do not change with time.

For the devices in particular that require either the input or extraction of mechanical work to change the state of the stream - for example a compressor or pump - we will define a *Second Law Efficiency*[4], which compares the actual work to the work of the ideal reversible device. This efficiency will be defined differently for each device, but it is worth noting here that it is fundamentally different from the previous efficiency we looked at, which is typically called a *First Law Efficiency* that compares the energy put in to the “usefull” energy extracted. The Second Law Efficiency is measurable and thus gives us the ability to model these devices as undergoing ideal reversible processes - which are typically easier to analyze - and then simply apply the efficiency directly in our analysis as we will see.

Compressor

A device that is capable of compressing a continuous stream of some working fluid - typically a gas - is fittingly called a *compressor*. There are many different implementations of this type of device, but they all take in a gas at P_1 and output it at P_2 such that $P_2 > P_1$. Fig. 5.9 shows the simplified diagram of a compressor with a stream entering at state 1 and leaving at state 2 as mechanical power, $\dot{W}$ is applied to bring the gas to a higher pressure. Writing the First Law for the idealized adiabatic compressor, we find that

$$\dot{E}_{CV} = \cancel{\dot{Q}_{net}} - \dot{W}_{ideal} + \dot{m}(h_1 - h_{2s}) \tag{5.68}$$

and thus

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[4] also called *isentropic efficiency*

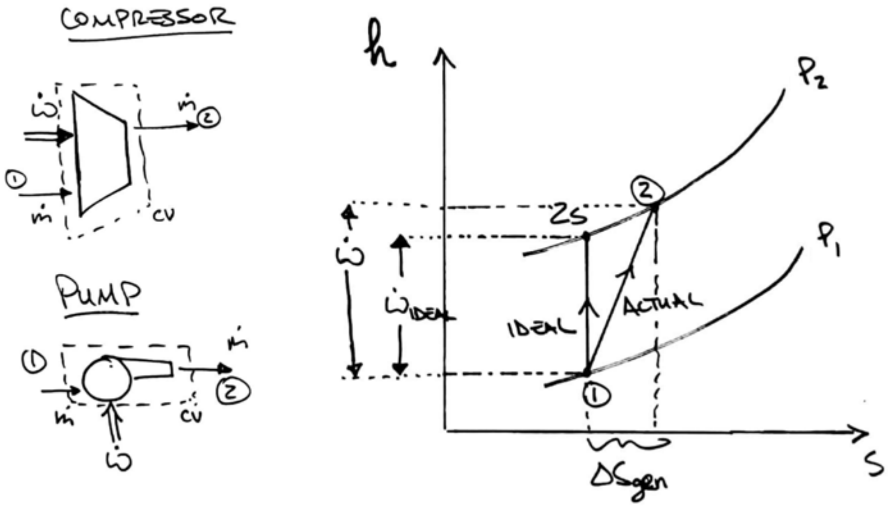

Figure 5.9: Compressor and pump control volume and corresponding h-s plot showing that generated entropy requires more work be added to achieve same pressure ratio, P_2/P_1.

$$\begin{aligned}\dot{W}_{ideal} &= -\dot{m}(h_{2s} - h_1) && (5.69)\\ &= -\dot{m}c_p(T_{2s} - T_1) && (5.70)\\ &= -\dot{m}c_pT_1(\frac{T_{2s}}{T_1} - 1) && (5.71)\end{aligned}$$

which we can relate to pressures P_1 and P_2 by applying our familiar adiabatic relationship between P and T. Substituting this expression into Eq. 5.69 gives us

$$\dot{W}_{ideal} = -\dot{m}c_pT_1\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] \tag{5.72}$$

We can then define our Second Law Efficiency for the compressor, η_c^{II}, as

$$\eta_c^{II} = \frac{\dot{W}_{ideal}}{\dot{W}_{actual}} \tag{5.73}$$

and thus if we are given this efficiency, we can compute the actual work required to change the stream from state 1 to 2 using a non-ideal compressor as

$$\dot{W}_{actual} = \frac{1}{\eta_c^{II}} \dot{m} c_p T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \tag{5.74}$$

because we can easily compute $\dot{W}_{ideal}$ and can measure $\dot{W}_{actual}$ for a range of different states, we can get a well-defined value for η_c^{II} in practice. Typical Second Law Efficiencies range from 0.7-0.9.

To characterize the entropy generated in an actual compressor, we can write the Second Law for a non-ideal compressor as

$$\begin{aligned}
\cancel{\dot{S}_{CV}} &= \cancel{\sum_i \frac{\dot{Q}_i}{T_i}} + \dot{m}(s_1 - s_2) + \dot{S}_{gen} && (5.75)\\
\Rightarrow \dot{S}_{gen} &= \dot{m}(s_2 - s_1) && (5.76)\\
&= \dot{m} \left[c_p \ln \frac{T_2}{T_1} - \widetilde{R} \ln \frac{P_2}{P_1} \right] && (5.77)\\
&= \dot{m} \left[c_p \ln \left(1 + \frac{1}{\eta_c^{II}} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \right) - \widetilde{R} \ln \frac{P_2}{P_1} \right] && (5.78)
\end{aligned}$$

where we can easily see that for $\eta_c^{II} = 1$, $\dot{S}_{gen} = 0$. Graphically, this relationship between irreversibility and enthalpy - and thus work required to compress the gas - can be clearly illustrated by plotting the process on an *h*-*s* diagram as shown in Fig. 5.9. As shown here, the ideal process is *isentropic* and thus represented by a vertical line on this plot connecting isobars at P_1 and P_2. On these plots "2s" represents the idealized state 2. In reality, if entropy is generated in this process, the enthalpy required to achieve the same pressure increase will be greater as shown here. Because the work required for this process is directly proportional to the change in enthalpy, then the actual process will require more work as well, as we showed analytically here.

Pump

A *pump* is essentially just a compressor but one that is typically used with incompressible fluids like water instead. It can be represented on a similar *h*-*s* diagram as shown in Fig. 5.9. Because the fluid is incompressible, several simplifications can be made in the characterization of this type of device. Writing the First Law, rearranging to solve for the input work, and substituting in our expression for enthalpy for a solid or incompressible fluid:

$$\dot{E}_{CV} = \cancel{\dot{Q}_{net}} - \dot{W}_{ideal} + \dot{m}(h_1 - h_{2s}) \tag{5.79}$$

$$\Rightarrow \dot{W}_{ideal} = \dot{m}(h_1 - h_2) \tag{5.80}$$

$$= \dot{m}[c(T_1 - T_2) + (P_1 - P_2)v] \tag{5.81}$$

where v is the fluid specific volume. To figure out the relationship between T_1 and T_2 for the ideal case, we can write the Second Law and show that

$$\cancel{\dot{S}_{CV}} = \cancel{\sum_i \frac{Q_i}{T_i}} + \dot{m}(s_1 - s_{2s}) + \cancel{\dot{S}_{gen}} \tag{5.82}$$

$$\Rightarrow s_1 - s_{2s} = 0 \tag{5.83}$$

$$c \ln \frac{T_{2s}}{T_1} = 0 \tag{5.84}$$

$$\Rightarrow T_{2s} = T_1 \tag{5.85}$$

As before, we can define a Second Law Efficiency, η_p^{II}, such that

$$\dot{W}_{actual} = \frac{\dot{W}_{ideal}}{\eta_p^{II}} = \frac{1}{\eta_p^{II}}\dot{m}(P_2 - P_1)v \tag{5.86}$$

which is also useful in determining the temperature rise of the fluid in the non-ideal case:

$$\dot{m}[c(T_2 - T_1) + (P_2 - P_1)v] = \frac{1}{\eta_p^{II}}\dot{m}(P_2 - P_1)v \tag{5.87}$$

$$\Rightarrow T_2 - T_1 = \frac{1}{c}(P_2 - P_1)v\left(\frac{1}{\eta_p^{II}} - 1\right) \tag{5.88}$$

This allows us to compute the entropy generated as

$$\dot{S}_{gen} = \dot{m}(s_2 - s_1) = \dot{m}c \ln \frac{T_2}{T_1} \tag{5.89}$$

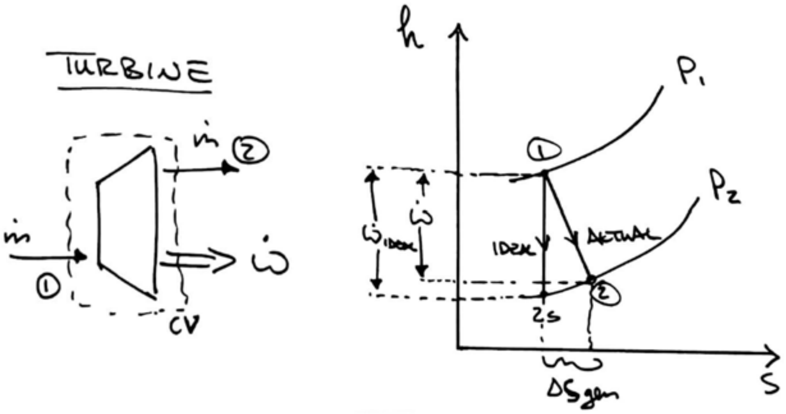

Figure 5.10: Turbine control volume and corresponding *h*-*s* plot showing that the actual work extracted is limited by the generated entropy.

Turbine

A *turbine* is the opposite of a compressor and pump in that it takes in a stream a reduces its enthalpy by expanding it, extracting mechanical work in the process. Again we can start with the First Law for a gas to analyze the ideal device and then define an efficiency to relate its performance to an actual turbine:

$$\cancel{\dot{E}_{CV}} = \cancel{\dot{Q}_{net}} - \dot{W}_{ideal} + \dot{m}(h_1 - h_{2s}) \tag{5.90}$$

$$\Rightarrow \dot{W}_{ideal} = \dot{m}(h_1 - h_{2s}) \tag{5.91}$$

where $2s$ on the h-s diagram in Fig. 5.10 indicates the endpoint of the idealized isentropic expansion process. As before, we define a Second Law Efficiency to relate this ideal work to the work done by an actual turbine:

$$\dot{W}_{actual} = \eta_T^{II} \dot{W}_{ideal} \tag{5.92}$$

$$= \eta_T^{II} \dot{m} c_p T_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right] \tag{5.93}$$

With this information, we can use the First Law for an ideal gas to establish a relationship between T_2 and T_1 as

$$(T_2 - T_1) = \eta_T^{II} T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \tag{5.94}$$

which enables us to solve for the entropy generated in this process as

$$\dot{S}_{gen} = \dot{m} \left[c_p \ln \frac{T_2}{T_1} - \widetilde{R} \ln \frac{P_2}{P_1} \right] \tag{5.95}$$

As we did with the pump, we can also analyze a turbine assuming that the stream is comprised of incompressible fluid. For this case,

$$\dot{W}_{actual} = \eta_T^{II} \dot{W}_{ideal} = \eta_T^{II} \dot{m}(P_1 - P_2)v \tag{5.96}$$

where $\Delta T = 0$ across the ideal process if no entropy is generated. The entropy generated for the real process can be solved exactly as we did for the pump case.

Heat Exchanger

The final continuous flow device we will briefly look at here is the *heat exchanger*, which unlike the compressor, pump, and turbine serves to transfer heat between two streams. As shown in Fig. 5.11, heat exchangers can operate in *parallel flow* or *counter flow* configurations, both of which transfer heat continuously along their length. Writing the First Law for control volumes surrounding each of the streams, we have

$$\cancel{\dot{E}_{CV,B}} = \dot{Q} - \cancel{\dot{W}} + [\dot{m}(h_2 - h_1)]_A \tag{5.97}$$

and

$$\cancel{\dot{E}_{CV,A}} = -\dot{Q} - \cancel{\dot{W}} + [\dot{m}(h_2 - h_1)]_B \tag{5.98}$$

because the heat flux leaving one stream is equal and opposite in magnitude to the heat flux entering the other stream, we can relate these two equations as

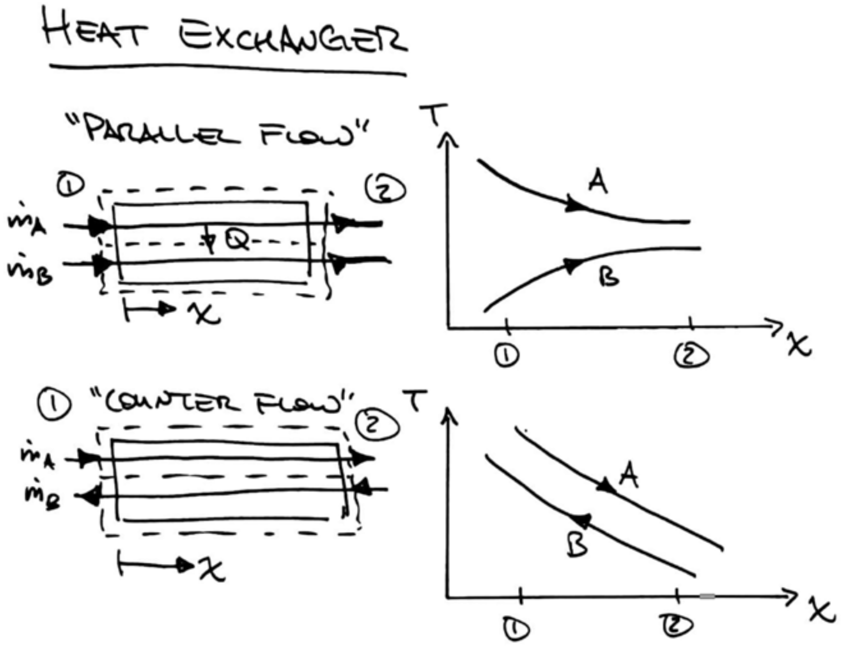

Figure 5.11: Two common heat exchanger configurations that facilitate a heat transfer, Q, between two streams.

$$[\dot{m}(h_2 - h_1)]_A = -[\dot{m}(h_2 - h_1)]_B = \dot{Q} \tag{5.99}$$

The actual physics determining how this heat transfer occurs is beyond the scope of this text but is covered in detail in most previous heat transfer textbooks [Mills]. What Eq. 5.99 tells us, however, is that if we can measure the enthalpy of either stream at the inlet and outlet, we can determine the amount of heat transferred between the two streams. In order to compute the entropy generated from this process, we would need to be able to say something about the temperature profile along the length of the heat exchanger. This is dependent on the various parameters of the exchanger itself.

Additionally, heat can only flow where there is temperature difference between the two streams and the heat flux is proportional to the temperature difference. For this reason the counter flow configuration is capable of maintaining a larger temperature difference over the entire length and is therefore often favored for applications requiring a continuous flow heat exchanger. Despite the *effectiveness* of the heat exchanger, considerable entropy will be generated in this process as a result of the intentional heat transfer across as large a temperature difference as possible.

5.2.3 Continuous Power Cycles

Putting this all together, the previously discussed continuous flow devices can be used to generate power continuous via numerous different power cycles. In particular, we will look at what is arguably the oldest known power cycle, the *Rankine Cycle*, which underlies the operation of old steam engines and modern power plants that use geothermal, nuclear, or other external heat sources. We will also analyze the *Brayton Cycle*, which is the continuous analog to the Diesel Cycle. Like the Diesel Cycle, Brayton Cycle utilizes a combustible fuel source undergoing constant-pressure combustion to generate the thermal energy necessary to do net mechanical work. Instead of taking place in a piston, however, the Brayton Cycle uses a continuous compressor and turbine as configured in Fig. 5.13.

Rankine Cycle

The first known engine was the previously mentioned Aeolipile, which was a very rudimentary *steam engine* that uses an external heat source to vaporize water, causing the whole device to spin and perform mechanical work. Almost 2000 years later, in the 1700's CE, this cycle was improved upon to create what is now the modern *Rankine Cycle*. As shown in Fig. 5.12, a Rankine Cycle is a closed-loop, continuous power cycle that utilizes a pump, boiler or heat exchanger, turbine, and condenser. In the ideal cycle, between states 1 and 2, liquid water or some other working fluid in liquid phase is pumped isentropically to high pressure. Then heat is transferred to the fluid isobarically between states 2 and 3, first bringing the fluid to its saturation temperature, then vaporizing the fluid, and finally superheating the vapor, bringing it to state 3. The superheated vapor is then sent through a turbine where work is extracted as the vapor expands isentropically to state 4, which is typically at atmospheric pressure. Finally, between states 4 and 1, heat is rejected and the vapor condenses back into liquid phase isobarically to reset the cycle.

To analyze the ideal system, we can write the First Law for each process given our stated assumptions. Starting with the pumping process, we have from Eq. 5.81 that

$$\dot{W}_{pump} = \dot{W}^{1\to 2} = \dot{m}(h_1 - h_2) \tag{5.100}$$

$$= \dot{m}[c(T_1 - T_2) + (P_1 - P_2)v] \tag{5.101}$$

as no thermal energy transferred in or out of our control volume in the ideal case.

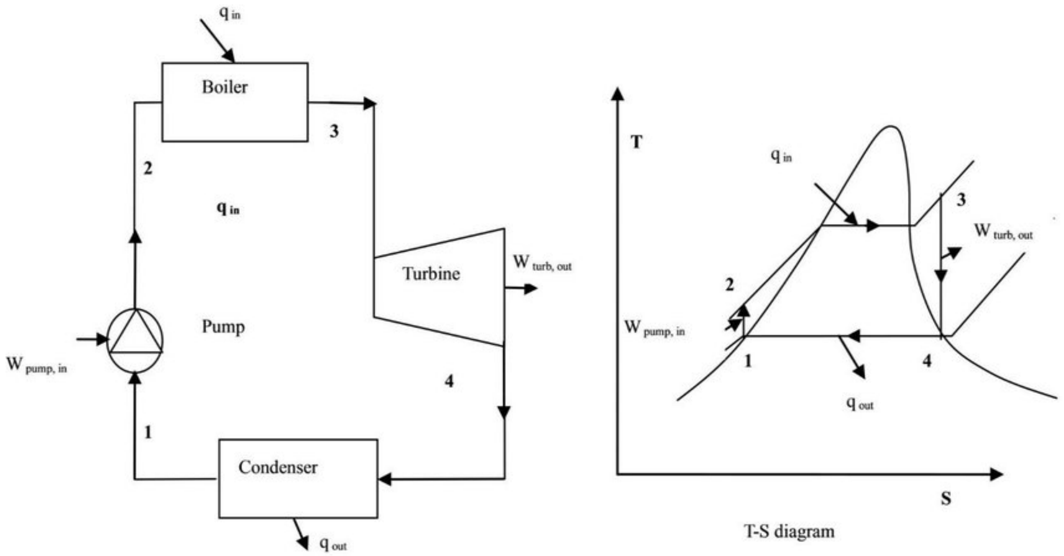

Figure 5.12: Ideal Rankine Cycle schematic and T-S diagram.

From state 2 to 3, we can again write the first law to relate the heat transferred, $\dot{Q}_{in} = \dot{Q}^{2\to 3}$ to the other state properties as

$$\cancel{\dot{E}_{CV}} = \dot{Q}^{2\to 3} - \cancel{\dot{W}^{2\to 3}} + \dot{m}(h_2 - h_3) \tag{5.102}$$

$$\Rightarrow Q^{2\to 3} = \dot{m}(h_3 - h_2) \tag{5.103}$$

It is important to keep track of what phase the working fluid is at the beginning and end of this process. While we do not need to know anything about how the phase change occurs, we do need to be able to fully characterize the state of the fluid at states 2 and 3 to determine h_2 and h_3. In the example cycle shown in Fig. 5.12, state 2 lies outside and to the left of the vapor dome, meaning that it will be completely in liquid phase in state 2. State 3 lies outside the dome and to the right, meaning that it will be completely in vapor phase at state 3. If state 3 instead terminates inside the vapor dome, then we need to know some additional piece of information about the working - e.g. the total specific volume or enthalpy - to also then determine the vapor quality.

For the expansion and work extraction process between states 3 and 4, the ideal work output is given by Eq. 5.72 as

$$\dot{W}_{turbine} = \dot{W}^{3\rightarrow 4} = \dot{m}(h_3 - h_4) \tag{5.104}$$

$$= -\dot{m}c_p T_3 \left[\left(\frac{P_4}{P_3} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \tag{5.105}$$

In practice, modern turbine blades can be easily damaged by the formation of water droplets during the expansion process, and thus Rankine Cycles are typically operated such that state 4 lies right on the vapor dome or just outside of it to ensure that the working fluid remains in vapor phase throughout.

With this information, we can compute the First Law efficiency for this cycle as

$$\eta_{Rankine} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} \tag{5.106}$$

$$= \frac{\dot{W}_{turbine} + \dot{W}_{pump}}{Q_{in}} \tag{5.107}$$

$$= \frac{(h_3 - h_4) + (h_1 - h_2)}{(h_3 - h_2)} \tag{5.108}$$

which holds regardless of whether or not the cycle is ideal. For the ideal cycle, however, we can substitute in our equations for the ideal pump and compressor work derived here.

For non-ideal Rankine Cycles, we must use the isentropic efficiencies of each component as previously discussed. Recall, for example, that the isentropic efficiency of the pump for this example is

$$\eta^{II}_{pump} = \frac{h_{2s} - h_1}{h_2 - h_1} \tag{5.109}$$

where the s subscript indicates the ideal enthalpy at that particular state. Typically, we can compute h_1 and h_{2s}, and there if we are given η^{II}_{pump}, we can solve for h_2 via Eq. 5.109. Via a similar process, we can solve for h_4 via the definition for a given isentropic efficiency for a turbine:

$$\eta^{II}_{turbine} = \frac{h_4 - h_3}{h_{4s} - h_3} \tag{5.110}$$

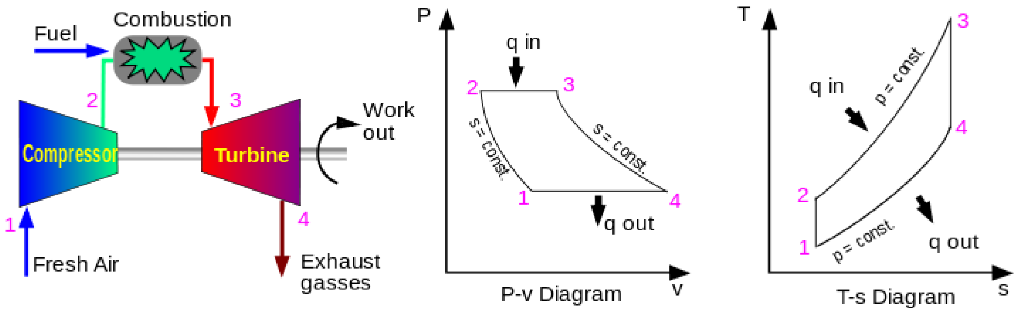

Figure 5.13: Continuous flow power cycle called the Brayton Cycle which is the continuous equivalent of the Diesel Cycle. Combustion happens from 2 → 3 at constant pressure.

Brayton Cycle

This cycle can be broken up into four main processes. First, air enters the compressor in state 1, where it is compressed adiabatically to state 2 with a higher pressure and temperature than in state 1. Next, fuel is injected into the flow and combusted to add heat to the system isobarically[5]. Between states 3 and 4, the hot, high-pressure gas expands adiabatically in a turbine, which outputs mechanical work and brings the products back to the initial pressure. Finally, heat is rejected isobarically and the process repeats. The power required to continuously compress the gas between states 1 and 2 is typically supplied directly by the turbine itself. Fig. 5.13 shows this process plotted on both P-V and T-S diagrams, both of which look very similar to that of the Diesel Cycle.

To determine the *First Law Efficiency* for this cycle, we can use the relationships we defined in the previous section to relate the various work and heat transfers for each process to system properties. As with any continuous power cycle, this efficiency is given by ratio of the net mechanical power, $\dot{W}_{net}$, to the heat added, $\dot{Q}_{in}$. For this cycle,

$$\dot{W}_{net} = \dot{W}_{turbine} - \dot{W}_{compressor} \tag{5.111}$$

$$= \dot{m}[(h_3 - h_4) - (h_2 - h_1)] \tag{5.112}$$

---

[5] For the ideal case analysis, we will ignore the change in mass due to this fuel injection.

where it is important to note that even though on the P-V diagram we can clearly see PV work being done for both constant pressure processes, this work is not extracted as mechanical work and instead captured by the change in enthalpy over those processes. This is different from the Diesel Cycle where mechanical work is extracted during the constant-pressure combustion as it is happening directly in the piston.

For the Brayton Cycle, the heat added is equal to

$$\dot{Q}_{in} = \dot{m}(h_3 - h_2) = \dot{m}c_p(T_3 - T_2) \tag{5.113}$$

We therefore compute the ideal efficiency directly as

$$\begin{aligned}
\eta_{Brayton} &= \frac{\dot{W}_{net}}{\dot{Q}_{in}} && (5.114)\\
&= \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} && (5.115)\\
&= \frac{(h_3 - h_2) - (h_1 - h_4)}{h_3 - h_2} && (5.116)\\
&= 1 - \frac{h_1 - h_4}{h_3 - h_2} && (5.117)\\
&= 1 - \frac{T_1 - T_4}{T_3 - T_2} && (5.118)\\
&= 1 - \frac{T_1}{T_2}\frac{(T_4/T_1 - 1)}{(T_3/T_2 - 1)} && (5.119)
\end{aligned}$$

where we can relate T_4/T_1 to T_3/T_2 by using the adiabatic expansion and compression relationships as we did with the Otto Cycle analysis to show that

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} \tag{5.120}$$

Thus,

$$\begin{aligned}
\eta_{Brayton} &= 1 - \frac{T_1}{T_2} && (5.121)\\
&= 1 - \left(\frac{P_1}{P_2}\right)^{\frac{\gamma-1}{\gamma}} && (5.122)
\end{aligned}$$

which interestingly looks very similar to the Otto Cycle efficiency. Again, this is due to the fact that no mechanical work is extracted during the combustion itself.

For the non-ideal or non-isentropic Brayton Cycle, the analysis becomes much more complex as we must model each process using the relationships we previously established. Starting with the compressor work, we have

$$\begin{aligned}
\dot{W}_{compressor} &= \dot{m}(h_2 - h_1) &(5.123)\\
&= \frac{1}{\eta_c^{II}}\dot{m}c_pT_1\left[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1\right] &(5.124)
\end{aligned}$$

where η_c^{II} is the given isentropic efficiency of the compressor. Similarly, we have for the turbine work that

$$\begin{aligned}
\dot{W}_{turbine} &= \dot{m}(h_4 - h_3) &(5.125)\\
&= \eta_T^{II}\dot{m}c_pT_3\left[1 - \left(\frac{P_4}{P_3}\right)^{\frac{\gamma-1}{\gamma}}\right] &(5.126)
\end{aligned}$$

which only holds for a *perfect* gas. If instead c_p is a function of temperature, care must be taken to evaluate h_4 and h_3 using empirically-derived formulae.

We can then determine the thermal energy input by looking at the heat released in the combustion reaction itself between states 2 and 3. Since this is a constant pressure combustion process, we can model this heat release by the change in enthalpy across the products and reactants. We can then compute the adiabatic flame temperature under these conditions to determine the temperature of the reaction products at state 3 and finally compute the First Law Efficiency by solving these equations simultaneously. Note that to be completely accurate, we would also need to take into account that for an actual power system, the specific heat of the working fluid(s) will not be constant with temperature, especially over the typically wide temperature range these systems operate under. In practice, computer simulations must be used to characterize realistic power systems. Real *power plants* that combust methane to generate mechanical power based on the Brayton Cycle do so at efficiencies up to 55%. These plants effectively recover much of the enthalpy contained within the hot gas exiting the turbine to extract work over multiple stages.

5.3 Gibbs Free Energy

Like we did with enthalpy, we will now define another quantity that is a combination of state properties, which as we will show has some utility for analyzing systems. To help characterize the amount of "useful" work, which we will define shortly, we will define a quantity called the *Gibbs Free Energy*, G, as

$$G \equiv H - TS = U + PV - TS \tag{5.127}$$

or in differential form as

$$dG = dH - d(TS) = dU + d(PV) - d(TS) \tag{5.128}$$

For a process in which both the temperature and pressure are held constant, this can be further reduced:

$$\begin{aligned} dG &= dU + d(PV) - d(TS) && (5.129)\\ &= dU + P\,dV + \cancel{V\,dP} - T\,dS - \cancel{S\,dT} && (5.130)\\ &= dU + P\,dV - T\,dS && (5.131) \end{aligned}$$

Following our methodology for determining the physical meaning of enthalpy, we can write the First and Second Law for an arbitrary steady-state continuous process that exchanges heat and work with environment at (P_a, T_a) and maintains constant pressure and temperature throughout:

$$\cancel{\dot{E}_{CV}} = \dot{Q} - \dot{W} + \dot{m}(h_1 - h_2) \tag{5.132}$$

and

$$\cancel{\dot{S}_{CV}} = \frac{\dot{Q}}{T_a} + \dot{m}(s_1 - s_2) + \dot{S}_{gen} \tag{5.133}$$

We can combine Eqs. 5.132 and 5.133 and solve for $\dot{W}$, giving us

$$\begin{aligned} \dot{W} &= \dot{m}(h_1 - h_2) - \dot{m}T_a(s_1 - s_2) - T_a\dot{S}_{gen} && (5.134)\\ &= \dot{m}[(h - T_a s)_1 - (h - T_a s)_2] - T_a\dot{S}_{gen} && (5.135)\\ &= \dot{m}(g_1 - g_2) - T_a\dot{S}_{gen} && (5.136) \end{aligned}$$

where g is the specific Gibbs Free Energy in units of energy per mass. This expression tells us that the maximum work that can be extracted from a power cycle requires that each process be reversible and thus that $\dot{S}_{gen} = 0$. The maximum work in this case can be expressed simply as

$$\dot{W}_{max} = \dot{m}(g_1 - g_2) \tag{5.137}$$

5.3.1 Availability

The Gibbs Free Energy again highlights the fact that the work that can be extracted from a stream over a process is limited directly by any irreversibility generated by the system. This relationship is derived directly from the Second Law, but it serves an important purpose to help illuminate this concept from another angle. This concept can be formalized to characterize the maximum amount of work that can be extracted from a system in communication with the environment at (P_a, T_a). A quantity called the *Availability* or *Exergy*, Ξ, is defined as

$$\Xi \equiv E + P_a V - T_a S \tag{5.138}$$

which allows us to characterize the "usefull" mechanical work that can be extracted generally as

$$\begin{aligned} W_{useful} &= -\Delta\Xi - T_a \Delta S_{gen} & (5.139)\\ &= -(\Delta E + P_a \Delta V - T_a \Delta S) - T_a \Delta S_{gen} & (5.140) \end{aligned}$$

by the Second Law.

Throughout all of this analysis it is important to understand that in terms of its conversion to mechanical work, not all thermal energy is treated equally. We have from the Carnot Efficiency of a reversible heat engine that the greater the difference in temperature between the hot and cold thermal reservoirs, the more work can be extracted for the same thermal energy input. As such, thermal energy has this notion of *quality* attached to it, with thermal energy at a higher temperature relative to its environment having a higher quality.

5.3.2 Chemical Equilibrium

In all systems, but in continuous flow power system in particular, we may have chemical reactions that are proceeding in both the forward and backward directions simultaneously. The rates of both reactions depend on the local concentrations of the products and reactants as we learned back in Chapter 3. We also talked about the equilibrium conditions of the reaction being established from the temperature-dependent rate constant, $k_p(T)$ as

$$\prod_i X_i^{\nu_i} \left(\frac{P}{P_0}\right)^{\sum_i \nu_i} = k_p(T) \tag{5.141}$$

At the time, we did not yet have the tools to derive where the mysterious k_p constant came from, but now that we have defined the Gibbs Free Energy, we can establish that the equilibrium conditions for a chemical reaction actually come from the even more fundamental notion that at equilibrium, the total Gibbs Free Energy of this system is minimized, or that

$$dG = 0 \tag{5.142}$$

To understand why this is the case, we need to augment the First Law equation we have been using up until this point to also include the change in energy that results from a change in the number of moles of a species in a reaction:

$$dU = dQ - dW + \sum_i \mu_i \, dN_i \tag{5.143}$$

where μ_i is the *chemical potential energy* and dN_i the change in number of moles of species i. We sum over all species to get the total change in chemical potential energy. The reason we did not include this before in our calculations is that by definition, at equilibrium, the total change in chemical potential must be zero and therefore this new term in the First Law expression is zero. That is,

$$\mu_1 \, dN_1 + \mu_2 \, dN_2 + ... = 0 \tag{5.144}$$

Substituting in our definition for dG in Eq. 5.128 into Eq. 5.143, we get

$$\underbrace{d(U + P\,dV - T\,dS)}_{\equiv dG} = dQ - \cancel{P\,dV} + \sum_i \mu_i \, dN_i + \cancel{P\,dV} - T\,dS \tag{5.145}$$

and then substituting our reversible Second Law equation in for dQ:

$$dG = \cancel{T\,dS} + \sum_i \mu_i \, dN_i - \cancel{T\,dS} \tag{5.146}$$

$$= \sum_i \mu_i \, dN_i \tag{5.147}$$

which is called the *Gibbs-Duhem* equation for constant pressure and temperature. Then at chemical equilibrium

$$dG = \sum_i \mu_i \, dN_i = 0 \tag{5.148}$$

Recall that by mass conservation, we have the relationship that for a chemical reaction, the rate of change of any one species in the products must be equal in magnitude and the opposite sign of the rate of change of any one species in the reactants. This is expressed simply as

$$-\frac{dN_i}{\nu_i} = \frac{dN_j}{\nu_j} \equiv d\lambda \tag{5.149}$$

where i is some reactant species and j is some product species, ν is the stoichiometric coefficient for the particular species, and $d\lambda$ is some constant. Therefore, Eq. 5.148 is equivalent to

$$dG = \left(\sum_i \mu_i \nu_i \right) d\lambda = 0 \tag{5.150}$$

and at equilibrium

$$\sum_i \nu_i \mu_i = 0 \tag{5.151}$$

Digging a bit deeper, we can relate this equilibrium constraint to state properties by using the definition that $G = H - TS$ as well as the constitutive relationships for an ideal gas:

$$\begin{aligned} G &= \sum_i \mu_i N_i = H - TS && (5.152) \\ &= \sum_i N_i \underbrace{\left[h^\circ_{f,i} + \int_{T_0}^{T} c_{p,i} \, dT - T \left(s^\circ_i + \int_{T_0}^{T} \frac{c_{p,i} \, dT}{T} - R \ln \frac{P_i}{P_0} \right) \right]}_{\equiv \mu_i} && (5.153) \end{aligned}$$

where it is clear that the term multiplying N_i is equivalent to μ_i by comparison. Note that here, P_i is the partial pressure of gas species i and is equal to

$$P_i = X_i P \tag{5.154}$$

by Dalton's Law. We can therefore rewrite our expression for μ_i using the total pressure P as

$$\mu_i = \underbrace{\left[h^\circ_{f,i} + \int_{T_0}^{T} c_{p,i}\, dT - T\left(s^\circ_i + \int_{T_0}^{T} \frac{c_{p,i}\, dT}{T}\right)\right]}_{\equiv \mu_i^+(T)} + RT\left(\ln\frac{P}{P_0} + \ln X_i\right) \tag{5.155}$$

or

$$\mu_i = \mu_i^+(T) + RT\ln\left(\frac{P}{P_0}\right) + RT\ln X_i \tag{5.156}$$

where the first term is defined as the purely temperature-dependent chemical potential energy, μ_i^+. Applying our equilibrium condition and pulling out the pressure and concentration terms, we have

$$\sum_i \mu_i\nu_i = \left(\sum_i \nu_i\mu_i^+(T)\right) + RT\left[\ln\left(\frac{P}{P_0}\right)^{\sum\nu_i} + \sum_i \ln X_i^{\nu_i}\right] = 0 \tag{5.157}$$

Rearranging, we find

$$\prod_i X_i^{\nu_i}\left(\frac{P}{P_0}\right)^{\sum\nu_i} = \exp\left(\frac{\sum\nu_i\mu_i^+(T)}{RT}\right) \equiv k_p(T) \tag{5.158}$$

which gives us an expression for $k_p(T)$. In practice, this quantity, as well as the chemical potential energy, is computed from empirical data.

Note that Eq. 5.156 is only valid for an ideal mixture, or one that obeys Raoult's Law, discussed previously in Section 3.2.3. For non-ideal mixtures, this expression is modified to include an empirically derived *activity coefficient*, γ, such that

$$\mu_i = \mu_i^+(T) + RT\ln\left(\frac{P}{P_0}\right) + RT\ln\gamma_i X_i \tag{5.159}$$

not to be confused with the heat capacity ratio.

5.4 The Anthropocene

In the story of climate change, the study of the thermodynamics and engineering behind heat engines and power generation brings us into the *Anthropocene*, a new geological epoch in which the Earth has been dramatically altered by human activity. From the discovery of fire nearly 2 million years ago to the mass combustion of fossil fuels in the present day, the accelerating expansion and energy consumption has pushed the Earth's many feedback loops so far off their natural equilibrium that the evidence can be seen in virtually every ecosystem on the planet, necessitating the demarcation of a new age. Thinking hypothetically to what the geologists of the far future might uncover about this era, it is likely that their geological observations - even in the absence of digital records - will point to an extremely short period of time in which the Earth experienced a major increase in both carbon dioxide concentrations and average global temperature, coupled with an equally severe reduction in sea ice and biodiversity. Additionally, given the wealth of detailed information *we* can glean about the Earth's history over the past 4 billion years, it might also be clear to the future geologists that this shift occurred in such way that had been yet unprecedented. They might be able to tell that this progression had to have occurred external to the natural carbon cycles that had governed the evolution of the planet up to that point with even more sudden and far-reaching than effects than those of the Cambrian Explosion.

Focusing back on the present, as a moment of self-awareness, we should recognize that the thermodynamical principles we have learned in this book thus far and their many scientific and engineering applications are nearly fully responsible for the transition from the Holocene to the Anthropocene. In fact, this particular branch of physics was rapidly developed largely in response to a growing demand for mechanical and later electrical power driving productivity and progress over the last several hundred years. From consumer products to military applications, thermodynamics has been applied at nearly every level in the development of what we consider modernity - including an era-defining change in our climate. As we continue on with this material, we will move to focus on the sustainable application of thermodynamics and the many technologies we may need to change course or in the event of a failure to do so - survive.

Before launching into potential solutions, however, we must take a closer look at the causes and effects of climate change to better understand the problem itself. First, as we learned in Chapter 2, as more CO_2, CH_4, and other greenhouse gases are added to the atmosphere, the global mean temperature rises as a result of the greenhouse effect - the atmosphere becomes a more effective insulator, trapping ever more thermal radiation from the Sun. We can measure the atmospheric CO_2 concentrations, for instance, and show that it is in fact driving an increase in the global mean temperature. The relationship between the two are not necessarily linear, however, as there are numerous positive feedback loops in the Earth's climate system that are both driven by global warming and human activity in such a way that results in even more warming than we would expect from just the *radiative forcing* from the greenhouse effect alone. For example, as sea ice melts, the once reflective white surfaces at the poles give way to a dark blue ocean that is more effective at absorbing incident solar radiation. At the same time, human expansion is resulting in mass deforestation that greatly hampers the Earth's ability to take up excess CO_2.

The important questions then become, 1) what is the exact relationship between greenhouse gas emissions and temperature rise? and 2) what are the ramifications of a warmer planet? Looking at the former, climate scientists typically frame this problem specifically as, if we double the concentration of CO_2 and equivalent greenhouse gases in our atmosphere relative to pre-industrial levels, what is the corresponding temperature rise? Taking the global average pre-industrial CO_2 concentration to be about 280 ppm, the question then is, what happens if we get to 560 ppm? Studies as early as 1979 have shown that this temperature rise will be somewhere between 1.5-4.5 °C, with more recent studies reducing this uncertainty to 2.5-3.2 °C [1]. As of writing this book in mid 2020, the global average CO_2 concentration is between 410-420 ppm, roughly halfway to the doubling point. Already, the global mean temperature has risen 1.1 °C above pre-industrial levels.

To answer the second question about what that temperature rise induced by greenhouse gas emissions means for the Earth and its various ecosystems, we can look to a comprehensive report issued by the Intergovernmental Panel on Climate Change (IPCC), a group of the world's leading climate scientists and economists. In their 2018 special report (SR15), they detail and compare the effects of both a +1.5 °C and +2 °C warming scenario, as well as make the well-supported case that the roughly 1 °C warming between 1850 and 2018 has already negatively impacted a wide swath of the Earth's climate system. Current observed effects include more frequent and severe heatwaves over virtually every landmass, more frequent heavy precipitation events and severe weather events, increased drought in the Mediterranean region, sea level rise, and a loss of biodiversity in many biomes, among many more. With an additional 0.5-1 °C warming, these consequences will likely be magnified, placing further strain on the many ecosystems that simply have not had time to adapt. Additionally, with this additional warming and associated increase

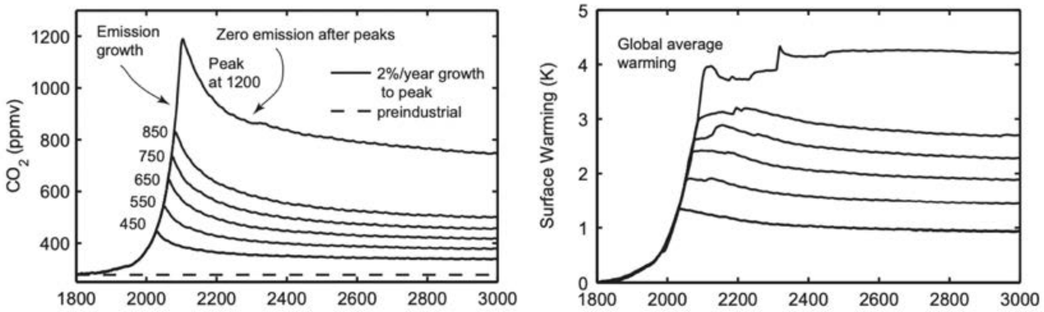

Figure 5.14: Plots showing how the carbon dioxide concentrations in the atmosphere and associated mean surface temperature increase can linger for over 1000 years even after emissions cease [3]. Image courtesy of Susan Solomon, Gian Kasper Plattner, et al. "Irreversible Climate Change due to Carbon Dioxide Emissions." *PNAS*. February 10, 2009. 106 (6) 1704–1709.

in carbon dioxide concentrations ocean acidification is expected greatly reduce the productivity of the oceans, threatening the food security of a major portion of the Earth's human population [2].

This report also showed that while the least of these effects can no longer be avoided, there remains a significant difference in their severity between the 1.5 and 2 °C warming scenarios. Limiting the warming to 1.5 °C - which is far lower than the well-established 2.5-3.2 °C climate sensitivity value we are hurtling towards - stands to greatly reduce the threat of mass extinction of insects, plants, and vertebrates, limit sea level rise, comparatively reduce the threat of severe forest fires, and even help limit the spread of disease. As detailed in this report, the case for preventing additional warming past 1.5 °C is well made, and though the Earth would still be left with many detrimental impacts of climate change that are already coming into focus, we made be able to avoid the worst of them. Regardless, there is yet some uncertainty surrounding several tipping points that, for example, would result in the majority of the Greenland and Antarctic ice sheets melting, resulting in a multi-meter sea level rises over next several centuries - which against the backdrop of even the human timeline, let alone evolution, is troublingly short.

The final point to reiterate about the Anthropocene here is that in some sense, humanity has pushed well past the point of no return on its far-reaching alteration of the natural world. Report after report details the loss of biodiversity, increase in extreme weather events, and more frequent flooding, among others, that are at this point *historical* - there is no hypothetical climate change. The climate *has* changed and we are at the point where we can play a role in limiting this change. What is important to note is that simply stop-ping carbon emissions, while extremely important, will not undo what has

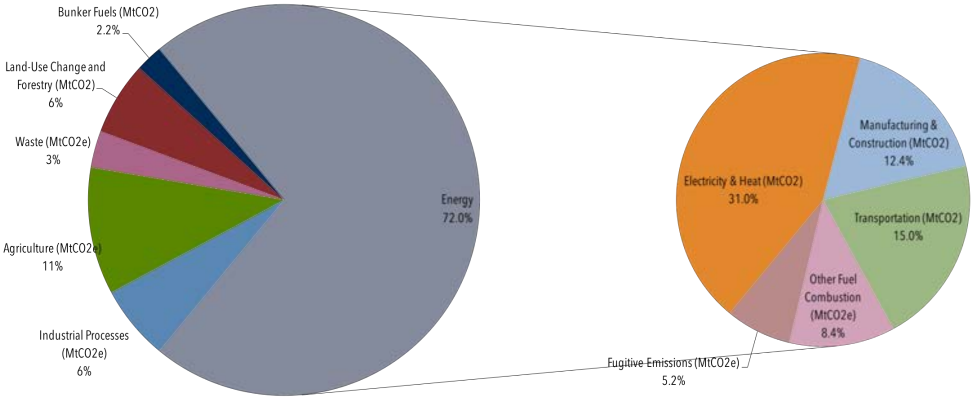

Figure 5.15: Global carbon emissions broken down by sector [source].

already been done. In a landmark study in 2009, Solomon et al showed that this climate *inertia* can be quantified. As illustrated in Fig. 5.14, without removing CO_2 from the atmosphere, its concentration will remain at its ele-vated value in the atmosphere for over 1000 years after the emissions cease, with the associated mean surface temperature rise stabilizing at its elevated value as well [3]. Indeed, we are pushing well past the limits of the Earth's own carbon feedback loops to regulate these added emissions as we approach a new equilibrium, further justifying giving this era its own name.

5.4.1 Current Climate Change Drivers

So to recap, we know with a high degree of certainty that humans are emitting more CO_2 that can be taken up by the Earth's natural carbon cycle, and that a doubling of concentrations above pre-industrial levels to 560 ppm would result in a temperature rise of 2.5-3.2 °C with a high degree of certainty. As the IPCC report shows, an Anthropocene characterized by even a 1.5-2 °C warming would be bad news for a majority of the Earth's ecosystems and would take thousands of years to recover from via the Earth's natural feedback mechanisms. That leaves us with the question of how do we stop this?

Before getting into the strategies for mitigating the ensuing climate crisis, it is first necessary to take a more detailed look at exactly where exactly these emissions are coming from. If we look to Fig. 5.15, we can see that the majority of the Earth's carbon emissions come from the energy sector and are driven by the combustion of fossil fuels in very heat engines we have learned about

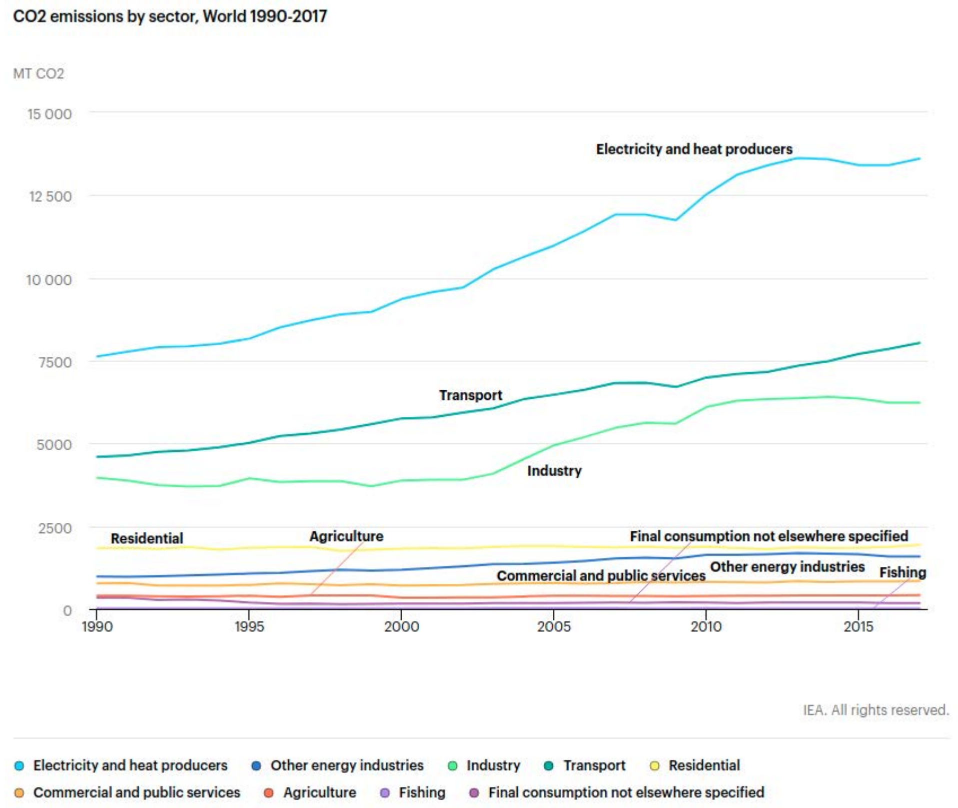

Figure 5.16: Global annual CO_2 emissions for each major carbon-intensive economic sector [IEA].

here. The International Energy Agency (IEA) maintains detailed reports on the global energy consumption and greenhouse gas emissions broken down by a variety of different categories and metrics. Fig. 5.16 shows a breakdown of global annual CO_2 emissions from 1990 to 2017 for key economic sectors. As is shown here, the top three most carbon-intensive sectors are electricity and heat production, transportation, and industry, which includes emissions associated with the production of raw materials and commodities[6].

Currently, the carbon emissions associated with electricity and heat production as well as transportation come from the direct combustion of fossil fuels. Of these emissions, we can see from Fig. 5.17 that as of 2017, the ma-

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[6] Aluminum production for example has significant carbon emissions from the electrochemical reaction that reduces aluminum from aluminum oxide.

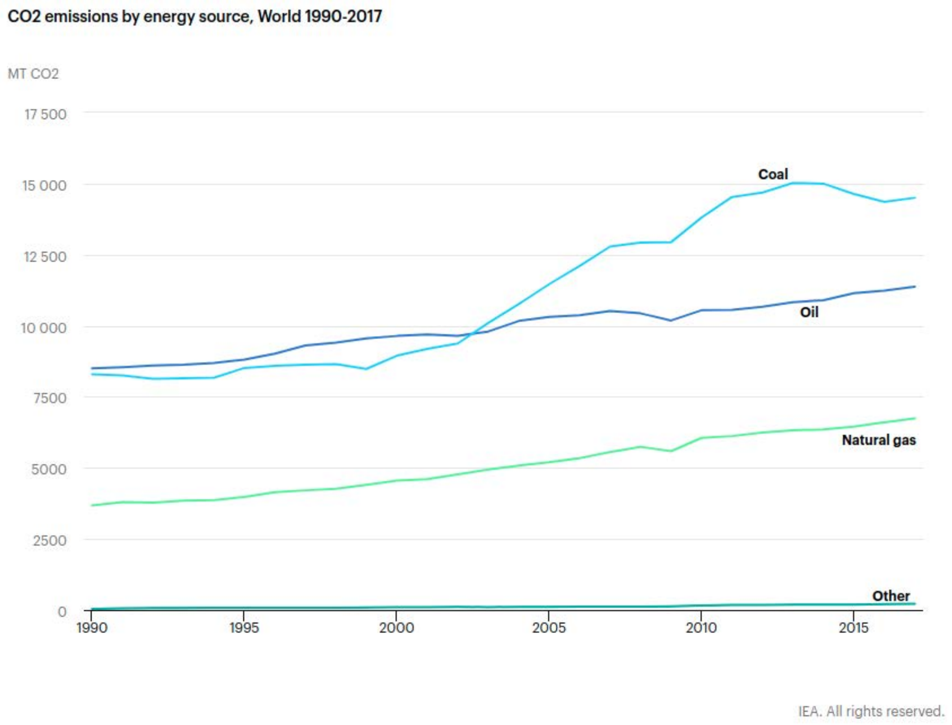

Figure 5.17: Global annual CO_2 emissions for each major carbon-intensive energy source [IEA].

jority still come from coal and oil, which is driven in part by the high carbon intensities of those fuel sources as well as their global ubiquity, as also illustrated in Fig. 5.19. The growth of natural gas emissions shown in this figure are largely due to the increasing prevalence of natural gas combustion plants that are displacing coal power plants, especially in the United States. The corresponding dip in coal emissions since 2013 are primarily a result of this shift towards natural gas usage as well and less so a result of the adoption of renewable energy sources, which we will soon discuss.

It is also important to note that in Fig. 5.17, the annual global carbon emissions associated with the combustion of fossil fuels continue to increase, despite the greater adoption of less carbon-intensive fuel sources and more efficient infrastructure. This disparity illustrates the second primary issue at play - the more efficient consumption of energy grows the global economy, which in turn drives more energy consumption. As shown in Fig. 5.18, the global annual energy consumption in nearly every economic sector is increasing

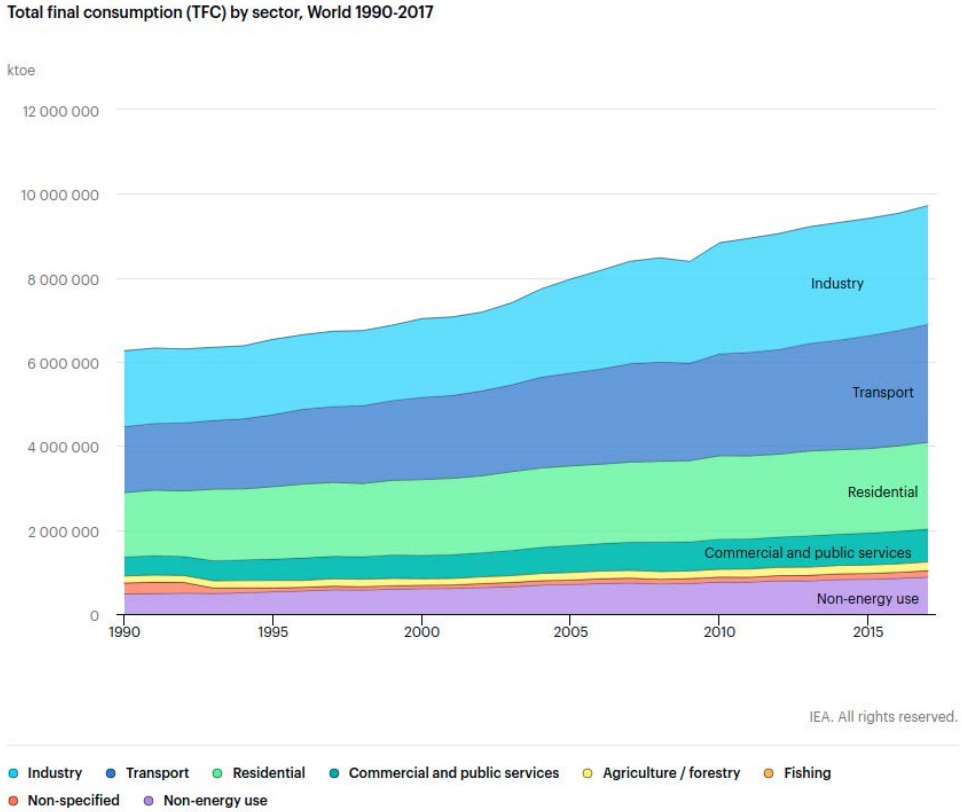

Figure 5.18: Total global annual energy consumption broken down into various economic sectors [IEA].

and so too is the total global annual energy consumption, making climate change mitigation an extremely challenging problem. This phenomenon helps to explain why in Fig. 5.19, we see the yearly consumption of fossil fuels increasing steadily. These trends are especially alarming given that there is an upper limit on *cumulative* carbon emissions since the Industrial Revolution associated with limiting global warming to a safer temperature increase. From just these four plots by IEA, we can paint a sobering picture of the total issue wherein both energy consumption and the proportional usage of fossil fuels are increasing.

This landscape consisting of these multiple compounding issues requires solutions that address both the reduction of energy consumption and greenhouse gas emissions. As we will see, however, these measures alone will likely not be

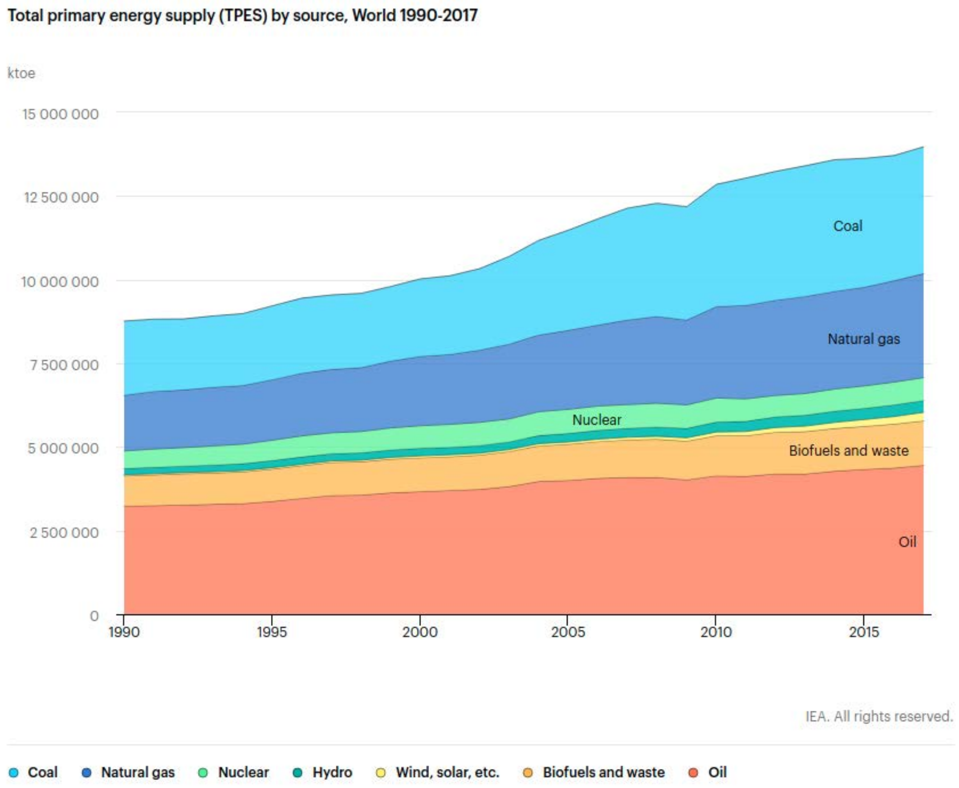
Total primary energy supply (TPES) by source, World 1990-2017

Figure 5.19: Total global primary energy supply broken down by source, showing that even though renewables are expanding, so too fossil fuels [IEA].

enough to mitigate the crisis and additional CO_2 will need to be taken from the atmosphere. It is perhaps safe to say that the tools built using the knowledge garnered through the study of thermodynamics have largely brought us to this critical tipping point and continue to push us well into uncharted territories. As we will soon see, however, these same principles might be able to be used to mitigate this crisis.

5.5 Summary

In this chapter we bridged the short gap between the discovery of fire and the first use of chemical combustion reactions to generate power, as well as the even shorter gap between what is considered the Industrial Revolution and the present self-ascribed *Anthropocene*. We took a detailed look at how the First and Second Laws of Thermodynamics can be used to construct heat engines to continuously convert the thermal energy released in combustion into mechanical work to meet the world's ever-growing energy demands, which account for the vast majority of anthropogenic greenhouse gas emissions. In looking at external and internal combustion engines, as well as continuous flow power systems, we developed a framework for determining how much mechanical work can be extracted for a given input of thermal energy, a relationship that defines the carbon emissions per unit output of energy associated with different fuel sources and power system architectures. Finally, we discussed the harm that these emissions have caused through climate change and the importance and urgency of reducing them to avoid a 1.5 °C warming.

Up to this point in the story of climate change, we have answered many of the questions pertaining to how we got here and why this is such an unprecedented and important problem to solve. Naturally then, the next question to tackle is how do we solve it?

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Chapter 6

A Return to Renewables

In the story of climate change, we are mostly caught up to the present, where the reality of a *climate crisis* is bearing down upon us. With the urgency of the issue and the many daunting challenges it presents humanity, there is not the option to *not* solve it if we wish to achieve climate stability with only a moderate global average temperature rise. Despite the severity and progression of this crisis - which has already resulted in a temperature rise of 1.1 °C above pre-industrial levels by mid 2020 - there is significant motivation to not let that warming exceed 1.5 °C. Indeed, every additional degree of warming presents more severe and wider reaching consequences for our species and the many ecosystems on which we rely, and makes it more difficult to reverse course. The transition to a carbon neutral and ultimately carbon negative society can no longer a question of *if* but rather *when* - the best science we have at our disposal tells us the sooner the better.

With the motivation in place for sweeping societal changes that move us towards global sustainability, we can begin to look at how this transition might occur and the tools we have at our disposal. In this and the following chapters, we will cover several key approaches, all of which will likely need to be implemented to some degree in parallel in order to make any substantial progress. First, in this chapter we will start with the biggest emissions source shown in Fig. 5.15 - energy conversion. In short, we must simply stop emitting CO_2 as a result of burning fossil fuels for energy to power our daily lives - not just make these processes more efficient. This means natural gas, coal, oil, and its derivatives must be eventually phased out in favor of *renewable* and *net neutral* energy sources like solar, wind, and geothermal. In the short term, carbon-neutral nuclear energy will also likely play an important role. We will look at the thermodynamics behind some of the most promising technologies in this space.

Next, to solve the intermittency issues posed by renewable energy sources - in particular solar and wind which both have guaranteed downtime - we will also need new and better ways to store energy that is collected when it is not needed for when it is. To this end, we will take a look at the thermodynamics of electrochemistry, which is the basis for most batteries used today, as well as physical means of storage that use gravitational potential energy to help flatten power generation curves. We will also look at the carbon-neutral generation and consumption of hydrogen as an effective means of storing and transporting energy as well. Combined, these technologies have the capability to help restore our ability to use rewewable energy to meet global demand sustainably.

6.1 Renewable and Carbon-Neutral Energy

Renewable energy encapsulates all sources of energy that *regenerate* naturally on a timescale comparable to that of its usage or that are expected to last far into the future - providing energy in a useful form for millions or even billions of years. These sources include the sun, wind, rain, tides, geothermal wells, and biofuels, which with the exception of geothermal wells[1] and lunar tides, are actually all different forms of solar energy as we learned in Chapter 2. This is to be expected, though, as from a pure thermodynamic systems perspective, nearly all of the energy that is continuously being added to the Earth system is solar radiation. Fossil fuels are stored solar energy as well, but we do not consider them renewable as it takes millions of years for them to regenerate naturally - much longer than the timescale on which we consume them today.

In reality, we know from the Laws of Thermodynamics that no source of energy is truly infinite and renewable. As the Second Law tells us, hot condensed energy has a tendency to cool and spread out until the point where no useful work can be extracted and entropy is maximized. Our Sun and geothermal wells are no different; however, while the Sun, like all stars, will eventually burn out, it is expected to have enough fuel for fusion to last for another 5 to 10 billion years - well past the point where the sun is expected to expand and swallow the Earth and this conversation becomes irrelevant. Similarly, the now extremely hot core of the Earth is expected to eventually cool and freeze as happened with Mars, but again not for billions of years. It is therefore safe to say that these sources are renewable on timescales that are compatible with the story of humanity and its utilization of energy.

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[1] though recall the thermal energy at the Earth's core is a remnant of the energy released from the supernova death of a star and is in a way solar energy, just not from our Sun.

In the story of climate change specifically, as we know all too well at this point, the consumption of *non*-renewable energy sources has led to the emission of greenhouse gases on a timescale that is incompatible with the rate of the natural sequestering of those emissions and subsequent regeneration of the energy sources. Moving forward, if humanity wishes to slow and ultimately stop the progression of climate change, one important strategy is to widely replace these fossil fuels with renewables to eliminate *net* emissions. An important distinction to make here is that renewable energy sources are not necessarily emission free; but rather, are *carbon-neutral* on a relatively short timescale. For example, biofuels derived from the processing of live organic plant matter can be combusted in place of fossil-based gasoline, diesel, and methane but still produce the same amount of emissions that the fuels they are replacing would. The key difference is that because the biofuels are produced from living or recently alive organic matter, the equivalent carbon emitted by their combustion will be taken out of the atmosphere when the plants, trees, etc. grow back within a few years. If this emission and reuptake cycle is short enough, the total average concentration of CO_2 will remain constant. Technically, even the carbon dioxide emitted from burning fossil fuels might eventually be taken back in by living organisms, but the time required for carbon neutrality is millions of years - much longer than the time expected for humans to exhaust fossil fuel reservoirs.

There is also a class of energy sources that are not renewable but are carbon-neutral and therefore will need to play a prominent role in climate change mitigation as well. In particular, fission-based *nuclear* energy requires the consumption of fissile radioisotopes of elements like uranium and plutonium to produce an enormous amount of heat and solid waste. If the heat released in the nuclear reactions is used to drive a Rankine cycle, no CO_2 is emitted in the steady-state energy production process and is thus considered to be carbon neutral. We will discuss this energy source as well as the previously mentioned renewable sources in greater detail here.

6.1.1 Solar Energy

Solar energy in the context of renewable energy typically refers to thermal radiation that is captured and either used or stored directly as thermal energy, converted to mechanical work via various types of heat engines, or used to provide electrical work through devices that utilize the *photovoltaic effect*. As shown in Fig. 6.1, there is a significant amount of energy that arrives at the Earth's surface; however, it is highly concentrated in certain regions, which is largely a function of weather and both the amount of types of vegetation.

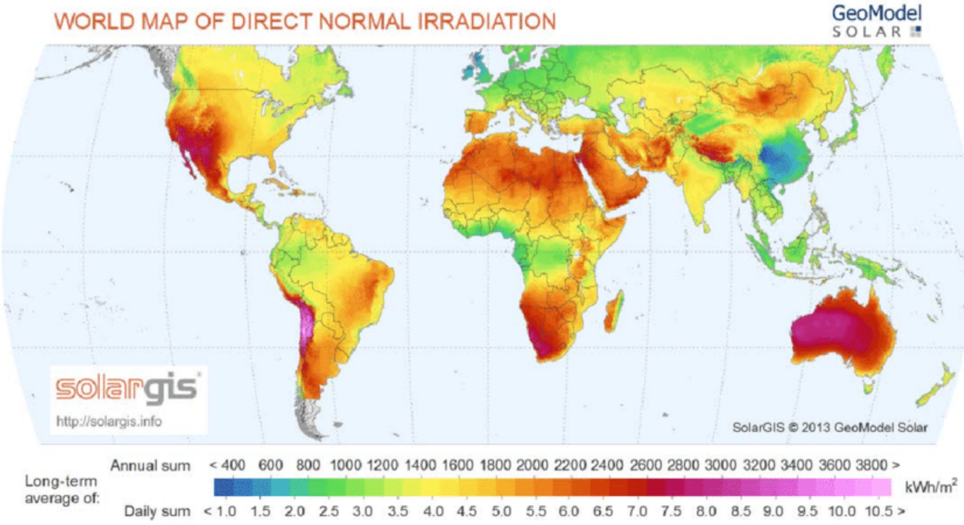

Figure 6.1: Average daily and annual global solar irradiance in kWh/m^2. *Direct normal* refers only to sunlight that arrives perpendicular to the Earth's surface [Solargis].

As expected, desert areas see the largest solar *irradiance* - radiative power or energy per unit area. To get a sense for how much is available, note that the current global energy demand is roughly 35,000 TWh per year. At a solar irradiance of 2,500 kWh/yr-m^2, this would require a surface area of about 14,000 km^2, not including efficiencies of energy conversion[2]. For reference, the area of Nevada, which sees some of the highest solar irradiance in the United States, is over 286,000 km^2! From Fig. 6.1, we can easily see that even at low energy conversion efficiencies, there is more than enough solar energy present to meet the world's energy demands many times over. The question then becomes, how can we actually utilize this energy?

For the direct thermal energy utilization, there is not much else in terms of thermodynamics that can be said beyond what we discussed in Chapter 2. On a practical note, much of the energy used globally is needed as heat directly to drive a wide array of industrial processes, space heating, cooking, and water purification and *desalination* in many parts of the world. As we learned, high frequency solar radiation is absorbed by gray bodies and re-emitted as lower frequency thermal radiation. The temperature and therefore internal energy

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[2] With a capacity factor of 0.25 and a First Law efficiency of 0.2, this value becomes 280,000 km^2.

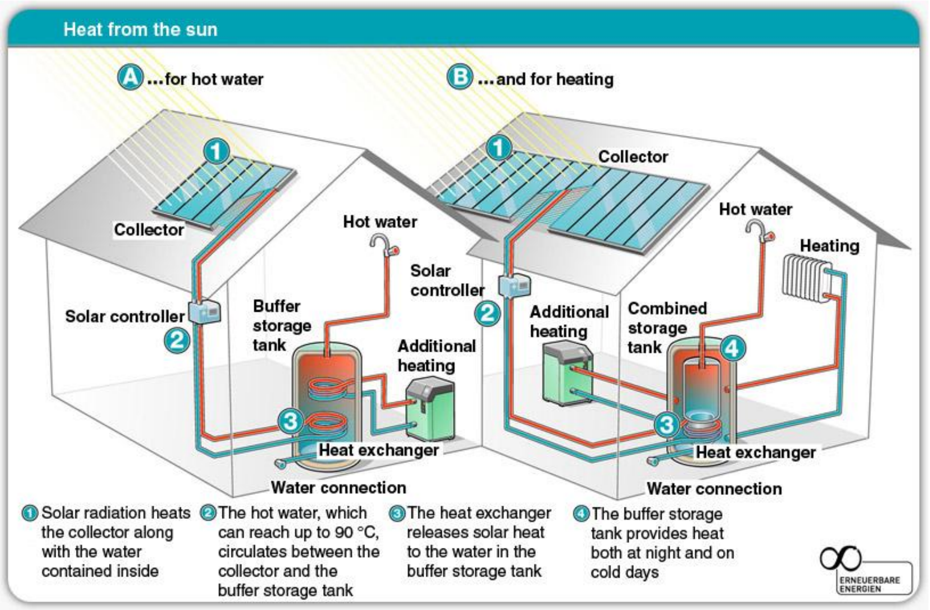

Figure 6.2: Example home system that uses solar thermal energy directly to provide water and space heating demands [source].

of the bodies adjusts such that in equilibrium, the heat fluxes in and out are perfectly balanced. In fact, the outer layer of the Sun itself is in such an equilibrium as gamma rays and other extremely high frequency radiation released in the nuclear fusion reactions at the Sun's core are absorbed by the mostly hydrogen and helium gases in the outer layers, which then re-emit lower frequency radiation. The temperature of this outer layer reaches about 5800 K under these equilibrium conditions.

On Earth, this phenomenon is used to provide solar-powered heating and cooling for water and air at the residential scale. For example, vacuum-insulated solar *collectors* with high emissivities are placed on roofs to absorb solar radiation without significant heat loss to the environment. A working fluid is circulated through the collector where it heats up and then transfers that heat to the residential hot water line or to a radiator to heat internal rooms. Fig. 6.2 shows two example configurations of this type of system, which can be used to supply seasonal heating needs. Because solar energy is inherently intermittent, excess energy must be stored to supply heating power overnight, for example. Several thermal energy storage mechanisms have been already been discussed previously and we will go into greater detail later in

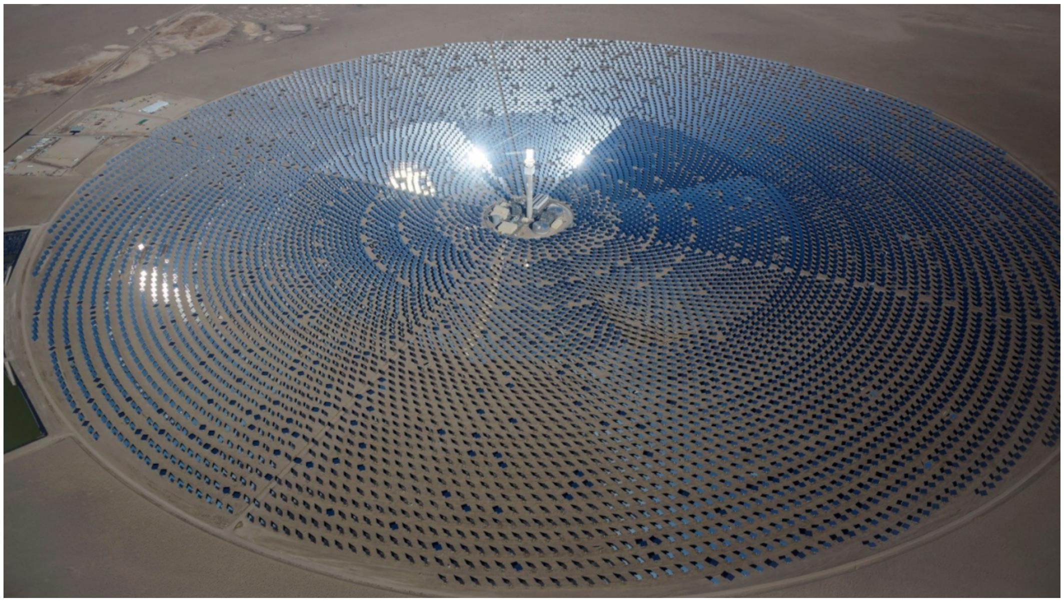

Figure 6.3: 110 MW Crescent Dunes Concentrated Solar Power plant in Nevada, US which uses a giant mirror array to direct sunlight to heat a working fluid at the top of a central tower. This high temperature working fluid - typically molten salt - is then used as the high temperature thermal reservoir for a power cycle [source]. Image courtesy of DOE.

this chapter.

Mechanical Work Conversion

If instead mechanical work is needed, solar thermal energy can be used to drive a heat engine via one of the many external heating-based architectures we previously discussed - Stirling or Rankine Cycles, for example. To achieve the high temperatures necessary for high First Law efficiencies, giant mirror arrays are typically used to capture a wide area of sunlight and direct it towards a central thermal reservoir that absorbs the radiation to heat an internal working fluid. This fluid, typically molten salt heated in the range of 400-750 °C, can then be used as the heat source to run a power cycle nearby. Fig. 6.3 shows an example plant located in the United States in the desert in Nevada. Here, each mirror in the array is capable of tracking the sun, continuously directing the sunlight at the central thermal reservoir tower.

In this type of solar-thermal power system, the overall efficiency is a factor of several different sources of energy loss. First, the mirrors themselves will not be able to perfectly reflect incident radiation due to dust accumulation and manufacturing defects and thus have an associated efficiency, η_{mirror}. Additionally, as is evident from Fig. 6.3, the fact that the top of the thermal tower appears bright white means that a potentially significant amount of thermal radiation is being emitted from the thermal reservoir itself. This radiated energy is lost to the environment and cannot be converted to work. This efficiency, η_r, is given as

$$\eta_r = 1 - \frac{Q_{out}}{Q_{in}} \tag{6.1}$$

where Q_{out} is given by the Stefan-Boltzmann equation as

$$Q_{out} = A\varepsilon\sigma T_H^4 \tag{6.2}$$

where A is the surface area of the high temperature thermal reservoir and T_H is its temperature. Q_{in} is a function of the solar irradiance $\dot{q}''_{solar}$, the concentration factor C, A, the absorptivity of the reservoir α, and the mirror efficiency as

$$Q_{in} = \eta_{mirror}\alpha\dot{q}''_{solar}CA \tag{6.3}$$

and thus

$$\eta_r = 1 - \frac{\varepsilon\sigma T_H^4}{\eta_{mirror}\alpha\dot{q}''_{solar}C} \tag{6.4}$$

Finally, the power conversion cycle will have a First Law efficiency, η_{cycle}, which in the ideal case is equal to the Carnot Efficiency, $1 - T_a/T_H$. In the ideal case, the total efficiency, η_{total} is given as

$$\begin{aligned} \eta_{total} &= \eta_r\eta_{cycle} && (6.5) \\ &= \left(1 - \frac{\sigma T_H^4}{\dot{q}''_{solar}C}\right)\left(1 - \frac{T_a}{T_H}\right) && (6.6) \end{aligned}$$

Here ε, α, and η_{mirror} are all assumed to be equal to 1 for the ideal case. It is interesting to note here that there are competing phenomena governing the performance of this type of system - a higher temperature thermal reservoir means higher Carnot efficiency but also means greater heat loss to thermal radiation. As a result, if we plot the efficiency as a function of this top temperature, we would expect there to be a maximum efficiency at some temperature value roughly in between the two values where Eq. 6.5 is equal

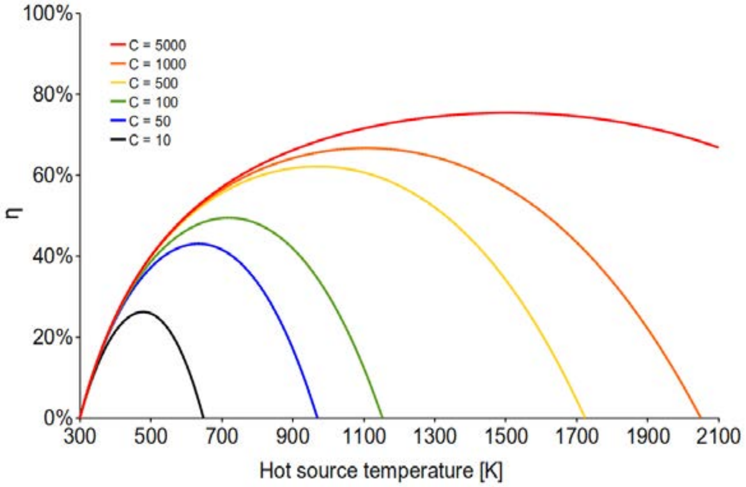

Figure 6.4: Total ideal efficiency of a concentrated solar power plant as a function of T_H shown for different concentration factors, C [source].

to zero - $T_H = (\dot{q}''_{solar}C/\sigma)^{1/4}$ and $T_H = T_a$. Indeed, Fig. 6.4 shows the total efficiency plotted as function of T_H for several concentration factors, C, and we can see that as expected, there exists a temperature at which the efficiency is a maximum. This poses some interesting design considerations to be made when installing and operating such a power plant. Given that the solar irradiance fluctuates throughout the day, care must taken to ensure that the efficiencies are balanced with energy demand. It may make sense, for example, to direct some of the sunlight away from the thermal reservoir during peak solar hours to avoid some losses associated with going to higher top temperatures.

Photovoltaics

In the mechanical energy conversion systems we have discussed so far, what has been implicit but not mentioned explicitly is that much of the mechanical work produced is immediately converted to electricity, typically at very high efficiencies[3]. Despite the high mechanical-to-electrical efficiency, the overall performance, however, is limited by the Carnot Efficiency, which again is a statement of the Second Law. If solar energy is available and electricity is needed, the heat engine can be bypassed and electricity can be generated

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[3] For example, Siemens generators can achieve efficiencies $> 99\%$ for converting mechanical to electrical work.

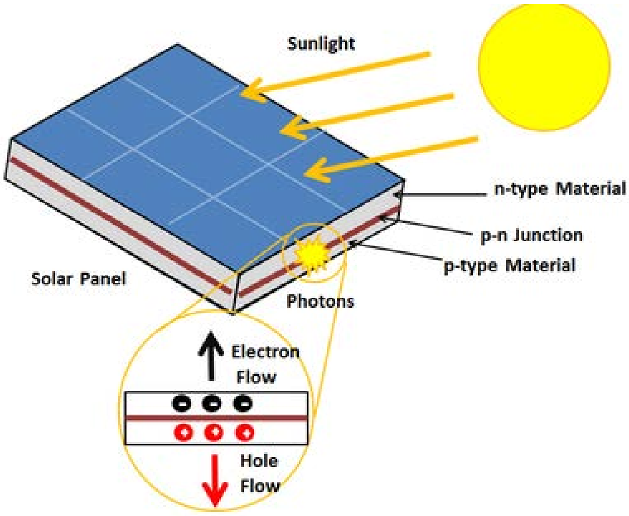

Figure 6.5: Basic operation of a photovoltaic (PV) cell [source].

directly via the *photovoltaic* effect.

In order to completely understand the photovoltaic effect, it is necessary to know several concepts from electromagnetism and quantum mechanics and is therefore beyond the scope of this text. The simplified explanation, however, is that when *photons*[4] strikes an electron, it brings the electron to a higher energy state. When two different types of materials with different amounts of *free* electrons and positive charge carriers are brought together, photons that strike at the interface of the materials cause different levels of excitation in both material, generating an imbalance in charge and thus a *voltage*. As shown in Fig. 6.5, this voltage is then able to drive a net flow of electrons called current. As these electrons flow around a circuit, electrical work can be extracted as

$$W_e = IV \tag{6.7}$$

where I and V are the current through and voltage across the *photovoltaic (PV) cell*. Interestingly, though we will not derive it here, the *open-cell* voltage of a PV cell with no current flowing is proportional to the *thermal voltage*, V_T, equal to

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[4] The quantized particle representation of a light wave (radiation).

$$V_T = \frac{k_B T}{q} \tag{6.8}$$

where k_B is the familiar Boltzmann Constant and q is the charge of a single electron[5]. The open-cell voltage, V_{OC} is given as

$$V_{OC} \approx V_T \ln\left(\frac{I_L}{I_0}\right) \tag{6.9}$$

where I_L is the current induced by the photovoltaic effect and I_0 is the *reverse saturation current*. While those terms may seem obscure, it is important to understand that this voltage difference is a function of the cell temperature.

When placed into a *circuit*, the voltage of a PV cell will vary as a function of how much current is flowing. As Fig. 6.6 shows, for a typical PV cell, the current remains roughly constant over a wide range of cell voltages and then abruptly drops to zero at the open-cell voltage. Viewed another way, as the current produced by the cell increases, its voltage drops. Since power is the product of current and voltage, we can plot this as a function of voltage as well, as shown in Fig. 6.6 in blue. As expected, the maximum power point is achieved near the *knee* in the I-V curve. In practice, PV cells are designed to run at this point, and the current is controlled externally to ensure maximum power output.

From a practical engineering perspective, we can treat a PV cell as a *current source* with a First Law efficiency, η_{PV}, equal to

$$\eta_{PV} = \frac{IV}{\dot{Q}_{solar}} \tag{6.10}$$

where $\dot{Q}_{solar}$ is the incident solar irradiance. Fig. 6.7 shows how this efficiency has improved for production solar cells since the 1990's. Currently, high-efficiency solar cells can convert up to 25% of the incoming solar radiation to electrical power. It has been shown that for a single interface absorbing sunlight, the maximum theoretical efficiency is around 30% in what is called the *Shockley-Queisser Limit* [1]. Higher efficiencies around 45% can be achieved with multiple interfaces that are tailored to specific bands within the solar spectrum. Compared to the ideal efficiencies that can be achieved for high-temperature concentrated solar power shown in Fig. 6.4, however, PV cell efficiencies are much lower. That said, by comparison, PV cells are much more flexible in terms of how and where they can be installed. In particular,

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[5] $1.602176634\text{x}10^{-19}$ Coulombs

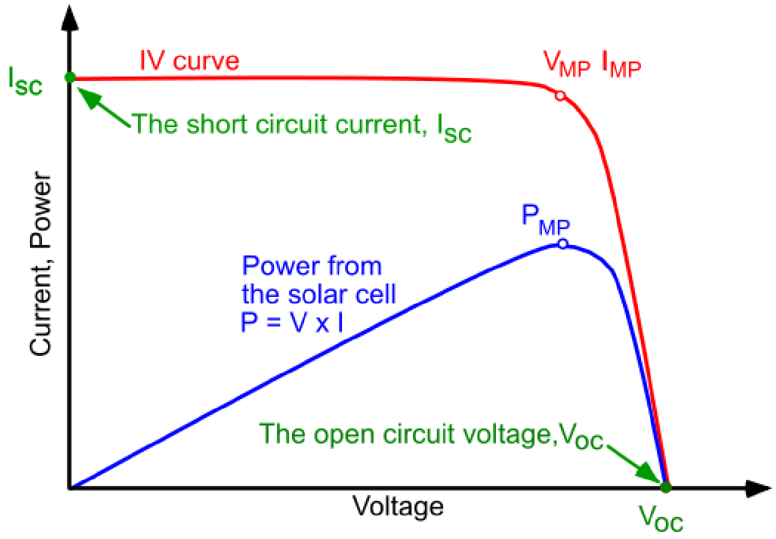

Figure 6.6: Current-Voltage and Power-Voltage curves for a typical solar cell [source].

concentrated solar power plants must be constructed in wide open areas and require a significant amount of specialized materials and equipment to operate at high temperatures. In comparison, solar panels can be placed on rooftops in cities as they require little extra infrastructure or space. Indeed, both energy conversion strategies are highly important for mitigating climate change as they serve different purposes and usage cases.

6.1.2 Wind Energy

Wind energy is another manifestation of solar energy. Even though solar radiation provides a more-or-less constant heat flux into the thermodynamic climate system, it does not do so uniformly, causing the temperatures of the air and various bodies of water to vary significantly over the Earth's surface. We can observe easily, for instance, that the weather in Antarctica is different than in the Middle East. As we would expect, these global temperature *gradients* in both the oceans and atmospheric create pressure gradients as well that drive the flow of water and air from regions of high temperature and pressure to regions of lower temperature and pressure. We call the moving water *currents* and the air *wind*. Moving a fluid across a pressure drop requires work as we have learned, and in the climate system, the energy driving these processes

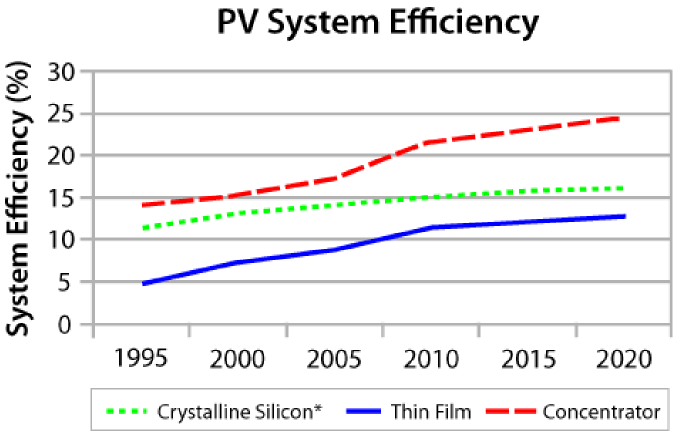

Figure 6.7: Average solar cell efficiencies for several production-ready technologies. In lab settings, efficiencies as high as 47% have been reported for *multi-junction* solar cells capable of extracting electrical work from a broader range of the solar spectrum. Image courtesy of DOE.

comes largely from the Sun[6].

Looking at the First Law for a stream of moving between two points in the atmosphere, as shown in Fig. 6.8, we see that

$$\cancel{\dot{E}_{CV}} = \dot{Q} - \dot{W} + \dot{m}\left[(h_1 - h_2) + \frac{1}{2}(|\vec{v}_1|^2 - |\vec{v}_2|^2)\right] \tag{6.11}$$

$$\tag{6.12}$$

where we have introduced a new term to keep track of the macroscopic *kinetic* energy of the flow. For wind comprised of an ideal gas, heat transfer to and from the control volume is typically negligible and thus can be considered roughly adiabatic. The work extracted is thus

$$\dot{W} = \dot{m}\left[c_p(T_1 - T_2) + \frac{1}{2}(|\vec{v}_1|^2 - |\vec{v}_2|^2)\right] \tag{6.13}$$

The turbines we have studied previously extract energy from the flow by lowering the stream's enthalpy; however, with wind turbines, this energy is

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[6] Some energy also comes from lunar tides. Also much of the observed weather patterns comes from the fact that the Earth is rotating and result *Coreolis* forces; however, these forces do not require nor do any work.

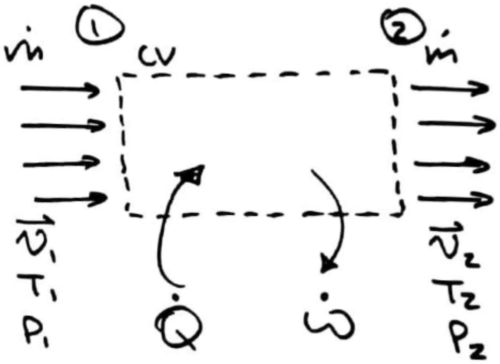

Figure 6.8: General control volume for fluid stream.

instead extracted from the stream's kinetic energy as it passes through the turbine blades. Specifically, momentum is transferred from the wind to each blade, causing it to rotate and slowing the velocity of the stream. For the type of horizontal-axis turbine shown in Fig. 6.9, we can draw a control volume around the air stream before and after the turbine as in Fig. 6.10. To compute the maximum work we can extract from this type of configuration, we can start by applying conservation of mass. We know that mass must enter and exit the control volume at the same rate, and thus

$$\dot{m} = \rho A_1 v_1 = \rho A_2 v_2 = \rho A v \tag{6.14}$$

where A and v are the cross-sectional area and velocity at the turbine[7]. This gives us a relationship between the two cross-sectional areas and velocities as

$$A_1 v_1 = A_2 v_2 = A v \tag{6.15}$$

Clearly, because the stream slows, it must expand to match the incoming mass flow rate. To compute the ideal mechanical power, we can assume in the ideal case that the wind density and temperature does not change between states 1 and 2. Under this assumption, Eq. 6.13, gives us

$$\dot{W} = \frac{1}{2}\dot{m}(v_1^2 - v_2^2) \tag{6.16}$$

$$= \frac{1}{2}\rho A v(v_1^2 - v_2^2) \tag{6.17}$$

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[7] The vector notation has been dropped for clarity. $v_i \equiv |\vec{v}_i|$.

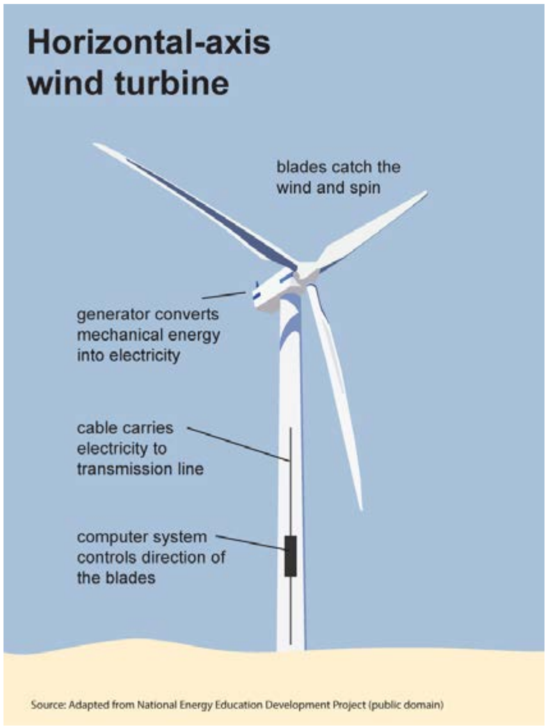


Image courtesy of EIA.

Figure 6.9: Schematic of a typical horizontal-axis wind turbine [EIA].

To solve for $|\vec{v}|$, we can compute the mechanical power extracted by the turbine by looking at the force, F, that must be applied by the turbine blades to slow the flow. The force is simply the time rate of change of momentum, which in this case is

$$F = \Delta \dot{p} = \dot{m}(v_1 - v_2) \tag{6.18}$$
$$= \rho A v (v_1 - v_2) \tag{6.19}$$

The power at the turbine is the product of force and velocity, which gives us

$$\dot{W} = Fv = \rho A v^2 (v_1 - v_2) \tag{6.20}$$

Now we have two equivalent expressions for $\dot{W}$ and so can equate them to solve for $|\vec{v}|$:

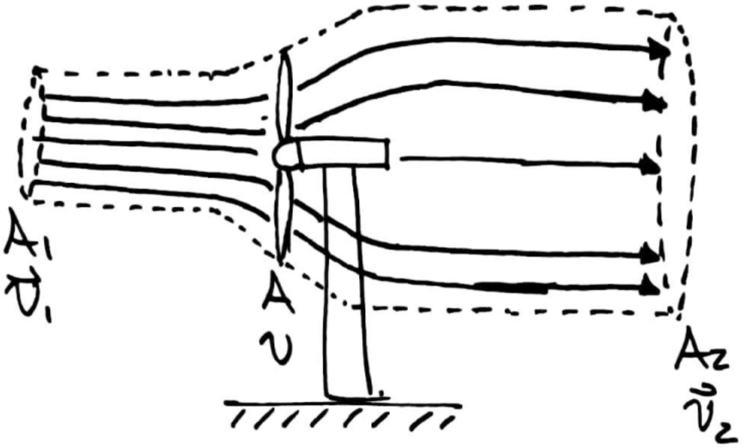


Figure 6.10: Control volume for air passing through wind turbine. As air slows across the turbine, it must expand to obey conservation of mass.

$$\frac{1}{2}\cancel{\rho A}v(v_1^2 - v_2^2) = \cancel{\rho A}v^2(v_1 - v_2) \tag{6.21}$$

$$\frac{1}{2}(v_1 + v_2)\cancel{(v_1 - v_2)} = v\cancel{(v_1 - v_2)} \tag{6.22}$$

$$\Rightarrow v = \frac{1}{2}(v_1 + v_2) \tag{6.23}$$

which is simply the average of the initial and final velocities. Plugging this expression for v back into Eq. 6.17, we get

$$\dot{W} = \frac{1}{4}\rho A(v_1 + v_2)(v_1^2 - v_2^2) \tag{6.24}$$

or

$$\dot{W} = \frac{1}{4}\rho A v_1^3 \left[1 + \left(\frac{v_2}{v_1}\right) - \left(\frac{v_2}{v_1}\right)^2 - \left(\frac{v_2}{v_1}\right)^3\right] \tag{6.25}$$

Intuitively, we might expect there to be a maximum value for the power that can be extracted by a turbine. If $v_2/v_1 = 1$, no power is extracted from the wind as its kinetic energy remains the same; however, as v_2/v_1 approaches 0, a considerable pressure builds up as air slowing down after the turbine prevents new air from passing through. This pressure starts to detract from the work we can extract. Indeed, if we set the first derivative of Eq. 6.25 with respect to v_2/v_1, which we will call ξ, we find that

$$\frac{d}{d\xi}\dot{W} = 0 \tag{6.26}$$

$$\frac{1}{4}\rho A v_1^3 \left(1 - 2\xi - 3\xi^2\right) = 0 \tag{6.27}$$

$$\left(x - \frac{1}{3}\right)(x+1) = 0 \tag{6.28}$$

which gives us roots at 1/3 and -1. Since v_2/v_1 is positive, we know then that the maximum power occurs at $v_2/v_1 = 1/3$. Plugging this value into Eq. 6.25 yields the maximum power

$$\dot{W}_{max} = \frac{8}{27}\rho A v_1^3 \tag{6.29}$$

To determine a maximum First Law efficiency, this value can be divided by the power of a stream with the same cross-sectional area of the turbine traveling at v_1 $(1/2\dot{m}v_1^2 = 1/2Av_1^3)$:

$$\eta_{turbine,max} = \frac{\frac{8}{27}\rho A v_1^3}{\frac{1}{2}A v_1^3} \tag{6.30}$$

$$= \frac{16}{27} = 0.593 \tag{6.31}$$

which is called the *Betz Limit*. In reality, actual wind turbines will experience loss due to *turbulence* and thermal dissipation that generates entropy and therefore detracts from the maximum work that can be extracted from the stream. Modern turbines, however, can reach efficiencies of up to 0.5, or about 84% of the Betz Limit, in ideal conditions.

While this performance metric is important for evaluating a single turbine, the analysis gets much more complex when you have a field of wind turbines as shown in Fig. 6.11. Given that the air that has passed through the turbine slows down considerably and in the real case can be quite turbulent, wind turbines cannot be placed close together or both will suffer a loss in efficiency and performance. In practice, large wind turbines are typically placed 150-200 m apart, leading to the important question: how much power can be generated per unit area? Or in other words, what is the total effective power density of a wind farm? Given these spacing requirements, at peak capacity, large farms

Figure 6.11: Wind farm showing multiple wind turbines [Photograph by Inga Spence / Alamy Stock Photo].

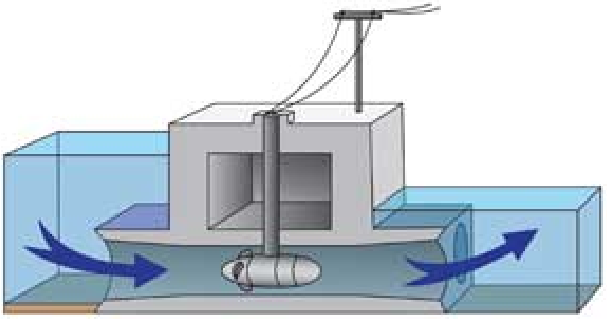
in the 200 MW range average about 10 W/m^2. It is tempting to compare this value with solar irradiance, but it is worth noting that wind power is typically used where solar power is impractical due to geography or low solar irradiance.

6.1.3 Hydropower

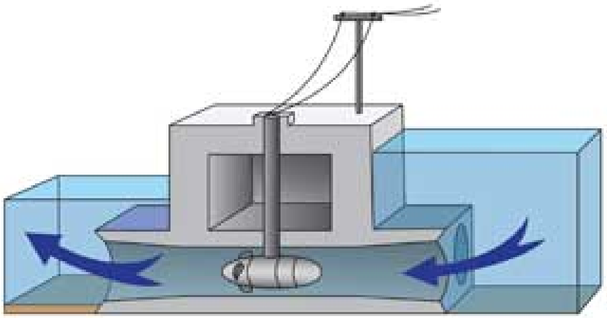
Hydropower is exactly analogous to wind power in that we can extract energy from a stream by reducing its kinetic energy. In the case of hydropower, this energy is extracted from literal streams, rivers, and other sources of flowing water. Instead of being driven by thermal gradients as with wind, the energy here is largely the result of the conversion of gravitational potential energy to kinetic energy as the water flows from high to lower elevations. In the end, though, this is still solar powered as the sun-driven water cycle transports water from low to higher geographic regions via evaporation and precipitation. Thermodynamically, we can treat wind ad hydro energy sources similarly and thus the equations for power extraction will be nearly identical, with the primary modifications occurring in the density of the fluids.

Tidal Energy

A subset of hydropower is power extracted from flowing water that moves as a result of the tidal forces of both the Sun and Moon. As the tides go in and out,



Tide Coming In



Tide Going Out

Figure 6.12: A turbine capturing tidal energy. Power is generated both as the tide comes in and goes out [NASA]. Image courtesy of NASA.

turbines can be used to extract work from the stream as shown in Fig. 6.12. The world's largest tidal power plant is the Sihwa Lake Tidal Power Station in South Korea and is capable of producing 254 MW at peak power. Like with wind and solar, however, this power is not continuous as kinetic energy can only be converted to work during the tidal transitions. As we will discuss later, energy storage is necessary in practice for smoothing out these dips in power production.

6.1.4 Geothermal

We know from our study of the Second Law of Thermodynamics that we need two thermal reservoirs at different temperatures to convert thermal energy to net work in a cycle. On Earth, we happen to have a staggering temperature gradient between the Earth's surface and core, which can reach temperatures well over 5,000 K as shown in Fig. 6.13. This thermal energy is a combination

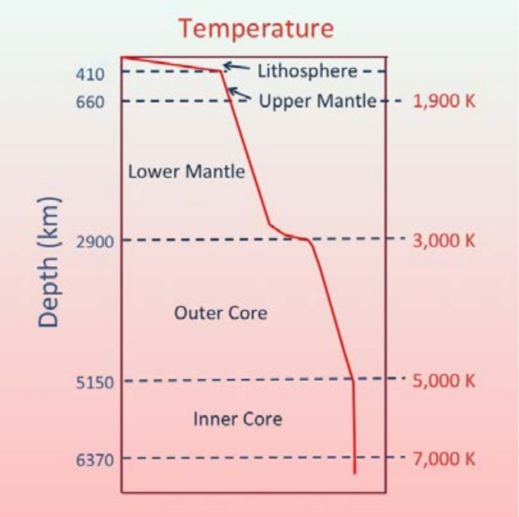


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Figure 6.13: Temperature profile of the Earth as a function of depth [source].

of thermal energy left over from the formation of the Earth - *primordial heat* - and *radioactive decay* of elements like uranium and plutonium at the core.

In terms of thermodynamics, a Carnot Cycle operating between the Earth's core at 5,000 K and surface at 300 would have an efficiency of

$$\begin{aligned} \eta_{Carnot} &= 1 - \frac{T_L}{T_H} && (6.32)\\ &= 1 - \frac{300}{5000} && (6.33)\\ &= 0.94 && (6.34) \end{aligned}$$

and the vast thermal mass (mcT) of the Earth would in theory be able supply a large fraction of human energy needs for millions of years. As is to be expected, there are numerous complications that prevents the ubiquity of geothermal power.

In practice, to extract energy from the thermal resources of the Earth's interior, water is pumped in deep wells where it is turned to steam, sent back to the surface, and used to power a Rankine Cycle to extract mechanical work. The steam is condensed and cooled using the ambient thermal reservoir and the cycle repeats. Fig. 6.14 shows exactly this process in a typical geothermal plant architecture. If the efficiency and Earth's heat capacity are so high, what are the caveats then? Well, to achieve the super hot temperatures required for

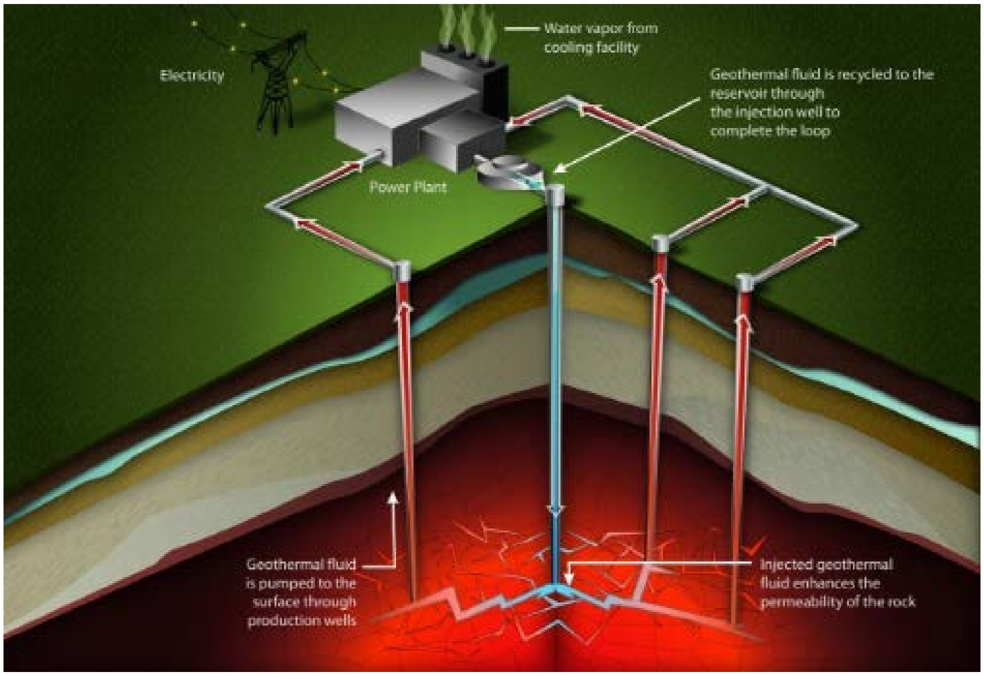

Image courtesy of DOE.

Figure 6.14: Geothermal well and associated power plant [USDOE].

high First Law efficiencies, it is necessary to drill upwards of a kilometer into the Earth, which is a significant and costly engineering challenge. Additionally, the thermal gradient is not uniform across the Earth's surface and is function of geography and geology, so even figuring out where would be a good location for geothermal power plants can be tricky. Regardless, given the carbon-neutral and nearly renewable nature of this energy source, it will need to play a large part in mitigating climate change.

6.1.5 Nuclear

While not technically renewable, nuclear energy derived from either the *fission* and decay of heavy, *radioactive* elements like uranium and plutonium or the *fusion* of light elements like hydrogen is carbon-neutral and provides an extremely large amount of energy per input fuel mass. Additionally, nuclear fuel sources are relatively abundant in nature, especially in the case of hydrogen-fed fusion. Thus, nuclear energy plays a crucial role in helping to bridge the gap between fossil fuels and true renewable energy, though its use - particularly via the fission of radioactive elements - has met significant hurdles as a result of public perception, politics, and concern about weaponization and waste management. Nuclear fusion solves most of these issues, but it is much more difficult to perform and to date, no utility-scale fusion reactor exists.

Thermodynamically, nuclear reactions are fundamentally different than the chemical reactions we previously looked at. In fission and fusion reactions, energy is not released via the change in bond energies, but rather in the loss of mass. Counter to what we have assumed for the majority of the content in this book, mass is not actually a conservative quantity but is instead another form of energy that can be converted to and from other forms. Einstein showed that the energy equivalent of *rest mass*[8] is equivalent to

$$E = mc^2 \tag{6.35}$$

where c is the speed of light in a vacuum. In nuclear fission, for example, a radioactivae and *fissile* isotope[9] of uranium, typically U-235, is bombarded with a neutron, causing its nucleus to split into various lighter element isotopes, including barium and krypton isotopes, and some neutrons. For this reaction, if we were to exactly measure all of the mass of the products and the reactants, we would find that mass of the products is about 0.1% less than that of the reactants. Because energy must be conserved, that converted mass is contained in the kinetic energy of the product neutrons as well as high-energy gamma radiation that released as well. It is evident from Eq. 6.35 that even though a small amount of mass is converted, c is equal to roughly 3x10^8 m/s and thus the overall energy release is enormous. The resultant energy density of fissile uranium fuel is roughly 144,000,000 MJ/kg, which is more than *two million* times greater than the heating value of any fossil fuel.

In a nuclear power plant, nuclear fission is carried out in an insulated container filled with water and some other materials to help control the reaction. The constant fission causes the entire volume to heat up, and this thermal energy is used as the heat input to a Rankine Cycle that extracts this energy as mechanical work, as shown in Fig. 6.15. While nuclear fission can be slowed using various techniques in these types of plants, it can never be completely stopped. As a result, nuclear power plants must always be producing power. In fact, the Rankine Cycle is crucial for cooling the nuclear reactor, preventing a runaway *meltdown* scenario. As a result of several notable such meltdown accidents, public and political perception of nuclear power is negative; however, nuclear fission-based energy actually remains the safest source of energy.

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[8] mass at rest relative to a fixed, non-accelerating reference frame. Relativistic physics of mass moving is a rich subject but well beyond the scope of this material.

[9] the same element but with a different number of neutrons

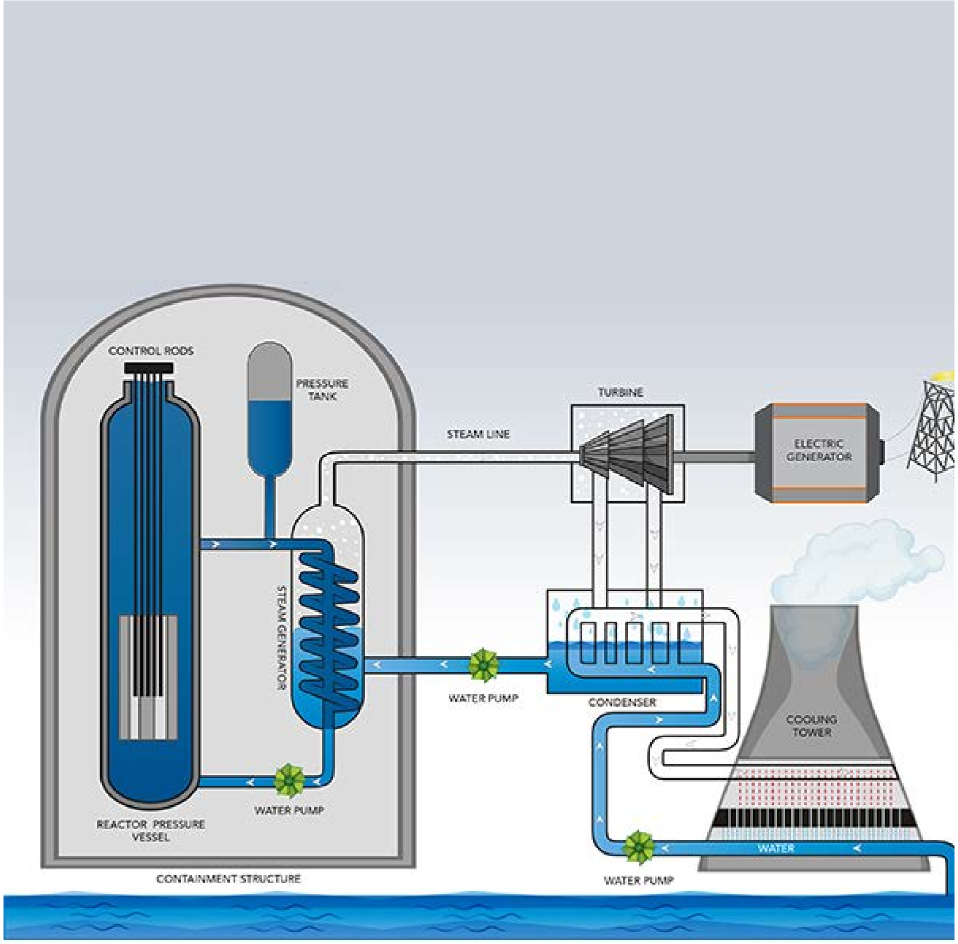

Figure 6.15: Schematic of a typical fission nuclear reactor power plant [US-DOE]. Image courtesy of DOE.

Also, while the radioactive fission products are highly toxic and dangerous to all life, the amount of waste per energy produced is extremely small given the high energy content of the fuel itself. Modern nuclear plants are able to handle this waste safely and effectively, but perception remains unchanged. It is also important to note that the only emissions from these plants is water vapor ejected from the turbine and thus is otherwise completely carbon neutral environmentally benign.

Fusion

In nuclear fusion, isotopes of hydrogen - deuterium and tritium - are brought together under extreme temperatures and pressures, forcing their nuclei to fuse, converting rest mass into kinetic and radiative energy for much the same reason as the fission reactions. The same reaction is what powers the cores of stars. Compared to fission, the energy density of this hydrogen fuel input is even greater, coming in at roughly 338,000,000 MJ/kg. Moreover, given the fact that hydrogen can be made easily via the *electrolysis* of water as we will soon discuss, the fuel source is practically endless. Unlike with fission, the byproduct of fusion is simply helium, which is not only non-toxic but also a highly valuable and otherwise dwindling resource. Clearly, nuclear fusion is an ideal power source; however, it is incredibly difficult to sustain in a controllable manner as the temperature required - 150,000,000 K - is far too high for any known material to sustain. Leading fusion reactor designs, including that by an international fusion project, ITER, hold the reaction as a plasma contained within a magnetic field. The complexity of the system and the required energy input to heat the plasm has prohibited the successful construction of a fusion plant that releases net energy, though as has been the case for decades, success is thought to be imminent.

6.1.6 Biofuels

The last energy source we will briefly discuss here is *biofuel*, which is chemically equivalent to many of the fossil fuels that helped bring humanity into this climate crisis; however, unlike fossil fuels, biofuels are produced and consumed on a similar timescale as it takes for the source biomass itself to grow. As shown by Solomon et al [2], CO_2 can remain in the atmosphere for hundreds to thousands of years, and so fuel production cycles on the order of tens of years can be considered carbon neutral, depending on the carbon intensity of the energy used in processing. The most common biofuel, ethanol, for instance, is derived from the fermentation of sugars found in corn and other harvested crops. The combustion of ethanol for power, as discussed in Chapter 3 and given by Eq. 3.71, releases CO_2 that is in theory offset by the CO_2 sequestered when the base crops regrow. In reality, however, emissions associated with the fermentation and refinement processes, as well as with the subsequent transportation of the ethanol fuel can lead to quite a high carbon intensity. As we will discuss later in this chapter, synthetic fuels produced directly from CO_2 may be a better alternative for a net carbon-neutral fuel.

6.2 Renewable Heat to Work

In many of the renewable energy sources we have discussed here, the energy is delivered to the user as heat, which can be at high temperatures in the cases of concentrated solar, deep-well geothermal, and nuclear, for example. Given the implications of the Second Law of Thermodynamics and the Carnot Theorem, there is this notion that the same quantity of thermal energy at different temperatures is not equal in terms of our ability to do useful work. Indeed, we know from the Carnot Efficiency - the maximum efficiency that can be achieved by a heat engine operating between two thermal reservoirs - that the greater the temperature difference between your heat source and cold sink, the greater the efficiency. The *quality* or *grade* of a heat source attempts to capture this observation, with heat at higher temperatures having a higher grade.

This is of course not new information for us at this point, but it is also worth noting that lower grade heat sources place additional limitations on how thermal energy is converted to work. External heat engines that operate on the Stirling Cycle using air as a working fluid, for example, require much larger heat exchangers to produce the same amount of power at lower temperatures, making them more expensive and impractical for all but industrial uses. Additionally, Rankine Cycles require the phase change of the working fluid, and thus the top temperature must be at or above the saturation temperature of the working fluid at the operating pressure, which can be quite high. To use water as a working fluid, this requires that the top temperature be in excess of 300-400 °C. Often, renewable-generated heat comes in well below these temperatures in practice, requiring that a different form of heat engine be used.

6.2.1 Low Temperature Heat Engines

As previously mentioned, a Stirling Engine can work well as a low-temperature heat engine; however, this architecture suffers from a low *power density* at lower temperatures, requiring prohibitively large and expensive components in many applications. Instead, low grade heat can be converted effectively to mechanical work in what is called an *Organic Rankine Cycle* (ORC). Such a cycle is the same as the normal Rankine Cycle, except that it utilizes a working fluid compatible with the suppressed temperature range. Ideal working fluids tend to be volatile organic liquids like butane, propane, toluene, pentane, and even ethanol, for instance, which is where the cycle gets its name. These fluids all have saturation temperatures much lower than water for the same pressures and are thus ideal for this type of cycle.

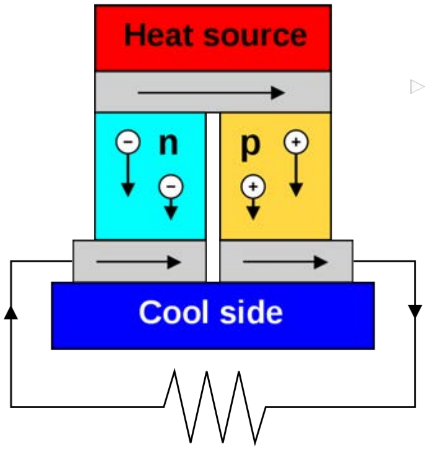

Figure 6.16: Thermoelectric or *Seebeck* effect that allows electrical work to be extracted from a temperature gradient. Here two materials with different levels of negative and positive charge carriers experience a net diffusion of electrons in one direction, generating current in the process [source].

Another architecture that is gaining traction is a Rankine Cycle that uses supercritical CO_2 as a working fluid. CO_2 has a critical temperature of only 31 °C, which enables the extraction of work from very low grade thermal energy, even waste heat from the output of power plants. This ability is important in terms of climate change mitigation, as there are many yet untapped renewable energy resources at these lower temperatures and can stand to make existing power extraction more efficient as well. The primary downside to both organic and supercritical CO_2-based Rankine Cycles is that higher pressures are required, making the systems more costly to build. Also, the release of some of these organic working fluid vapors into the atmosphere might negate their role and worth in carbon mitigation.

6.2.2 Thermoelectric Generator

Like with photovoltaic cells, we often want electrical work as a our final output. In a very similar manner as the photovoltaic effect, the *thermoelectric* or *Seebeck* effect enables a temperature gradient applied between the p-n junction - the interface between two dissimilarly doped semiconductors - and the outer ends of each semiconductor to develop an electrical potential across those ends. Note that this is partially what enables a potential difference to develop across a PV cell, but in this case, only conductive sensible thermal energy is supplied. A device that uses this phenomenon to generate electricity directly from a thermal gradient is called a *thermoelectric generator* (TEG), and typically only has an efficiency of around 5-8%, largely due to resistive losses. Despite this low efficiency, however, their compact nature and the fact that they are *solid state* - i.e. have no moving parts - makes them useful in many applications[10]. A TEG can be operated in reverse as a heat pump by supplying current to generate a thermal gradient. Such a system is called a *Peltier* cooler.

6.3 Energy Storage

Despite the significant quantity of renewable energy sources available on average, in particular those forms that are derived from solar irradiance directly, many are only available intermittently. In a fixed location on Earth, for example, the sun only shines bright enough to extract substantial electrical work for 6-8 hours a day, and wind energy may be even less predictable. As a result, the degree to which renewables are available is characterized by a *capacity factor* - the average fraction of time they are able to supply usable energy. For solar and wind at the grid scale, this capacity factor is around 20-35%. Nuclear has a capacity factor near 100% to avoid the previously discussed issues with meltdowns. The energy demand, however, may drop at times, but never completely to zero for many regions - cities in particular - and thus is not compatible with low-capacity-factor energy sources on their own. To mitigate this issue, renewables must generate excess power when they can and store the extra energy for when their output cannot meet demand. Here, we will discuss several key energy storage technologies.

6.3.1 Electrochemical Energy Storage

Perhaps the most ubiquitous form of energy storage that modern humans interact with on a daily basis is electrochemical energy storage - *batteries* that store and release *electrical* potential energy via *electro*chemical reactions. Zooming in to the atomic level, individual atoms and atomic compounds are made up of

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[10] The radioisotope thermoelectric generator (RTG) on the NASA Curiosity Mars Rover converts thermal energy released from its decaying plutonium fuel source to electricity directly using an array of TEGs.

electrons, protons, and neutrons such that in their neutral state, the negative and positive charges of the electrons and protons respectively balance out exactly. Some atoms, however, have a stronger affinity for electrons than others based on their atomic structure. Thus, when certain pairs of dissimilar atoms - typically metals - are placed in close proximity, electrons can travel between them. This makes one more negative than the other, creating an *electric field*, and if we can physically separate the dissimilar metals, an *electrical potential*, or *voltage* difference is established. Mathematically, this this potential difference, $\Delta\Phi$, is given as

$$\begin{aligned} \Delta\Phi &= \Phi_2 - \Phi_1 && (6.36) \\ &= \int_1^2 -\vec{E} \cdot d\vec{l} && (6.37) \end{aligned}$$

which is the *dot product* of the electric field along the path of separation. We will not show this here, but it is important to note that this potential is a state property and therefore is independent of the path of separation. Also like with entropy, we typically choose a reference value against which we can compare these potentials.

On its own, Φ has units of Volts in SI units which is equivalent to energy per *charge*, or Joules per Coulomb. From this, we can see directly that if we have a system that moves a charge through an electric field such that its electrical potential changes, the potential energy of the system will change as well. Consequently,

$$\begin{aligned} \Delta U_e &= U_2 - U_1 && (6.38) \\ &= q(\Phi_2 - \Phi_1) && (6.39) \end{aligned}$$

where q is the charge. Energy stored in this way can be released in a *circuit* by establishing an electrical potential difference and allowing electrons or other charge carriers to move from high to low potential. The movement of these charge carriers is called *current*. This energy release at the atomic level is simply a force applied by the electric field on the charge over some distance and is thus exactly equal to our previous definition of work. For this reason, the change in potential is often called the *electromotive force* or *EMF*. We can therefore include the work done by moving an electrical charge through a potential difference in our First Law definition:

$$dU = dQ - dW_{mechanical} - dW_{electrical} \tag{6.40}$$

$$= dQ - P\,dV - q\,d\Phi \tag{6.41}$$

While we will not discuss electromagnetism in much greater detail in this text, we will see how the laws of thermodynamics enable us to predict the energy storage capability of various combinations of dissimilar atoms or compounds. As usual we will look at the steady state equilibrium conditions of the system, this time for a typical battery *cell* in which two dissimilar metals with different electron affinities are used to create a potential difference.

Daniell Cell

A simple battery cell configuration is the *Daniell Cell* in which zinc and copper, two metals with different electron affinities, are used to drive current through a circuit and do electrical work. Fig. 6.17 shows a typical cell in which the zinc and copper *electrodes* are placed in separate *electrolyte* solutions containing water and some dissolved salts of each element - zinc sulfate ($ZnSO_4$) and copper sulfate ($CuSO_4$), for example. Zinc atoms have a lower affinity for electrons than copper atoms, and thus when connected by a conductor, electrons will move from the zinc electrode, called the *anode* to the copper electrode, called the *cathode*.

At the anode, zinc is *oxidized* and loses two electrons by the following oxidation reaction:

$$\mathrm{Zn} \rightleftharpoons \mathrm{Zn}^{2+} + 2\,\mathrm{e}^- \tag{6.42}$$

where Zn^{2+} indicates that the zinc has lost two electrons and thus has a positive charge with a magnitude twice that of a single electron. We call the new charged atoms *ions*. Similarly, on the cathode side, copper ions dissolved in the solution each gain two electrons from the zinc to form neutral cooper by the following reduction reaction:

$$\mathrm{Cu}^{2+} + 2\,\mathrm{e}^- \rightleftharpoons \mathrm{Cu} \tag{6.43}$$

All the while this is occurring, positively and negatively charged salts travel in opposite directions towards the cathode and anode respectively via a salt

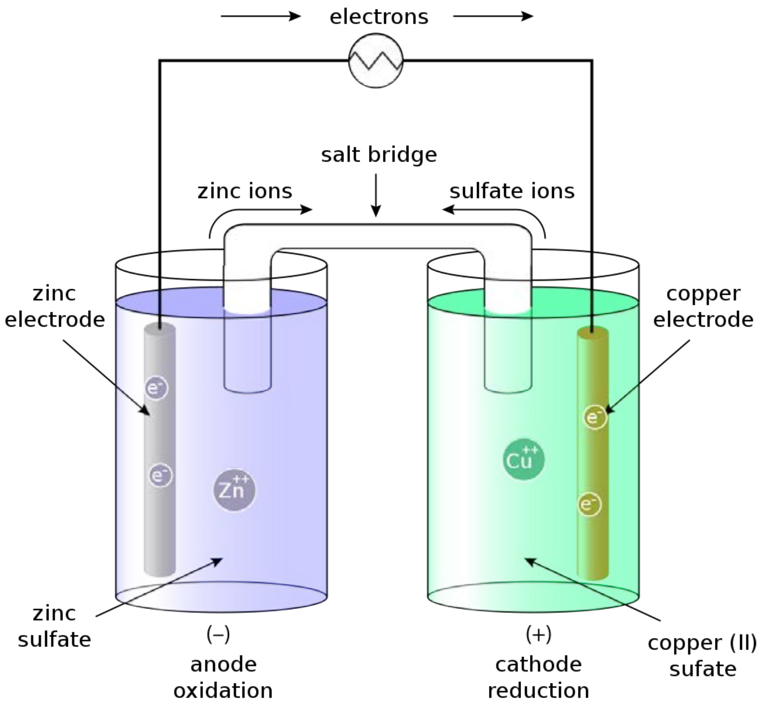

Figure 6.17: Simple electrochemical or galvanic battery cell called a *Daniell Cell* that uses zinc and copper electrodes to drive current through a circuit until the zinc is fully depleted [source]. Image courtesy of Rehua on Wikimedia. License CC BY.

bridge, which is a simple tube or absorbent paper sheet containing some electrolyte. This allows the reactions to proceed while zinc is removed from the anode and copper ions precipitate onto the copper electrode.

We know that in equilibrium, the molar change in Gibbs Free Energy, dg, must be zero for each reaction. Recall that for a chemical reaction, we have the general Gibbs-Duhem expression for the change in Gibbs Free Energy per mole:

$$dg = -s\,dT + v\,dP + \sum_i \mu_i\,dN_i \tag{6.44}$$

or for constant pressure and temperature processes,

$$dg = \sum_i \mu_i\,dN_i \tag{6.45}$$

For electrochemical reactions, we must add an additional term to also account for the change in electrical potential energy associated with a change in concentration of a particular species, dN_i,

$$dg = \sum_i (\mu_i + q_i \Phi)\, dN_i \tag{6.46}$$

where

$$q_i = z_i F \tag{6.47}$$

Here, z_i is the charge of the species (e.g. +2 for Zn^{2+}), and F is the Faraday constant[11]. Note that the right-hand side in parentheses for Eq.6.46 is defined as the electrochemical potential for species, i, denoted as η_i.

For the Daniell Cell used here, we can safely assume that reactions all happen at constant temperature and pressure, allowing us establish the equilibrium condition for each reaction using Eq. 6.46. First for the zinc oxidation reaction, we have

$$dg_{\mathrm{Zn}^{2+}} + dg_{\mathrm{Zn}} = 0 \tag{6.48}$$

$$(\eta\, dN_i)_{\mathrm{Zn}^{2+}} + (\eta\, dN_i)_{\mathrm{Zn}} = 0 \tag{6.49}$$

where from conservation of mass, we know

$$dN_{\mathrm{Zn}^{2+}} + dN_{\mathrm{Zn}} = 0 \tag{6.50}$$

$$\Rightarrow dN_{\mathrm{Zn}^{2+}} = -dN_{\mathrm{Zn}} \tag{6.51}$$

and thus

$$\eta_{\mathrm{Zn}^{2+}} = \eta_{\mathrm{Zn}} \tag{6.52}$$

$$\mu_{\mathrm{Zn}^{2+}} + 2F\Phi_a = \mu_{\mathrm{Zn}} \tag{6.53}$$

where Φ_a is the electrical potential of the zinc anode.

Similarly for the copper reduction reaction,

---

[11] Equal to 96485.33... C/mol and is equivalent to Avogadro's number times the charge of a single electron.

$$\mu_{\mathrm{Cu}^{2+}} + 2F\Phi_c = \mu_{\mathrm{Cu}} \tag{6.54}$$

where Φ_c is the electrical potential of the copper cathode, which is referenced to the same arbitrary reference potential as Φ_a for the anode. The cell potential at equilibrium can then be found by taking the difference Eqs. 6.53 and 6.54 to find $\Phi_a - \Phi_c$, giving us:

$$2F(\Phi_a - \Phi_c) = (\mu_{\mathrm{Zn}} - \mu_{\mathrm{Cu}}) + (\mu_{\mathrm{Cu}^{2+}} - \mu_{\mathrm{Zn}^{2+}}) \tag{6.55}$$

$$\Rightarrow \Phi_a - \Phi_c = \frac{1}{2F}\left[(\mu_{\mathrm{Zn}} - \mu_{\mathrm{Zn}^{2+}}) + (\mu_{\mathrm{Cu}^{2+}} - \mu_{\mathrm{Cu}})\right] \tag{6.56}$$

$$= \frac{-\Delta g_{overall}}{2F} = \mathrm{EMF} \tag{6.57}$$

In its most general form, Eq. 6.57 is given as

$$\mathrm{EMF} = \frac{-\Delta g_{overall}}{zF} \tag{6.58}$$

and is called the *Nernst Equation*. In this analysis, at equilibrium, this electrical potential difference or EMF is called the open-circuit voltage. In reality, once current starts flowing this voltage will drop due to resistance and other losses. To compute the open-circuit voltage, however, we can go back to our expression for the chemical potential of an ideal mixture, which gives

$$\mu_i = \mu_i^+(T) + RT\left[\ln\left(\frac{P}{P_0}\right) + \ln X_i\right] \tag{6.59}$$

which at constant pressure is simply

$$\mu_i = \mu_i^+(T) + RT\ln X_i \tag{6.60}$$

for a single species. The overall change in Gibbs Free Energy is given as

$$dg_{overall} = \sum_i \mu_i\, dN_i \tag{6.61}$$

$$= \sum_i \left(\mu_i^+(T)\nu_i + RT\nu_i \ln X_i\right) \tag{6.62}$$

$$= \sum_i \mu_i^+(T)\nu_i + RT\ln\left(\prod_i X_i^{\nu_i}\right) \tag{6.63}$$

where ν_i is the stoichiometric coefficient of species i[12]. This equation is usually valid for low concentrations. For non-ideal mixtures, we need to utilize the activity coefficient as previously discussed, which gives us

$$
\begin{aligned}
dg_{overall} &= \sum_i \mu_i^+(T)\nu_i + RT\ln\left(\prod_i (\gamma_i X_i)^{\nu_i}\right) && (6.64)\\
&= \sum_i \mu_i^+(T)\nu_i + RT\ln\left(\prod_i (a_i)^{\nu_i}\right) && (6.65)\\
& && (6.66)
\end{aligned}
$$

where a_i is the *activity* of the species.

Putting this all together, we get that the open circuit EMF is

$$
\begin{aligned}
\text{EMF} &= \frac{-\Delta g_{overall}}{zF} && (6.67)\\
&= \frac{-\sum_i \mu_i^+(T)\nu_i}{zF} - \frac{RT}{zF}\ln\left(\prod_i a_i^{\nu_i}\right) && (6.68)\\
&= \text{EMF}^\circ(T) - \frac{RT}{zF}\ln\left(\prod_i a_i^{\nu_i}\right) && (6.69)
\end{aligned}
$$

where $\text{EMF}^\circ(T)$ is the standard cell potential at a given temperature and is derived from experimental measurements.

For our zinc-copper Daniell Cell, we have the total reaction:

$$\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu} \tag{6.70}$$

for which the standard cell potentials for the zinc and copper *half* reactions are given at standard temperature as -0.763 V and 0.337 V respectively. The total standard cell potential is therefore $0.337 - (-0.763) = 1.1V$, and thus the actual EMF is given by

$$\text{EMF} = 1.1 \text{ V} - \frac{RT}{2F}\ln\left(\frac{a_{\text{Zn}^{2+}} \cdot a_{\text{Cu}}}{a_{\text{Zn}} \cdot a_{\text{Cu}^{2+}}}\right) \tag{6.71}$$

---

[12] recall that the products have negative stoichiometric coefficients.

for pure solids, the activity is equal to 1 and thus we can simplify this further as

$$\mathrm{EMF} = 1.1\ \mathrm{V} - \frac{RT}{2F}\ln\left(\frac{a_{\mathrm{Zn}^{2+}}}{a_{\mathrm{Cu}^{2+}}}\right) \tag{6.72}$$

where again the activity is typically a function of both the composition and temperature of the mixture and must be taken from experimental data. Note that this type of electrochemical cell is generally called a *Galvanic Cell.*

Rechargeable Electrochemical Batteries

What was implicit in our analysis of the simple Daniell Cell - and is true for all Galvanic cells - was that the stored energy is actually in the fact that the zinc starts out as a pure elemental electrode and that there are already Cu^{2+} ions in solution on the cathode side. The energy extracted as current initially went into reducing the zinc and liberating copper ions so that the reduction-oxidation reaction could later take place, much like our combustion reactions from Chapter 3, which were also reduction-oxidation reactions. Over the life of the electrochemical cell, electrons can only be transported as long as there is pure reduced zinc on the anode and there are Cu^{2+} ions in solution, and as the battery operates, more and more zinc dissolves into solution and copper ions reattach to the copper electrode.

In the Daniell Cell analyzed here, the two half reactions are reversible in theory. If instead a reverse voltage is applied, electrons will flow from the cathode to the anode, causing the reverse reactions to occur; however, in practice, for this type of battery, it is difficult to get the zinc to precipitate back onto the anode with out forming *dendrites* - long spindly formations that dramatically decrease the performance of the cell and can even cause short a short circuit between the anode and cathode. Consequently, this type of battery is not considered to be *rechargeable* in that the potential energy cannot be appreciably restored by simply reversing the direction of the current. Such a battery is typically called a *primary battery.*

Conversely, a *secondary* or rechargeable battery is one in which the chemistry can be reversed successfully by running the cell in reverse. Most alkaline batteries can be recharged several times before their performance degrades to the point where the cell is no longer usable. A major innovation came in the 1970's when it was discovered that cathodes made from lithium cobalt dioxide ($LiCoO_2$) were stable enough to undergo hundreds of recharge cycles and exhibit high energy densities. In the years since, *Li-ion* batteries have

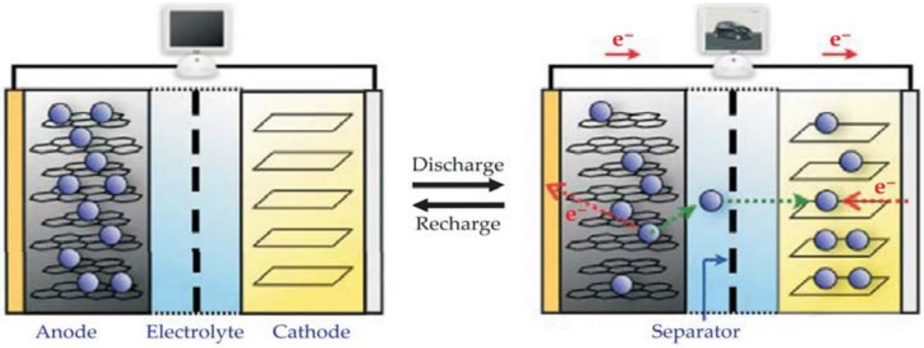

Figure 6.18: Li-ion battery architecture that uses a $LiCoO_2$ cathode and graphite anode.

emerged as the leading electrochemical-based energy storage technologies. In these cells, the charge carrier is lithium, which during discharge is the result of the following oxidation reaction on a graphite-lithium anode:

$$C_6Li \longrightarrow 6\,C_{gr} + Li^+ + e^- \tag{6.73}$$

and subsequent reduction reaction in the cathode:

$$CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2 \tag{6.74}$$

State of the art Li-ion batteries can achieve specific energies and energy densities up to 265 Wh/kg and 700 Wh/L respectively.

6.3.2 Thermal Energy Storage

Another leading strategy for energy storage involves storing energy as heat - either in the latent heat of a *phase change material* (PCM) or as sensible heat. In either case, excess electrical or mechanical work generated by some energy conversion process is dissipated as thermal energy, which is then stored and later extracted using a heat engine, PV cells, or TEGs depending on the temperature of the available heat. As discussed earlier, the stored thermal energy can also be used directly as heat as well.

Because thermal energy has the tendency to spread out and diffuse irreversibly by the Second Law of Thermodynamics, it is inevitable that some energy will "leak out" of any heat storage system. Also, we know well by now that there are limitations on the First Law efficiencies of each of these various energy conversion processes. It is therefore important to define the concept of a *round-trip* efficiency, which is ratio of how much energy we get out in the form we want to the amount of energy we put in originally. If we only need thermal energy as our output, the round-trip efficiency is given as

$$\eta_{round-trip} = \frac{Q_{out}}{Q_{in}} \tag{6.75}$$

$$= \frac{Q_{in} - Q_{lost}}{Q_{in}} \tag{6.76}$$

where Q_{lost} is the thermal energy lost to the environment during the storage period. If instead we need the energy back out as electrical or mechanical work, we must then also apply the First Law efficiency of whatever energy conversion process is used. For this case,

$$\eta_{round-trip} = \eta_{conversion} \left(\frac{Q_{in} - Q_{lost}}{Q_{in}} \right) \tag{6.77}$$

The keys to a high round-trip efficiency are therefore to increase the efficiency of the energy conversion process and limit the lost heat. For the former, there are thermodynamic limits that place upper bounds on $\eta_{conversion}$. For heat engines in particular, we know that the higher the temperature at which the heat is stored, the higher the efficiency. Unfortunately, the amount of heat lost is also proportional to temperature, with higher temperatures leading to more heat loss over the same storage period, as we would expect. Physically, conductive heat transfer obeys *Fourier's Law*, which gives the heat flux, $\dot{q}$, in units of power per unit area - W/m^2 in SI units - as

$$\dot{q} = -k \nabla T \tag{6.78}$$

where ∇ T is the spatial *gradient* of temperature. In one dimension, this equation is equal to

$$\dot{q} = -k \frac{dT}{dx} \tag{6.79}$$

which shows us that a greater difference in temperature across the same distance will lead to a higher heat flux. In general, heat will be lost to conduction, thermal radiation, and *convection*[13]. The heat flux from our storage system at temperature T_s to the environment at T_a can be approximated as

$$\dot{Q}_{lost} = hA(T_s - T_a) \tag{6.80}$$

where h is an empirical *heat transfer coefficient* with units of W/m^2-K and A is the surface area over which the heat transfer occurs. The total heat lost over a storage period τ is then

$$Q_{lost} = \int_0^\tau hA(T_s - T_a)dt \tag{6.81}$$

where T_s, T_a, and even h, may change over the storage period.

In practice, h can be reduced by adding various types of insulation to the storage system, but can never be brought to 0. Thus a trade-off emerges between needing high temperatures for efficient energy conversion but also low enough temperatures or sufficient insulation to reduce losses. For latent heat storage, the primary benefit is that thermal energy can be stored at *constant temperature*, as we know from our analysis of phase changes from earlier. This helps to reduce losses in the case where the energy is needed back out as work. For these applications, substances with high melting points are typically used. Various salts or even silicon, which have melting points around 800 °C and 1,400 °C respectively, are common choices. In practice, however, these materials are often heated well past their melting points, adding thermal energy as *sensible heat*, which follows our usual expression for internal energy

$$Q_{stored} = mc\Delta T \tag{6.82}$$

where m and c are the storage material mass and specific heat capacity respectively.

6.3.3 Other Forms

Finally, in terms of energy storage, there are numerous other technologies that are being explored at the grid-scale, though we will not go into too much detail here.

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[13] conduction to a fluid

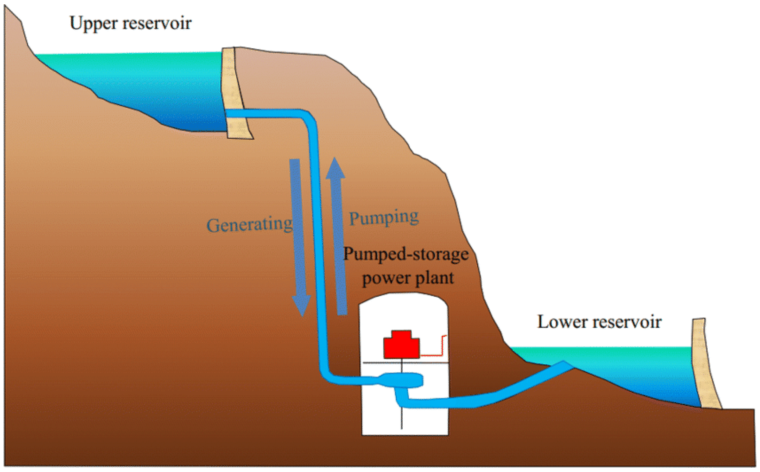

Figure 6.19: Schematic of a pumped-hydro storage system. Excess electricity is used to pump water from a lower reservoir to a higher one and then when energy is needed, the water flows back through the pump in the opposite direction to generate electrical power.

Pumped-Hydro

First, there are number of promising gravity-based storage technologies. For instance, *pumped-hydro storage* is basically a hydro-electric dam that can also run in reverse. As discussed earlier, hydro-power benefits from the natural water cycle using solar energy to transport water from a lower to a higher geographic region; however, this flow of energy is subject to natural weather patterns, which may be unpredictable. Pumped-hydro removes some of this uncertainty by using excess renewable electricity to pump water from a lower to a higher reservoir as shown in Fig. 6.19. Then when electricity demand exceeds that which can be produced by the renewable sources, water is released from the upper reservoir and flows the opposite direction through the pump to generate electricity. This is enabled by the fact that electric motors can operate in reverse to generate current from an input of mechanical work. It is believed that there is enough natural change in elevation throughout across the Earth to meet most of the world's energy storage needs. Presently, there are political and economic hurdles to implementing these systems.

Compressed-Air Energy Storage

Another leading energy storage technology is *compressed-air energy storage* (CAES), where excess mechanical or electrical work is used to run a compressor to compress air to high pressures. Here the energy is stored both as PV work and thermal energy. In this paradigm, the gas can be compressed adiabatically or isothermally, and either stored isochorically or isobarically. In all combinations, the theoretical round-trip efficiency is 100%, but in practical systems, irreversibility cannot be completely avoided, as the gas will heat up substantially during the compression process. In the adiabatic case, the final temperature after compression, T_2, is given as

$$T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} \tag{6.83}$$

if we assume constant volume gas storage - which in practice can be achieved by compressing gas in a naturally occurring cavern, porous rock bed, or human-made tank - we can compute the work per unit mass from the First Law as

$$\begin{aligned} w_{c,s} &= -(u_2 - u_1) && (6.84)\\ &= -c_v(T_2 - T_a) && (6.85)\\ &= c_v T_a(1 - \frac{T_2}{T_a}) && (6.86)\\ &= c_v T_a \left[1 - \left(\frac{P_2}{P_a}\right)^{\frac{\gamma-1}{\gamma}}\right] && (6.87) \end{aligned}$$

which also assumes no other losses. As discussed in Chapter 5, the real compressor will have some isentropic efficiency, η_c^{II}, that increases the work required by a factor of $1/\eta_c^{II}$ and thus:

$$w_c = \frac{c_v T_a}{\eta_c^{II}} \left[1 - \left(\frac{P_2}{P_a}\right)^{\frac{\gamma-1}{\gamma}}\right] \tag{6.88}$$

When energy is needed, this compressed air is released, and is expanded through a turbine to extract work. Due to the symmetry of the problem, we can compute the turbine work as

$$\begin{aligned}
w_{t,s} &= -(u_3 - u_2) \qquad (6.89)\\
&= -c_v(T_a - T_2) \qquad (6.90)\\
&= -c_v T_a(1 - \frac{T_2}{T_a}) \qquad (6.91)\\
&= -c_v T_a \left[1 - \left(\frac{P_2}{P_a}\right)^{\frac{\gamma-1}{\gamma}}\right] \qquad (6.92)
\end{aligned}$$

for the ideal case and

$$w_t = \eta_t^{II} c_v T_a \left[1 - \left(\frac{P_2}{P_a}\right)^{\frac{\gamma-1}{\gamma}}\right] \tag{6.93}$$

for the real case, where η_t^{II} is the isentropic efficiency of the turbine. The round-trip efficiency is then

$$\begin{aligned}
\eta_{round-trip} &= \left|\frac{w_{out}}{w_{in}}\right| \qquad (6.94)\\
&= \left|\frac{w_t}{w_c}\right| \qquad (6.95)\\
&= \eta_t^{II}\eta_c^{II} \qquad (6.96)
\end{aligned}$$

as we would expect.

In the isothermal case, we can determine the round-trip efficiency by a similar process. Looking at the First Law for the compression case, we have

$$\begin{aligned}
\Delta u &= q_{out} - w_{c,s} \qquad (6.97)\\
\Rightarrow w_{c,s} &= q_{out} - \cancelto{0}{\Delta u} \qquad (6.98)
\end{aligned}$$

where we know $\Delta u = c_v \Delta T = 0$ for an isothermal process. Also, intuitively we know that in order for the gas to maintain the same temperature throughout the process, heat must be transferred from the gas to its surroundings. To determine the magnitude of this heat transfer, we look tp the Second Law:

$$\Delta s = \frac{q_{out}}{T_a} + \Delta s_{gen} \tag{6.99}$$

$$\cancelto{0}{c_p \ln \frac{V_2}{V_1}} + c_v \ln \frac{P_2}{P_a} = \frac{q_{out}}{T_a} + \Delta s_{gen} \tag{6.100}$$

$$\Rightarrow q_{out} = T_a \left(c_v \ln \frac{P_2}{P_1} - \Delta s_{gen} \right) \tag{6.101}$$

For the ideal case, $\Delta s_{gen} = 0$, giving us

$$w_{c,s} = c_v T_a \ln \frac{P_2}{P_a} \tag{6.102}$$

which by comparison to the adiabatic case, is considerably less work for the same pressure difference. We can lump all of the inefficiencies for this process together again as an isentropic efficiency, giving us the actual work of compression as

$$w_c = \frac{c_v T_a}{\eta_c^{II}} \tag{6.103}$$

By symmetry, the expansion process must also absorb the same amount of heat, giving us the ideal work extracted as

$$w_{t,s} = c_v T_a \ln \frac{P_a}{P_2} \tag{6.104}$$

and the real work as

$$w_t = \eta_t^{II} c_v T_a \ln \frac{P_a}{P_2} \tag{6.105}$$

giving us the same round-trip efficiency as with the adiabatic case,

$$\eta_{round-trip} = \eta_t^{II} \eta_c^{II} \tag{6.106}$$

Ideally, the isothermal process is preferred as it requires less work to achieve the same pressure ratio and there is no potential for heat loss during the storage

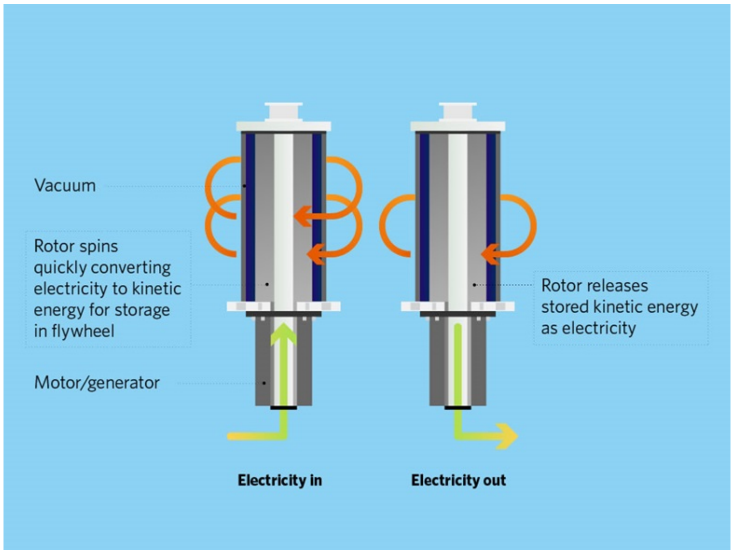

Figure 6.20: Basic inertial energy storage mechanism using a rotating flywheel to store energy as rotational kinetic energy [IESO].

period as the gas is at the same temperature as the environment; however, in practice it is difficult to achieve isothermal compression and requires multiple stages where the gas is cooled irreversibly in between. Thus, CAES systems typically operate closer to the adiabatic regime. Also, while we assumed constant volume processes here, constant pressure processes are also favored in the ideal case, as they allow for work to be extracted over the total expansion of the gas. This requires an expandable reservoir, though, which can add complexity and cost to a large storage project. In many cases, natural caverns already exist that form an ideal storage reservoir for the compressed air.

Flywheels

The final energy storage system we will discuss briefly here is *inertial* energy storage, in which energy is stored as macroscopic kinetic energy. One common approach is to use excess electricity to spin a motor attached to a mass with a large moment of inertia to high angular velocities, allowing energy to be stored as

$$E_{flywheel} = \frac{1}{2} I \omega^2 \tag{6.107}$$

where I is the moment of inertia and ω is the angular velocity. The mass is then electrically decoupled from the motor, and the mass's kinetic energy is held roughly constant. When energy is needed back out, the spinning mass couples back to electric motor, generating electrical work. As shown in Fig. 6.20, this type of energy storage mechanism is typically placed in a vacuum with magnetic couplings, resulting in very little frictional losses or dissipation throughout the energy storage cycle. The state-of-the-art flywheel energy storage systems can achieve round-trip efficienies above 85%.

6.4 Summary

The main issue with burning fossil fuels for energy from a climate change perspective is that the CO_2 combustion products are being added to the atmosphere at a much greater rate than they are naturally removed. Given the comparatively long timescales required for forming coal, oil, and natural gas, these energy sources are considered non-*renewable*. Fortunately, there exist abundant *renewable* energy sources that can supply global human energy demands without emitting CO_2 and other greenhouse gases and further contributing to climate change. Sources like solar, wind, geothermal, and tidal energy together supply significantly more power on average than we consume, and thus they are playing a crucial role in slowing greenhouse gas emissions. In this chapter, we looked a several of these sources from a thermodynamics perspective, as well as some technologies used in the conversion of low temperature renewable thermal energy to work. Finally, because renewables, while abundant, typically provide power intermittently, new and efficient energy storage systems are required for bridging the gaps between demand and power generation capacity. To that end, we analyzed electrochemical, thermal, gravitational, and inertial storage.

It is clear from a thermodynamics perspective that our global energy needs can be met many times over with renewable energy sources, coupled with adequate energy storage; however, from a geopolitics and socioeconomics perspective, this transition from fossil fuels to carbon neutral energy infrastructure cannot occur instantaneously. Consequently, additional technologies will be necessary to mitigate the climate crisis while this transition is carried out in the background. This is where we are going next.

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Chapter 7

Mitigating the Climate Crisis

The global conversion from fossil fuels to renewable energy sources is a function of economic resources and political will and therefore has not been a swift process. At the same time, immediate action must be taken to eliminate carbon emissions from existing energy conversion infrastructure. This can be accomplished in a variety of ways via carbon capture and storage at the source of emissions, separating CO_2 out of the atmosphere, or replacing the fuels themselves with synthetic, carbon-neutral alternatives that existing infrastructure can use directly. In this chapter, we will look at the thermodynamics behind a few of these carbon sequestration methods and how in some cases, they can exacerbate the problem. Additionally, many major industrial processes aluminum smelting, for example, currently emit a significant amount of CO_2 as a result of chemistry underlying their operation. We will briefly look at some of these processes to understand where a significant source of emissions continue to come from and how those might be mitigated.

Finally, as a last-ditch effort in the event of emissions exceeding the IPCC targets, humanity may need to turn to major geoengineering projects to attempt to cool the Earth directly and manipulate the climate on a global scale. While considerable effort has been made towards establishing new technologies that could theoretically accomplish such a complex task, however, we are still a long way off from being able to both execute some of these strategies or even fully understand the other effects they may have on global ecosystems and weather. Nevertheless, we will apply some of our knowledge of thermodynamics to explore some of the leading concepts. At the rate global atmospheric CO_2 concentrations continue to rise, these technologies are becoming increasingly more relevant to the conversation on how to manage the climate crisis.

7.1 Artificial Carbon Capture

The material developed in Chapters 3 and 4 shows us that a) the oxidation of hydrocarbons and other carbon-based fossil fuels results in the emission of CO_2 and various other greenhouse gases as direct products of combustion reactions and b) due to the entropy generated in the mixing of these gases with atmosphere, there is mandatory work associated with their subsequent separation and capture. Because of point b) here, there are significant energy-saving benefits to capturing the gases as they are emitted and before they mix with the rest of the atmosphere. While this practice would help reduce point-of-use emissions going forward once implemented, there would still be significant emissions unaccounted for along the pipeline from fuel extraction to use. Also carbon capture at the source is often infeasible, and thus for these reasons, greenhouse gases must still be captured directly from the atmosphere as well. Both of these climate change mitigation strategies are discussed further here.

7.1.1 Carbon Capture and Storage (CCS)

We showed in Chapter 4 that the minimum amount of energy required to separate a component gas of mole fraction, X_i, from a mixture of various other gases is given by

$$w_{min} = -RT\left[\ln X_i + \frac{1-X_i}{X_i}\ln(1-X_i)\right] \tag{7.1}$$

per mole of component gas i, where R is the ideal gas constant, and T is the temperature at which the separation is carried out. Fig. 4.18 shows this function plotted over a component mole fraction range of 0 to 1, illustrating that the amount of energy required to separate a single gas from a mixture decreases to zero as the concentration of that gas increases to 1. The second law efficiency (i.e. w_{min}/w_{actual}) for typical separation plants is on the range of 5-40% [1], further compounding this issue. Avoiding this challenge altogether is the foundation of *Carbon Capture and Storage (CCS)* methods that remove CO_2 from the point of production where concentrations are significantly higher than in the atmosphere. It is also important to note, however, that power plants with CCS implemented incur an efficiency penalty, so the favorable thermodynamics associated with the separation become less so.

CCS methods specifically involve separating CO_2 from other gases at the points of generation (e.g. power plants and concrete manufacturers), compressing it to a liquid, and transporting it for storage in wells underground

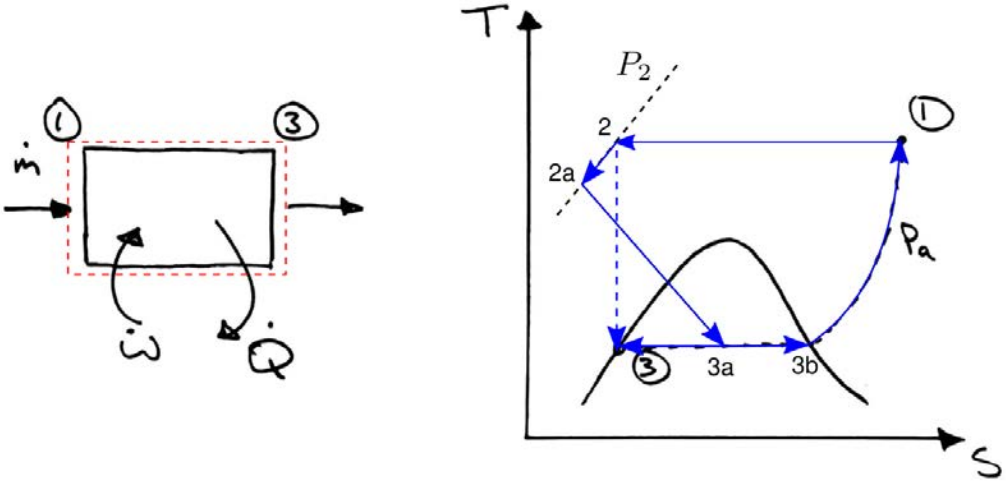

Figure 7.1: General control volume for a liquefaction process (left) and T-s diagram for the ideal *Linde-Hampson Cycle* with the dashed blue line and actual Linde-Hampson Cycle with the solid blue lines (right).

or deep in the ocean. These solutions typically involve flowing exhaust gas with high concentrations of CO_2 past solid absorbents like CaO and amino acid salts or liquid adsorbents like various hydrotalcites and other ionic liquids that selectively absorb or adsorb the greenhouse gas. Once separated, these sorbents can typically be regenerated using thermal energy to release the gas for subsequent compression, transportation, and storage. CCS can also be performed efficiently using polymer-based gas separation membranes to selectively remove CO_2 from the other various flue gases [2].

Gas Liquefaction

A key step that contributes to the energy requirements of CCS is the liquefaction of the captured CO_2. This process is often necessary, as storing gaseous CO_2 is difficult and requires a prohibitively large amount of volume. As we have done before, we can compute the minimum work required for this process by formulating a general control volume and thermodynamic cycle to represent this process, as shown in Fig. 7.1. Here we see the T-s diagram for two versions of the *Linde-Hampson Cycle* in which a gas at atmospheric pressure is compressed isothermally and then expanded in a number of different ways to cool and condense it into a liquid, also at atmospheric pressure.

For the ideal case, we can write the First and Second Laws for the control volume shown in Fig. 7.1 as

$$\cancelto{0}{\dot{E}_{CV}} = \dot{Q} - \dot{W} + \dot{m}(h_1 - h_3) \tag{7.2}$$

and

$$\cancelto{0}{\dot{S}_{CV}} = \frac{\dot{Q}}{T_a} + \dot{m}(s_1 - s_3) + \dot{S}_{gen} \tag{7.3}$$

Setting $\dot{S}_{gen} = 0$ for the ideal case and combining, we find that the minimum work per mass of gas converted to liquid is given by

$$w_{min} = -[(h_3 - h_1) - T_a(s_3 - s_1)] \tag{7.4}$$

which you can see is the change in availability or exergy across this cycle. The expansion process for this ideal case is represented by the dashed blue line on the T-s diagram in Fig. 7.1, indicating that the gas expands isentropically until it just intersects the vapor dome on the saturated liquid side at state 3. Here the produced liquid is also at atmospheric as shown by the fact that it lies on the same isobar as state 1 at P_a.

In reality, isentropic expansion is not possible, and thus a more a realistic process is shown in the solid blue lines in Fig. 7.1. From state 2a to 3a, the compressed gas is expanded through a *throttle valve*, which holds enthalpy constant through this extremely fast expansion process[1]. Because considerable entropy is generated, however, 3a typically lies inside the vapor, meaning that only some of the gas is converted to liquid. In practice, the liquid is separated and the remaining cold gas is sent back through the cycle. To save energy, this cold gas is used to cool the input gas from state 2 to 2a, bringing it back up to T_a in the process.

To determine the Second Law efficiency for this non-ideal but practical Linde-Hampson cycle, we can note that in both cases the same amount of work is required in the compression process; however, in the real case, work cannot be extracted during the expansion process as it is *isenthalpic* as previously noted. Also, not all of the gas is converted to liquid and the remaining gas must be sent through the cycle again. For this case, we can therefore compute the work required by simply dividing the work required for the isothermal compression process by the liquid quality of the outputs:

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[1] typically called a *flash* process

$$w = \frac{1}{1 - X_{3a}}[(h_1 - h_2) - T_a(s_1 - s_2)] \tag{7.5}$$

where X_{3a} is the vapor quality after the expansion process and thus $1 - X_{3a}$ is the liquid quality. To determine the vapor quality at state 3a, we can perform an energy balance across the *isenthalpic* expansion process form state 2a to 3a.

$$\begin{aligned}
\cancel{\dot{m}}h_{2a} &= \cancel{\dot{m}}[(1 - X_{3a})h_3 + X_{3a}h_{3b}] \qquad (7.6)\\
\Rightarrow X_{3a}(h_{3b} - h_3) &= h_{2a} - h_3 \qquad (7.7)\\
\Rightarrow X_{3a} &= \frac{h_{2a} - h_3}{h_{3b} - h_3} \qquad (7.8)\\
& \qquad (7.9)
\end{aligned}$$

We can simplify this further by noting that change in enthalpy of the remaining gas between states 3b and 1 must exactly be the change in enthalpy between states 2 and 2a, taking into account that there is less mass of gas after the expansion process:

$$\begin{aligned}
\cancel{\dot{m}}X_{3a}(h_1 - h_{3b}) &= \cancel{\dot{m}}(h_2 - h_{2a}) \qquad (7.10)\\
\Rightarrow h_{2a} &= h_2 - X_{3a}(h_1 - h_{3b}) \qquad (7.11)
\end{aligned}$$

plugging this back into 7.8 and performing some algebra, we find that

$$\begin{aligned}
X_{3a} &= \frac{h_2 - h_3}{h_1 - h_3} \qquad (7.12)\\
\Rightarrow 1 - X_{3a} &= \frac{h_1 - h_2}{h_1 - h_3} \qquad (7.13)
\end{aligned}$$

and thus

$$w = \frac{h_1 - h_3}{h_1 - h_2}[(h_1 - h_2) - T_a(s_1 - s_2)] \tag{7.14}$$

Depending on the gas, relative concentration, and its input conditions, this liquefaction process can be highly energy-intensive. For natural gas-fueled power plants, the capture and liquefaction of CO_2 can result in a First Law efficiency loss of 10-15%, requiring that more natural gas be burned to meet the demand. If the carbon dioxide can be effectively sequestered, however, this additional cost is well worth it. As we will see, however, storing the captured CO_2 is difficult and can cause additional problems.

Carbon Storage

Once compressed and liquefied, the CO_2 must be stored to prevent re-emission back into the atmosphere. The most promising methods laid out by the IPCC include mineralization, oceanic, and geological storage [3]. With mineral-based storage, CO_2 is reacted with inorganic elements to produce solid carbonates in a process similar to the natural weathering limestone to produce calcium carbonate. This enables the formation of carbonated solids that can be stored indefinitely without concern for leakage. While effective, this process can be cost prohibitive [4].

In oceanic storage, CO_2 is injected deep into the ocean where it can dissolve due to higher solubility in colder water or form heavier hydrates that sink to the bottom. There exist significant concerns, however, that the rapid increase in CO_2 and potential subsequent acceleration of ocean acidification can negatively impact marine life, ultimately causing a net-negative effect on the climate [2].

Finally, the most commonly used storage method is geological storage, in which liquid CO_2 is pumped underground into depleted oil and gas reservoirs, coal seams, or brackish aquifers. While this is the cheapest and easiest method for storing the captured gas, there can often be high leakage rates back into the atmosphere, negating its positive effects in the long term. Additionally, this method is typically used in conjunction with Enhanced Oil Recovery (EOR) and Enhanced Gas Recovery (EGR) whereby pumping liquid CO_2 into depleted oil fields enables the collection of additional oil and gas, ultimately offsetting a large fraction of the net carbon mitigation [3][2].

7.1.2 Direct Air Capture

Despite the unfavorable energy requirements given by Eq. 7.1 and shown in Fig. 4.18, it is still necessary to remove CO_2 from the atmosphere as supported by the arguments made by Solomon et al [5]. Given that molar concentrations of CO_2 in the atmosphere are around 410 ppm, the minimum work required to separate out the greenhouse gas from the air at 300 K is a substantial 500 MJ per metric ton CO_2 (140 kWh per metric ton CO_2). Regardless, many technologies are under development to accomplish this as efficiently as possible.

Direct Air Capture (DAC) generally refers to the sequestration of CO_2 from ambient air away from any CO_2 sources, where it exists in low concentrations. Many similar techniques used for CCS can also be used in DAC applications and have been seen as an ideal starting point given the significant oil and gas industry-funded development to date. Other promising approaches have been developed as well, including advanced chemisorbent materials like amine-modified mesoporous silica (e.g. TEPA-SBA-15), physisorbent materials like zeolite and metal organic frameworks (e.g. Mg-MOF-74/Mg-dobdc) [6], and ultramicroporous materials like MOOFOUR-1-Ni [7]. These materials exhibit exceptional selectivity to adsorbing CO_2 over other atmospheric gases and aerosols and can release the molecules upon heating. While promising, current limitations in manufacturing for these materials stand as a significant barrier to adoption in this space. Once the CO_2 is sequestered, this captured gas can then be stored using the previously discussed techniques. Recent research has shown that this gas can also be directly converted into alcohols like methanol to be used later as a near carbon-neutral fuel source [8].

7.1.3 Climatological Impacts of Carbon Capture

With CCS technologies, there is an inherent trade off between reducing CO_2 concentrations in power plant exhaust gases and maintaining high plant efficiencies. As previously described, work energy is required thermodynamically for any gas separation method, and for storage, additional work must be expended to liquefy and transport the captured CO_2. Even though the concentration of CO_2 is high in the power plant exhaust gases, this reduction in least work can be offset by these other factors. One of the most important factors for influencing the global climate in particular is the method of CO_2 storage and the leakage rate of the stored gas from that reservoir. Given that one of the most popular locations for carbon storage is porous geologic formations with potentially high leakage rates, this factor has a significant impact on the efficacy of CCS technologies today.

Studies have shown that for low enough gas retention times, CCS can exacerbate AGW. One study in particular found that AGW abatement is a strong function of gas retention times of the storage sites. Stone et al developed a climate model to compute the radiative forcing and resultant mean atmospheric temperature change as a function of CCS adoption rate, efficiency penalty, and residence time of the storage site, defined simply as the site storage capacity divided by the leakage rate. Fig. 7.2 shows that for a fixed efficiency penalty of 0.25, net cumulative emissions may still be significant when using storage sites with a finite leak rate, even if 100% of global carbon emissions from power plants can be captured. When looking at a 500 year analysis window, storage site residence times must exceed 100 years in order to break even with plants running without CCS [9]. The authors here additionally suggest that the use of storage with low residence times may be useful for AGW mitigation strate-

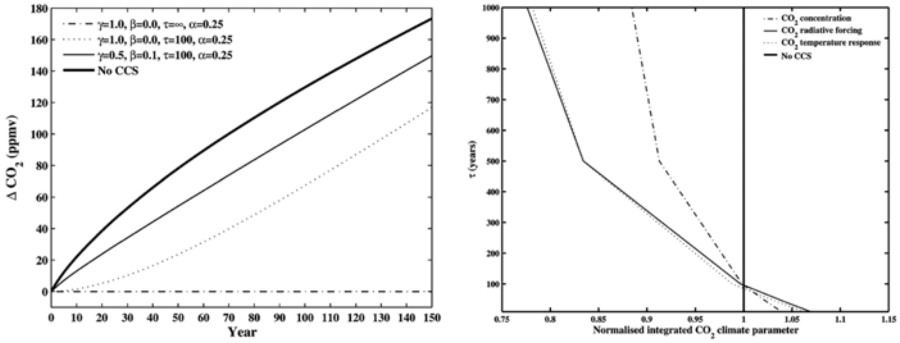

Figure 7.2: Model results for cumulative carbon emissions over time as a function of fraction of global carbon emissions suitable for CCS, γ, fraction of emissions released by each plant into atmosphere, α, and storage residence time τ (left) and abatement of AGW causes and effects due to CCS as function of τ for 500 year analysis window (right) [9].

gies which allow near-term CO_2 concentration peaks followed by stabilization in order to reduce the total cost of CO_2 reduction [10]. These strategies have shown to be risky, however, as they could potentially result in drastic overshoot of target stabilization levels. Stone et al suggest that short term storage underground may provide a less risky alternative to this strategy, though this approach has yet to be validated.

DAC approaches to AGW mitigation are virtually the same as CCS from a climatological perspective. It is important to note, however, that the costs of DAC are significantly higher than that for CCS given that concentrations of CO_2 in the atmosphere are roughly 300 times less than in the flue gases of power plants. At an estimated cost of \$1000/tCO_2, DAC will likely prove too expensive to be implemented in the near term unless significant government subsidies are leveraged [1][11]. More recent research has shown this price could be brought down to \$309/tCO_2 with more sustainable construction practices and reduced grid-level carbon intensity [12]. CCS, at an estimated \$80/tCO_2, is currently economically viable when used with Enhanced Oil/Gas Recovery; however, this reduces its effectiveness as an AGW mitigation strategy as more fossil fuels are extracted for subsequent burning.

7.1.4 Synthetic Fuels

Another approach to sequestering carbon is to pull it from the air to make fuels directly, creating a net carbon-neutral fuel production system. Similar to the biofuels discussed previously, this approach involves capturing the CO_2 combustion products of various carbon and hydrocarbon oxidation reactions and recycling them into new fuel. If the additional energy input to the system is derived from a carbon-neutral renewable like solar, geothermal, or wind, the total synthetic fuel process can be considered carbon-neutral as well.

Bosch Reaction

Going back to one of the first reactions we looked at in Chapter 3 - the combustion of pure carbon in oxygen to form carbon dioxide - we discussed that the reverse reaction of decomposing CO_2 back into elemental carbon and oxygen is extremely difficult and energy intensive. A much easier reaction to carry and one that has a similar end result is the *Bosch Reaction*:

$$\mathrm{CO}_{2(g)} + 2\,\mathrm{H}_{2(g)} \longrightarrow \mathrm{C}_{(\mathrm{s})} + 2\,\mathrm{H_2O}_{(\mathrm{g})} \tag{7.15}$$

where gaseous carbon dioxide and hydrogen are reacted at high temperatures in the presence of various metal catalysts like iron and nickel to form elementary carbon and water. This total reaction is actually comprised of the following intermediate reactions:

$$\mathrm{CO}_{2(g)} + \mathrm{H}_{2(g)} \rightleftharpoons \mathrm{CO}_{(\mathrm{g})} + \mathrm{H_2O}_{(\mathrm{g})} \tag{7.16}$$

$$\mathrm{CO}_{(\mathrm{g})} + \mathrm{H}_{2(g)} \longrightarrow \mathrm{C}_{(\mathrm{s})} + \mathrm{H_2O}_{(\mathrm{g})} \tag{7.17}$$

where the first is the familiar water-gas shift reaction and the second is dissociation of *syngas* into the final reaction products.

If we compute $\Delta_f h_{rxn}$ for the overall reaction at 600 °C, we find roughly 100 kJ/mol CO_2 (2.3 kJ/g CO_2) is *released* in the reaction. Indeed, this exothermic reaction actually releases thermal energy. This is largely due to the high chemical potential of the hydrogen gas reactant, and in practice, energy would be required to produce the hydrogen needed for this reaction. If this hydrogen is generated using renewable energy sources, though, this entire process is carbon negative. The carbon product can then either be stored easily as a solid or combusted to form a carbon-neutral energy loop. As with biofuels and all carbon-neutral synthetic fuels, the primary benefit to using this process is that existing fossil-fuel combustion infrastructure can still be used with these new fuels as drop-in replacements, saving a significant amount on capital costs and making widespread adoption more likely.

Sabatier Reaction

The natural gas equivalent to the Bosch Reaction is the *Sabatier Reaction*:

$$CO_{2(g)} + 4\,H_{2(g)} \longrightarrow CH_{4(g)} + 2\,H_2O_{(\mathrm{g})} \tag{7.18}$$

where instead of producing elemental carbon, more hydrogen is consumed - again in the presence of a metal catalyst - and methane is produced instead. For this reaction, 182 kJ/mol CO_2 (4.13 kJ/g CO_2) is released, with the thermal energy again coming from the high chemical potential of the hydrogen.

Like with the Bosch Reaction, the methane product of the Sabatier Reaction can then be combusted in existing natural gas power plant infrastructure as a carbon-neutral fuel replacement. To make this reaction a carbon-negative process, however, additional methane pyrolysis can be performed to dissociate the gas into elemental carbon and hydrogen:

$$CH_{4(g)} \longrightarrow 2\,H_{2(g)} + C_{(\mathrm{s})} \tag{7.19}$$

This reaction requires a considerable amount of thermal energy as expected - on the order of 90.4 kJ/mol CH_4 (5.6 kJ/g CH_4k). In practice, this accomplished by bubbling methane through molten metals between 1000-1200 °C. The solid carbon product can then easily be stored or sold for processing in various other industries[2].

CO_2 to Methanol

Finally, carbon dioxide can be extracted from the atmosphere or hydrocarbon combustion products to produce methanol, ethanol, and other alcohols that can serve as high-density, easy-to-store liquid fuels. The reaction that produces methanol (CH_3OH) is carried out as follows:

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[2] Numerous companies are currently using this pure carbon to generate inks and dyes used in packaging and textiles as a way to economically incentivize carbon capture.

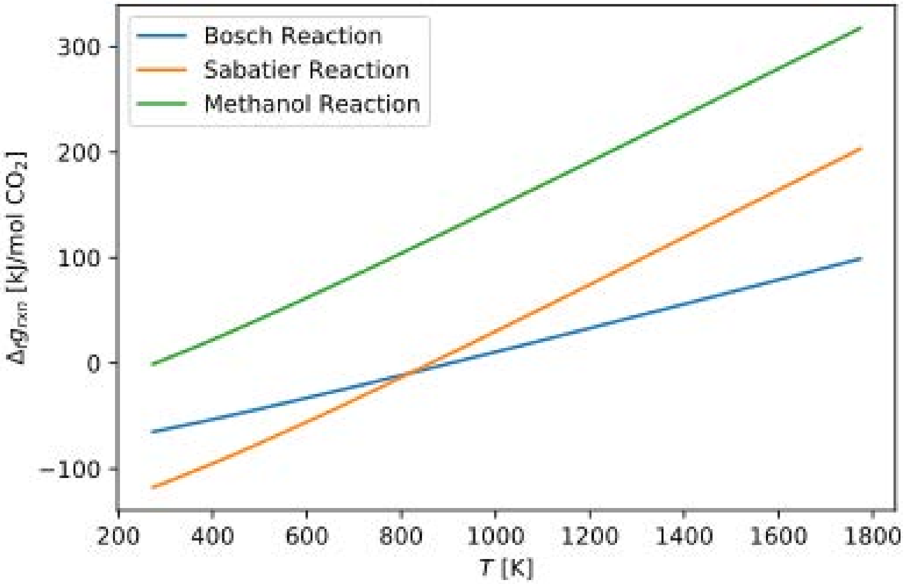

Figure 7.3: $\Delta_f g_{rxn}$ for the three carbon sequestration reactions discussed here, all at 1 bar. The lowest $\Delta_f g_{rxn}$ at a given temperature is the most favorable reaction to occur at that temperature.

$$CO_{2(g)} + 3\,H_{2(g)} \longrightarrow CH_3OH_{(g)} + H_2O_{(g)} \tag{7.20}$$

where the gaseous methanol can then be condensed and easily kept as a liquid at room temperature. This reaction releases 60.4 kJ/mol CO_2 (1.37 kJ/g CO_2).

For each of these reactions presented here, the reactants include carbon dioxide and hydrogen, so a natural question that arises is: how are the product species controlled? The answer is complex and beyond the scope of this text; however, we can get a sense for which reaction is most favorable at a given temperature by finding which has the lowest $\Delta_f g_{rxn}$. As shown in Fig. 7.3, the Sabatier Reaction is favored at temperatures up to roughly 800 K, and the Bosch Reaction is favored above 800 K. The complete answer to which reaction will occur, however, requires careful control of any intermediate reactions, the concentrations of hydrogen relative to carbon dioxide, and the selection of catalysts that favor one reaction over the other [13]. Thus, even though the methanol reaction is never thermodynamically most favorable here under standard conditions without intervention, the use of catalysts can change the picture dramatically and enable the reaction to proceed.

7.2 De-carbonizing Industries

As Fig. 5.15 shows, another large portion of anthropogenic carbon emissions comes from industrial processes like the manufacturing of raw materials and bulk chemicals. While there are certainly carbon emissions associated with energy required for transporting and supplying electricity and thermal energy to these processes, the bulk of these emissions are actually associated with the various chemical reactions required that produce carbon dioxide or methane as a byproduct. While there exists a plethora of different processes that fall into this category, we will only look at two here as an example of the thermochemistry involved in these carbon emissions and where we might be able to make them carbon neutral.

7.2.1 Aluminum Smelting

Globally, 64 million metric tons (Mt) of primary aluminum are produced from the reduction of Bauxite ore each year using an electrolytic process, and as shown in Figure 7.4, this value is expected to increase to over 70 Mt/yr by the end of 2020. Moreover, longer term projections show global aluminum demand increasing to roughly 150 Mt/yr by 2050 [14]. Over 25% of this aluminum produced globally goes to transportation industries including automotive, rail, and aerospace, while another 20% goes into construction materials. Packaging and electrical equipment each comprise 15% of this total production and the remaining goes into consumer products, machinery, powder metallurgy, and the deoxidation of steel [15].

Aluminum is not only one of the most widely used metals, it is also one of the costliest to produce in terms of both required energy and carbon emissions. After aluminum oxide (Al_2O_3), is extracted from Bauxite ore, it is reduced to pure aluminum via the Hall-Heroult process, in which the Al_2O_3, is first dissolved in molten Cryolite (Na_3AlF_6), enabling the oxygen to be removed via electrolysis at carbon electrodes by the following total reaction:

$$2\,\mathrm{Al_2O_3} + 3\,\mathrm{C} \longrightarrow 4\,\mathrm{Al} + 3\,\mathrm{CO_2} \tag{7.21}$$

which is comprised of the two electrochemical half reactions at the cathode and anode respectively:

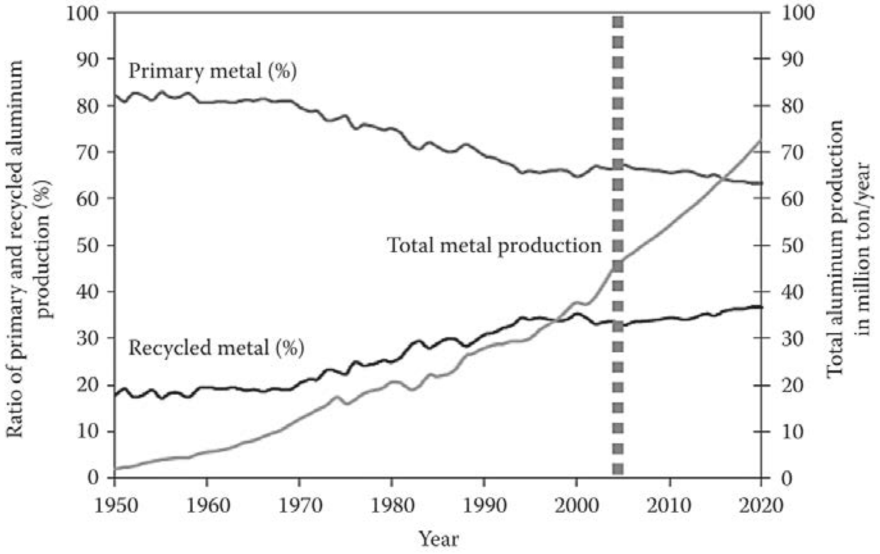

Figure 7.4: Percentage of recycled aluminum in primary production and global aluminum production rates from 1950 to the present [16].

$$Al^{3+} + 3\,e^{-} \longrightarrow Al \tag{7.22}$$

$$C_{(gr)} + 2\,O^{2-} \longrightarrow CO_2 + 4\,e^{-} \tag{7.23}$$

where the aluminum and oxygen ions in each reaction are a result of the dissociation in the electrolyte. Fig. 7.5 shows a Hall-Heroult Cell that carries out these reactions.

The Hall-Heroult process requires a significant amount of energy, equal to 14,000 kWh/ton of aluminum averaged globally, and in total consumes 3.5% of global electricity production. Additionally, regardless of the carbon intensity of the electricity used to carry out the electrolysis step, as shown in Equation 7.21, this process directly results in the generation of carbon dioxide. In total, the production of aluminum results in the release of 13 tons of CO_2e per ton of aluminum, over 70% of which comes from the Hall-Heroult process alone [18][19].

Globally, this process accounts for 830 Mt of CO_2e annually, nearly 1% of the world's total carbon emissions [14]. Recycling aluminum avoids this

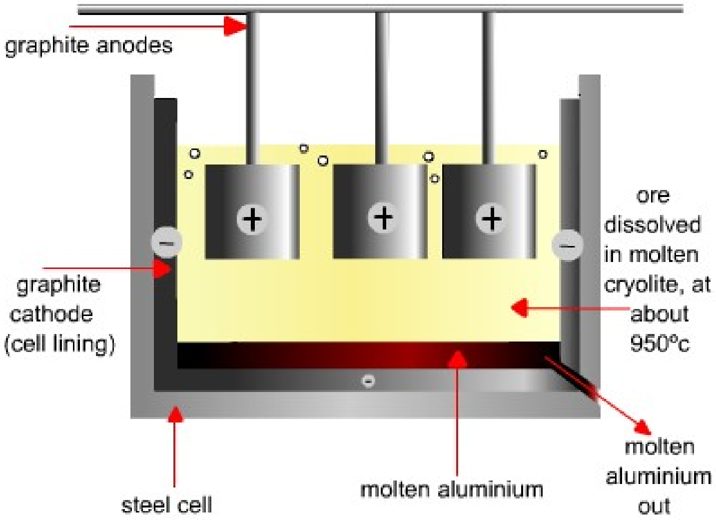

Figure 7.5: Hall-Heroult Cell used in the reduction of pure aluminum from aluminum oxide. Aluminum oxide is first dissolved into a molten electrolyte and then reduced via electrolysis across graphite electrodes. CO_2 is released in the process [17].

Hall-Heroult process, significantly reducing the total carbon intensity of the resultant aluminum. Therefore, with demand for aluminum expected to increase by 130% by 2050, coupled with the increasing urgency of reducing global carbon emissions to slow the rate of anthropogenic climate change, there is significant motivation to improve the efficacy and adoption of aluminum recycling to reduce primary production.

The ultimate solution to removing carbon emissions from the aluminum production process, however, will require a move towards the use of carbon-free electrodes to perform the electrolysis. The use of an *inert anode* in this context would theoretically eliminate the carbon emissions associated with aluminum production if the electricity supplied were also carbon-neutral. The development of these anodes has been slow, as it has been challenging to find a material that promotes the aluminum reduction reaction while also not corroding in the molten electrolyte. Success has been found in using electrodes comprised of various combinations of nickel, lithium, tin, lead, copper, and cobolt [20]. Recently, Elysis, a collaboration between the major Canadian primary aluminum producers has announced the development of a production-scale plant that will use such inert anodes, forging a path forward to decarbonize this industry.

7.2.2 Hydrogen Production

The other major industry we will touch on in this section is hydrogen production. As discussed previously, the combustion of hydrogen only produces water and is thus a good candidate for storing excess energy produced by various renewable energy sources. The global demand for hydrogen far exceeds what can produced by this excess energy, however, as it is used in many different industries, including fertilizer production, oil refining, and even electronics manufacturing. In fertilizer production, for example, ammonia (NH_3) is a critical ingredient that is produced synthetically via the *Haber-Bosch* process:

$$3\,H_2 + N_2 \longrightarrow 2\,NH_3 \tag{7.24}$$

which of course requires large amounts of hydrogen.

The cheapest - and therefore most widespread - method for producing the hydrogen needed for these industries is *steam methane reforming* in which methane is reacted with water at high temperatures in the presence of a nickel catalyst to produce hydrogen and carbon monoxide:

$$CH_{4(g)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + 3\,H_{2(g)} \tag{7.25}$$

Additional hydrogen can then be produced via the water-gas shift reaction, giving us a total reaction:

$$CH_{4(g)} + 2\,H_2O_{(g)} \rightleftharpoons CO_{2(g)} + 4\,H_{2(g)} \tag{7.26}$$

This reaction is highly endothermic, requiring a large thermal energy input of roughly 48 kJ/mol H_2. As a result of the CO_2 released in this reaction, the production of hydrogen currently has a large carbon footprint, which is further compounded by the fugitive emissions associated with the mining and transportation of the natural gas required for these reactions. Consequently, we stand to benefit greatly from the development of new processes that reduce these emissions. Carbon-neutral hydrogen can be produced, for example, via the methane pyrolysis reaction discussed previously and given by Eq. 7.19, which produces hydrogen gas and solid carbon that can be easily filtered out and stored. Additionally, this hydrogen can be produced directly from water via electrolysis, but currently the economics are in favor of using steam methane reforming[3].

7.3 Geoengineering

Up to this point, our discussion on climate crisis mitigation has been centered on the technologies and practices that, if implemented on a global scale, would drastically limit or even eliminate anthropogenic carbon emissions. What if these solutions are not adopted or fail to work as planned? This question brings us into another realm of mitigation strategies that attempt to modify the climate and various biospheres *directly* in what is typically referred to as *geoengineering*. It has been shown that various types of direct climate intervention can have far-reaching and quick-acting affects, but as of writing this text, climate forecasting models are not powerful enough to fully model the impacts, making such interventions risky as well. Here we will discuss a few proposed strategies in this category.

7.3.1 Biosequestration

Earlier we discussed artificial carbon capture as a way to remove greenhouse gases from the atmosphere to offset emissions from industry. Another leading approach to sequestering atmospheric CO_2 involves much less technological development than the previously described methods. This approach, called biosequestration, leverages the use of natural carbon sinks to sequester the greenhouse gas via reforestation to repair ecosystems damaged by human land use and afforestation to provide additional sinks that did not previously exist. In principle, CO_2 is consumed via photosynthetic processes to form cellulose and other carbon-based plant products that store carbon in solid form. Plants, trees, and other vegetation undergo aerobic respiration and therefore emit roughly as much CO_2 as they consume in steady state operations, however, as they grow, they store more carbon in their added biomass. Additionally, as plants die, their biomass becomes incorporated into soils, giving rise to a potentially significant carbon inventory in terrestrial soils within old-growth forests. In total, these terrestrial sinks are able to sequester carbon at roughly 2.4 Pg C (9.2 Pg CO_2 equivalent) per year globally [21][22]. Pan et al estimate

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[3] Given the abundance and ease of extracting methane, it is unlikely that the economics will work against its use unless governments enact legislations like a *carbon tax* that penalizes companies from using carbon-intensive processes.

Figure 7.6: Mangrove forest in Gazi, Kenya showing the tortuous root system that increases carbon sequestration capabilities [23].

that when accounting for current deforestation, the net sink is 1.1 Pg C per year.

Biosequestration also encompasses the sequestering of CO_2 in marine-based ecosystems. Carbon that is captured and stored in the plant matter of mangroves, seagrass, and other marine-based plants, is referred to as "blue carbon" and serves as a significant global carbon sink. Compared to terrestrial sinks, marine-based sinks comprise a significantly smaller area; however, marine-based sinks sequester carbon at a similar rate globally. For example, carbon is buried in mangroves, salt marshes, and seagrass bed at a rate of 30 to 100 Tg C per year in each ecosystem, compared with 50-80 Tg C per year for tropical and boreal forests. In terms of global carbon sequestration rates, blue carbon sinks in mangroves, salt marshes, and seagrass beds alone have a global capacity as high as 0.2 Pg C per year. One of the primary reasons these carbon sinks are so effective is that their complex root structures, coupled with tidal inundation and tidal-driven mixing, enable them to trap and incorporate carbon-rich particles from the water into the local sediment [23]. Fig. 7.6 shows an example mangrove forest in Gazi, Kenya, which exhibits this complex root network.

Finally, biosequestration can also refer to the use of biomass to offset carbon emissions in other industries. One obvious application is to simply burn wood or methane off-gassed from the anaerobic digestion of organic matter instead of fossil fuels [24][25]. In theory, these fuels are carbon neutral, as the carbon they release upon burning was taken in from the atmosphere relatively recently. Inefficiencies of transporting and processing these fuels results in net carbon emissions; however, these fuels may serve as a less detrimental source of energy during the transition from fossil fuels to even less carbon-intensive solar and wind energy sources. Additionally, wood may also be able to replace products that would otherwise be manufactured from aluminum or steel, whose production results in the release of significant amounts of CO_2, thereby potentially offsetting significant carbon emissions.

There are numerous beneficial feedback loops in regards to how atmospheric CO_2 concentrations affect biomass-based carbon sinks. It has long been understood, for example, that increased concentrations enable plants to grow more quickly and use less water in the process, potentially introducing a negative feedback loop to help stabilize CO_2 concentrations [26]. More recently, researches have begun to understand the more complex ways in which the Earth's forests affect the climate on the whole. Most notably, while forests provide a potentially large global carbon sink, they also have the ability to both warm and cool the climate by lowering surface albedo and increasing cooling via evapotranspiration. For example, the decrease in surface albedo due to boreal forestation in high latitudes has been shown to increase local warming, especially in snow covered regions where the forests mask the increased albedo due to snow and ice formations [27]. Globally, these forests can still provide a net cooling effect due to sequestered carbon, but with significantly reduced efficacy.

Tropical forests, on the other hand, have a greater potential to cool the planet as the decrease in albedo is more than compensated by additional evaporation rates as a result of transpiration [28]. As shown in Fig. 7.7, deforestation of tropical forests has a significant impact on global mean temperature rise, due both to their significant carbon stocks and these secondary cooling effects. In this simulation produced by Bala et al, it was also shown that the deforestation of of boreal forests results in a slight global cooling effect, further illustrating the importance of these secondary climatological effects [28]. Consequently, when considering afforestation as a means of AGW mitigation, it is important to consider not only how much land to convert or restore, but also where.

Marine-based biosequestration also has additional benefits and drawbacks from a climatological perspective. First, mangroves and seagrass beds help to prevent coastal erosion, which if left unabated can accelerate the leaching of organic carbon and ultimately reduce the carbon sequestration capabilities of those ecosystems. It has been shown that clearing mangrove forests, for example, can result in a 50% decrease of sedimentary carbon stocks over an 8

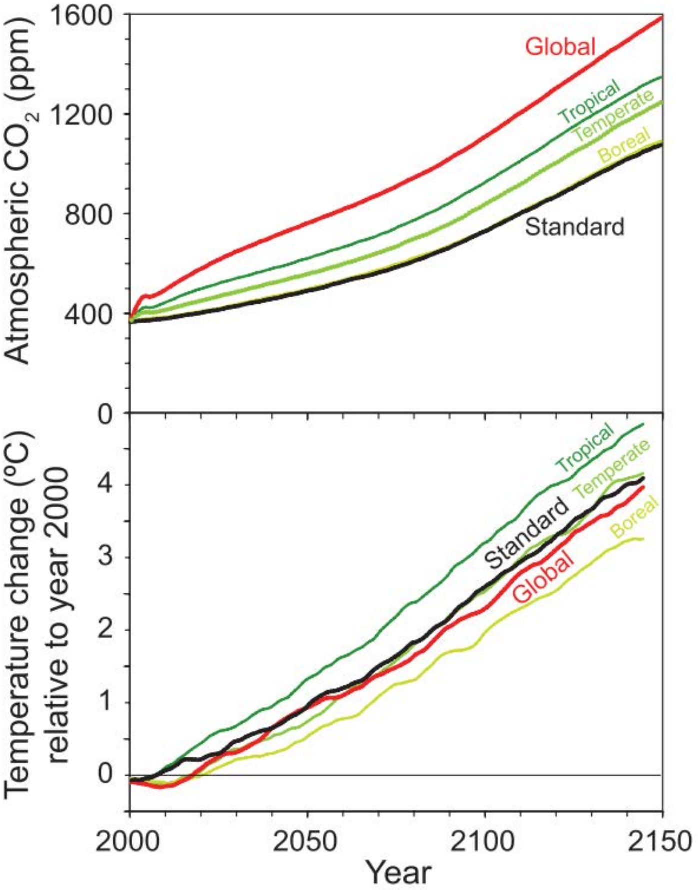
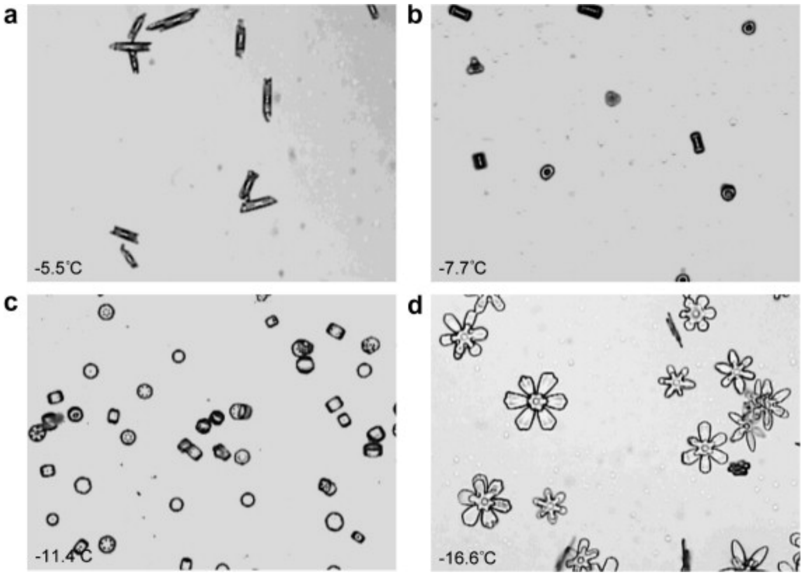


Figure 7.7: Effect of deforestation on global atmospheric CO_2 concentrations and mean temperature rise broken out by forest type [28].

Image courtesy of G. Bala, K. Caldeira, et al. "Combined Climate and Carbon-cycle Effects of Large-scale Deforestation." *PNAS*. 104 (16) 6550–6555, 4 2007



Courtesy Elsevier, Inc., http://www.sciencedirect.com. Used with permission.

Figure 7.8: Nano-scale silver iodide particles acting as nucleation sites for water crystal (ice) growth [31].

year period [23]. Additionally, mangroves in particular are resilient to changes in sea level, making them a potentially ideal tool for mitigating AGW [29]. Counter to these positive effects, it has been shown recently that mangrove forests emit methane in rates that can reduce their global warming offset potential by 20% globally [30].

7.3.2 Cloud Seeding

Going back to Chapter 2, we learned that the driving mechanism behind climate change is the greenhouse effect, and up until now, we have primarily been focused on mitigation strategies that reduce the amount of greenhouse gases being emitted from anthropogenic sources. What if instead we could limit the amount of sunlight that arrives at the Earth's surface? Indeed, if we can increase the Earth's *albedo*, more sunlight will be reflected back into space and the energy input term in our First Law equation will be reduced. As a result, the total Earth-climate thermodynamic system will experience a drop in temperature to equilibrate to the reduced solar energy input. This theory is the driving justification for *cloud seeding*, in which bright white clouds are used to reflect sunlight.

This solution may seem counter-intuitive, as in previous chapters we dis-

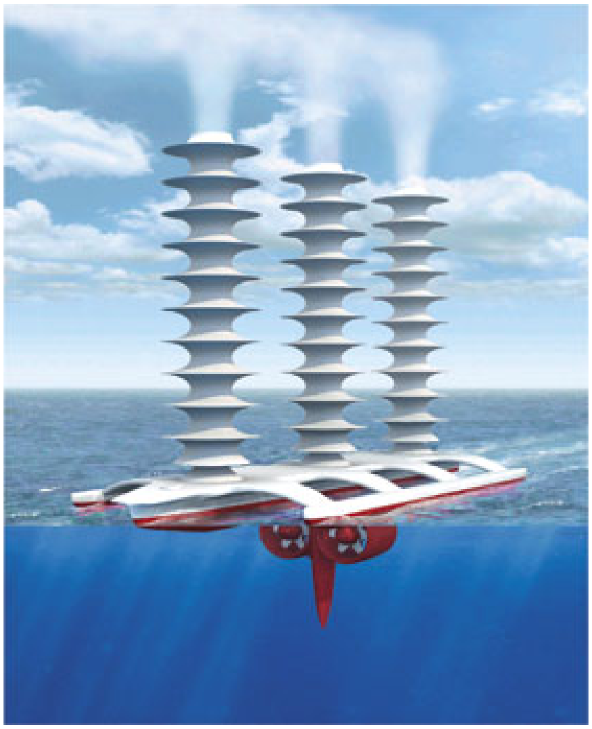


Figure 7.9: Concept for using a ship to seed clouds over the open oceans [32].

cussed the fact that water vapor is a potent greenhouse gas itself, and therefore if clouds are made of water vapor, would adding clouds to the atmosphere exacerbate the issue? The key to making cloud seeding an effective climate change mitigation approach is that the water vapor is already in the atmosphere and that by adding *seeds* or more specifically, *nucleation sites*, that water vapor will form droplets and or crystallize, forming a bright could. As Fig. 7.8 shows, certain aerosol-based seeds like nano-scale silver iodide particles are capable of promoting water crystal (ice) growth, which in turn can yield large clouds capable of reflecting a significant amount of sunlight. At a large scale, these silver iodide particles or similar could be injected into the atmosphere using planes, ships, or other ground-based generation systems. Fig. 7.9 shows an example of a ship that could be used to seed clouds over the open oceans. Eventually, precipitation will remove these particles from the atmosphere and they will need to be replaced.

While current climate models are unable to predict the total global effects of cloud brightening and seeding or any mitigation strategy that generally attempts to increase the Earth's albedo, they do indicate that on average, these practices have the ability to reduce many of the negative effects associated with climate change. Specifically, most models point to the strong trend that reducing solar radiation results in fewer and less powerful hurricanes and typhoons [33][34], as well as reducing the rate of sea-level rise [35], buying humanity more time to reduce and eliminate carbon emissions. Critics of such practices claim that while storm intensity is reduced in some regions, other regions may also see increased storm activity or even drought as a result, which would would exacerbate the negative impacts of climate change for some [36][37][38], though recent studies have shown that magnitude of these negative impacts are not as significant as was previously thought [39]. Regardless, it is highly important that the global impacts - positive and negative - are well understood to ensure that climate change is not just being mitigated for those who can afford to implement the solutions, pushing the negative impacts off onto those who cannot [4].

7.3.3 Other Future Strategies

The two strategies discussed thus far for using nature-based interventions to slow the climate crisis are arguably the most thoroughly researched and developed, and they also have the greatest potential to be implemented on global scale due with the necessary geopolitical and socioeconomic will. There are a few other interesting concepts to discuss briefly, though they are likely farther away from being implementable in the near future.

Space Mirrors

First, following the motivation for cloud seeding and brightening, space mirrors - mirrors attached to a fleet of controllable satellites in orbit around Earth - have also been suggested as a means of effectively increasing the albedo of the Earth thermodynamic system. As illustrated in Fig. 7.10, these mirrors simply reflect incoming sunlight to reduce the total solar flux that arrives at the Earth's surface, thereby limiting the greenhouse effect. These satellite mirrors could be placed precisely in *geosynchronous* orbit to limit the solar flux in certain regions - much like in cloud seeding - or placed to always be between the

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[4] Another book could (and should) be dedicated to the ways in which thermodynamics and the resultant climate change have disproportionally negatively impacted lower-income and non-white communities and the reader is encouraged to explore the IPCC report [3] for more specifics.

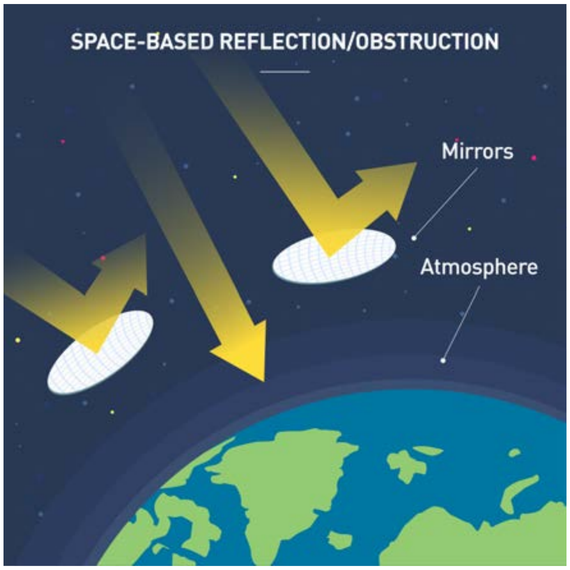

Figure 7.10: Concept for using mirrors in orbit around Earth to reflect incoming sunlight, reducing the solar flux to the Earth's surface, thereby slowing climate change [source].

sun and the Earth, casting an ever-moving shadow. In either case, these mirrors have the benefit of not needing to continuously inject potentially harmful aerosols in to the atmosphere, however the logistical challenges and associated cost make this solution quite difficult to implement on a short timescale.

Making New Sea Ice

Also along the lines of increasing the Earth's albedo, another proposed climate crisis mitigation strategy is to use solar energy to produce giant ice cubes in the Arctic Ocean to combat the loss in albedo associated with melting sea ice. Fig. 7.11 shows an artistic rendering of a fleet of these ice makers producing hexagonal ice cubes at a rate comparable to the rate of ice loss. Ignoring cost and other potential barriers to adoption, we can use our knowledge of thermodynamics knowledge to perform a First Law analysis to determine if this concept is even possible.

To assess feasibility from an energy availability perspective, we can assume that the energy required to freeze these ice cubes from solar PV panels and then determine roughly how much solar panel area would be required to produce

Figure 7.11: Artistic rendering of machines that could be used to replace sea ice in the Arctic Ocean to combat sea ice loss [source].

the ice that is lost each year. To begin with this analysis, we need to know first how much ice we would need to make each year. Fig. 7.12 is a plot showing the extent of Arctic sea ice and how over time, even though the values fluctuate over the course of a year, over tens of years, there is a clear average trend downwards. From this data, it is evident that the Arctic loses roughly 70,800 square km per year [NSIDC].

Assuming that the only energy we must supply is in the latent heat associated with the phase change between liquid water and ice - and ignoring the presence of the salt and other dissolved solids for now - the energy required per year is simply

$$E_{ice} = A_{loss} t_{ice} \rho_{water} h_{sf} \tag{7.27}$$

where A_{loss} is the are of sea ice lost each year, t_{ice} is the thickness of the ice cube we are using to replace the lost ice, ρ_{water} is the density of water, and h_{sf} is the latent heat of fusion of pure water. Taking the values for these variables given in Table 7.1, we can estimate the energy required to replace the sea ice per year as 2.35x10^{13} MJ, which would be roughly 4% of the total energy usage of the world. While this seems like a lot, what we are really interested in how much solar panel area we would need.

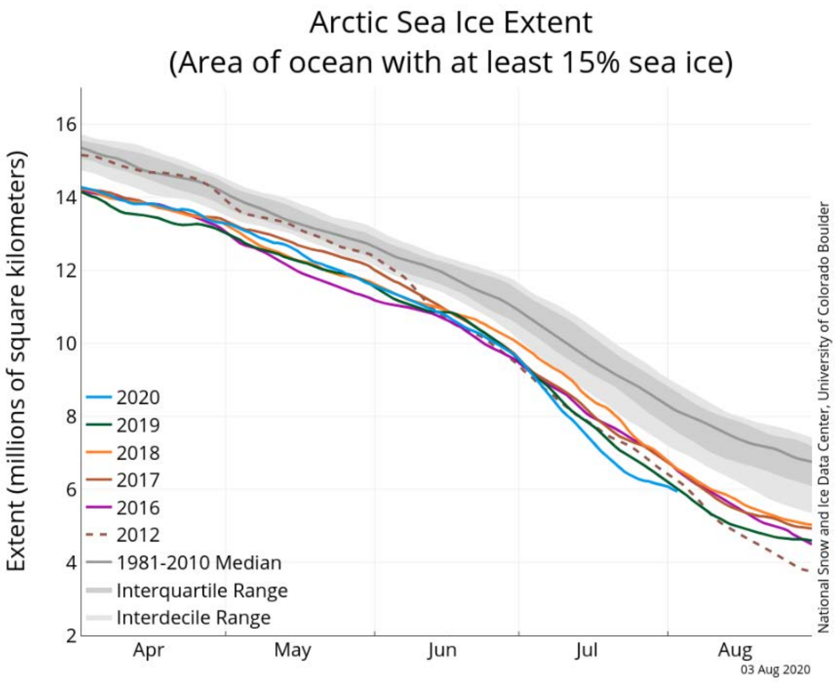

Figure 7.12: Decline of July sea ice extent [NSIDC].

To compute the solar area, we must assume that the solar panels have some First Law efficiency, η_{PV}, the sun has an average constant solar irradiance, q''_{solar} when the sun is shining, and that the solar energy has a capacity factor - the fraction of time the sun is shining - of C. The total available electrical power we have at our disposal then is

$$\dot{E}_e = \eta_{PV} C q''_{solar} A_{solar} \tag{7.28}$$

where A_{solar} is the total solar panel area. To compute this area, we can solve for A_{solar} noting that

$$\dot{E}_e \tau_{year} = E_{ice} \tag{7.29}$$

where τ is the time period over which this analysis is performed - 1 year in this case. This gives us

Table 7.1: Variable values used in Arctic Ice Maker feasibility analysis.

Variable	Value	Units
A_{loss}	70,800	km^2
h_{sf}	334	kJ/kg
t_{ice}	1	m
ρ_{water}	997	kg/m^3
q''_{solar}	800	W/m^2
η_{PV}	0.15	-
C_{solar}	0.25	-

$$A_{solar} = \frac{E_{ice}}{\eta_{PV} C q''_{solar} \tau_{year}} \tag{7.30}$$

Plugging in numbers from Table 7.1, we find that the total solar panel area required is 25,000 km^2, which while considerably less than area of sea ice lost per year, is still a considerable amount of surface area. Additionally, marine environments pose engineering challenges, including corrosion and salt spray reducing the efficiency of the solar panels. Therefore, while theoretically possible, it is unlikely that this strategy will be feasible with existing technology and resources.

7.4 Summary

Capturing CO_2 via both artificial and natural methods has the potential to offset the nearly 42 Gt CO_2 emitted each year by human activity; however there are some potential factors that may limit the efficacy of these approaches. Artificial carbon sequestration, for example, relies heavily on the ability able to reliably store the captured gas. CCS technologies, by which carbon is sequestered from the output of power plant exhaust gases, may result in net additional carbon emissions over a long time horizon when used in conjunction with storage sites with high leakage rates. Renewable-driven DAC technologies avoid this effect to some degree, but their significant implementation costs (\$1,000 per ton CO_2) have proven to be prohibitive. Regardless, as fossil fuels are increasingly phased out over the next century, the total impact of CCS will become reduced as additional CO_2 emissions ideally wane. Consequently, DAC will become crucial to avoid the long-term warming trend after emissions cease as predicted by Solomon et al.

We then discussed the importance of removing carbon emissions associated with industrial processes like aluminum smelting and hydrogen production, which current rely on chemical reactions that result in the release of carbon dioxide as a byproduct. Such practices will eventually need to be converted to carbon-neutral processes to mitigate the climate crisis.

In addition to these artificial approaches, carbon can also be captured effectively and cheaply with comparatively minimal technological requirements via biosequestration. Currently, in total, terrestrial and marine-based plants and trees together take in on the order of 10 Gt CO_2 per year. Even doubling the amount of forested area would capture less than half of additional anthropogenic emissions, which on its own is insufficient from a carbon perspective; however, as previously described, the effects of afforestation on mean temperature is a strong function of the type and location of the forests. Afforestation in the tropics, for example, may have significant additional cooling benefits due to increased evapotranspiration and negligible changes in albedo.

Finally, in this chapter, we also discussed several other means of artificially increasing the Earth's albedo using cloud seeding and the more hypothetical - for now - space mirror and Arctic sea ice maker concepts. More research must be done, however, in order to determine the total impacts of these practices to ensure that the problems are not just being solved for some and exacerbated for others. Regardless, given the scale of the crisis and the difficulty in implementing many of these solutions, it is likely that the Earth will continue to warm over the next several decades. In the final chapter, we will explore how we can use thermodynamics to adapt to a climate that has already changed, helping to bridge the gap between where we are now and a sustainable world.

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A Call to Action

Armed with the scientific knowledge presented in this book, humanity has constructed a global society that is as magnificent as it is unsustainable. The electricity that drives innovation and furthers scientific progress, the many modes of transportation that connect people across the Earth, and the industrial processes that bring us raw materials for construction, medicine, and agriculture are all made possible by exploiting the Laws of Thermodynamics. While it is difficult to argue that these advances do not benefit humanity, it is just as difficult to argue that the path to getting here was not fraught with injustice and that even in the modern age, all people benefit equally. Additionally, we are seeing clearly that these advances have come at a largely ignored cost - the stability of the climate. This cost will be inescapable for most in the upcoming century but ironically is being largely paid for now by those who have reaped the least reward from the systems at the root of it.

It is important to understand that thermodynamics and science in general is not inherently good nor evil. The laws of physics exist whether or not we are around to observe and formalize them; however, we have the ability to choose which areas of physics we explore and what applications come from our discoveries. In fact, stepping back and looking at where our knowledge is concentrated tells as much of a story as the knowledge itself. For example, we know the thermodynamics properties - specific heat, enthalpy, and entropy - of virtually every substance on Earth that could conceivably be involved in combustion reactions. These data are the result of the push for developing fuel for rockets and power generation in the 20th century. As another example, we know so much about nuclear fuel from our deep scientific investigations during the development of thermo-nuclear weapons in World War II. Of course, whether or not scientists should be held responsible for the applications of their discoveries is a matter of moral framework, but the point here is that we can learn a lot about our priorities by observing what we choose to investigate. Too often, this reflection comes too late if at all[5] and hidden behind many

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[5] See Einstein and Oppenheimer responses to use of the atomic bombs in World War II.

layers of irresponsible reverence for the scientific process.

I therefore urge you to keep in mind as you continue on with your education and careers that the knowledge base presented to you is always malleable. Of course as we learn more through experimentation and observation, we refine this knowledge, but more importantly, the information taught in books and classes - including this one - is only the cross section of the given field that the author or teacher thinks is most important to cover. Again, the collection of the information itself was subject to historical biases and societal priorities. Going forward, the tools you are given are not necessarily the tools you will need or should even use. Before the photovoltaic effect was discovered, it was likely difficult to imagine generating power without combustion. As we continue, we may find that entirely new fields of science must be developed to achieve the solutions that are in line with our imagined future, and it is of utmost importance that you do not shy away from that notion. The way things were are not how they must be.

Regardless, we are now at the point where the impending climate crisis - and its many derivative socioeconomic crises - leaves us an diminishingly slim grace period for realizing too late that our actions are causing more problems than they are solving. Going forward, the repercussions of progress must be evaluated *before* it is made, and we must use our imagination of what an equitable and sustainable future looks like to guide what we choose to explore. The now cliche statement of “With great knowledge comes great responsibility” could not ring truer than it does today. Indeed, it is now our responsibility to use the knowledge that brought on these crises to change course. Fortunately, the Laws of Thermodynamics are behind many of the leading solutions that hold promise for doing just that.

Despite detailing over and over the gravity of the crisis we find ourselves in near the beginning of the 21st century, the point of this text was not to instill fear or despair - just the opposite in fact. There is nothing in the physics we learned that told us that turning things around was an impossible or even extremely difficult task from a technological perspective. An equitable and sustainable path forward is clearly laid out for us, but it will require unprecedented effort from everyone to follow it. Whether you consider yourself current or future technologists, innovators, engineers, scientists, entrepreneurs, artists, or even consumers, we all have a role to play, as the problems are as much social as they are technical. In fact, a diversity of perspective is *necessary* to ensure we moving towards solutions that benefit all.

Finally, if it was not clear up until now, the format we employed here for teaching thermodynamics - one in which we question *why* and *how* we came upon this information, as well as *what* we have done with it - is just as important as the thermodynamics itself. The dismantling of "colonial"[6] mindsets with which science has historically been taught and conducted is occurring in many fields and is an exciting and extremely promising revolution in both education and problem solving. Your responsibility now is to spread this way of thinking to whatever fields you find yourself in. Whatever roles you see yourself as playing in this climate crisis, I implore you to include "educator" and "activist" as well. This is a solvable problem but not within many of our existing societal frameworks, especially where those frameworks have been manipulated to contribute negatively to the problem. It is time we collectively re-imagine what we want the world to look like and work together to re-build it in that image.

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[6] driven by a sense of Darwinian competition and a focus on achievement and derived economic prosperity

Resource: Thermodynamics and Climate Change
Peter Godart