# 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

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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 m²/kg-s². 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/s² at the Earth's surface.
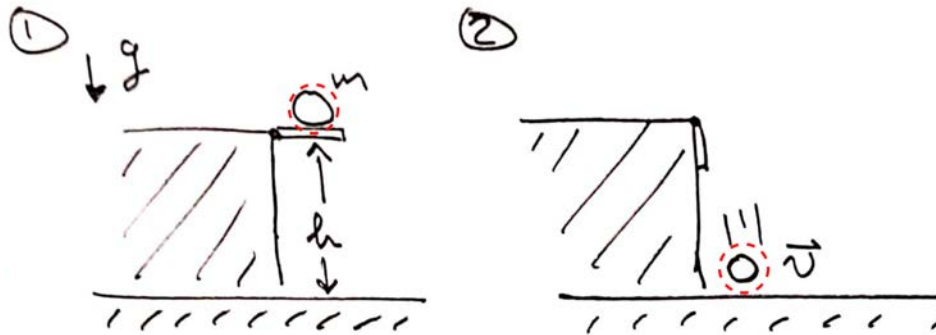
Figure 2.1: Two "thermodynamic" states for the stone drop example. Dashed red circle shows the control volume. Note that in the case of gravitational potential energy, technically the force of gravity and thus any potential difference requires 2 bodies. Here, the mass of the Earth is also implicitly 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 $\sigma$ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8}$ 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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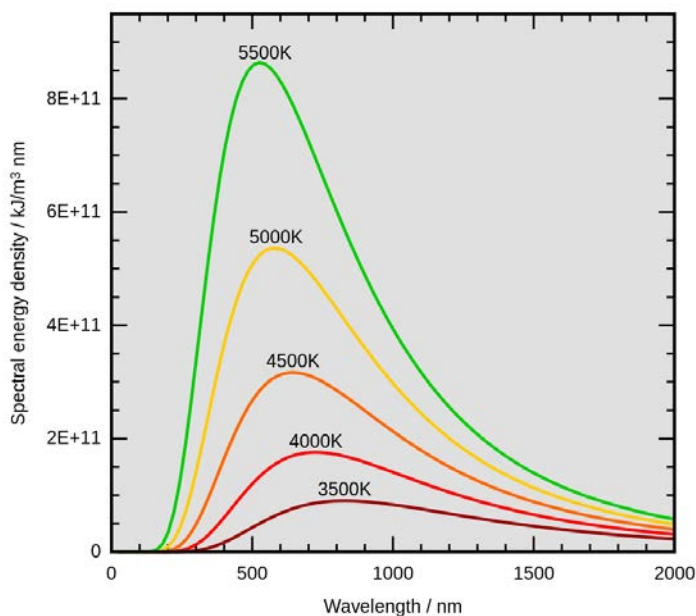[14]Atoms have electronics and protons that can separate slightly, creating net regions of negative and positive charge.

Image courtesy of 4C 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.

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

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[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, $\lambda$, 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 ($6.626 \times 10^{-34}$ J-s), $c$ is the speed of light in the medium[18], and $k_B$ is the Boltzmann Constant ($1.38 \times 10^{-23}$ 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 $3 \times 10^8$ 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*, $\varepsilon$ and appears in a simplified power equation as

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

where $\varepsilon$ can vary from 0 to 1. In reality, $\varepsilon$ 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 $\rho$ 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

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

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

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

Plugging Eq. 2.18 into Eq. 2.17 yields

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

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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.

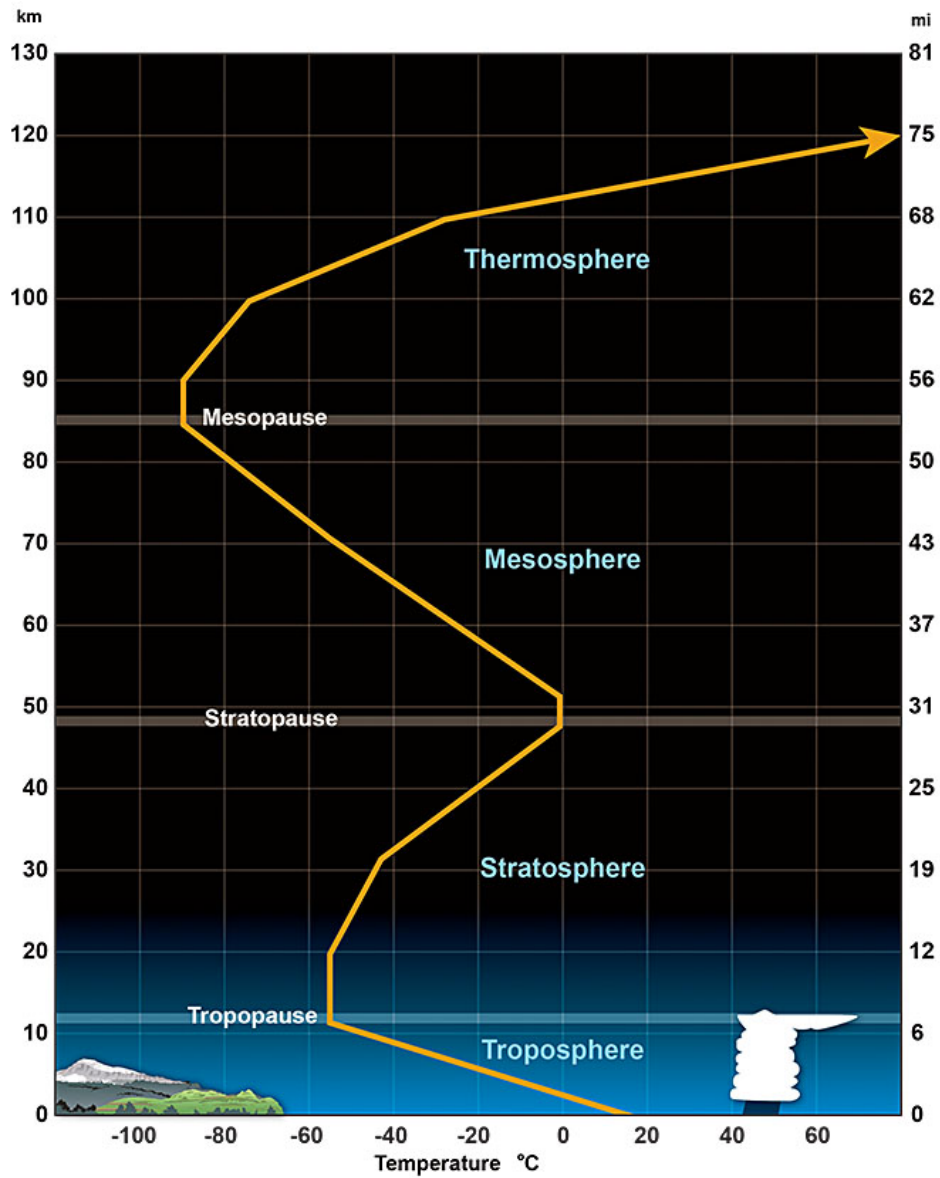[27]We use *fluid* in this text to mean either a liquid and a gas, as is commonly done in this field.

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, $\Delta T$. 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 $\Delta T$. 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.
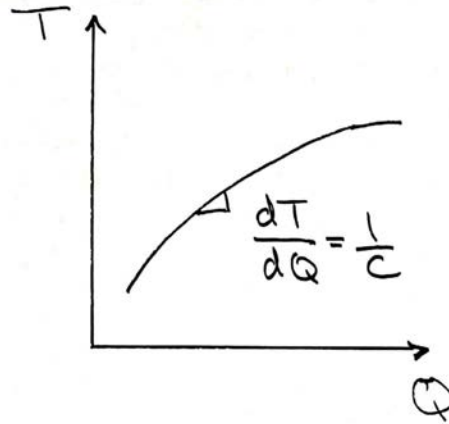
Figure 2.4: $T$-$Q$ diagram for solids and liquids.

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

$$E_1 = \frac{1}{2}mv^2 + mcT_1 \qquad (2.28)$$

and in state 2 after it has come to rest as

$$E_2 = mcT_2 \qquad (2.29)$$

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

$$\Delta E = E_2 - E_1 = \cancel{Q} - \cancel{W} \qquad (2.30)$$

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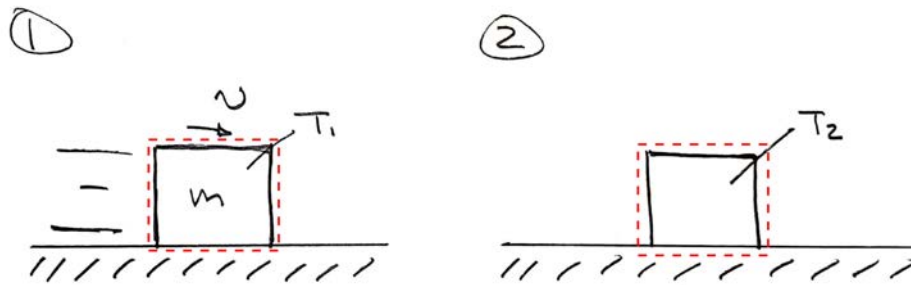
Figure 2.5: Two states for mass sliding on a surface with friction and ultimately coming to a stop.

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

Annual ocean heat content compared to average (1993-2018)
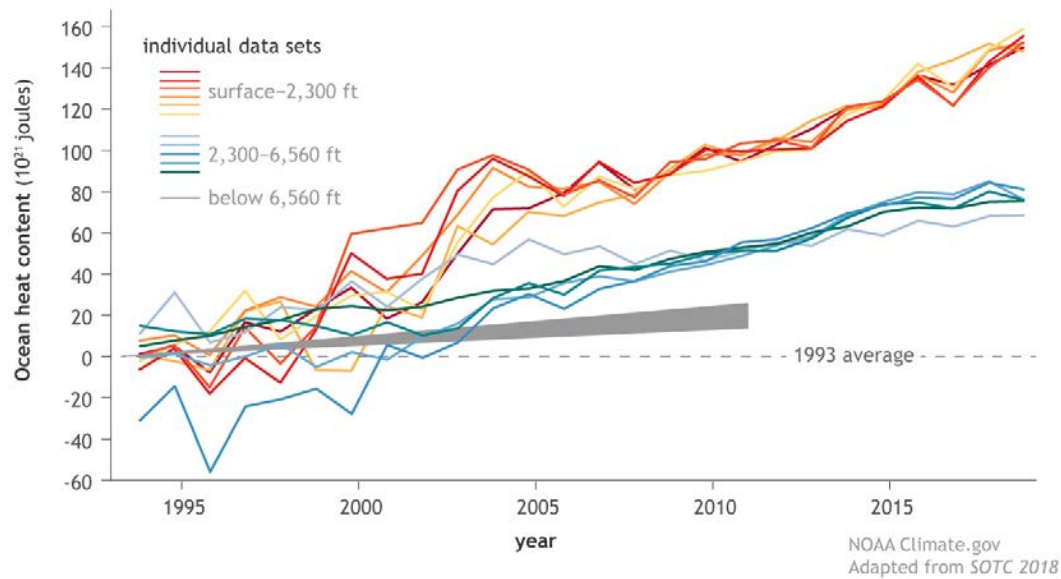


Figure 2.6: Plot of the ocean heat content showing it steadily rising as a result of human activity [NOAA]. **Image courtesy of NOAA.**

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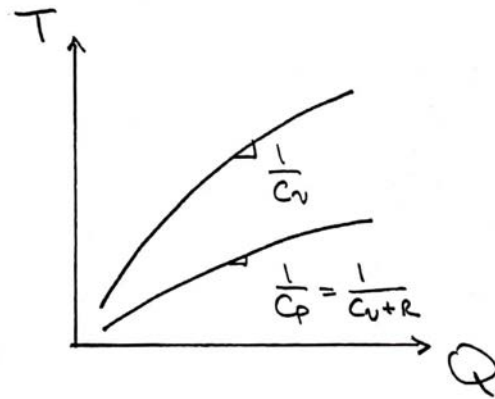
$$dU = dQ - dW = dQ - P\,dV \tag{2.34}$$

50

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

$$(C_p - C_v) \, d\!\!\!/T = m \widetilde{R} \, d\!\!\!/T \tag{2.38}$$

giving us the final relationship that

51

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

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, $\gamma$, 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:

$$dU = \not{d}Q - dW \tag{2.41}$$

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 $\gamma$ 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:
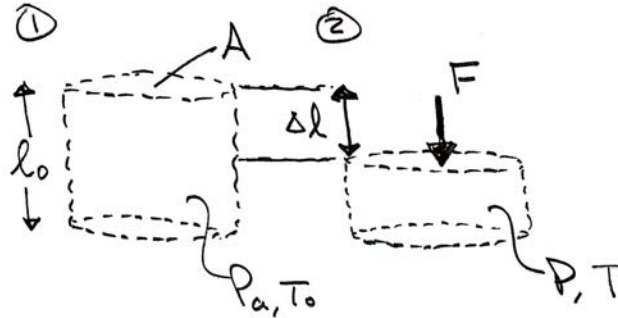
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[32]$C_p = mc_p$ and $C_v = mc_v$

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 $\Delta l$, we can rewrite Eq. 2.48 replacing $P$ with $F/A$ to yield

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

which appears to be a non-linear spring with a spring constant of $A P_a l_0^{\gamma}$. 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
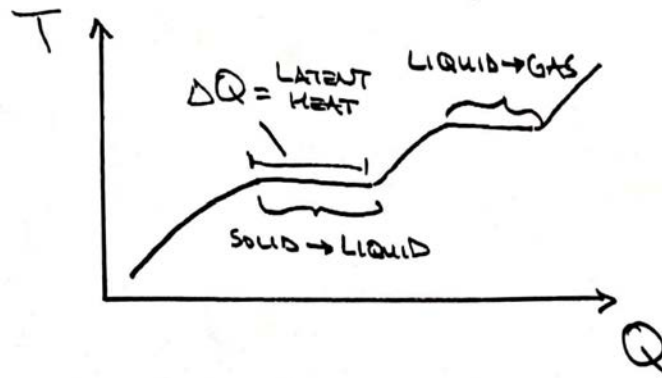
Figure 2.9: $T$-$Q$ diagram for substance undergoing phase changes. During each phase change, the temperature remains constant.

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 $\Delta h$ 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
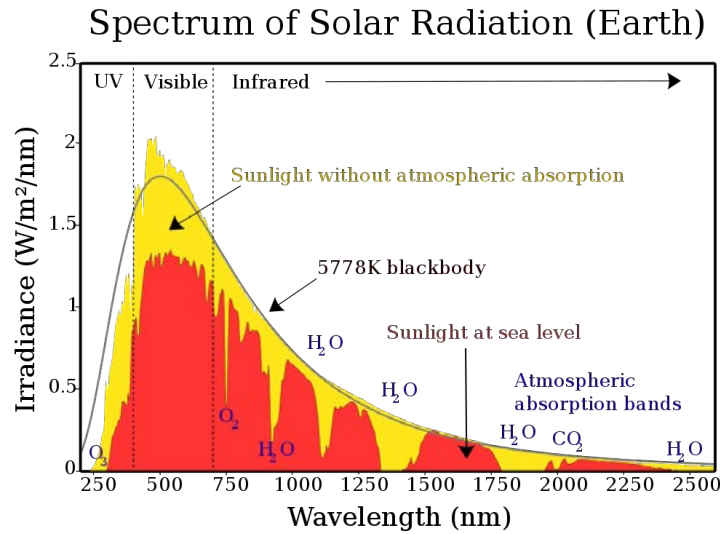


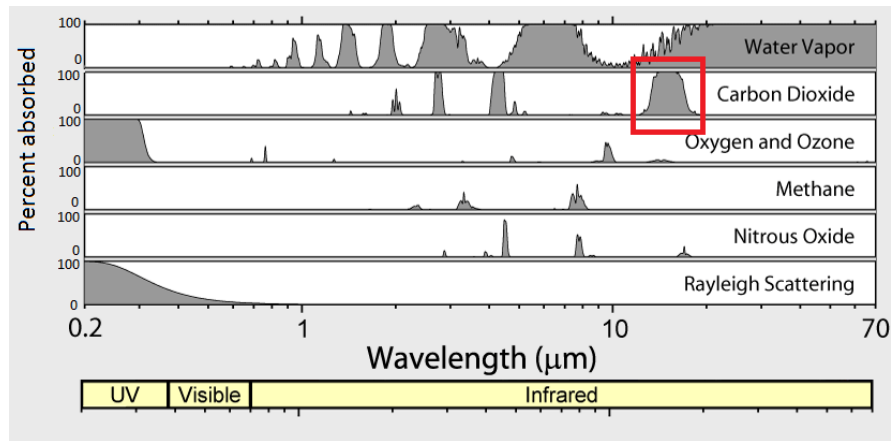Figure 2.10: The absorption of sunlight by various molecules in the atmosphere. Image courtesy of Robert A. Rohde on Wikimedia. License: CC BY-SA. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

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

consumption of nearly 13 TW.

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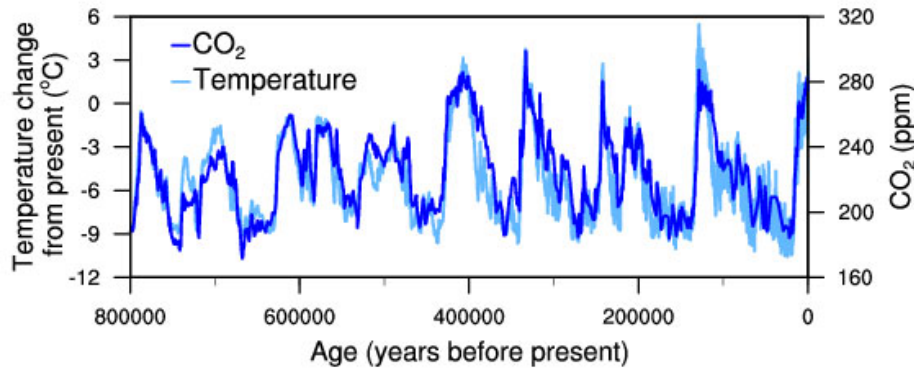
Figure 2.12: Historical carbon dioxide concentration and mean Earth surface temperature. **Image courtesy of NOAA.**

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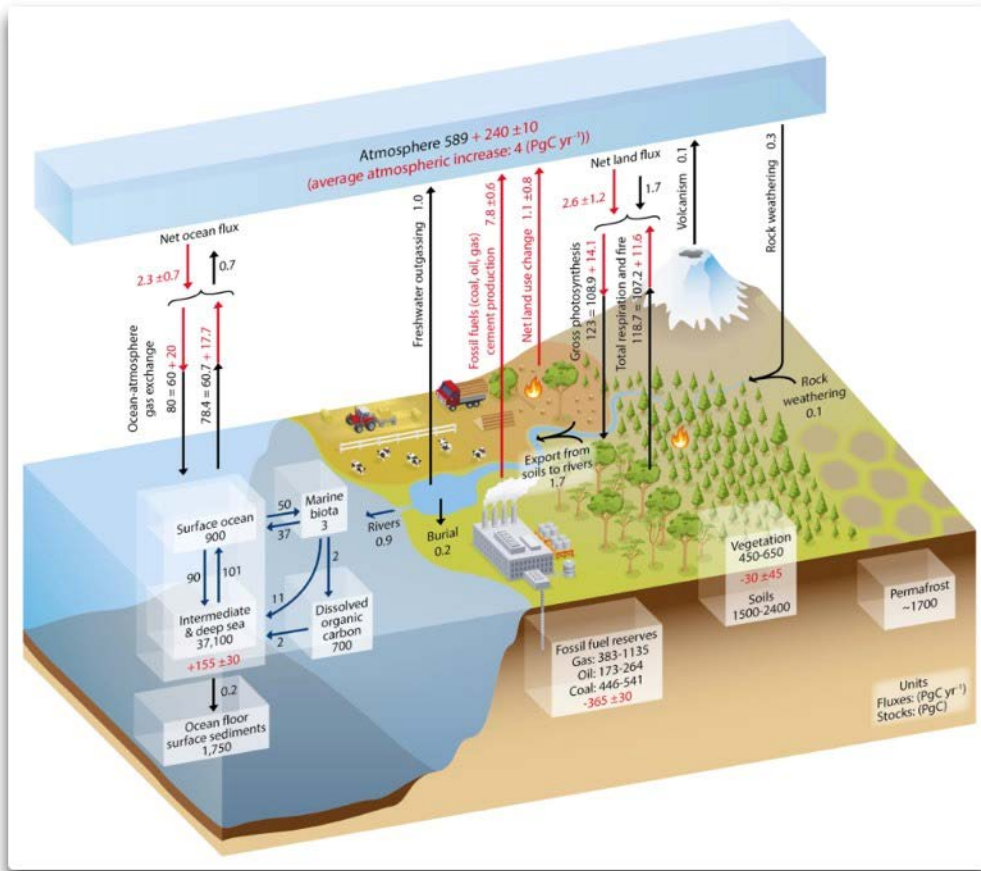
Figure 2.13: Graphical depiction of the carbon cycle [1].

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 ($CaCO_3$). $CO_2$dissolves 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 $CO_2$.
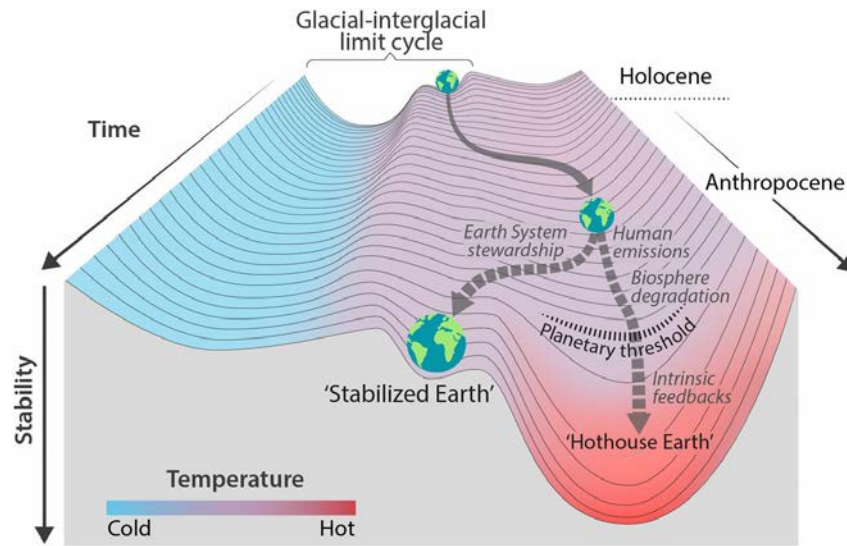
Figure 2.14: Possible states for the Earth's climate, showing the very stable glacial and "hothouse" scenarios [2]. Image courtesy of Will Steffen, Johan Rockström, et al. "Trajectories of the Earth System in the Anthropocene." *PNAS*. August 6, 2018. 115 (33) 8252–8259.

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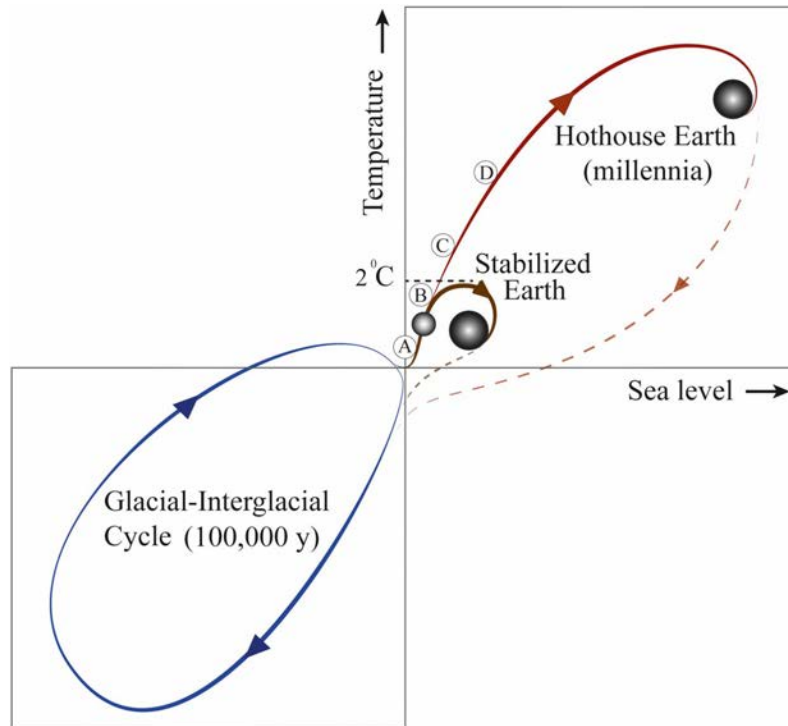
Figure 2.15: Possible trajectories for Earth's climate illustrating the long timescales for the glacial cycles and "hothouse Earth" scenario.

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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