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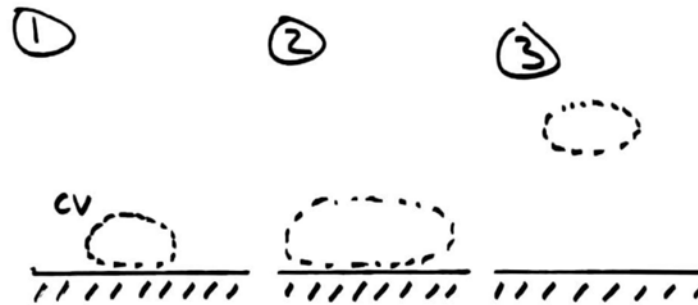
Figure 4.2: Example process of parcel of air being heated by Earth's surface, expanding, rising, and cooling.

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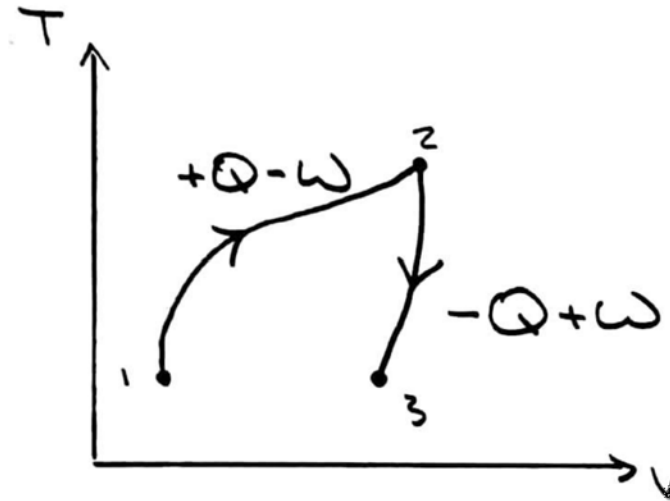
Figure 4.3: Example thermodynamic process for air parcel system plotted as Temperature-Volume curve. Note states and 3 do not necessarily have the same temperature and these curves are drawn arbitrarily for some unknown process.

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*.
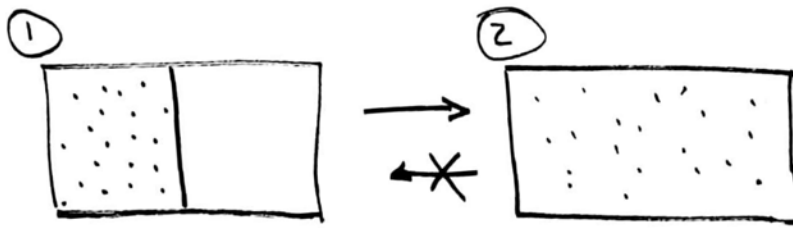
Figure 4.4: Irreversible gas diffusion process.

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

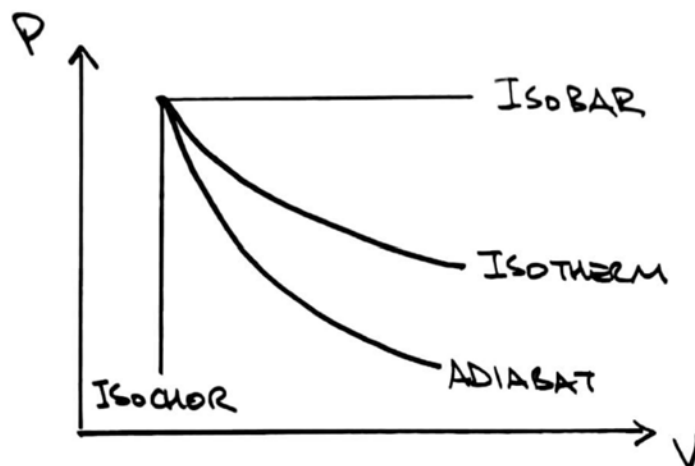[2]From our definition of work, W, this ensures that $dW = 0$.

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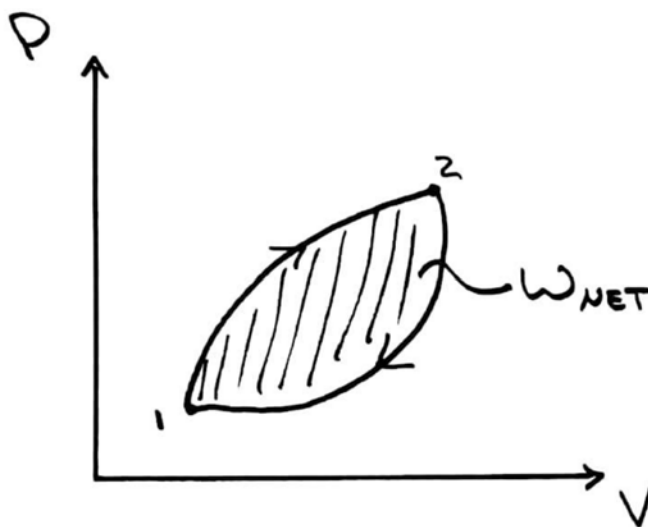
Figure 4.6: Thermodynamic cycle example with final and initial states being equivalent. Here the volume contained within the curve is the net work done by the system, $\oint P\,dV$.

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 $1 \rightarrow 2$, 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 $2 \rightarrow 3$, the gas expands *adiabatically*, bringing its temperature down to T_L.
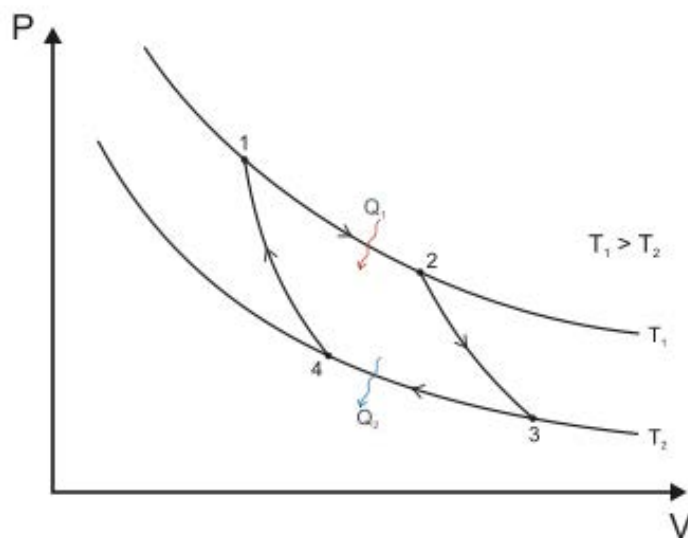
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[3]a body with a theoretically infinite heat capacity

Figure 4.7: Carnot Cycle plotted on *P-V* diagram. Processes 1 → 2 and 3 → 4 are carried out isothermally, while 2 → 3 and 4 → 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 → 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
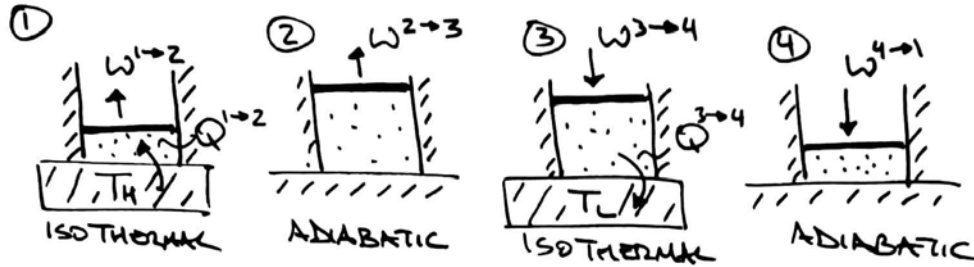
Figure 4.8: Carnot Cycle diagram. Ideal gas is in thermal communication with two different thermal reservoirs at T_H and T_L respectively.

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

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

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

$$Q_{net} = \oint dQ = Q_{in} - Q_{out} \tag{4.9}$$
$$= Q^{1\rightarrow 2} - Q^{3\rightarrow 4} \tag{4.10}$$

$$W_{net} = \oint dW = W_{out} - W_{in} \tag{4.11}$$
$$= W^{1\rightarrow 2} + W^{2\rightarrow 3} - W^{3\rightarrow 4} - W^{4\rightarrow 1} \tag{4.12}$$

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 $Q^{1\rightarrow 2}$. From Eq. 4.8, we see that

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

and thus the efficiency is given as

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

$$= \frac{W_{net}}{Q^{1\to2}} \tag{4.15}$$

$$= \frac{Q^{1\to2} - Q^{3\to4}}{Q^{1\to2}} \tag{4.16}$$

$$= 1 - \frac{Q^{3\to4}}{Q^{1\to2}} \tag{4.17}$$

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 $Q^{1\to2}$ and $Q^{3\to4}$ using the First Law and the Ideal Gas Law. First, to compute, $Q^{1\to2}$, 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

$$\Delta U^{1\to2} = Q^{1\to2} - W^{1\to2} \tag{4.18}$$

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:

$$Q^{1\to2} = W^{1\to2} \tag{4.19}$$

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

$$W^{1\to2} = \int_{V_1}^{V_2} P\, dV \tag{4.20}$$

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

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

and thus

$$Q^{1\to2} = m\widetilde{R}T_H \ln\frac{V_2}{V_1} \tag{4.23}$$

By this same reasoning, $Q^{3\to4}$, 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
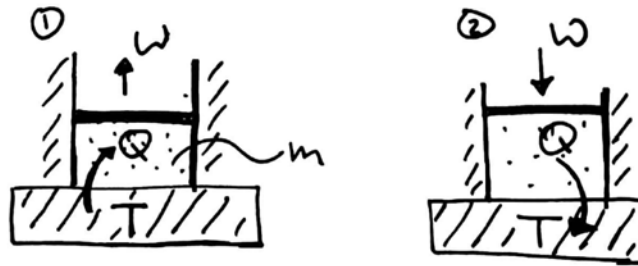
Figure 4.9: Reversible isothermal cycle with zero net work. Gas and thermal reservoir remain at temperature T throughout the whole cycle.

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

$$\Delta U^{1\to2} = Q^{1\to2} - W^{1\to2} \tag{4.35}$$

$$\underline{mc_v(T - T)} = Q^{1\to2} - W^{1\to2} \tag{4.36}$$

$$\Rightarrow W^{1\to2} = Q^{1\to2} \tag{4.37}$$

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

$$W^{2\to1} = Q^{2\to1} \tag{4.38}$$

Writing the first law for the cycle, we have

$$\Delta U_{\widetilde{cycle}} = Q_{net} - W_{net} \tag{4.39}$$

$$\Rightarrow W_{net} = Q_{net} \tag{4.40}$$

$$\oint dW = \oint dQ \tag{4.41}$$

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 $W^{1\to2}$ is given by

$$W^{1\to2} = \int_1^2 P\,dV \tag{4.42}$$

then

$$W^{2\to1} = \int_2^1 P\,dV = -\int_1^2 P\,dV \tag{4.43}$$

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,

$$Q^{1\to2} = -Q^{2\to1} \tag{4.45}$$

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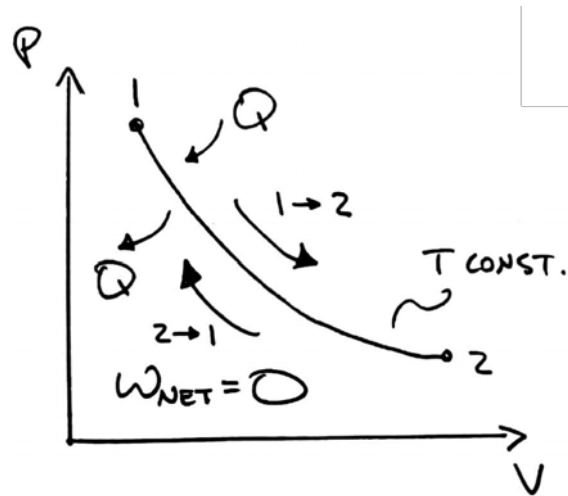
Figure 4.10: *P-V* diagram for isothermal cycle in Fig. 4.9

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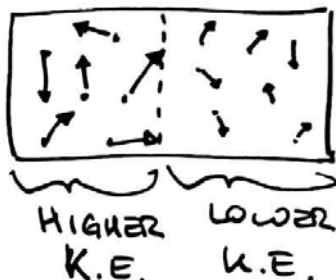[4]See Fermi *Thermodynamics* Chapter 3 for a excellent proof of this [2].

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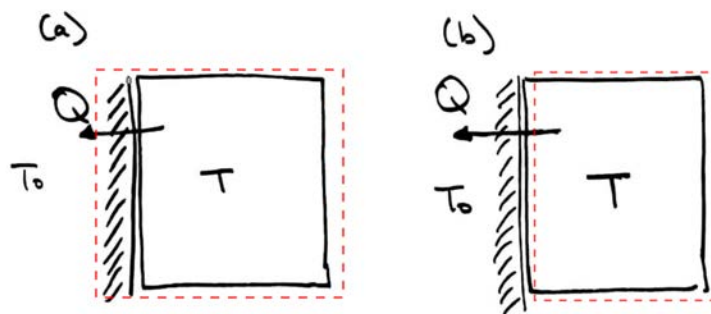
Figure 4.12: Two ways to draw a control volume (red) for the same heat transfer problem involving a transfer Q between a mass at temperature T and a thermal reservoir at T_0. (a) has a CV boundary inside the thermal reservoir and (b) just inside the mass. Assuming a discontinuous temperature change at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

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

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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,

$$dS = \frac{mc_v \, dT + P \, dV}{T} \tag{4.72}$$

$$= \frac{mc_v \, dT}{T} + \frac{m\widetilde{R}T \, dV}{TV} \tag{4.73}$$

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:

$$s_2 - s_1 = c_p \ln \frac{T_2}{T_1} - \widetilde{R} \ln \frac{P_2}{P_1} \tag{4.76}$$

$$= c_p \ln \frac{V_2}{V_1} + c_v \ln \frac{P_2}{P_1} \tag{4.77}$$

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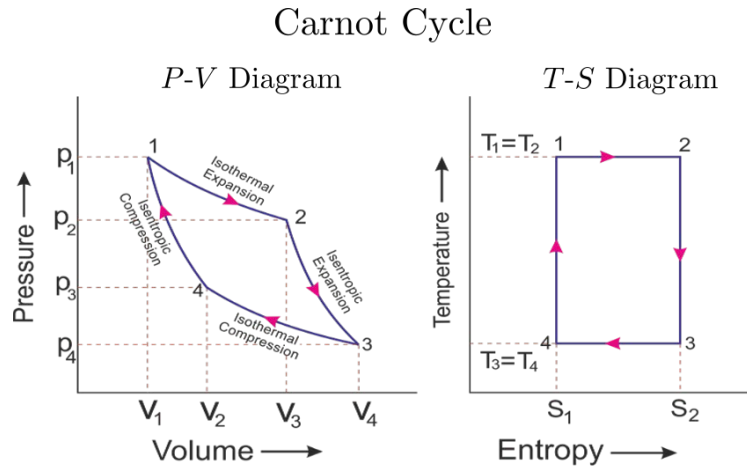
Figure 4.13: Property plots for the Carnot Cycle. Reversible adiabatic processes are *isentropic* and are given by vertical lines on a T-S diagram.

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

$$Q_{net} = \oint dQ = \oint T\, dS \qquad (4.78)$$

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 re-statement 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:

$$\Delta U_{\overbrace{cycle}} = Q_{net} - W_{net} \tag{4.84}$$
$$0 = (T\Delta S_{\overbrace{cycle}} - T\Delta S_{gen}) - W_{net} \tag{4.85}$$
$$\Rightarrow W_{net} = -T\Delta S_{gen} \tag{4.86}$$

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 ($h = u + PV$):
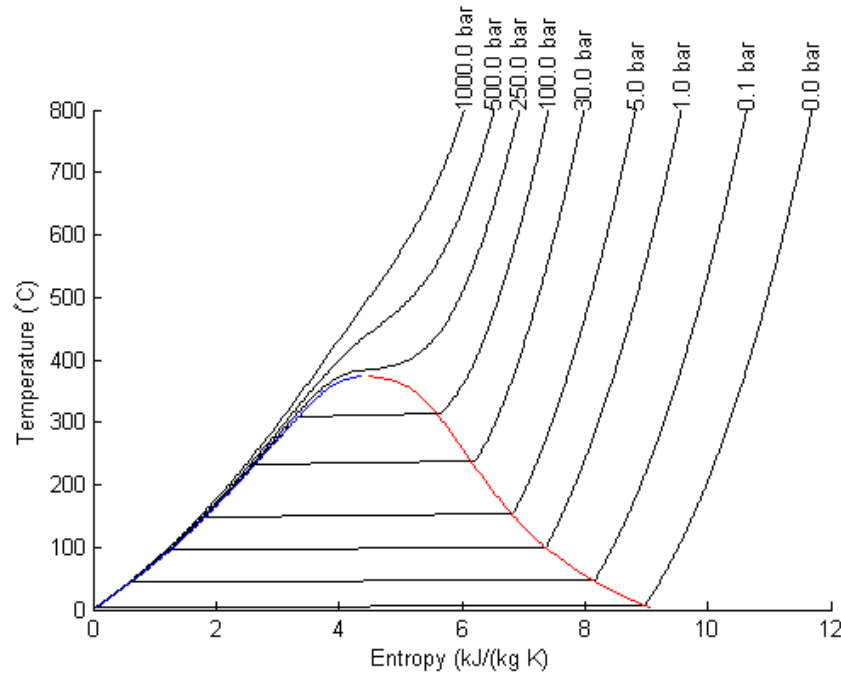
Figure 4.14: Saturation or vapor dome plotted for a substance on a T-s diagram. The black lines represent isobars on this plot, showing constant pressure phase change processes.

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

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

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

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.

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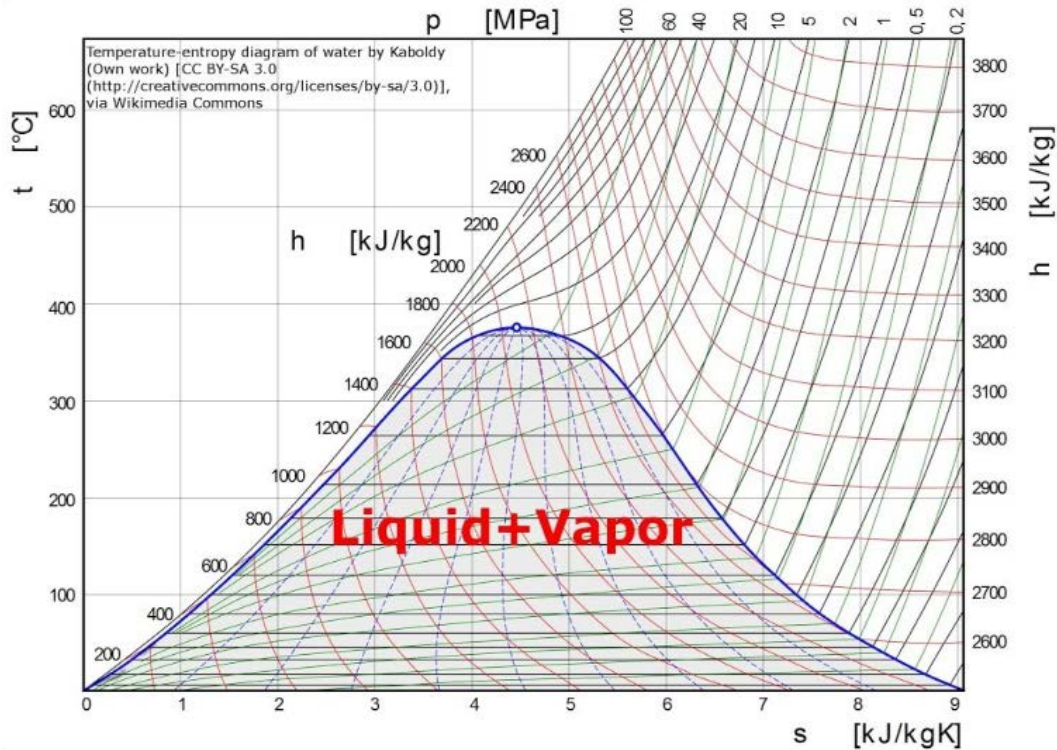Figure 4.15: Vapor dome of water plotted on a T-s diagram showing lines of constant pressure and enthalpy.

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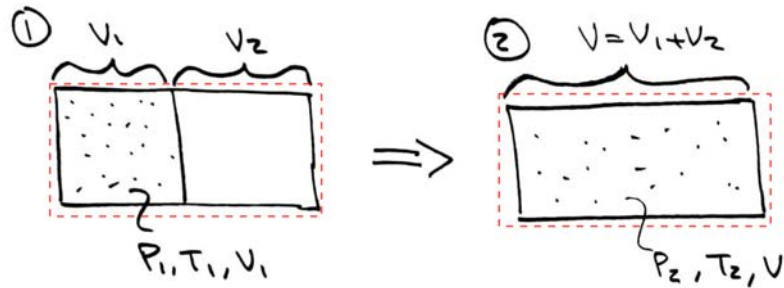
Figure 4.16: A perfect gas occupying part of a volume, V, in state 1. In between states 1 and 2, the barrier is removed and the gas can move to fill the remaining volume, coming to equilibrium at state 2. Control volume is shown in red.

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

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$$\Delta U = \cancel{Q} - \cancel{W} \tag{4.96}$$

$$mc_v(T_2 - T_1) = 0 \tag{4.97}$$

$$\Rightarrow T_2 = T_1 \tag{4.98}$$

and from the Second Law that

$$\Delta S = \int_1^2 \cancel{\frac{dQ}{T}} + \Delta S_{gen} \tag{4.99}$$

$$\Rightarrow \Delta S_{gen} = \Delta S = S_2 - S_1 \tag{4.100}$$

$$= mc_v \cancel{\ln \frac{T_2}{T_1}}^{0} + m\widetilde{R} \ln \frac{V}{V_1} \tag{4.101}$$

$$= m\widetilde{R} \ln \frac{V}{V_1} \tag{4.102}$$

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

$$T_1 V_1^{\gamma-1} = T_2 V^{\gamma-1} \tag{4.103}$$

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

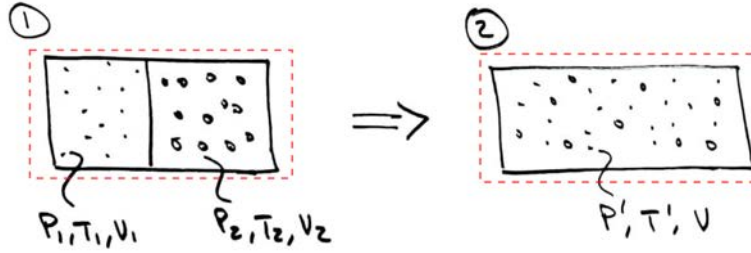and if we plug this relationship into our Second Law formula for a perfect gas to eliminate T, we find that

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.

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

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

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

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

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

$$= 0 \tag{4.110}$$

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:

$$m_1 = \frac{P_1 V_1}{\widetilde{R} T_1} = Xm \tag{4.111}$$

and

$$m_2 = \frac{P_2 V_2}{\widetilde{R} T_2} = (1-X)m \tag{4.112}$$

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:

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

where if $T_1 = T_2 = T$, then

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

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:

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

Solving for V_1 and V_2 gives us

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

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

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

$$V = V_1 + V_2 \tag{4.122}$$

$$= \frac{(1 - X) m \widetilde{R} T}{P} + \frac{(1 - X) m \widetilde{R} T}{P} \tag{4.123}$$

$$= \frac{m \widetilde{R} T}{P} \tag{4.124}$$

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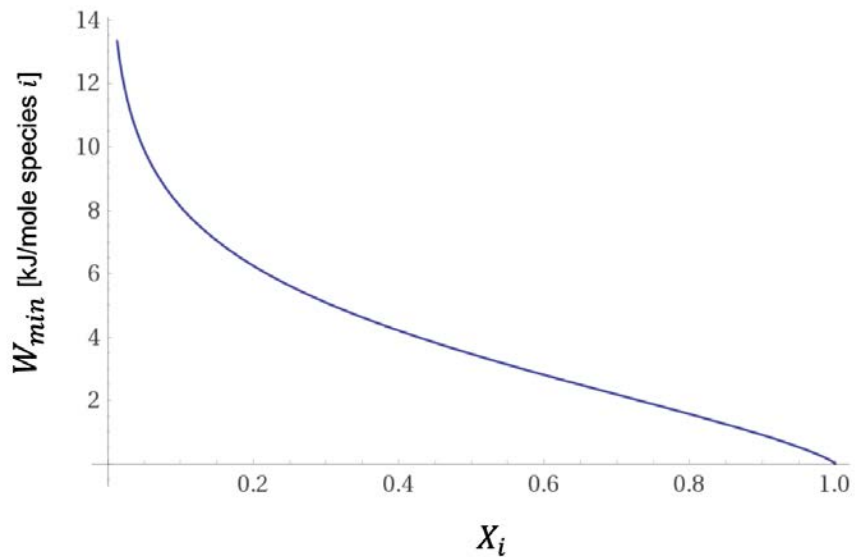
Figure 4.18: Minimum work of separation of gas species i in a mixture per mole of that gas.

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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