

Chapter 5

Engines, Power, and the Anthropocene

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

In the previous chapter, we showed that undoing carbon emissions by directly separating out CO₂ molecules from the air requires a substantial amount of energy, and while possible, this process would need to be carried out using entirely renewable sources to avoid exacerbating the energy usage to carbon emission feedback loop. While this process, called *Direct Air Capture (DAC)*, will need to be a prominent component of climate change mitigation - especially as humanity draws every closer to several dangerous climatological tipping points triggered by rising CO₂ concentrations - it is also essential that greenhouse gas emissions be curtailed and ultimately stopped at the source. To begin to understand the magnitude of these human-generated emissions, we will now look at the thermodynamics behind one of the largest collective carbon emitters of the “unnatural” world - engines.

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

5.1 Engines

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

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

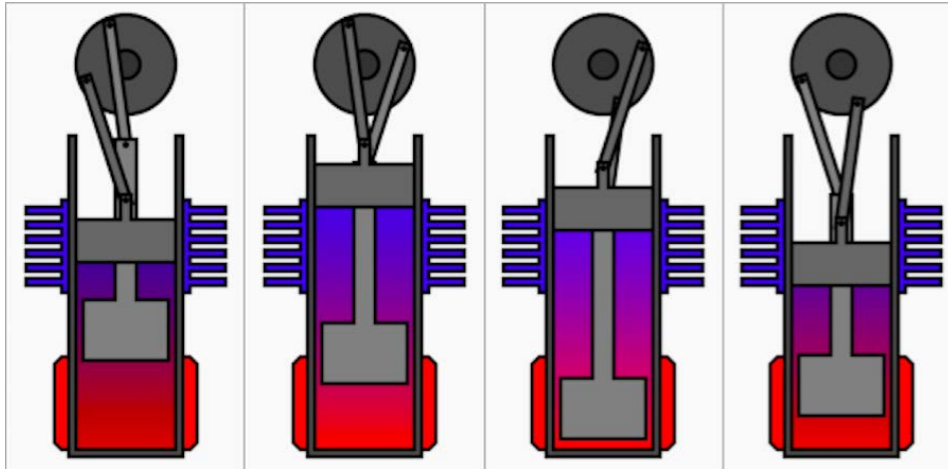


Figure 5.1: Four main stages of a Stirling Cycle. First the displacer forces the gas to be in contact with the hot reservoir, causing the gas to expand and do work via the top piston. The flywheel attached to both the piston and displacer then forces the displacer down, pushing the gas to the top part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

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5.1.1 External Combustion Engines

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

Stirling Engine

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

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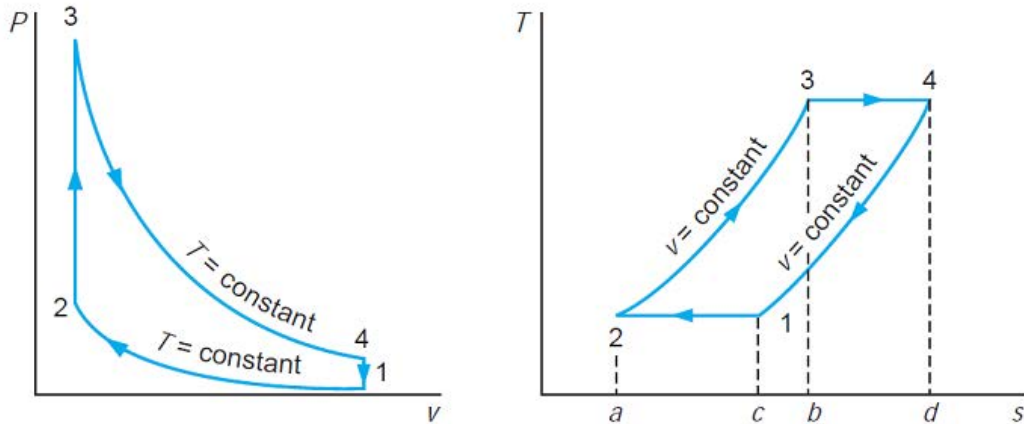


Figure 5.2: P - V and T - S diagrams for a Stirling Cycle. Note the key difference between this and an Otto cycle is that the expansion and compression happen isothermally instead of isentropically.

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

To determine the efficiency for this system, we can start by looking at the heat added, Q_{in} , over the course of a cycle. Here, heat is transferred to the gas from states $2 \rightarrow 3$ and $3 \rightarrow 4$ and can be expressed mathematically by writing the First Law for each process as

$$\Delta U^{2 \rightarrow 3} = Q^{2 \rightarrow 3} - \cancel{W^{2 \rightarrow 3}} \quad (5.1)$$

$$U_3 - U_2 = Q^{2 \rightarrow 3} \quad (5.2)$$

$$\Rightarrow Q^{2 \rightarrow 3} = U_3 - U_2 \quad (5.3)$$

$$= mc_v(T_H - T_L) \quad (5.4)$$

and

$$\Delta U^{3 \rightarrow 4} = Q^{3 \rightarrow 4} - W^{3 \rightarrow 4} \quad (5.5)$$

$$mc_v(\overbrace{T_H - T_H}^0) = Q^{3 \rightarrow 4} - W^{3 \rightarrow 4} \quad (5.6)$$

$$\Rightarrow Q^{3 \rightarrow 4} = W^{3 \rightarrow 4} \quad (5.7)$$

$$= \int_3^4 P dV \quad (5.8)$$

$$= m\tilde{R}T_H \int_{V_3}^{V_4} \frac{dV}{V} \quad (5.9)$$

$$= m\tilde{R}T_H \ln \frac{V_4}{V_3} \quad (5.10)$$

It is important to note here that the heat added from states 2 to 3 and 4 to 1 are equal and opposite in magnitude by this same logic. Typically, we call this the *regenerated heat* as this can be supplied by the thermal mass of the cylinder itself. That is to say from states 4 to 1, heat with a magnitude of $mc_v(T_H - T_L)$ is rejected to the cylinder walls, which is then completely reabsorbed by the gas - or regenerated - from states 2 to 3. Thus the total extra heat that we need to keep the engine running is just

$$Q_{in} = Q^{3 \rightarrow 4} = m\tilde{R}T_H \ln \frac{V_4}{V_3} \quad (5.11)$$

The net work, W_{net} , is computed by similar logic as

$$W_{net} = W^{3 \rightarrow 4} + W^{1 \rightarrow 2} \quad (5.12)$$

$$= m\tilde{R} \left[T_H \ln \frac{V_4}{V_3} + T_L \ln \frac{V_2}{V_1} \right] \quad (5.13)$$

but since $V_1 = V_4$ and $V_2 = V_3$,

$$W_{net} = m\tilde{R}(T_H - T_L) \ln \frac{V_4}{V_3} \quad (5.14)$$

Putting this all together, we can solve for the efficiency of the ideal Stirling cycle as

$$\eta_{Stirling} = \frac{W_{net}}{Q_{in}} \quad (5.15)$$

$$= \frac{m\tilde{R}(T_H - T_L) \ln \frac{V_4}{V_3}}{m\tilde{R}T_H \ln \frac{V_4}{V_3}} \quad (5.16)$$

$$= \frac{T_H - T_L}{T_H} \quad (5.17)$$

$$= 1 - \frac{T_L}{T_H} \quad (5.18)$$

$$= \eta_{Carnot} \quad (5.19)$$

which is exactly equal to the Carnot efficiency! Now we did not say anything about the reversibility of this cycle up until now, but looking carefully at each process, as long as the work is carried out infinitely slowly and all heat is transferred across zero temperature difference, this cycle is indeed reversible. For the regeneration step in particular to be reversible, the cylinder walls must always be the same temperature as the gas locally. The fact that we can recover the Carnot efficiency from this analysis of a completely different reversible cycle operating between two thermal reservoirs further supports the validity of the Second Law of Thermodynamics.

In reality, a Stirling engine will not exactly follow the cycle diagrams in Fig. 5.2 but instead will be closer to the bold curve shown in Fig. 5.3. This actual cycle will not be perfectly reversible and will therefore have an efficiency lower than η_{Carnot} , which again is consistent with the Second Law. In practice, Stirling engines can be made with extremely high efficiencies but typically do not scale well for many applications. Interestingly, because this cycle is reversible, we can run it backwards to get extremely efficient cooling via the heat pump effect previously discussed. This type of device - called a Stirling Cooler - is used in laboratories to achieve extremely cold temperatures down to 10 K or so.

5.1.2 Internal Combustion Engines

Another extremely common engine archetype is the *internal combustion engine* for which the heat driving the cycle is released in such a way that it makes direct contact with the working fluid or is released by the working fluid itself. This type of engine is most commonly used with the combustion of hydrocarbon fuels like gasoline and diesel and is used to power everything from cars to airplanes. While there are many different implementations of this architecture

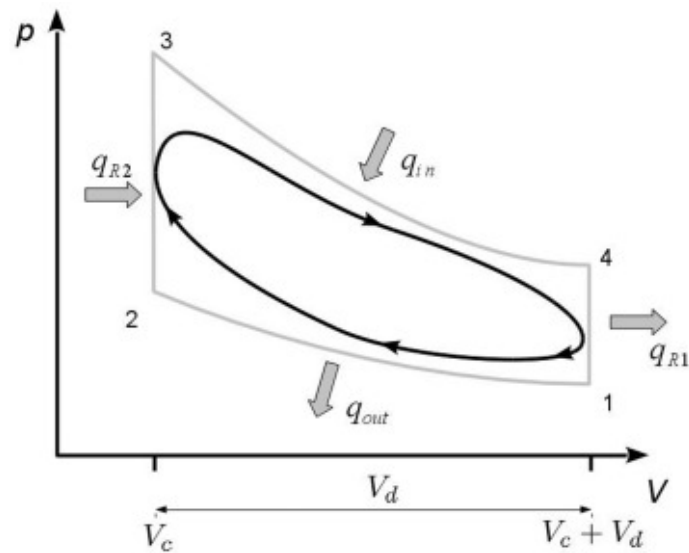


Figure 5.3: P - V diagram showing the path of an actual non-ideal Stirling Cycle in bold. In reality, it takes finite time to transfer heat to the working fluid and thus the heating does not happen isochorically.

with a plethora of compatible fuels, we will only look at a few of the most common here.

Otto Cycle

The *Otto Engine* - which operates on the *Otto Cycle* - powers virtually every internal combustion engine-based vehicle in the world. In this type of engine, vaporized liquid hydrocarbons and air are drawn into a piston, compressed, and ignited adiabatically using a spark plug to release thermal energy via a combustion reaction. The heat release causes the piston to expand isentropically¹ to do work, and the various combustion products are exhausted. Thus, this cycle is for an open system, so even though the exact molecules of gas are different from loop to loop, the cycle is still valid as long as the new reactants are brought in at the same thermodynamic state. Additionally, the idealized version of this cycle is shown in Fig. 5.4 and is theoretically reversible, though unlike with the Stirling and Carnot Cycles, there is a less clear notion of what the thermal reservoirs are.

¹Requires no friction and no heat transfer. The latter requirement can be achieved in practice if the time required for the piston stroke is sufficiently short. This tends to cause dissipation, however.

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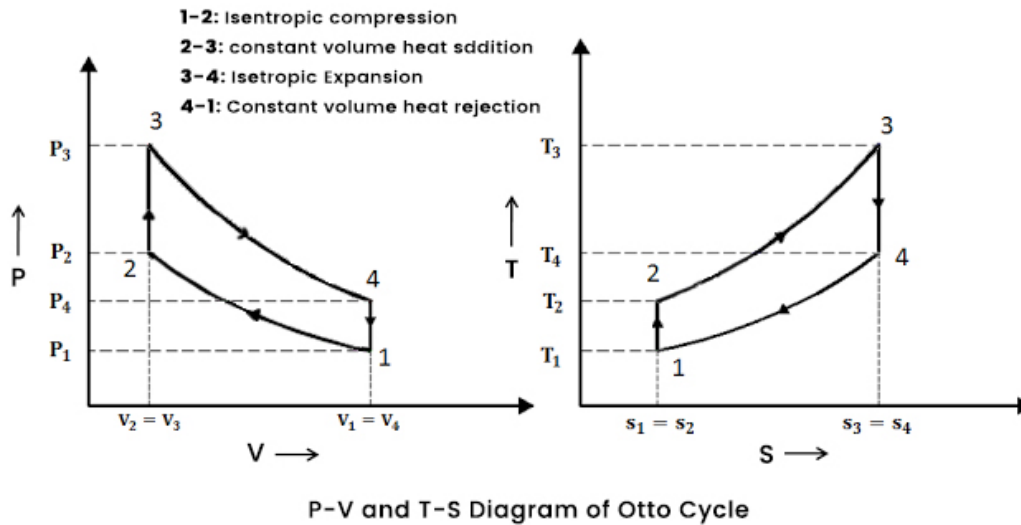


Figure 5.4: P - V and T - S diagrams for the Otto cycle used in many gasoline-powered internal combustion engines.

To determine the maximum efficiency of an Otto Engine, we can start by identifying the effective thermal energy input, Q_{in} , and net work W_{net} . Using the states as labeled in Fig. 5.4, we see that heating release occurs as a result of the combustion reaction between states 2 and 3. Writing the First Law for this process, we can immediately see that the work done is 0 as the combustion happens at constant volume:

$$U_3 - U_2 = Q^{2 \rightarrow 3} - \cancel{W^{2 \rightarrow 3}} = 0 \quad (5.20)$$

$$\Rightarrow Q^{2 \rightarrow 3} = U_3 - U_2 = Q_{in} \quad (5.21)$$

where U_3 is the internal energy of the products at T_3 and U_2 is the internal energy of the reactants at T_2 . We will hold off for now saying anything else about their values, as keeping track of the different species is tricky.

Similarly, we can write the heat rejected between states 4 and 1 as

$$Q^{4 \rightarrow 1} = U_4 - U_1 \quad (5.22)$$

Next, noting that processes $1 \rightarrow 2$ and $3 \rightarrow 4$ are isentropic (reversible adiabatic) we can express the net work by writing the First Law for the cycle:

$$\Delta U_{\text{cycle}} \overset{0}{=} Q_{\text{net}} - W_{\text{net}} \quad (5.23)$$

$$\Rightarrow W_{\text{net}} = Q^{2 \rightarrow 3} + Q^{4 \rightarrow 1} \quad (5.24)$$

and substitute in our expressions for $Q^{2 \rightarrow 3}$ and $Q^{4 \rightarrow 1}$ to yield

$$W_{\text{net}} = (U_3 - U_2) + (U_4 - U_1) \quad (5.25)$$

The efficiency can therefore be written as

$$\eta_{\text{Otto}} = \frac{W_{\text{net}}}{Q_{\text{in}}} \quad (5.26)$$

$$= \frac{(U_3 - U_2) + (U_4 - U_1)}{U_3 - U_2} \quad (5.27)$$

$$= 1 - \frac{U_4 - U_1}{U_3 - U_2} \quad (5.28)$$

where assuming that the products and reactants have the same non-temperature-dependent specific heats, we can write:

$$\eta_{\text{Otto}} = 1 - \frac{mc_v(T_4 - T_1)}{mc_v(T_3 - T_2)} \quad (5.29)$$

$$= 1 - \frac{T_4 - T_1}{T_3 - T_2} \quad (5.30)$$

$$= 1 - \left(\frac{T_1}{T_2}\right) \frac{T_4/T_1 - 1}{T_3/T_2 - 1} \quad (5.31)$$

As we did with the Carnot Cycle analysis earlier, we can use the adiabatic expansion and compression relationships to show that

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} \quad (5.32)$$

and thus

$$\eta_{\text{Otto}} = 1 - \frac{T_1}{T_2} \quad (5.33)$$

which has a similar form as the Carnot Efficiency but represents a physically different phenomena.

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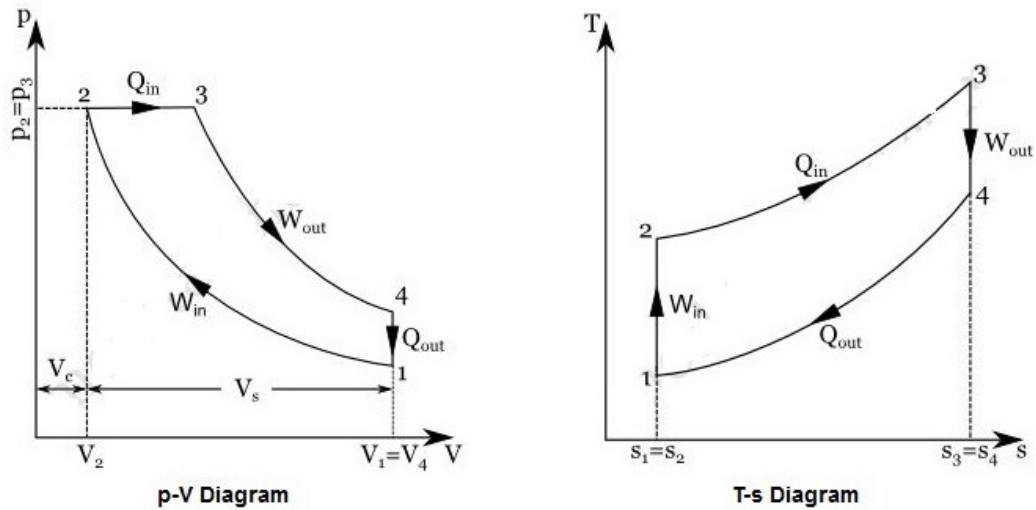


Figure 5.5: P - V and T - S diagrams for the Diesel cycle used in many diesel-powered internal combustion engines. The key difference between this and the Otto cycle is that combustion happens isobarically in the Diesel cycle and isochorically in the Otto cycle.

Finally, with Otto Engines, we typically know the minimum and maximum volumes of the piston well, so we will now get an expression for the efficiency in terms of those volumes, V_1 and V_2 . To do this, we can easily relate T_1/T_2 to V_1/V_2 again via the adiabatic compression relationship:

$$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1} \quad (5.34)$$

and thus

$$\eta_{Otto} = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1} = 1 - \frac{1}{r^{(\gamma-1)}} \quad (5.35)$$

where r is the *compression ratio* equal to V_1/V_2 . This is the maximum efficiency that an actual Otto Engine can achieve, and in reality heat loss to the environment and other irreversibility caused by friction and mixing of gases will detract from this efficiency.

Diesel Cycle

A similar process to the Otto Cycle is the *Diesel Cycle*, which differs from the Otto Cycle in that combustion happens at constant pressure instead of constant volume. Fig. 5.5 shows the property plots for the ideal reversible Diesel Cycle which look very similar to that of the Otto Cycle in Fig. 5.4, except for process 2 \rightarrow 3. The efficiency can be derived in a similar manner, though it is made more complex by the fact that the system does work during the combustion process. We will not derive that here, but it can be shown that the efficiency of this cycle is given by

$$\eta_{Diesel} = 1 - \frac{1}{r^{(\gamma-1)}} \left(\frac{\alpha^\gamma - 1}{\gamma(\alpha - 1)} \right) \quad (5.36)$$

where $\alpha = V_3/V_2$ and $r = V_1/V_2$.

We can see directly from Eq. 5.36 that the efficiency of the theoretical Diesel Engine is less than that of the equivalent Otto Cycle, though in practice, diesel engines are often more efficient for a variety of reasons we will not go into detail about here. One of the main reasons, however, is that in an internal combustion engine, a high compression ratio will cause the fuel to ignite before the piston reaches its minimum volume, wasting significant energy in the process. Diesel engines can achieve much higher compression ratios due to the fact that the combustion occurs at constant pressure and thus there is much more room to increase the pressure during the compression. In fact, because of this fact, diesel engines do not require a spark plug as the compression itself is what ignites the fuel.

Note that in internal combustion engines (and many external combustion engines as well), this cycle is occurring in several different pistons simultaneously, each operating out of phase from one another. This helps to ensure that the engine is balanced and that power is more or less being continuously produced over time. Additionally, engines and the devices that use them rely on the inertia of the engine itself to smooth out the operation. This can be accomplished with a heavy spinning mass called a *flywheel*, which helps to ensure that any other moving parts coupled to the engine - like the displacer in the Stirling Engine - continue to operate in between the power strokes of the engine. In some machines - cars, for example - the inertia of the machine itself helps to smooth things out. For this reason, most combustion engines cannot simply start self start; instead, they need a small electric motor to start the engine spinning in order to build up enough inertia to sustain the cycle².

²This is why you cannot start a gasoline-powered car, for example, when the battery is dead.

5.2 Continuous Flow Power Systems

Up until this point, we have been primarily discussing closed systems and their associated cycles with discrete *temporally sequential* processes. For example, a gas in a piston undergoes expansion or compression but at any given time, our control volume has a homogeneous state throughout and moves throughout the cycle sequentially one step at a time. While most combustion engines operate with multiple pistons running out of phase from one another, we still treat each piston as a separate cycle with a homogeneous internal state. Also even though internal combustion engines, for example, exhaust the working fluid at the end of the cycle and replace the fuel and oxidizer before beginning again, we are still able to analyze the cycle as if the same gas remained inside the whole time.

In contrast to these closed temporally sequential cycles, *continuous flow* or *continuous power* cycles are comprised of a flowing working fluid whose state changes continuously throughout the system. The cycle is happening such that states are better represented *spatially* in the system than temporally as is the case with the discrete closed systems we previously looked at. We just as easily represent these cycles on property plots as we can imagine tracking a small homogeneous packet of working fluid as it flows from one device to the next, even though in reality, all states in the cycle exist at the same time but separated in space. This concept will be made clear by looking at some example devices and cycles.

5.2.1 Open Systems

Before we begin describing systems, we need to first establish a framework for analyzing *open systems*, which unlike *closed* systems, allow mass to enter and exist the control volume. Just like with closed systems, however, we can track the energy of the *streams* in and out and relate those fluxes to the change in internal energy using the First Law. As shown in Fig. 5.6 a generalized control volume for such a system has mass flowing in and out with its own internal energy, useful work done continuously via *shear* stresses of the liquid, useful work done by the *normal* stresses (i.e. $\int P dV$), and heat transfer in and out. Because these systems are operating continuously, we replace our Δ operators for $\frac{d}{dt}$ operators in order to analyze how the system changes continuously with time. For energy contained within the control volume, E_{CV} , we have for example

$$\Delta E_{CV} \rightarrow \frac{d}{dt}(E_{CV}) \equiv \dot{E}_{CV} \quad (5.37)$$

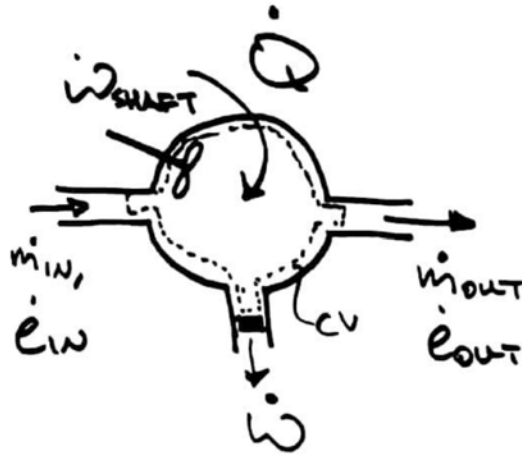


Figure 5.6: Generalized control volume for continuous flow open systems.

where \dot{E}_{CV} has units of energy per time or Watts in SI units.

Conservation of Mass

For the open systems we will look at in this text, mass is conserved, which can be expressed mathematically as

$$\frac{d}{dt}m_{CV} = \dot{m}_{in} - \dot{m}_{out} \quad (5.38)$$

which simply states that the rate of change of mass inside the control volume is equal to the difference in mass flow rates between the entering and exiting mass streams. Note that in steady state, $\frac{d}{dt}m_{CV} = 0$. Here \dot{m} is a *mass flow rate* in units of mass per time. Because there can be many streams coming in and leaving our system, Eq. 5.38 can be generalized to

$$\frac{d}{dt}m_{CV} = \left(\sum_i \dot{m}_i \right)_{in} - \left(\sum_i \dot{m}_i \right)_{out} \quad (5.39)$$

First Law

We can similarly write the First Law for open systems as

$$\dot{E}_{CV} = \left(\sum_i \dot{m}_i e_i \right)_{in} - \left(\sum_i \dot{m}_i e_i \right)_{out} + \dot{Q}_{net} - \dot{W}_{net} \quad (5.40)$$

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where e_i is the specific internal energy of stream i and can include kinetic energy, gravitational potential energy, etc. For fluids flowing in and out of the system, it is important to note that at the boundaries of our control volume, the fluid stream itself is doing mechanical work of the form $\int P dV$ as it will have some pressure acting over a volumetric displacement. By definition, we differentiate this work from any other work done by the *deformation* of the control volume or mechanical work done by a shaft that is stuck into the fluid³. The reason for this differentiation is that we can directly lump together the internal energy of the stream, u_i , and this PV flow work done by stream at the boundary as the *enthalpy* of the stream:

$$h_i = u_i + (Pv)_i \quad (5.41)$$

where v is the specific volume in units of volume per mass.

Thus, it is often common to write the first law as

$$\dot{E}_{CV} = \left[\sum \dot{m} \left(h + \frac{1}{2} w^2 + gz + \dots \right) \right]_{in} - \left[\sum \dot{m} \left(h + \frac{1}{2} w^2 + gz + \dots \right) \right]_{out} + \dot{Q}_{net} - \dot{W}_{net} \quad (5.42)$$

where h is the specific enthalpy of the stream, $1/2w^2$ the specific kinetic energy, gz the specific gravitational potential energy, and the ellipsis represents all other forms of energy relevant to the particular problem.

Second Law

Similarly, we can write the Second Law for our open system as

$$\dot{S}_{CV} = \left(\sum_i \dot{m}_i s_i \right)_{in} - \left(\sum_i \dot{m}_i s_i \right)_{out} + \sum \frac{Q_i}{T_i} + \dot{S}_{gen} \quad (5.43)$$

where for irreversible cycles, $\dot{S}_{gen} > 0$, and for reversible cycles, $\dot{S}_{gen} = 0$.

Examples

Let us look at two simple examples to illustrate how to use these principles in practice for open systems. Perhaps the simplest open system is an adiabatic

³We differentiate *shaft work* typically from PV work as shaft work requires that a shear stress be applied to some surface to spin a propeller for example vs PV work which requires that a normal stress be applied to a deforming boundary.

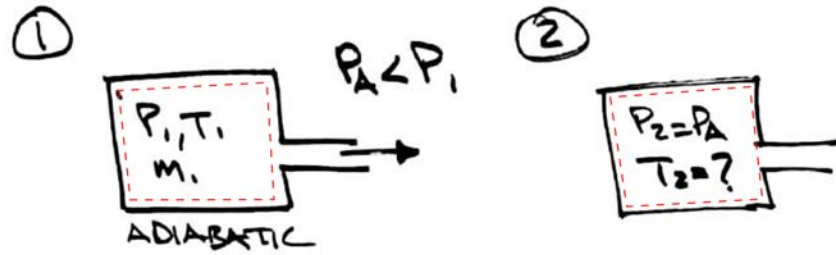


Figure 5.7: Example problem where a gas in an adiabatic container initially at some pressure $P_1 > P_a$ expands and exits the container.

container that is initially at some pressure, P_1 , that is greater than ambient pressure. Intuitively if open the container, the gas contained within it will rush out. The question is, what is the final temperature of the gas that remains within the control volume, as shown in Fig. 5.7? There are two ways to solve this problem. First, how we would have approached this previously would be by working backwards and only encompassing the gas that remains in the container at the end of the process in our control volume. We could then track these particles back to state 1 and realize that this gas is simply undergoing adiabatic expansion and then apply the appropriate relationships between P and T for an ideal gas. Because we are tracking the same particles of gas throughout the process and morphing our control volume continuously, we are actually treating this control volume as a closed system. This allows us to directly write

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (5.44)$$

Using our new understanding of open systems, we can also approach this problem by maintaining a fixed control volume as shown in Fig. 5.7 and keeping track of the gas that leaves the control volume between states 1 and 2. Writing the open system form of the First Law, we have

$$\dot{E}_{CV} = \cancel{(\dot{m}h)_{in}} - (\dot{m}h)_{out} + \cancel{\dot{Q}_{net}} - \cancel{\dot{W}_{net}} \quad (5.45)$$

where we can immediately cancel out terms due to the system being adiabatic and the fact that no work is being done other than by the stream itself exiting the container, which as we saw, is captured in the enthalpy term of the outgoing stream. Note we assume here that the macroscopic kinetic energy of the gas

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leaving is negligible. Recalling that $h = c_p T$ and $u = c_v T$ for an ideal gas, we can rewrite this expression as

$$\frac{d}{dt}(m c_v T) = -\dot{m}_{out} c_p T \quad (5.46)$$

where m is mass in the control volume at some time t . By conservation of mass we know that $\dot{m} = -\dot{m}_{out}$, and thus

$$\frac{d}{dt}(m c_v T) = -\dot{m}_{out} c_p T \quad (5.47)$$

$$\dot{m} c_v T + m c_v \dot{T} = \dot{m} c_p T \quad (5.48)$$

$$\Rightarrow m c_v \dot{T} = \dot{m} (c_p - c_v) T \quad (5.49)$$

$$\Rightarrow \frac{\dot{T}}{T} = \frac{c_p - c_v}{c_v} \frac{\dot{m}}{m} \quad (5.50)$$

$$= (\gamma - 1) \frac{\dot{m}}{m} \quad (5.51)$$

Switching the limits of integration from time to state variables of T and m and integrating both sides, we have

$$\int_{T_1}^{T_2} \frac{dT}{T} = (\gamma - 1) \int_{m_1}^{m_2} \frac{dm}{m} \quad (5.52)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{m_2}{m_1} \right)^{\gamma-1} \quad (5.53)$$

and finally using the ideal gas law to replace m with $\frac{PV}{RT}$, we get

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (5.54)$$

which is exactly what would have gotten using our first approach. While for this example, this open system approach was more convoluted, for many systems, we cannot easily track the motion of the individual particles and instead must use a fixed control volume.

Recall that this is the same result we obtained for a perfectly reversible adiabatic expansion process, and thus if we compute the entropy for our control volume over this process, we would indeed find that it is exactly 0. Intuitively, however, we would not expect the process of gas rushing out of a container into the surrounding air to be a reversible process. In reality it is not, but in



Figure 5.8: Example where an adiabatic container is initially at some pressure $P_1 < P_a$ and then opens to allow ambient air to rush in.

the way we defined our control volume, all irreversibility occurs *outside* the container and outside our control volume. This makes the math much easier.

We can also look at the opposite of this process, where instead we have the initial pressure inside the container less than ambient pressure such that when the container is opened, gas rushes in. We will take the same fixed control volume as in the previous example and as shown in Fig. 5.8. Clearly there will be irreversibility generated inside our control volume in this process due to mixing and dissipation; however, we can still write the First and Second Laws for this process. Starting with the First Law, again ignoring the macroscopic kinetic energy of the gas coming in, we have that

$$\dot{E}_{CV} = (\dot{m}h)_{in} - \cancel{(\dot{m}h)_{out}} + \overset{0}{\dot{Q}_{net}} - \overset{0}{\dot{W}_{net}} \quad (5.55)$$

As before, we can substitute our expressions for internal energy and enthalpy to yield

$$\frac{d}{dt}(mc_v T) = \dot{m}c_p T_a \quad (5.56)$$

where T_a is the ambient temperature of the entering gas - the temperature at the boundary where we are tracking the enthalpy. Using the ideal gas law and the relationship that $R = c_v/(\gamma - 1)$, this expression is equivalent to

$$\frac{d}{dt} \left(\frac{PV}{\gamma - 1} \right) = \dot{m}c_p T_a \quad (5.57)$$

Switching the limits of integration and integrating:

$$\frac{V}{\gamma - 1} \int_{P_1}^{P_2} dP = c_p T_a \int_{m_1}^{m_2} dm \quad (5.58)$$

$$\Rightarrow \frac{(P_2 - P_1)V}{\gamma - 1} = (m_2 - m_1)c_p T_a \quad (5.59)$$

$$= \left(\frac{P_2 V}{\tilde{R} T_2} - \frac{P_1 V}{\tilde{R} T_1} \right) c_p T_a \quad (5.60)$$

For $P_1 = 0$, this simplifies to the expression:

$$T_2 = \gamma T_a \quad (5.61)$$

We can write the Second Law for this example to characterize the irreversibility generated by this process as

$$\dot{S}_{CV} = (\dot{m}s)_{in} - \cancel{(\dot{m}s)_{out}} + \sum_i \cancel{\frac{Q_i}{T_i}} + \dot{S}_{gen} \quad (5.62)$$

Because entropy as used here is a relative quantity, we must choose some reference against which to measure the change in entropy throughout the process. If we choose the reference state to be (T_a, P_a) , then we conveniently find that

$$s_{in} - s_0 = c_p \ln \frac{T_a}{T_a} - \tilde{R} \ln \frac{P_a}{P_a} = 0 \quad (5.63)$$

and after integrating Eq. 5.62 and taking $P_1 = 0$,

$$\Delta S_{gen} = m_2(s_2 - s_0) - \cancel{m_1(s_1 - s_0)} \quad (5.64)$$

$$= m_2 \left(c_p \ln \frac{T_2}{T_a} - \tilde{R} \ln \frac{P_a}{P_a} \right) \quad (5.65)$$

$$= m_2 c_p \ln \frac{\gamma T_a}{T_a} \quad (5.66)$$

$$= m_2 c_p \ln \gamma \quad (5.67)$$

For gases, $\gamma > 1$, and thus the $\Delta S_{gen} > 0$ as we would expect for this irreversible process. Note that in the above analysis, we assumed that the system inside the control volume started as a perfect vacuum with zero mass, and therefore $S_1 = 0$. In this process, the irreversibility comes from the diffusion of the gas entering the container and the ensuing dissipation that drives an increase in the temperature of the gas.

5.2.2 Power Conversion Devices

With an understanding of how the First and Second Laws are formulated for open and continuous flow systems, we can now take a high level look at a class of devices that are used in the various processes of power cycles. These so-called *power conversion devices* are used to manipulate the thermodynamic state of a stream, extracting or supply net work or net heat to the stream in the process. On our cycle diagrams, each one of these devices typically represents a single process taking the system from one well-defined state to the next. For each of the following devices, we are interested in characterizing the subsystem at *steady-state* - where total internal energy and mass within the control volume at any given time do not change with time.

For the devices in particular that require either the input or extraction of mechanical work to change the state of the stream - for example a compressor or pump - we will define a *Second Law Efficiency*⁴, which compares the actual work to the work of the ideal reversible device. This efficiency will be defined differently for each device, but it is worth noting here that it is fundamentally different from the previous efficiency we looked at, which is typically called a *First Law Efficiency* that compares the energy put in to the “useful” energy extracted. The Second Law Efficiency is measurable and thus gives us the ability to model these devices as undergoing ideal reversible processes - which are typically easier to analyze - and then simply apply the efficiency directly in our analysis as we will see.

Compressor

A device that is capable of compressing a continuous stream of some working fluid - typically a gas - is fittingly called a *compressor*. There are many different implementations of this type of device, but they all take in a gas at P_1 and output it at P_2 such that $P_2 > P_1$. Fig. 5.9 shows the simplified diagram of a compressor with a stream entering at state 1 and leaving at state 2 as mechanical power, \dot{W} is applied to bring the gas to a higher pressure. Writing the First Law for the idealized adiabatic compressor, we find that

$$\dot{E}_{CV} = \cancel{\dot{Q}_{net}} - \dot{W}_{ideal} + \dot{m}(h_1 - h_{2s}) \quad (5.68)$$

and thus

⁴also called *isentropic efficiency*

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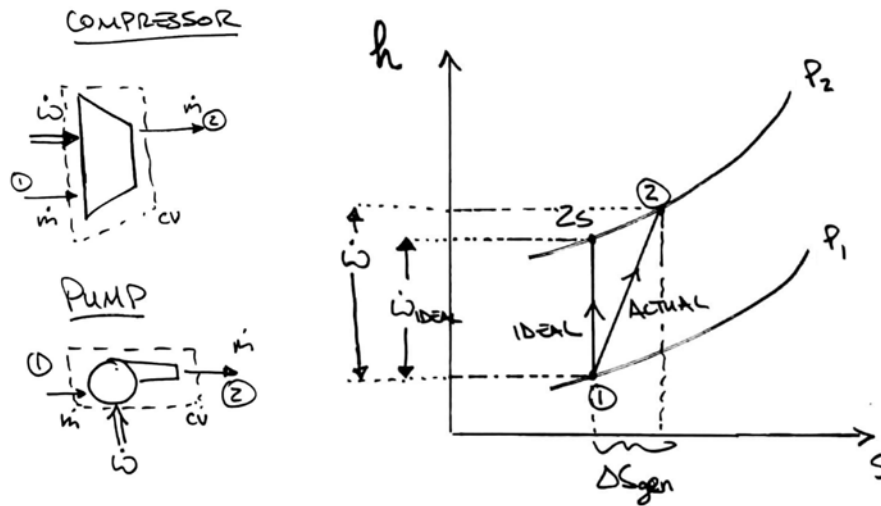


Figure 5.9: Compressor and pump control volume and corresponding h - s plot showing that generated entropy requires more work be added to achieve same pressure ratio, P_2/P_1 .

$$\dot{W}_{ideal} = -\dot{m}(h_{2s} - h_1) \quad (5.69)$$

$$= -\dot{m}c_p(T_{2s} - T_1) \quad (5.70)$$

$$= -\dot{m}c_p T_1 \left(\frac{T_{2s}}{T_1} - 1 \right) \quad (5.71)$$

which we can relate to pressures P_1 and P_2 by applying our familiar adiabatic relationship between P and T . Substituting this expression into Eq. 5.69 gives us

$$\dot{W}_{ideal} = -\dot{m}c_p T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (5.72)$$

We can then define our Second Law Efficiency for the compressor, η_c^{II} , as

$$\eta_c^{II} = \frac{\dot{W}_{ideal}}{\dot{W}_{actual}} \quad (5.73)$$

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and thus if we are given this efficiency, we can compute the actual work required to change the stream from state 1 to 2 using a non-ideal compressor as

$$\dot{W}_{actual} = \frac{1}{\eta_c^{II}} \dot{m} c_p T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (5.74)$$

because we can easily compute \dot{W}_{ideal} and can measure \dot{W}_{actual} for a range of different states, we can get a well-defined value for η_c^{II} in practice. Typical Second Law Efficiencies range from 0.7-0.9.

To characterize the entropy generated in an actual compressor, we can write the Second Law for a non-ideal compressor as

$$\cancel{\dot{S}_{CV}} = \cancel{\sum_i \frac{Q_i}{T_i}} + \dot{m}(s_1 - s_2) + \dot{S}_{gen} \quad (5.75)$$

$$\Rightarrow \dot{S}_{gen} = \dot{m}(s_2 - s_1) \quad (5.76)$$

$$= \dot{m} \left[c_p \ln \frac{T_2}{T_1} - \tilde{R} \ln \frac{P_2}{P_1} \right] \quad (5.77)$$

$$= \dot{m} \left[c_p \ln \left(1 + \frac{1}{\eta_c^{II}} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \right) - \tilde{R} \ln \frac{P_2}{P_1} \right] \quad (5.78)$$

where we can easily see that for $\eta_c^{II} = 1$, $\dot{S}_{gen} = 0$. Graphically, this relationship between irreversibility and enthalpy - and thus work required to compress the gas - can be clearly illustrated by plotting the process on an h - s diagram as shown in Fig. 5.9. As shown here, the ideal process is *isentropic* and thus represented by a vertical line on this plot connecting isobars at P_1 and P_2 . On these plots “2s” represents the idealized state 2. In reality, if entropy is generated in this process, the enthalpy required to achieve the same pressure increase will be greater as shown here. Because the work required for this process is directly proportional to the change in enthalpy, then the actual process will require more work as well, as we showed analytically here.

Pump

A *pump* is essentially just a compressor but one that is typically used with incompressible fluids like water instead. It can be represented on a similar h - s diagram as shown in Fig. 5.9. Because the fluid is incompressible, several

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simplifications can be made in the characterization of this type of device. Writing the First Law, rearranging to solve for the input work, and substituting in our expression for enthalpy for a solid or incompressible fluid:

$$\dot{E}_{CV} = \cancel{\dot{Q}_{net}} - \dot{W}_{ideal} + \dot{m}(h_1 - h_{2s}) \quad (5.79)$$

$$\Rightarrow \dot{W}_{ideal} = \dot{m}(h_1 - h_2) \quad (5.80)$$

$$= \dot{m}[c(T_1 - T_2) + (P_1 - P_2)v] \quad (5.81)$$

where v is the fluid specific volume. To figure out the relationship between T_1 and T_2 for the ideal case, we can write the Second Law and show that

$$\cancel{\dot{S}_{CV}} = \sum_i \cancel{\frac{Q_i}{T_i}} + \dot{m}(s_1 - s_{2s}) + \cancel{\dot{S}_{gen}} \quad (5.82)$$

$$\Rightarrow s_1 - s_{2s} = 0 \quad (5.83)$$

$$c \ln \frac{T_{2s}}{T_1} = 0 \quad (5.84)$$

$$\Rightarrow T_{2s} = T_1 \quad (5.85)$$

As before, we can define a Second Law Efficiency, η_p^{II} , such that

$$\dot{W}_{actual} = \frac{\dot{W}_{ideal}}{\eta_p^{II}} = \frac{1}{\eta_p^{II}} \dot{m}(P_2 - P_1)v \quad (5.86)$$

which is also useful in determining the temperature rise of the fluid in the non-ideal case:

$$\dot{m}[c(T_2 - T_1) + (P_2 - P_1)v] = \frac{1}{\eta_p^{II}} \dot{m}(P_2 - P_1)v \quad (5.87)$$

$$\Rightarrow T_2 - T_1 = \frac{1}{c}(P_2 - P_1)v \left(\frac{1}{\eta_p^{II}} - 1 \right) \quad (5.88)$$

This allows us to compute the entropy generated as

$$\dot{S}_{gen} = \dot{m}(s_2 - s_1) = \dot{m}c \ln \frac{T_2}{T_1} \quad (5.89)$$

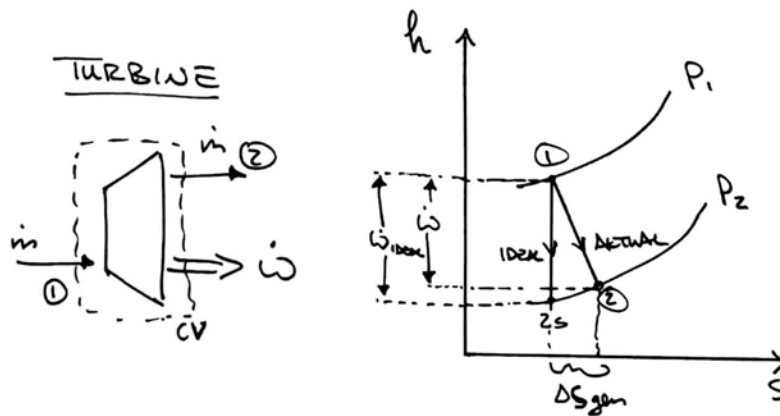


Figure 5.10: Turbine control volume and corresponding h - s plot showing that the actual work extracted is limited by the generated entropy.

Turbine

A *turbine* is the opposite of a compressor and pump in that it takes in a stream and reduces its enthalpy by expanding it, extracting mechanical work in the process. Again we can start with the First Law for a gas to analyze the ideal device and then define an efficiency to relate its performance to an actual turbine:

$$\dot{E}_{CV} = \dot{Q}_{net} - \dot{W}_{ideal} + \dot{m}(h_1 - h_{2s}) \quad (5.90)$$

$$\Rightarrow \dot{W}_{ideal} = \dot{m}(h_1 - h_{2s}) \quad (5.91)$$

where $2s$ on the h - s diagram in Fig. 5.10 indicates the endpoint of the idealized isentropic expansion process. As before, we define a Second Law Efficiency to relate this ideal work to the work done by an actual turbine:

$$\dot{W}_{actual} = \eta_T^H \dot{W}_{ideal} \quad (5.92)$$

$$= \eta_T^H \dot{m} c_p T_1 \left[1 - \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \right] \quad (5.93)$$

With this information, we can use the First Law for an ideal gas to establish a relationship between T_2 and T_1 as

$$(T_2 - T_1) = \eta_T^I T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (5.94)$$

which enables us to solve for the entropy generated in this process as

$$\dot{S}_{gen} = \dot{m} \left[c_p \ln \frac{T_2}{T_1} - \tilde{R} \ln \frac{P_2}{P_1} \right] \quad (5.95)$$

As we did with the pump, we can also analyze a turbine assuming that the stream is comprised of incompressible fluid. For this case,

$$\dot{W}_{actual} = \eta_T^I \dot{W}_{ideal} = \eta_T^I \dot{m} (P_1 - P_2) v \quad (5.96)$$

where $\Delta T = 0$ across the ideal process if no entropy is generated. The entropy generated for the real process can be solved exactly as we did for the pump case.

Heat Exchanger

The final continuous flow device we will briefly look at here is the *heat exchanger*, which unlike the compressor, pump, and turbine serves to transfer heat between two streams. As shown in Fig. 5.11, heat exchangers can operate in *parallel flow* or *counter flow* configurations, both of which transfer heat continuously along their length. Writing the First Law for control volumes surrounding each of the streams, we have

$$\cancel{\dot{E}_{CV,B}} = \dot{Q} - \cancel{\dot{W}} + [\dot{m}(h_2 - h_1)]_A \quad (5.97)$$

and

$$\cancel{\dot{E}_{CV,A}} = -\dot{Q} - \cancel{\dot{W}} + [\dot{m}(h_2 - h_1)]_B \quad (5.98)$$

because the heat flux leaving one stream is equal and opposite in magnitude to the heat flux entering the other stream, we can relate these two equations as

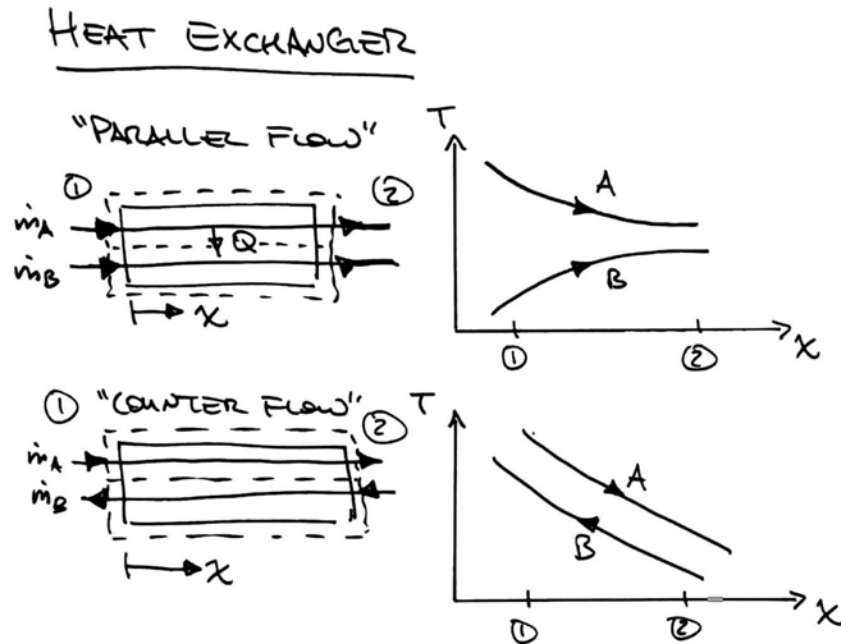


Figure 5.11: Two common heat exchanger configurations that facilitate a heat transfer, \dot{Q} , between two streams.

$$[\dot{m}(h_2 - h_1)]_A = -[\dot{m}(h_2 - h_1)]_B = \dot{Q} \quad (5.99)$$

The actual physics determining how this heat transfer occurs is beyond the scope of this text but is covered in detail in most previous heat transfer textbooks [Mills]. What Eq. 5.99 tells us, however, is that if we can measure the enthalpy of either stream at the inlet and outlet, we can determine the amount of heat transferred between the two streams. In order to compute the entropy generated from this process, we would need to be able to say something about the temperature profile along the length of the heat exchanger. This is dependent on the various parameters of the exchanger itself.

Additionally, heat can only flow where there is temperature difference between the two streams and the heat flux is proportional to the temperature difference. For this reason the counter flow configuration is capable of maintaining a larger temperature difference over the entire length and is therefore often favored for applications requiring a continuous flow heat exchanger. Despite the *effectiveness* of the heat exchanger, considerable entropy will be generated in this process as a result of the intentional heat transfer across as large a temperature difference as possible.

5.2.3 Continuous Power Cycles

Putting this all together, the previously discussed continuous flow devices can be used to generate power continuously via numerous different power cycles. In particular, we will look at what is arguably the oldest known power cycle, the *Rankine Cycle*, which underlies the operation of old steam engines and modern power plants that use geothermal, nuclear, or other external heat sources. We will also analyze the *Brayton Cycle*, which is the continuous analog to the Diesel Cycle. Like the Diesel Cycle, the Brayton Cycle utilizes a combustible fuel source undergoing constant-pressure combustion to generate the thermal energy necessary to do net mechanical work. Instead of taking place in a piston, however, the Brayton Cycle uses a continuous compressor and turbine as configured in Fig. 5.13.

Rankine Cycle

The first known engine was the previously mentioned Aeolipile, which was a very rudimentary *steam engine* that uses an external heat source to vaporize water, causing the whole device to spin and perform mechanical work. Almost 2000 years later, in the 1700's CE, this cycle was improved upon to create what is now the modern *Rankine Cycle*. As shown in Fig. 5.12, a Rankine Cycle is a closed-loop, continuous power cycle that utilizes a pump, boiler or heat exchanger, turbine, and condenser. In the ideal cycle, between states 1 and 2, liquid water or some other working fluid in liquid phase is pumped isentropically to high pressure. Then heat is transferred to the fluid isobarically between states 2 and 3, first bringing the fluid to its saturation temperature, then vaporizing the fluid, and finally superheating the vapor, bringing it to state 3. The superheated vapor is then sent through a turbine where work is extracted as the vapor expands isentropically to state 4, which is typically at atmospheric pressure. Finally, between states 4 and 1, heat is rejected and the vapor condenses back into liquid phase isobarically to reset the cycle.

To analyze the ideal system, we can write the First Law for each process given our stated assumptions. Starting with the pumping process, we have from Eq. 5.81 that

$$\dot{W}_{pump} = \dot{W}^{1 \rightarrow 2} = \dot{m}(h_1 - h_2) \quad (5.100)$$

$$= \dot{m}[c(T_1 - T_2) + (P_1 - P_2)v] \quad (5.101)$$

as no thermal energy is transferred in or out of our control volume in the ideal case.

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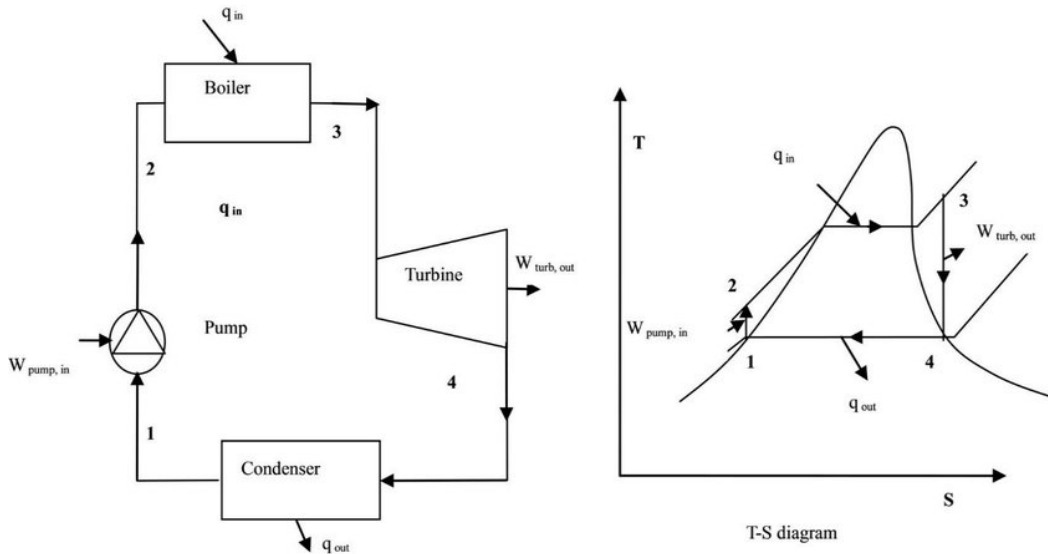


Figure 5.12: Ideal Rankine Cycle schematic and T - S diagram.

From state 2 to 3, we can again write the first law to relate the heat transferred, $\dot{Q}_{in} = \dot{Q}^{2 \rightarrow 3}$ to the other state properties as

$$\cancel{E_{CV}} = \dot{Q}^{2 \rightarrow 3} - \cancel{W^{2 \rightarrow 3}} + \dot{m}(h_2 - h_3) \quad (5.102)$$

$$\Rightarrow \dot{Q}^{2 \rightarrow 3} = \dot{m}(h_3 - h_2) \quad (5.103)$$

It is important to keep track of what phase the working fluid is at the beginning and end of this process. While we do not need to know anything about how the phase change occurs, we do need to be able to fully characterize the state of the fluid at states 2 and 3 to determine h_2 and h_3 . In the example cycle shown in Fig. 5.12, state 2 lies outside and to the left of the vapor dome, meaning that it will be completely in liquid phase in state 2. State 3 lies outside the dome and to the right, meaning that it will be completely in vapor phase at state 3. If state 3 instead terminates inside the vapor dome, then we need to know some additional piece of information about the working - e.g. the total specific volume or enthalpy - to also then determine the vapor quality.

For the expansion and work extraction process between states 3 and 4, the ideal work output is given by Eq. 5.72 as

$$\dot{W}_{turbine} = \dot{W}^{3 \rightarrow 4} = \dot{m}(h_3 - h_4) \quad (5.104)$$

$$= -\dot{m}c_p T_3 \left[\left(\frac{P_4}{P_3} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (5.105)$$

In practice, modern turbine blades can be easily damaged by the formation of water droplets during the expansion process, and thus Rankine Cycles are typically operated such that state 4 lies right on the vapor dome or just outside of it to ensure that the working fluid remains in vapor phase throughout.

With this information, we can compute the First Law efficiency for this cycle as

$$\eta_{Rankine} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} \quad (5.106)$$

$$= \frac{\dot{W}_{turbine} + \dot{W}_{pump}}{\dot{Q}_{in}} \quad (5.107)$$

$$= \frac{(h_3 - h_4) + (h_1 - h_2)}{(h_3 - h_2)} \quad (5.108)$$

which holds regardless of whether or not the cycle is ideal. For the ideal cycle, however, we can substitute in our equations for the ideal pump and compressor work derived here.

For non-ideal Rankine Cycles, we must use the isentropic efficiencies of each component as previously discussed. Recall, for example, that the isentropic efficiency of the pump for this example is

$$\eta_{pump}^{II} = \frac{h_{2s} - h_1}{h_2 - h_1} \quad (5.109)$$

where the s subscript indicates the ideal enthalpy at that particular state. Typically, we can compute h_1 and h_{2s} , and there if we are given η_{pump}^{II} , we can solve for h_2 via Eq. 5.109. Via a similar process, we can solve for h_4 via the definition for a given isentropic efficiency for a turbine:

$$\eta_{turbine}^{II} = \frac{h_4 - h_3}{h_{4s} - h_3} \quad (5.110)$$

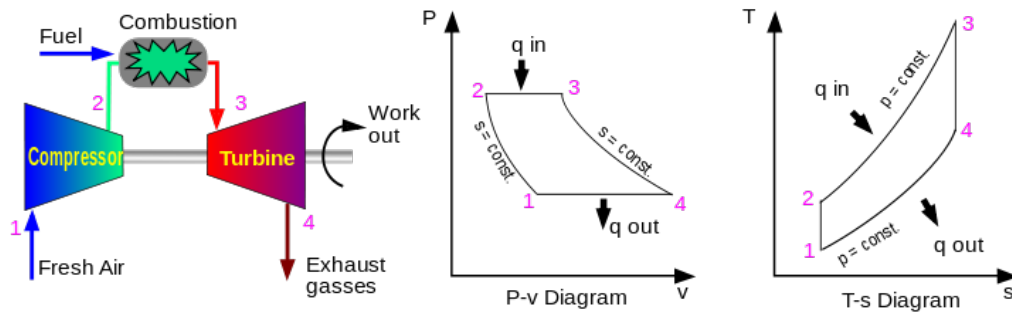


Figure 5.13: Continuous flow power cycle called the Brayton Cycle which is the continuous equivalent of the Diesel Cycle. Combustion happens from $2 \rightarrow 3$ at constant pressure.

Brayton Cycle

This cycle can be broken up into four main processes. First, air enters the compressor in state 1, where it is compressed adiabatically to state 2 with a higher pressure and temperature than in state 1. Next, fuel is injected into the flow and combusted to add heat to the system isobarically⁵. Between states 3 and 4, the hot, high-pressure gas expands adiabatically in a turbine, which outputs mechanical work and brings the products back to the initial pressure. Finally, heat is rejected isobarically and the process repeats. The power required to continuously compress the gas between states 1 and 2 is typically supplied directly by the turbine itself. Fig. 5.13 shows this process plotted on both P - V and T - S diagrams, both of which look very similar to that of the Diesel Cycle.

To determine the *First Law Efficiency* for this cycle, we can use the relationships we defined in the previous section to relate the various work and heat transfers for each process to system properties. As with any continuous power cycle, this efficiency is given by ratio of the net mechanical power, \dot{W}_{net} , to the heat added, \dot{Q}_{in} . For this cycle,

$$\dot{W}_{net} = \dot{W}_{turbine} - \dot{W}_{compressor} \quad (5.111)$$

$$= \dot{m}[(h_3 - h_4) - (h_2 - h_1)] \quad (5.112)$$

⁵For the ideal case analysis, we will ignore the change in mass due to this fuel injection.

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where it is important to note that even though on the P - V diagram we can clearly see PV work being done for both constant pressure processes, this work is not extracted as mechanical work and instead captured by the change in enthalpy over those processes. This is different from the Diesel Cycle where mechanical work is extracted during the constant-pressure combustion as it is happening directly in the piston.

For the Brayton Cycle, the heat added is equal to

$$\dot{Q}_{in} = \dot{m}(h_3 - h_2) = \dot{m}c_p(T_3 - T_2) \quad (5.113)$$

We therefore compute the ideal efficiency directly as

$$\eta_{Brayton} = \frac{\dot{W}_{net}}{\dot{Q}_{in}} \quad (5.114)$$

$$= \frac{(h_3 - h_4) - (h_2 - h_1)}{h_3 - h_2} \quad (5.115)$$

$$= \frac{(h_3 - h_2) - (h_1 - h_4)}{h_3 - h_2} \quad (5.116)$$

$$= 1 - \frac{h_1 - h_4}{h_3 - h_2} \quad (5.117)$$

$$= 1 - \frac{T_1 - T_4}{T_3 - T_2} \quad (5.118)$$

$$= 1 - \frac{T_1 (T_4/T_1 - 1)}{T_2 (T_3/T_2 - 1)} \quad (5.119)$$

where we can relate T_4/T_1 to T_3/T_2 by using the adiabatic expansion and compression relationships as we did with the Otto Cycle analysis to show that

$$\frac{T_4}{T_1} = \frac{T_3}{T_2} \quad (5.120)$$

Thus,

$$\eta_{Brayton} = 1 - \frac{T_1}{T_2} \quad (5.121)$$

$$= 1 - \left(\frac{P_1}{P_2} \right)^{\frac{\gamma-1}{\gamma}} \quad (5.122)$$

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which interestingly looks very similar to the Otto Cycle efficiency. Again, this is due to the fact that no mechanical work is extracted during the combustion itself.

For the non-ideal or non-isentropic Brayton Cycle, the analysis becomes much more complex as we must model each process using the relationships we previously established. Starting with the compressor work, we have

$$\dot{W}_{compressor} = \dot{m}(h_2 - h_1) \quad (5.123)$$

$$= \frac{1}{\eta_c^{II}} \dot{m} c_p T_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad (5.124)$$

where η_c^{II} is the given isentropic efficiency of the compressor. Similarly, we have for the turbine work that

$$\dot{W}_{turbine} = \dot{m}(h_4 - h_3) \quad (5.125)$$

$$= \eta_T^{II} \dot{m} c_p T_3 \left[1 - \left(\frac{P_4}{P_3} \right)^{\frac{\gamma-1}{\gamma}} \right] \quad (5.126)$$

which only holds for a *perfect* gas. If instead c_p is a function of temperature, care must be taken to evaluate h_4 and h_3 using empirically-derived formulae.

We can then determine the thermal energy input by looking at the heat released in the combustion reaction itself between states 2 and 3. Since this is a constant pressure combustion process, we can model this heat release by the change in enthalpy across the products and reactants. We can then compute the adiabatic flame temperature under these conditions to determine the temperature of the reaction products at state 3 and finally compute the First Law Efficiency by solving these equations simultaneously. Note that to be completely accurate, we would also need to take into account that for an actual power system, the specific heat of the working fluid(s) will not be constant with temperature, especially over the typically wide temperature range these systems operate under. In practice, computer simulations must be used to characterize realistic power systems. Real *power plants* that combust methane to generate mechanical power based on the Brayton Cycle do so at efficiencies up to 55%. These plants effectively recover much of the enthalpy contained within the hot gas exiting the turbine to extract work over multiple stages.

5.3 Gibbs Free Energy

Like we did with enthalpy, we will now define another quantity that is a combination of state properties, which as we will show has some utility for analyzing systems. To help characterize the amount of “useful” work, which we will define shortly, we will define a quantity called the *Gibbs Free Energy*, G , as

$$G \equiv H - TS = U + PV - TS \quad (5.127)$$

or in differential form as

$$dG = dH - d(TS) = dU + d(PV) - d(TS) \quad (5.128)$$

For a process in which both the temperature and pressure are held constant, this can be further reduced:

$$dG = dU + d(PV) - d(TS) \quad (5.129)$$

$$= dU + P dV + V dP - T dS - S dT \quad (5.130)$$

$$= dU + P dV - T dS \quad (5.131)$$

Following our methodology for determining the physical meaning of enthalpy, we can write the First and Second Law for an arbitrary steady-state continuous process that exchanges heat and work with environment at (P_a, T_a) and maintains constant pressure and temperature throughout:

$$\dot{E}_{CV} = \dot{Q} - \dot{W} + \dot{m}(h_1 - h_2) \quad (5.132)$$

and

$$\dot{S}_{CV} = \frac{\dot{Q}}{T_a} + \dot{m}(s_1 - s_2) + \dot{S}_{gen} \quad (5.133)$$

We can combine Eqs. 5.132 and 5.133 and solve for \dot{W} , giving us

$$\dot{W} = \dot{m}(h_1 - h_2) - \dot{m}T_a(s_1 - s_2) - T_a\dot{S}_{gen} \quad (5.134)$$

$$= \dot{m}[(h - T_a s)_1 - (h - T_a s)_2] - T_a\dot{S}_{gen} \quad (5.135)$$

$$= \dot{m}(g_1 - g_2) - T_a\dot{S}_{gen} \quad (5.136)$$

where g is the specific Gibbs Free Energy in units of energy per mass. This expression tells us that the maximum work that can be extracted from a

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power cycle requires that each process be reversible and thus that $\dot{S}_{gen} = 0$. The maximum work in this case can be expressed simply as

$$\dot{W}_{max} = \dot{m}(g_1 - g_2) \quad (5.137)$$

5.3.1 Availability

The Gibbs Free Energy again highlights the fact that the work that can be extracted from a stream over a process is limited directly by any irreversibility generated by the system. This relationship is derived directly from the Second Law, but it serves an important purpose to help illuminate this concept from another angle. This concept can be formalized to characterize the maximum amount of work that can be extracted from a system in communication with the environment at (P_a, T_a) . A quantity called the *Availability* or *Exergy*, Ξ , is defined as

$$\Xi \equiv E + P_a V - T_a S \quad (5.138)$$

which allows us to characterize the “useful” mechanical work that can be extracted generally as

$$W_{useful} = -\Delta\Xi - T_a \Delta S_{gen} \quad (5.139)$$

$$= -(\Delta E + P_a \Delta V - T_a \Delta S) - T_a \Delta S_{gen} \quad (5.140)$$

by the Second Law.

Throughout all of this analysis it is important to understand that in terms of its conversion to mechanical work, not all thermal energy is treated equally. We have from the Carnot Efficiency of a reversible heat engine that the greater the difference in temperature between the hot and cold thermal reservoirs, the more work can be extracted for the same thermal energy input. As such, thermal energy has this notion of *quality* attached to it, with thermal energy at a higher temperature relative to its environment having a higher quality.

5.3.2 Chemical Equilibrium

In all systems, but in continuous flow power system in particular, we may have chemical reactions that are proceeding in both the forward and backward directions simultaneously. The rates of both reactions depend on the local concentrations of the products and reactants as we learned back in Chapter 3. We

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also talked about the equilibrium conditions of the reaction being established from the temperature-dependent rate constant, $k_p(T)$ as

$$\prod_i X_i^{\nu_i} \left(\frac{P}{P_0} \right)^{\sum_i \nu_i} = k_p(T) \quad (5.141)$$

At the time, we did not yet have the tools to derive where the mysterious k_p constant came from, but now that we have defined the Gibbs Free Energy, we can establish that the equilibrium conditions for a chemical reaction actually come from the even more fundamental notion that at equilibrium, the total Gibbs Free Energy of this system is minimized, or that

$$dG = 0 \quad (5.142)$$

To understand why this is the case, we need to augment the First Law equation we have been using up until this point to also include the change in energy that results from a change in the number of moles of a species in a reaction:

$$dU = dQ - dW + \sum_i \mu_i dN_i \quad (5.143)$$

where μ_i is the *chemical potential energy* and dN_i the change in number of moles of species i . We sum over all species to get the total change in chemical potential energy. The reason we did not include this before in our calculations is that by definition, at equilibrium, the total change in chemical potential must be zero and therefore this new term in the First Law expression is zero. That is,

$$\mu_1 dN_1 + \mu_2 dN_2 + \dots = 0 \quad (5.144)$$

Substituting in our definition for dG in Eq. 5.128 into Eq. 5.143, we get

$$\underbrace{d(U + P dV - T dS)}_{\equiv dG} = dQ - P dV + \sum_i \mu_i dN_i + P dV - T dS \quad (5.145)$$

and then substituting our reversible Second Law equation in for dQ :

$$dG = T dS + \sum_i \mu_i dN_i - T dS \quad (5.146)$$

$$= \sum_i \mu_i dN_i \quad (5.147)$$

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which is called the *Gibbs-Duhem* equation for constant pressure and temperature. Then at chemical equilibrium

$$dG = \sum_i \mu_i dN_i = 0 \quad (5.148)$$

Recall that by mass conservation, we have the relationship that for a chemical reaction, the rate of change of any one species in the products must be equal in magnitude and the opposite sign of the rate of change of any one species in the reactants. This is expressed simply as

$$-\frac{dN_i}{\nu_i} = \frac{dN_j}{\nu_j} \equiv d\lambda \quad (5.149)$$

where i is some reactant species and j is some product species, ν is the stoichiometric coefficient for the particular species, and $d\lambda$ is some constant. Therefore, Eq. 5.148 is equivalent to

$$dG = \left(\sum_i \mu_i \nu_i \right) d\lambda = 0 \quad (5.150)$$

and at equilibrium

$$\sum_i \nu_i \mu_i = 0 \quad (5.151)$$

Digging a bit deeper, we can relate this equilibrium constraint to state properties by using the definition that $G = H - TS$ as well as the constitutive relationships for an ideal gas:

$$G = \sum_i \mu_i N_i = H - TS \quad (5.152)$$

$$= \sum_i N_i \underbrace{\left[h_{f,i}^\circ + \int_{T_0}^T c_{p,i} dT - T \left(s_i^\circ + \int_{T_0}^T \frac{c_{p,i} dT}{T} - R \ln \frac{P_i}{P_0} \right) \right]}_{\equiv \mu_i} \quad (5.153)$$

where it is clear that the term multiplying N_i is equivalent to μ_i by comparison. Note that here, P_i is the partial pressure of gas species i and is equal to

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$$P_i = X_i P \quad (5.154)$$

by Dalton's Law. We can therefore rewrite our expression for μ_i using the total pressure P as

$$\mu_i = \underbrace{\left[h_{f,i}^\circ + \int_{T_0}^T c_{p,i} dT - T \left(s_i^\circ + \int_{T_0}^T \frac{c_{p,i} dT}{T} \right) \right]}_{\equiv \mu_i^+(T)} + RT \left(\ln \frac{P}{P_0} + \ln X_i \right) \quad (5.155)$$

or

$$\mu_i = \mu_i^+(T) + RT \ln \left(\frac{P}{P_0} \right) + RT \ln X_i \quad (5.156)$$

where the first term is defined as the purely temperature-dependent chemical potential energy, μ_i^+ . Applying our equilibrium condition and pulling out the pressure and concentration terms, we have

$$\sum_i \mu_i \nu_i = \left(\sum_i \nu_i \mu_i^+(T) \right) + RT \left[\ln \left(\frac{P}{P_0} \right)^{\sum \nu_i} + \sum_i \ln X_i^{\nu_i} \right] = 0 \quad (5.157)$$

Rearranging, we find

$$\prod_i X_i^{\nu_i} \left(\frac{P}{P_0} \right)^{\sum \nu_i} = \exp \left(\frac{\sum \nu_i \mu_i^+(T)}{RT} \right) \equiv k_p(T) \quad (5.158)$$

which gives us an expression for $k_p(T)$. In practice, this quantity, as well as the chemical potential energy, is computed from empirical data.

Note that Eq. 5.156 is only valid for an ideal mixture, or one that obeys Raoult's Law, discussed previously in Section 3.2.3. For non-ideal mixtures, this expression is modified to include an empirically derived *activity coefficient*, γ , such that

$$\mu_i = \mu_i^+(T) + RT \ln \left(\frac{P}{P_0} \right) + RT \ln \gamma_i X_i \quad (5.159)$$

not to be confused with the heat capacity ratio.

5.4 The Anthropocene

In the story of climate change, the study of the thermodynamics and engineering behind heat engines and power generation brings us into the *Anthropocene*, a new geological epoch in which the Earth has been dramatically altered by human activity. From the discovery of fire nearly 2 million years ago to the mass combustion of fossil fuels in the present day, the accelerating expansion and energy consumption has pushed the Earth's many feedback loops so far off their natural equilibrium that the evidence can be seen in virtually every ecosystem on the planet, necessitating the demarcation of a new age. Thinking hypothetically to what the geologists of the far future might uncover about this era, it is likely that their geological observations - even in the absence of digital records - will point to an extremely short period of time in which the Earth experienced a major increase in both carbon dioxide concentrations and average global temperature, coupled with an equally severe reduction in sea ice and biodiversity. Additionally, given the wealth of detailed information *we* can glean about the Earth's history over the past 4 billion years, it might also be clear to the future geologists that this shift occurred in such way that had been yet unprecedented. They might be able to tell that this progression had to have occurred external to the natural carbon cycles that had governed the evolution of the planet up to that point with even more sudden and far-reaching than effects than those of the Cambrian Explosion.

Focusing back on the present, as a moment of self-awareness, we should recognize that the thermodynamical principles we have learned in this book thus far and their many scientific and engineering applications are nearly fully responsible for the transition from the Holocene to the Anthropocene. In fact, this particular branch of physics was rapidly developed largely in response to a growing demand for mechanical and later electrical power driving productivity and progress over the last several hundred years. From consumer products to military applications, thermodynamics has been applied at nearly every level in the development of what we consider modernity - including an era-defining change in our climate. As we continue on with this material, we will move to focus on the sustainable application of thermodynamics and the many technologies we may need to change course or in the event of a failure to do so - survive.

Before launching into potential solutions, however, we must take a closer look at the causes and effects of climate change to better understand the problem itself. First, as we learned in Chapter 2, as more CO₂, CH₄, and other greenhouse gases are added to the atmosphere, the global mean temperature rises as a result of the greenhouse effect - the atmosphere becomes a more

effective insulator, trapping ever more thermal radiation from the Sun. We can measure the atmospheric CO₂ concentrations, for instance, and show that it is in fact driving an increase in the global mean temperature. The relationship between the two are not necessarily linear, however, as there are numerous positive feedback loops in the Earth's climate system that are both driven by global warming and human activity in such a way that results in even more warming than we would expect from just the *radiative forcing* from the greenhouse effect alone. For example, as sea ice melts, the once reflective white surfaces at the poles give way to a dark blue ocean that is more effective at absorbing incident solar radiation. At the same time, human expansion is resulting in mass deforestation that greatly hampers the Earth's ability to take up excess CO₂.

The important questions then become, 1) what is the exact relationship between greenhouse gas emissions and temperature rise? and 2) what are the ramifications of a warmer planet? Looking at the former, climate scientists typically frame this problem specifically as, if we double the concentration of CO₂ and equivalent greenhouse gases in our atmosphere relative to pre-industrial levels, what is the corresponding temperature rise? Taking the global average pre-industrial CO₂ concentration to be about 280 ppm, the question then is, what happens if we get to 560 ppm? Studies as early as 1979 have shown that this temperature rise will be somewhere between 1.5-4.5 °C, with more recent studies reducing this uncertainty to 2.5-3.2 °C [1]. As of writing this book in mid 2020, the global average CO₂ concentration is between 410-420 ppm, roughly halfway to the doubling point. Already, the global mean temperature has risen 1.1 °C above pre-industrial levels.

To answer the second question about what that temperature rise induced by greenhouse gas emissions means for the Earth and its various ecosystems, we can look to a comprehensive report issued by the Intergovernmental Panel on Climate Change (IPCC), a group of the world's leading climate scientists and economists. In their 2018 special report (SR15), they detail and compare the effects of both a +1.5 °C and +2 °C warming scenario, as well as make the well-supported case that the roughly 1 °C warming between 1850 and 2018 has already negatively impacted a wide swath of the Earth's climate system. Current observed effects include more frequent and severe heatwaves over virtually every landmass, more frequent heavy precipitation events and severe weather events, increased drought in the Mediterranean region, sea level rise, and a loss of biodiversity in many biomes, among many more. With an additional 0.5-1 °C warming, these consequences will likely be magnified, placing further strain on the many ecosystems that simply have not had time to adapt. Additionally, with this additional warming and associated increase

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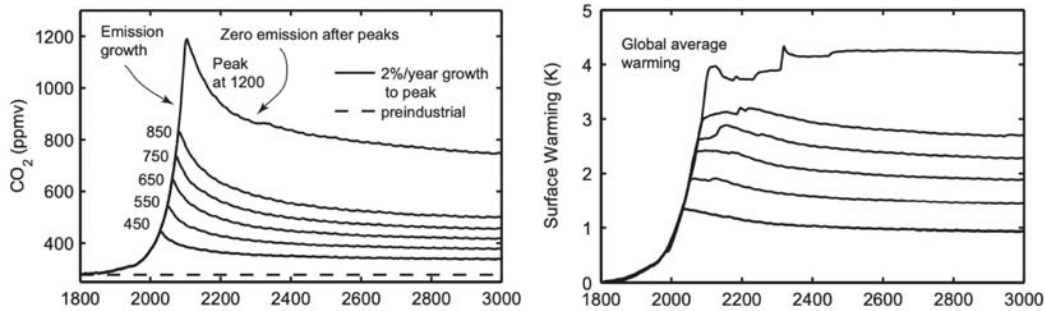


Figure 5.14: Plots showing how the carbon dioxide concentrations in the atmosphere and associated mean surface temperature increase can linger for over 1000 years even after emissions cease [3]. Image courtesy of Susan Solomon, Gian Kasper Plattner, et al. "Irreversible Climate Change due to Carbon Dioxide Emissions." *PNAS*. February 10, 2009. 106 (6) 1704–1709.

in carbon dioxide concentrations ocean acidification is expected greatly reduce the productivity of the oceans, threatening the food security of a major portion of the Earth's human population [2].

This report also showed that while the least of these effects can no longer be avoided, there remains a significant difference in their severity between the 1.5 and 2 °C warming scenarios. Limiting the warming to 1.5 °C - which is far lower than the well-established 2.5-3.2 °C climate sensitivity value we are hurtling towards - stands to greatly reduce the threat of mass extinction of insects, plants, and vertebrates, limit sea level rise, comparatively reduce the threat of severe forest fires, and even help limit the spread of disease. As detailed in this report, the case for preventing additional warming past 1.5 °C is well made, and though the Earth would still be left with many detrimental impacts of climate change that are already coming into focus, we made be able to avoid the worst of them. Regardless, there is yet some uncertainty surrounding several tipping points that, for example, would result in the majority of the Greenland and Antarctic ice sheets melting, resulting in a multi-meter sea level rises over next several centuries - which against the backdrop of even the human timeline, let alone evolution, is troublingly short.

The final point to reiterate about the Anthropocene here is that in some sense, humanity has pushed well past the point of no return on its far-reaching alteration of the natural world. Report after report details the loss of biodiversity, increase in extreme weather events, and more frequent flooding, among others, that are at this point *historical* - there is no hypothetical climate change. The climate *has* changed and we are at the point where we can play a role in limiting this change. What is important to note is that simply stop-ping carbon emissions, while extremely important, will not undo what has

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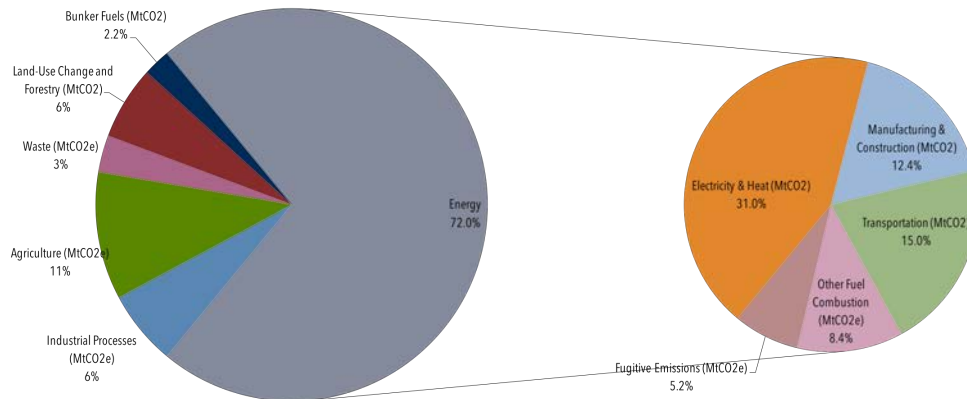


Figure 5.15: Global carbon emissions broken down by sector [source].

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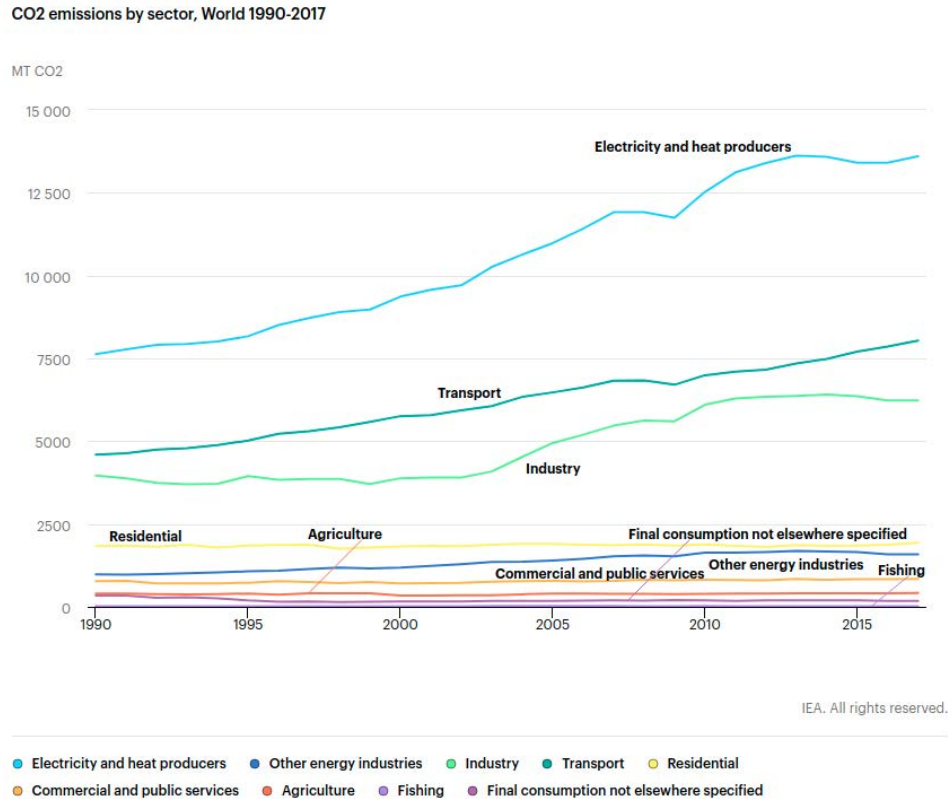
already been done. In a landmark study in 2009, Solomon et al showed that this climate *inertia* can be quantified. As illustrated in Fig. 5.14, without removing CO₂ from the atmosphere, its concentration will remain at its elevated value in the atmosphere for over 1000 years after the emissions cease, with the associated mean surface temperature rise stabilizing at its elevated value as well [3]. Indeed, we are pushing well past the limits of the Earth's own carbon feedback loops to regulate these added emissions as we approach a new equilibrium, further justifying giving this era its own name.

5.4.1 Current Climate Change Drivers

So to recap, we know with a high degree of certainty that humans are emitting more CO₂ that can be taken up by the Earth's natural carbon cycle, and that a doubling of concentrations above pre-industrial levels to 560 ppm would result in a temperature rise of 2.5-3.2 °C with a high degree of certainty. As the IPCC report shows, an Anthropocene characterized by even a 1.5-2 °C warming would be bad news for a majority of the Earth's ecosystems and would take thousands of years to recover from via the Earth's natural feedback mechanisms. That leaves us with the question of how do we stop this?

Before getting into the strategies for mitigating the ensuing climate crisis, it is first necessary to take a more detailed look at exactly where exactly these emissions are coming from. If we look to Fig. 5.15, we can see that the majority of the Earth's carbon emissions come from the energy sector and are driven by the combustion of fossil fuels in very heat engines we have learned about

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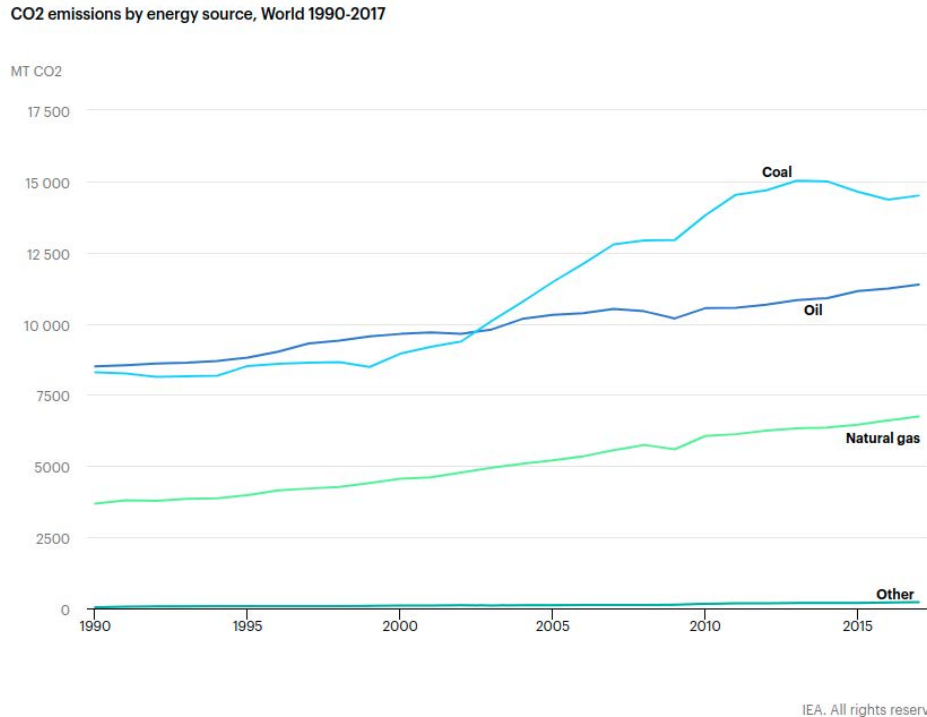
Figure 5.16: Global annual CO₂ emissions for each major carbon-intensive economic sector [IEA].

here. The International Energy Agency (IEA) maintains detailed reports on the global energy consumption and greenhouse gas emissions broken down by a variety of different categories and metrics. Fig. 5.16 shows a breakdown of global annual CO₂ emissions from 1990 to 2017 for key economic sectors. As is shown here, the top three most carbon-intensive sectors are electricity and heat production, transportation, and industry, which includes emissions associated with the production of raw materials and commodities⁶.

Currently, the carbon emissions associated with electricity and heat production as well as transportation come from the direct combustion of fossil fuels. Of these emissions, we can see from Fig. 5.17 that as of 2017, the ma-

⁶Aluminum production for example has significant carbon emissions from the electrochemical reaction that reduces aluminum from aluminum oxide.

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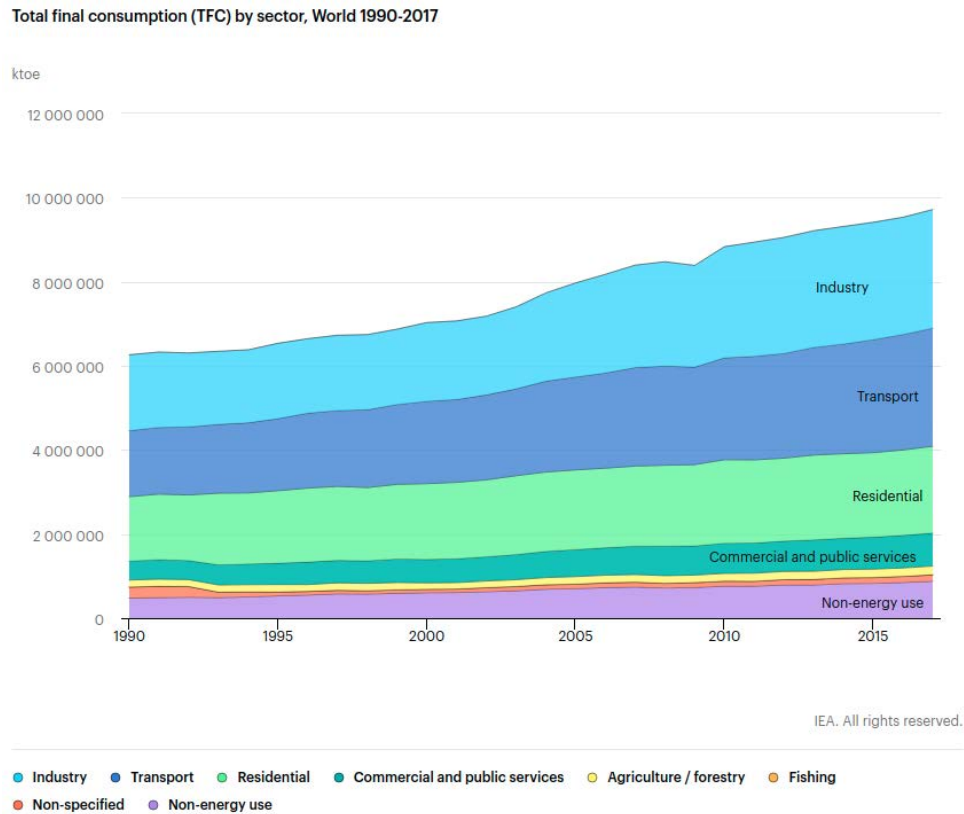
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Figure 5.17: Global annual CO₂ emissions for each major carbon-intensive energy source [IEA].

majority still come from coal and oil, which is driven in part by the high carbon intensities of those fuel sources as well as their global ubiquity, as also illustrated in Fig. 5.19. The growth of natural gas emissions shown in this figure are largely due to the increasing prevalence of natural gas combustion plants that are displacing coal power plants, especially in the United States. The corresponding dip in coal emissions since 2013 are primarily a result of this shift towards natural gas usage as well and less so a result of the adoption of renewable energy sources, which we will soon discuss.

It is also important to note that in Fig. 5.17, the annual global carbon emissions associated with the combustion of fossil fuels continue to increase, despite the greater adoption of less carbon-intensive fuel sources and more efficient infrastructure. This disparity illustrates the second primary issue at play - the more efficient consumption of energy grows the global economy, which in turn drives more energy consumption. As shown in Fig. 5.18, the global annual energy consumption in nearly every economic sector is increasing

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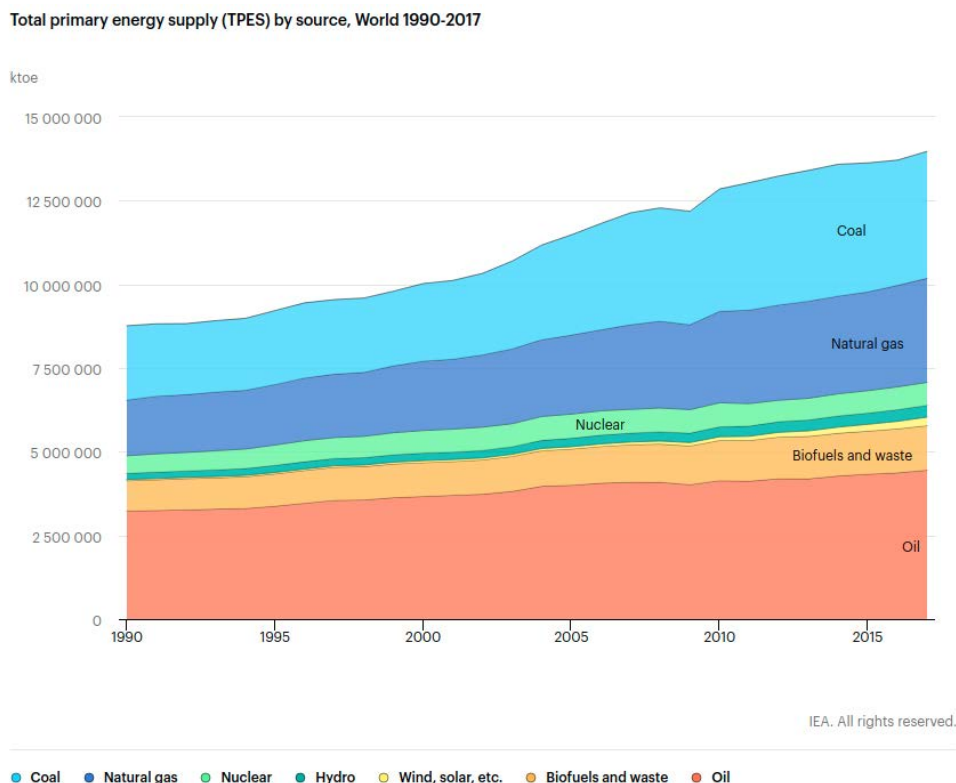
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Figure 5.18: Total global annual energy consumption broken down into various economic sectors [IEA].

and so too is the total global annual energy consumption, making climate change mitigation an extremely challenging problem. This phenomenon helps to explain why in Fig. 5.19, we see the yearly consumption of fossil fuels increasing steadily. These trends are especially alarming given that there is an upper limit on *cumulative* carbon emissions since the Industrial Revolution associated with limiting global warming to a safer temperature increase. From just these four plots by IEA, we can paint a sobering picture of the total issue wherein both energy consumption and the proportional usage of fossil fuels are increasing.

This landscape consisting of these multiple compounding issues requires solutions that address both the reduction of energy consumption and greenhouse gas emissions. As we will see, however, these measures alone will likely not be

5.5. SUMMARY



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Figure 5.19: Total global primary energy supply broken down by source, showing that even though renewables are expanding, so too fossil fuels [IEA].

enough to mitigate the crisis and additional CO_2 will need to be taken from the atmosphere. It is perhaps safe to say that the tools built using the knowledge garnered through the study of thermodynamics have largely brought us to this critical tipping point and continue to push us well into uncharted territories. As we will soon see, however, these same principles might be able to be used to mitigate this crisis.

5.5 Summary

In this chapter we bridged the short gap between the discovery of fire and the first use of chemical combustion reactions to generate power, as well as the even shorter gap between what is considered the Industrial Revolution and the present self-ascribed *Anthropocene*. We took a detailed look at how the First

and Second Laws of Thermodynamics can be used to construct heat engines to continuously convert the thermal energy released in combustion into mechanical work to meet the world's ever-growing energy demands, which account for the vast majority of anthropogenic greenhouse gas emissions. In looking at external and internal combustion engines, as well as continuous flow power systems, we developed a framework for determining how much mechanical work can be extracted for a given input of thermal energy, a relationship that defines the carbon emissions per unit output of energy associated with different fuel sources and power system architectures. Finally, we discussed the harm that these emissions have caused through climate change and the importance and urgency of reducing them to avoid a 1.5 °C warming.

Up to this point in the story of climate change, we have answered many of the questions pertaining to how we got here and why this is such an unprecedented and important problem to solve. Naturally then, the next question to tackle is how do we solve it?

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