Chapter 6

A Return to Renewables

In the story of climate change, we are mostly caught up to the present, where the reality of a *climate crisis* is bearing down upon us. With the urgency of the issue and the many daunting challenges it presents humanity, there is not the option to *not* solve it if we wish to achieve climate stability with only a moderate global average temperature rise. Despite the severity and progression of this crisis - which has already resulted in a temperature rise of 1.1 °C above pre-industrial levels by mid 2020 - there is significant motivation to not let that warming exceed 1.5 °C. Indeed, every additional degree of warming presents more severe and wider reaching consequences for our species and the many ecosystems on which we rely, and makes it more difficult to reverse course. The transition to a carbon neutral and ultimately carbon negative society can no longer a question of *if* but rather *when* - the best science we have at our disposal tells us the sooner the better.

With the motivation in place for sweeping societal changes that move us towards global sustainability, we can begin to look at how this transition might occur and the tools we have at our disposal. In this and the following chapters, we will cover several key approaches, all of which will likely need to be implemented to some degree in parallel in order to make any substantial progress. First, in this chapter we will start with the biggest emissions source shown in Fig. 5.15 - energy conversion. In short, we must simply stop emitting CO_2 as a result of burning fossil fuels for energy to power our daily lives - not just make these processes more efficient. This means natural gas, coal, oil, and its derivatives must be eventually phased out in favor of *renewable* and *net neutral* energy sources like solar, wind, and geothermal. In the short term, carbon-neutral nuclear energy will also likely play an important role. We will look at the thermodynamics behind some of the most promising technologies in this space.

Next, to solve the intermittency issues posed by renewable energy sources - in particular solar and wind which both have guaranteed downtime - we will also need new and better ways to store energy that is collected when it is not needed for when it is. To this end, we will take a look at the thermodynamics of electrochemistry, which is the basis for most batteries used today, as well as physical means of storage that use gravitational potential energy to help flatten power generation curves. We will also look at the carbon-neutral generation and consumption of hydrogen as an effective means of storing and transporting energy as well. Combined, these technologies have the capability to help restore our ability to use rewewable energy to meet global demand sustainably.

6.1 Renewable and Carbon-Neutral Energy

Renewable energy encapsulates all sources of energy that *regenerate* naturally on a timescale comparable to that of its usage or that are expected to last far into the future - providing energy in a useful form for millions or even billions of years. These sources include the sun, wind, rain, tides, geothermal wells, and biofuels, which with the exception of geothermal wells[1] and lunar tides, are actually all different forms of solar energy as we learned in Chapter 2. This is to be expected, though, as from a pure thermodynamic systems perspective, nearly all of the energy that is continuously being added to the Earth system is solar radiation. Fossil fuels are stored solar energy as well, but we do not consider them renewable as it takes millions of years for them to regenerate naturally - much longer than the timescale on which we consume them today.

In reality, we know from the Laws of Thermodynamics that no source of energy is truly infinite and renewable. As the Second Law tells us, hot condensed energy has a tendency to cool and spread out until the point where no useful work can be extracted and entropy is maximized. Our Sun and geothermal wells are no different; however, while the Sun, like all stars, will eventually burn out, it is expected to have enough fuel for fusion to last for another 5 to 10 billion years - well past the point where the sun is expected to expand and swallow the Earth and this conversation becomes irrelevant. Similarly, the now extremely hot core of the Earth is expected to eventually cool and freeze as happened with Mars, but again not for billions of years. It is therefore safe to say that these sources are renewable on timescales that are compatible with the story of humanity and its utilization of energy.

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[1]though recall the thermal energy at the Earth's core is a remnant of the energy released from the supernova death of a star and is in a way solar energy, just not from our Sun.

In the story of climate change specifically, as we know all too well at this point, the consumption of *non*-renewable energy sources has led to the emission of greenhouse gases on a timescale that is incompatible with the rate of the natural sequestering of those emissions and subsequent regeneration of the energy sources. Moving forward, if humanity wishes to slow and ultimately stop the progression of climate change, one important strategy is to widely replace these fossil fuels with renewables to eliminate *net* emissions. An important distinction to make here is that renewable energy sources are not necessarily emission free; but rather, are *carbon-neutral* on a relatively short timescale. For example, biofuels derived from the processing of live organic plant matter can be combusted in place of fossil-based gasoline, diesel, and methane but still produce the same amount of emissions that the fuels they are replacing would. The key difference is that because the biofuels are produced from living or recently alive organic matter, the equivalent carbon emitted by their combustion will be taken out of the atmosphere when the plants, trees, etc. grow back within a few years. If this emission and reuptake cycle is short enough, the total average concentration of CO_2 will remain constant. Technically, even the carbon dioxide emitted from burning fossil fuels might eventually be taken back in by living organisms, but the time required for carbon neutrality is millions of years - much longer than the time expected for humans to exhaust fossil fuel reservoirs.

There is also a class of energy sources that are not renewable but are carbon-neutral and therefore will need to play a prominent role in climate change mitigation as well. In particular, fission-based *nuclear* energy requires the consumption of fissile radioisotopes of elements like uranium and plutonium to produce an enormous amount of heat and solid waste. If the heat released in the nuclear reactions is used to drive a Rankine cycle, no CO_2 is emitted in the steady-state energy production process and is thus considered to be carbon neutral. We will discuss this energy source as well as the previously mentioned renewable sources in greater detail here.

6.1.1 Solar Energy

Solar energy in the context of renewable energy typically refers to thermal radiation that is captured and either used or stored directly as thermal energy, converted to mechanical work via various types of heat engines, or used to provide electrical work through devices that utilize the *photovoltaic effect*. As shown in Fig. 6.1, there is a significant amount of energy that arrives at the Earth's surface; however, it is highly concentrated in certain regions, which is largely a function of weather and both the amount of types of vegetation.
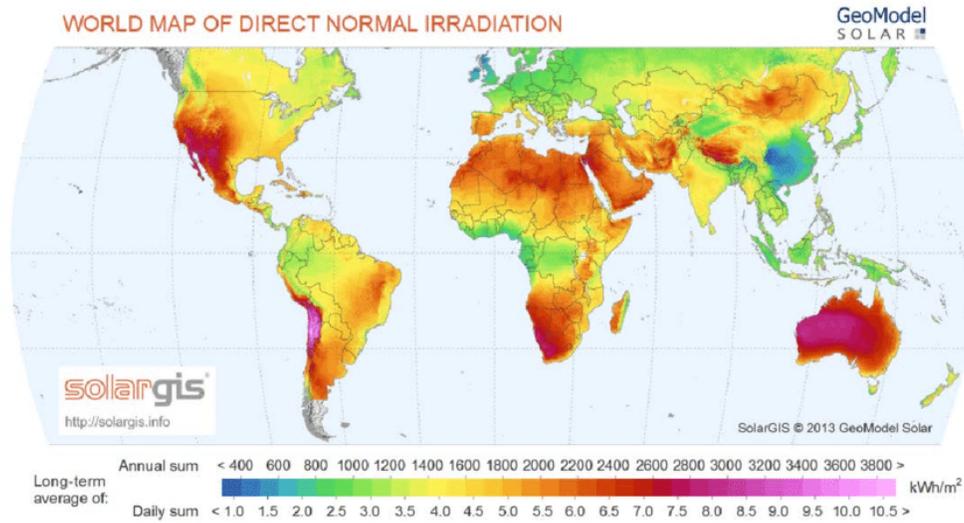
Figure 6.1: Average daily and annual global solar irradiance in kWh/m^2. *Direct normal* refers only to sunlight that arrives perpendicular to the Earth's surface [Solargis].

As expected, desert areas see the largest solar *irradiance* - radiative power or energy per unit area. To get a sense for how much is available, note that the current global energy demand is roughly 35,000 TWh per year. At a solar irradiance of 2,500 kWh/yr-m^2, this would require a surface area of about 14,000 km^2, not including efficiencies of energy conversion[2]. For reference, the area of Nevada, which sees some of the highest solar irradiance in the United States, is over 286,000 km^2! From Fig. 6.1, we can easily see that even at low energy conversion efficiencies, there is more than enough solar energy present to meet the world's energy demands many times over. The question then becomes, how can we actually utilize this energy?

For the direct thermal energy utilization, there is not much else in terms of thermodynamics that can be said beyond what we discussed in Chapter 2. On a practical note, much of the energy used globally is needed as heat directly to drive a wide array of industrial processes, space heating, cooking, and water purification and *desalination* in many parts of the world. As we learned, high frequency solar radiation is absorbed by gray bodies and re-emitted as lower frequency thermal radiation. The temperature and therefore internal energy

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[2]With a capacity factor of 0.25 and a First Law efficiency of 0.2, this value becomes 280,000 km^2.
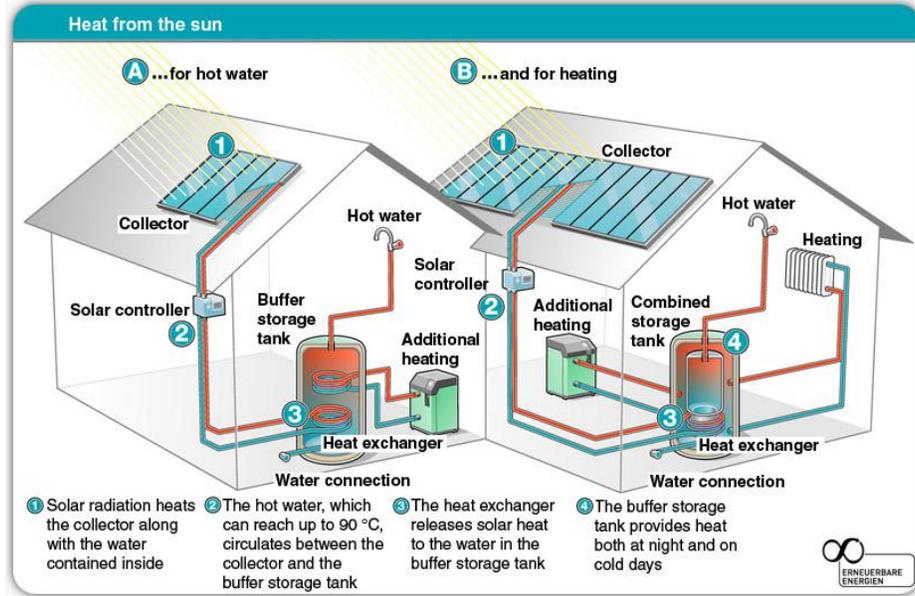
Figure 6.2: Example home system that uses solar thermal energy directly to provide water and space heating demands [source].

of the bodies adjusts such that in equilibrium, the heat fluxes in and out are perfectly balanced. In fact, the outer layer of the Sun itself is in such an equilibrium as gamma rays and other extremely high frequency radiation released in the nuclear fusion reactions at the Sun's core are absorbed by the mostly hydrogen and helium gases in the outer layers, which then re-emit lower frequency radiation. The temperature of this outer layer reaches about 5800 K under these equilibrium conditions.

On Earth, this phenomenon is used to provide solar-powered heating and cooling for water and air at the residential scale. For example, vacuum-insulated solar *collectors* with high emissivities are placed on roofs to absorb solar radiation without significant heat loss to the environment. A working fluid is circulated through the collector where it heats up and then transfers that heat to the residential hot water line or to a radiator to heat internal rooms. Fig. 6.2 shows two example configurations of this type of system, which can be used to supply seasonal heating needs. Because solar energy is inherently intermittent, excess energy must be stored to supply heating power overnight, for example. Several thermal energy storage mechanisms have been already been discussed previously and we will go into greater detail later in

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Figure 6.3: 110 MW Crescent Dunes Concentrated Solar Power plant in Nevada, US which uses a giant mirror array to direct sunlight to heat a working fluid at the top of a central tower. This high temperature working fluid - typically molten salt - is then used as the high temperature thermal reservoir for a power cycle [source]. **Image courtesy of DOE.**

this chapter.

Mechanical Work Conversion

If instead mechanical work is needed, solar thermal energy can be used to drive a heat engine via one of the many external heating-based architectures we previously discussed - Stirling or Rankine Cycles, for example. To achieve the high temperatures necessary for high First Law efficiencies, giant mirror arrays are typically used to capture a wide area of sunlight and direct it towards a central thermal reservoir that absorbs the radiation to heat an internal working fluid. This fluid, typically molten salt heated in the range of 400-750 °C, can then be used as the heat source to run a power cycle nearby. Fig. 6.3 shows an example plant located in the United States in the desert in Nevada. Here, each mirror in the array is capable of tracking the sun, continuously directing the sunlight at the central thermal reservoir tower.

In this type of solar-thermal power system, the overall efficiency is a factor of several different sources of energy loss. First, the mirrors themselves

will not be able to perfectly reflect incident radiation due to dust accumulation and manufacturing defects and thus have an associated efficiency, η_{mirror}. Additionally, as is evident from Fig. 6.3, the fact that the top of the thermal tower appears bright white means that a potentially significant amount of thermal radiation is being emitted from the thermal reservoir itself. This radiated energy is lost to the environment and cannot be converted to work. This efficiency, η_r, is given as

$$\eta_r = 1 - \frac{Q_{out}}{Q_{in}} \tag{6.1}$$

where Q_{out} is given by the Stefan-Boltzmann equation as

$$Q_{out} = A\varepsilon\sigma T_H^4 \tag{6.2}$$

where A is the surface area of the high temperature thermal reservoir and T_H is its temperature. Q_{in} is a function of the solar irradiance $\dot{q}''_{solar}$, the concentration factor C, A, the absorptivity of the reservoir α, and the mirror efficiency as

$$Q_{in} = \eta_{mirror}\alpha\dot{q}''_{solar}CA \tag{6.3}$$

and thus

$$\eta_r = 1 - \frac{\varepsilon\sigma T_H^4}{\eta_{mirror}\alpha\dot{q}''_{solar}C} \tag{6.4}$$

Finally, the power conversion cycle will have a First Law efficiency, η_{cycle}, which in the ideal case is equal to the Carnot Efficiency, $1 - T_a/T_H$. In the ideal case, the total efficiency, η_{total} is given as

$$\eta_{total} = \eta_r\eta_{cycle} \tag{6.5}$$

$$= \left(1 - \frac{\sigma T_H^4}{\dot{q}''_{solar}C}\right)\left(1 - \frac{T_a}{T_H}\right) \tag{6.6}$$

Here ε, α, and η_{mirror} are all assumed to be equal to 1 for the ideal case. It is interesting to note here that there are competing phenomena governing the performance of this type of system - a higher temperature thermal reservoir means higher Carnot efficiency but also means greater heat loss to thermal radiation. As a result, if we plot the efficiency as a function of this top temperature, we would expect there to be a maximum efficiency at some temperature value roughly in between the two values where Eq. 6.5 is equal

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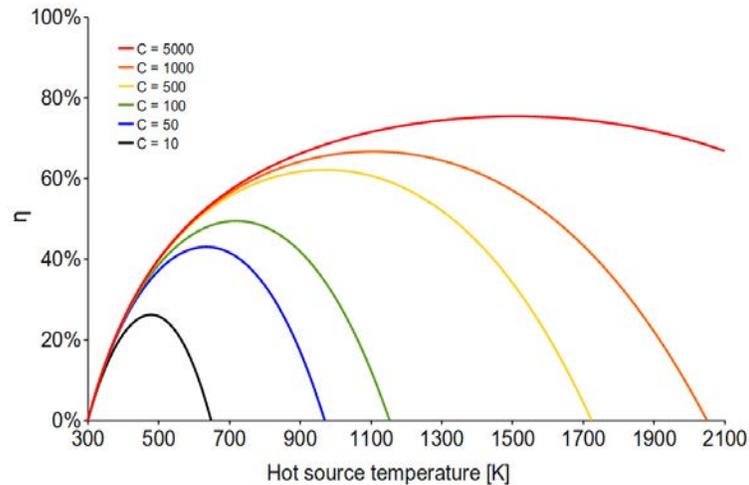
Image courtesy of MarcChambon on Wikimedia. License: CC BY-SA. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use.

Figure 6.4: Total ideal efficiency of a concentrated solar power plant as a function of T_H shown for different concentration factors, C [source].

to zero - $T_H = (\dot{q}''_{solar} C / \sigma)^{1/4}$ and $T_H = T_a$. Indeed, Fig. 6.4 shows the total efficiency plotted as function of T_H for several concentration factors, C, and we can see that as expected, there exists a temperature at which the efficiency is a maximum. This poses some interesting design considerations to be made when installing and operating such a power plant. Given that the solar irradiance fluctuates throughout the day, care must taken to ensure that the efficiencies are balanced with energy demand. It may make sense, for example, to direct some of the sunlight away from the thermal reservoir during peak solar hours to avoid some losses associated with going to higher top temperatures.

Photovoltaics

In the mechanical energy conversion systems we have discussed so far, what has been implicit but not mentioned explicitly is that much of the mechanical work produced is immediately converted to electricity, typically at very high efficiencies[3]. Despite the high mechanical-to-electrical efficiency, the overall performance, however, is limited by the Carnot Efficiency, which again is a statement of the Second Law. If solar energy is available and electricity is needed, the heat engine can be bypassed and electricity can be generated

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[3]For example, Siemens generators can achieve efficiencies $> 99\%$ for converting mechanical to electrical work.

Figure 6.5: Basic operation of a photovoltaic (PV) cell [source].

directly via the *photovoltaic* effect.

In order to completely understand the photovoltaic effect, it is necessary to know several concepts from electromagnetism and quantum mechanics and is therefore beyond the scope of this text. The simplified explanation, however, is that when *photons*[4] strikes an electron, it brings the electron to a higher energy state. When two different types of materials with different amounts of *free* electrons and positive charge carriers are brought together, photons that strike at the interface of the materials cause different levels of excitation in both material, generating an imbalance in charge and thus a *voltage*. As shown in Fig. 6.5, this voltage is then able to drive a net flow of electrons called current. As these electrons flow around a circuit, electrical work can be extracted as

$$W_e = IV \tag{6.7}$$

where I and V are the current through and voltage across the *photovoltaic (PV) cell*. Interestingly, though we will not derive it here, the *open-cell* voltage of a PV cell with no current flowing is proportional to the *thermal voltage*, V_T, equal to

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[4]The quantized particle representation of a light wave (radiation).

OCW V1

$$V_T = \frac{k_B T}{q} \tag{6.8}$$

where k_B is the familiar Boltzmann Constant and q is the charge of a single electron[5]. The open-cell voltage, V_{OC} is given as

$$V_{OC} \approx V_T \ln\left(\frac{I_L}{I_0}\right) \tag{6.9}$$

where I_L is the current induced by the photovoltaic effect and I_0 is the *reverse saturation current*. While those terms may seem obscure, it is important to understand that this voltage difference is a function of the cell temperature.

When placed into a *circuit*, the voltage of a PV cell will vary as a function of how much current is flowing. As Fig. 6.6 shows, for a typical PV cell, the current remains roughly constant over a wide range of cell voltages and then abruptly drops to zero at the open-cell voltage. Viewed another way, as the current produced by the cell increases, its voltage drops. Since power is the product of current and voltage, we can plot this as a function of voltage as well, as shown in Fig. 6.6 in blue. As expected, the maximum power point is achieved near the *knee* in the *I-V* curve. In practice, PV cells are designed to run at this point, and the current is controlled externally to ensure maximum power output.

From a practical engineering perspective, we can treat a PV cell as a *current source* with a First Law efficiency, η_{PV}, equal to

$$\eta_{PV} = \frac{IV}{\dot{Q}_{solar}} \tag{6.10}$$

where $\dot{Q}_{solar}$ is the incident solar irradiance. Fig. 6.7 shows how this efficiency has improved for production solar cells since the 1990's. Currently, high-efficiency solar cells can convert up to 25% of the incoming solar radiation to electrical power. It has been shown that for a single interface absorbing sunlight, the maximum theoretical efficiency is around 30% in what is called the *Shockley-Queisser Limit* [1]. Higher efficiencies around 45% can be achieved with multiple interfaces that are tailored to specific bands within the solar spectrum. Compared to the ideal efficiencies that can be achieved for high-temperature concentrated solar power shown in Fig. 6.4, however, PV cell efficiencies are much lower. That said, by comparison, PV cells are much more flexible in terms of how and where they can be installed. In particular,

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[5]1.602176634x10^{-19} Coulombs
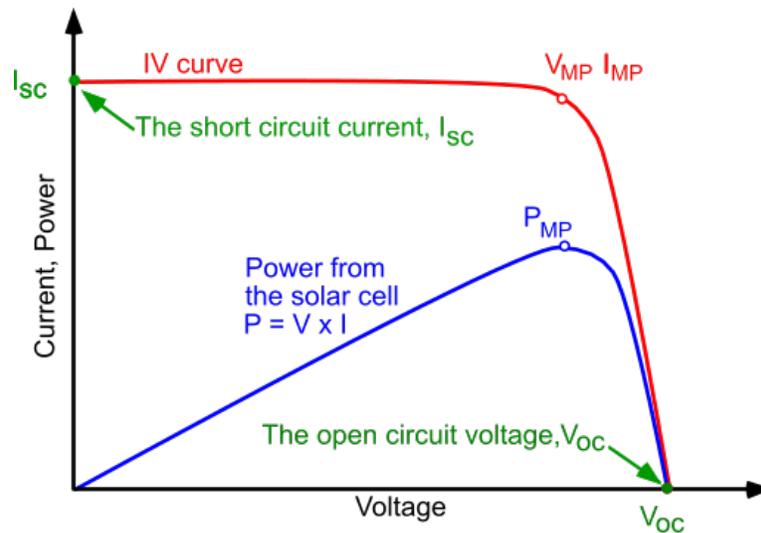
Figure 6.6: Current-Voltage and Power-Voltage curves for a typical solar cell [source].

concentrated solar power plants must be constructed in wide open areas and require a significant amount of specialized materials and equipment to operate at high temperatures. In comparison, solar panels can be placed on rooftops in cities as they require little extra infrastructure or space. Indeed, both energy conversion strategies are highly important for mitigating climate change as they serve different purposes and usage cases.

6.1.2 Wind Energy

Wind energy is another manifestation of solar energy. Even though solar radiation provides a more-or-less constant heat flux into the thermodynamic climate system, it does not do so uniformly, causing the temperatures of the air and various bodies of water to vary significantly over the Earth's surface. We can observe easily, for instance, that the weather in Antarctica is different than in the Middle East. As we would expect, these global temperature *gradients* in both the oceans and atmospheric create pressure gradients as well that drive the flow of water and air from regions of high temperature and pressure to regions of lower temperature and pressure. We call the moving water *currents* and the air *wind*. Moving a fluid across a pressure drop requires work as we have learned, and in the climate system, the energy driving these processes

PV System Efficiency
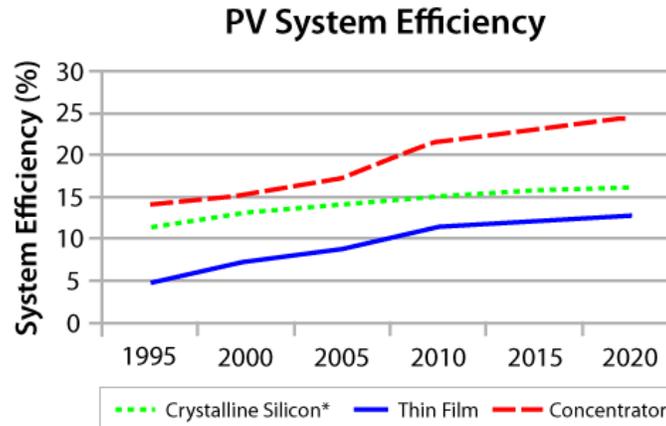
Figure 6.7: Average solar cell efficiencies for several production-ready technologies. In lab settings, efficiencies as high as 47% have been reported for *multi-junction* solar cells capable of extracting electrical work from a broader range of the solar spectrum. Image courtesy of DOE.

comes largely from the Sun[6].

Looking at the First Law for a stream of moving between two points in the atmosphere, as shown in Fig. 6.8, we see that

$$\cancel{\dot{E}_{CV}} = \dot{Q} - \dot{W} + \dot{m}\left[(h_1 - h_2) + \frac{1}{2}(|\vec{v_1}|^2 - |\vec{v_2}|^2)\right] \tag{6.11}$$

$$\tag{6.12}$$

where we have introduced a new term to keep track of the macroscopic *kinetic* energy of the flow. For wind comprised of an ideal gas, heat transfer to and from the control volume is typically negligible and thus can be considered roughly adiabatic. The work extracted is thus

$$\dot{W} = \dot{m}\left[c_p(T_1 - T_2) + \frac{1}{2}(|\vec{v_1}|^2 - |\vec{v_2}|^2)\right] \tag{6.13}$$

The turbines we have studied previously extract energy from the flow by lowering the stream's enthalpy; however, with wind turbines, this energy is

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[6]Some energy also comes from lunar tides. Also much of the observed weather patterns comes from the fact that the Earth is rotating and result *Coreolis* forces; however, these forces do not require nor do any work.
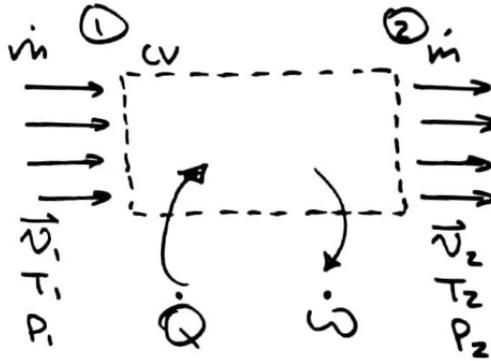
Figure 6.8: General control volume for fluid stream.

instead extracted from the stream's kinetic energy as it passes through the turbine blades. Specifically, momentum is transferred from the wind to each blade, causing it to rotate and slowing the velocity of the stream. For the type of horizontal-axis turbine shown in Fig. 6.9, we can draw a control volume around the air stream before and after the turbine as in Fig. 6.10. To compute the maximum work we can extract from this type of configuration, we can start by applying conservation of mass. We know that mass must enter and exit the control volume at the same rate, and thus

$$\dot{m} = \rho A_1 v_1 = \rho A_2 v_2 = \rho A v \tag{6.14}$$

where A and v are the cross-sectional area and velocity at the turbine[7]. This gives us a relationship between the two cross-sectional areas and velocities as

$$A_1 v_1 = A_2 v_2 = A v \tag{6.15}$$

Clearly, because the stream slows, it must expand to match the incoming mass flow rate. To compute the ideal mechanical power, we can assume in the ideal case that the wind density and temperature does not change between states 1 and 2. Under this assumption, Eq. 6.13, gives us

$$\dot{W} = \frac{1}{2}\dot{m}(v_1^2 - v_2^2) \tag{6.16}$$

$$= \frac{1}{2}\rho A v(v_1^2 - v_2^2) \tag{6.17}$$

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[7]The vector notation has been dropped for clarity. $v_i \equiv |\vec{v_i}|$.
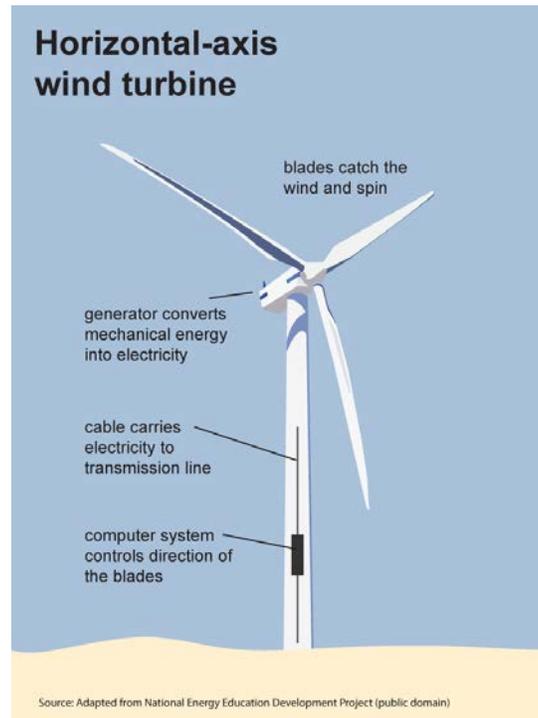
Image courtesy of EIA.

Figure 6.9: Schematic of a typical horizontal-axis wind turbine [EIA].

To solve for $|\vec{v}|$, we can compute the mechanical power extracted by the turbine by looking at the force, F, that must be applied by the turbine blades to slow the flow. The force is simply the time rate of change of momentum, which in this case is

$$F = \Delta\dot{p} = \dot{m}(v_1 - v_2) \tag{6.18}$$
$$= \rho A v(v_1 - v_2) \tag{6.19}$$

The power at the turbine is the product of force and velocity, which gives us

$$\dot{W} = Fv = \rho A v^2(v_1 - v_2) \tag{6.20}$$

Now we have two equivalent expressions for $\dot{W}$ and so can equate them to solve for $|\vec{v}|$:
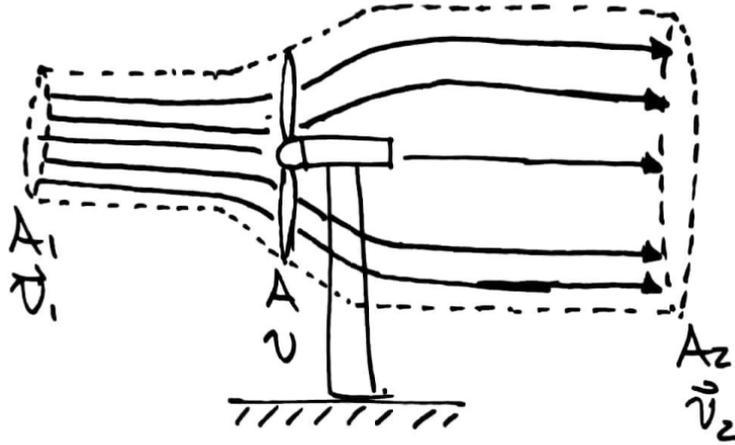
Figure 6.10: Control volume for air passing through wind turbine. As air slows across the turbine, it must expand to obey conservation of mass.

$$\frac{1}{2}\rho A v(v_1^2 - v_2^2) = \rho A v^2(v_1 - v_2) \tag{6.21}$$

$$\frac{1}{2}(v_1 + v_2)(v_1 - v_2) = v(v_1 - v_2) \tag{6.22}$$

$$\Rightarrow v = \frac{1}{2}(v_1 + v_2) \tag{6.23}$$

which is simply the average of the initial and final velocities. Plugging this expression for v back into Eq. 6.17, we get

$$\dot{W} = \frac{1}{4}\rho A(v_1 + v_2)(v_1^2 - v_2^2) \tag{6.24}$$

or

$$\dot{W} = \frac{1}{4}\rho A v_1^3 \left[1 + \left(\frac{v_2}{v_1}\right) - \left(\frac{v_2}{v_1}\right)^2 - \left(\frac{v_2}{v_1}\right)^3\right] \tag{6.25}$$

Intuitively, we might expect there to be a maximum value for the power that can be extracted by a turbine. If $v_2/v_1 = 1$, no power is extracted from the wind as its kinetic energy remains the same; however, as v_2/v_1 approaches 0, a considerable pressure builds up as air slowing down after the turbine prevents new air from passing through. This pressure starts to detract from

the work we can extract. Indeed, if we set the first derivative of Eq. 6.25 with respect to v_2/v_1, which we will call ξ, we find that

$$\frac{d}{d\xi}\dot{W} = 0 \tag{6.26}$$

$$\frac{1}{4}\rho A v_1^3 \left(1 - 2\xi - 3\xi^2\right) = 0 \tag{6.27}$$

$$\left(x - \frac{1}{3}\right)(x + 1) = 0 \tag{6.28}$$

which gives us roots at 1/3 and -1. Since v_2/v_1 is positive, we know then that the maximum power occurs at $v_2/v_1 = 1/3$. Plugging this value into Eq. 6.25 yields the maximum power

$$\dot{W}_{max} = \frac{8}{27}\rho A v_1^3 \tag{6.29}$$

To determine a maximum First Law efficiency, this value can be divided by the power of a stream with the same cross-sectional area of the turbine traveling at v_1 ($1/2\dot{m}v_1^2 = 1/2Av_1^3$):

$$\eta_{turbine,max} = \frac{\frac{8}{27}\rho A v_1^3}{\frac{1}{2}Av_1^3} \tag{6.30}$$

$$= \frac{16}{27} = 0.593 \tag{6.31}$$

which is called the *Betz Limit*. In reality, actual wind turbines will experience loss due to *turbulence* and thermal dissipation that generates entropy and therefore detracts from the maximum work that can be extracted from the stream. Modern turbines, however, can reach efficiencies of up to 0.5, or about 84% of the Betz Limit, in ideal conditions.

While this performance metric is important for evaluating a single turbine, the analysis gets much more complex when you have a field of wind turbines as shown in Fig. 6.11. Given that the air that has passed through the turbine slows down considerably and in the real case can be quite turbulent, wind turbines cannot be placed close together or both will suffer a loss in efficiency and performance. In practice, large wind turbines are typically placed 150-200 m apart, leading to the important question: how much power can be generated per unit area? Or in other words, what is the total effective power density of a wind farm? Given these spacing requirements, at peak capacity, large farms

Figure 6.11: Wind farm showing multiple wind turbines [Photograph by Inga
Spence / Alamy Stock Photo].

in the 200 MW range average about 10 W/m^2. It is tempting to compare this
value with solar irradiance, but it is worth noting that wind power is typically
used where solar power is impractical due to geography or low solar irradiance.

6.1.3 Hydropower

Hydropower is exactly analogous to wind power in that we can extract energy
from a stream by reducing its kinetic energy. In the case of hydropower, this
energy is extracted from literal streams, rivers, and other sources of flowing
water. Instead of being driven by thermal gradients as with wind, the energy
here is largely the result of the conversion of gravitational potential energy to
kinetic energy as the water flows from high to lower elevations. In the end,
though, this is still solar powered as the sun-driven water cycle transports wa-
ter from low to higher geographic regions via evaporation and precipitation.
Thermodynamically, we can treat wind ad hydro energy sources similarly and
thus the equations for power extraction will be nearly identical, with the pri-
mary modifications occurring in the density of the fluids.

Tidal Energy

A subset of hydropower is power extracted from flowing water that moves as a
result of the tidal forces of both the Sun and Moon. As the tides go in and out,
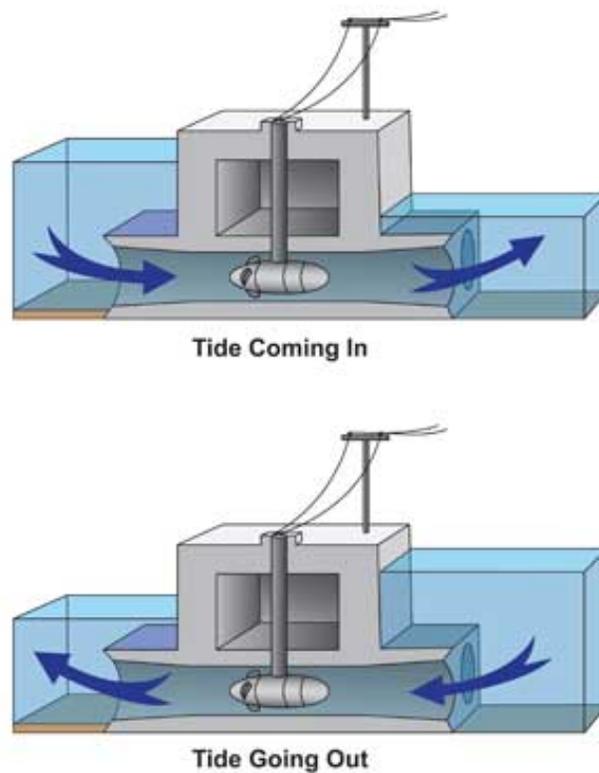
Figure 6.12: A turbine capturing tidal energy. Power is generated both as the tide comes in and goes out [NASA]. Image courtesy of NASA.

turbines can be used to extract work from the stream as shown in Fig. 6.12. The world's largest tidal power plant is the Sihwa Lake Tidal Power Station in South Korea and is capable of producing 254 MW at peak power. Like with wind and solar, however, this power is not continuous as kinetic energy can only be converted to work during the tidal transitions. As we will discuss later, energy storage is necessary in practice for smoothing out these dips in power production.

6.1.4 Geothermal

We know from our study of the Second Law of Thermodynamics that we need two thermal reservoirs at different temperatures to convert thermal energy to net work in a cycle. On Earth, we happen to have a staggering temperature gradient between the Earth's surface and core, which can reach temperatures well over 5,000 K as shown in Fig. 6.13. This thermal energy is a combination
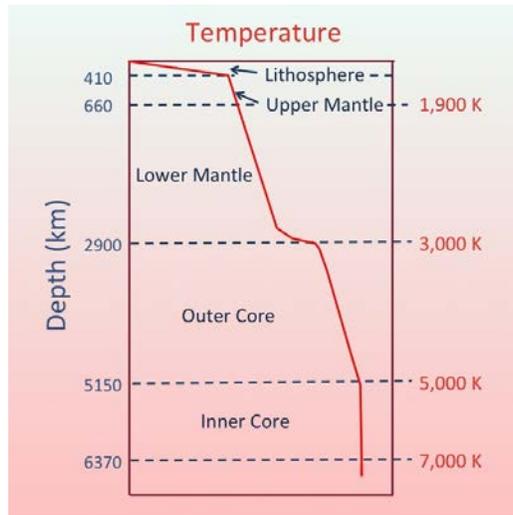
Figure 6.13: Temperature profile of the Earth as a function of depth [source].

of thermal energy left over from the formation of the Earth - *primordial heat* - and *radioactive decay* of elements like uranium and plutonium at the core.

In terms of thermodynamics, a Carnot Cycle operating between the Earth's core at 5,000 K and surface at 300 would have an efficiency of

$$\eta_{Carnot} = 1 - \frac{T_L}{T_H} \tag{6.32}$$

$$= 1 - \frac{300}{5000} \tag{6.33}$$

$$= 0.94 \tag{6.34}$$

and the vast thermal mass (mcT) of the Earth would in theory be able supply a large fraction of human energy needs for millions of years. As is to be expected, there are numerous complications that prevents the ubiquity of geothermal power.

In practice, to extract energy from the thermal resources of the Earth's interior, water is pumped in deep wells where it is turned to steam, sent back to the surface, and used to power a Rankine Cycle to extract mechanical work. The steam is condensed and cooled using the ambient thermal reservoir and the cycle repeats. Fig. 6.14 shows exactly this process in a typical geothermal plant architecture. If the efficiency and Earth's heat capacity are so high, what are the caveats then? Well, to achieve the super hot temperatures required for
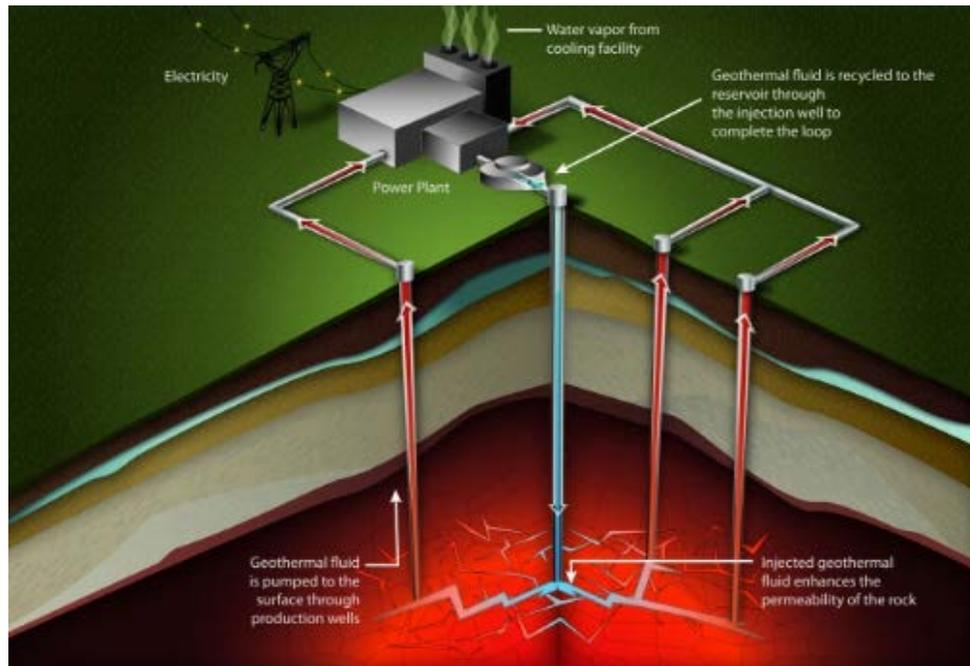
Image courtesy of DOE.

Figure 6.14: Geothermal well and associated power plant [USDOE].

high First Law efficiencies, it is necessary to drill upwards of a kilometer into the Earth, which is a significant and costly engineering challenge. Additionally, the thermal gradient is not uniform across the Earth's surface and is function of geography and geology, so even figuring out where would be a good location for geothermal power plants can be tricky. Regardless, given the carbon-neutral and nearly renewable nature of this energy source, it will need to play a large part in mitigating climate change.

6.1.5 Nuclear

While not technically renewable, nuclear energy derived from either the *fission* and decay of heavy, *radioactive* elements like uranium and plutonium or the *fusion* of light elements like hydrogen is carbon-neutral and provides an extremely large amount of energy per input fuel mass. Additionally, nuclear fuel sources are relatively abundant in nature, especially in the case of hydrogen-fed fusion. Thus, nuclear energy plays a crucial role in helping to bridge the gap between fossil fuels and true renewable energy, though its use - particularly via the fission of radioactive elements - has met significant hurdles as

a result of public perception, politics, and concern about weaponization and waste management. Nuclear fusion solves most of these issues, but it is much more difficult to perform and to date, no utility-scale fusion reactor exists.

Thermodynamically, nuclear reactions are fundamentally different than the chemical reactions we previously looked at. In fission and fusion reactions, energy is not released via the change in bond energies, but rather in the loss of mass. Counter to what we have assumed for the majority of the content in this book, mass is not actually a conservative quantity but is instead another form of energy that can be converted to and from other forms. Einstein showed that the energy equivalent of *rest mass*[8] is equivalent to

$$E = mc^2 \tag{6.35}$$

where c is the speed of light in a vacuum. In nuclear fission, for example, a radioactivae and *fissile* isotope[9] of uranium, typically U-235, is bombarded with a neutron, causing its nucleus to split into various lighter element isotopes, including barium and krypton isotopes, and some neutrons. For this reaction, if we were to exactly measure all of the mass of the products and the reactants, we would find that mass of the products is about 0.1% less than that of the reactants. Because energy must be conserved, that converted mass is contained in the kinetic energy of the product neutrons as well as high-energy gamma radiation that released as well. It is evident from Eq. 6.35 that even though a small amount of mass is converted, c is equal to roughly 3×10^8 m/s and thus the overall energy release is enormous. The resultant energy density of fissile uranium fuel is roughly 144,000,000 MJ/kg, which is more than *two million* times greater than the heating value of any fossil fuel.

In a nuclear power plant, nuclear fission is carried out in an insulated container filled with water and some other materials to help control the reaction. The constant fission causes the entire volume to heat up, and this thermal energy is used as the heat input to a Rankine Cycle that extracts this energy as mechanical work, as shown in Fig. 6.15. While nuclear fission can be slowed using various techniques in these types of plants, it can never be completely stopped. As a result, nuclear power plants must always be producing power. In fact, the Rankine Cycle is crucial for cooling the nuclear reactor, preventing a runaway *meltdown* scenario. As a result of several notable such meltdown accidents, public and political perception of nuclear power is negative; however, nuclear fission-based energy actually remains the safest source of energy.

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[8]mass at rest relative to a fixed, non-accelerating reference frame. Relativistic physics of mass moving is a rich subject but well beyond the scope of this material.

[9]the same element but with a different number of neutrons
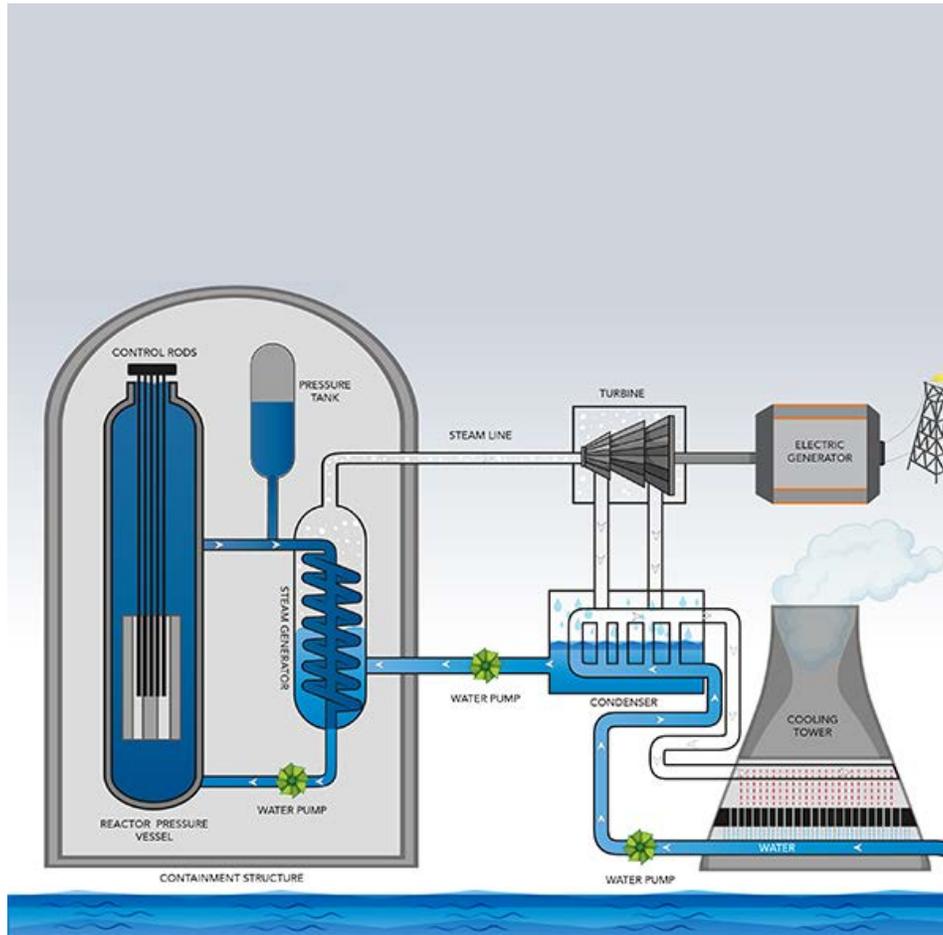
Figure 6.15: Schematic of a typical fission nuclear reactor power plant [US-DOE]. Image courtesy of DOE.

Also, while the radioactive fission products are highly toxic and dangerous to all life, the amount of waste per energy produced is extremely small given the high energy content of the fuel itself. Modern nuclear plants are able to handle this waste safely and effectively, but perception remains unchanged. It is also important to note that the only emissions from these plants is water vapor ejected from the turbine and thus is otherwise completely carbon neutral environmentally benign.

Fusion

In nuclear fusion, isotopes of hydrogen - deuterium and tritium - are brought together under extreme temperatures and pressures, forcing their nuclei to fuse, converting rest mass into kinetic and radiative energy for much the same reason as the fission reactions. The same reaction is what powers the cores of stars. Compared to fission, the energy density of this hydrogen fuel input is even greater, coming in at roughly 338,000,000 MJ/kg. Moreover, given the fact that hydrogen can be made easily via the *electrolysis* of water as we will soon discuss, the fuel source is practically endless. Unlike with fission, the byproduct of fusion is simply helium, which is not only non-toxic but also a highly valuable and otherwise dwindling resource. Clearly, nuclear fusion is an ideal power source; however, it is incredibly difficult to sustain in a controllable manner as the temperature required - 150,000,000 K - is far too high for any known material to sustain. Leading fusion reactor designs, including that by an international fusion project, ITER, hold the reaction as a plasma contained within a magnetic field. The complexity of the system and the required energy input to heat the plasm has prohibited the successful construction of a fusion plant that releases net energy, though as has been the case for decades, success is thought to be imminent.

6.1.6 Biofuels

The last energy source we will briefly discuss here is *biofuel*, which is chemically equivalent to many of the fossil fuels that helped bring humanity into this climate crisis; however, unlike fossil fuels, biofuels are produced and consumed on a similar timescale as it takes for the source biomass itself to grow. As shown by Solomon et al [2], CO_2 can remain in the atmosphere for hundreds to thousands of years, and so fuel production cycles on the order of tens of years can be considered carbon neutral, depending on the carbon intensity of the energy used in processing. The most common biofuel, ethanol, for instance, is derived from the fermentation of sugars found in corn and other harvested crops. The combustion of ethanol for power, as discussed in Chapter 3 and given by Eq. 3.71, releases CO_2 that is in theory offset by the CO_2 sequestered when the base crops regrow. In reality, however, emissions associated with the fermentation and refinement processes, as well as with the subsequent transportation of the ethanol fuel can lead to quite a high carbon intensity. As we will discuss later in this chapter, synthetic fuels produced directly from CO_2 may be a better alternative for a net carbon-neutral fuel.

6.2 Renewable Heat to Work

In many of the renewable energy sources we have discussed here, the energy is delivered to the user as heat, which can be at high temperatures in the cases of concentrated solar, deep-well geothermal, and nuclear, for example. Given the implications of the Second Law of Thermodynamics and the Carnot Theorem, there is this notion that the same quantity of thermal energy at different temperatures is not equal in terms of our ability to do useful work. Indeed, we know from the Carnot Efficiency - the maximum efficiency that can be achieved by a heat engine operating between two thermal reservoirs - that the greater the temperature difference between your heat source and cold sink, the greater the efficiency. The *quality* or *grade* of a heat source attempts to capture this observation, with heat at higher temperatures having a higher grade.

This is of course not new information for us at this point, but it is also worth noting that lower grade heat sources place additional limitations on how thermal energy is converted to work. External heat engines that operate on the Stirling Cycle using air as a working fluid, for example, require much larger heat exchangers to produce the same amount of power at lower temperatures, making them more expensive and impractical for all but industrial uses. Additionally, Rankine Cycles require the phase change of the working fluid, and thus the top temperature must be at or above the saturation temperature of the working fluid at the operating pressure, which can be quite high. To use water as a working fluid, this requires that the top temperature be in excess of 300-400 °C. Often, renewable-generated heat comes in well below these temperatures in practice, requiring that a different form of heat engine be used.

6.2.1 Low Temperature Heat Engines

As previously mentioned, a Stirling Engine can work well as a low-temperature heat engine; however, this architecture suffers from a low *power density* at lower temperatures, requiring prohibitively large and expensive components in many applications. Instead, low grade heat can be converted effectively to mechanical work in what is called an *Organic Rankine Cycle* (ORC). Such a cycle is the same as the normal Rankine Cycle, except that it utilizes a working fluid compatible with the suppressed temperature range. Ideal working fluids tend to be volatile organic liquids like butane, propane, toluene, pentane, and even ethanol, for instance, which is where the cycle gets its name. These fluids all have saturation temperatures much lower than water for the same pressures and are thus ideal for this type of cycle.
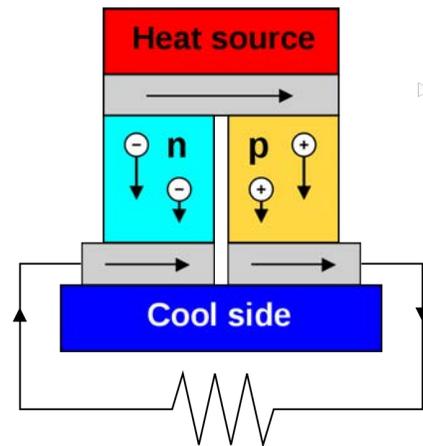
Figure 6.16: Thermoelectric or *Seebeck* effect that allows electrical work to be extracted from a temperature gradient. Here two materials with different levels of negative and positive charge carriers experience a net diffusion of electrons in one direction, generating current in the process [source].

Another architecture that is gaining traction is a Rankine Cycle that uses supercritical CO_2 as a working fluid. CO_2 has a critical temperature of only 31 °C, which enables the extraction of work from very low grade thermal energy, even waste heat from the output of power plants. This ability is important in terms of climate change mitigation, as there are many yet untapped renewable energy resources at these lower temperatures and can stand to make existing power extraction more efficient as well. The primary downside to both organic and supercritical CO_2-based Rankine Cycles is that higher pressures are required, making the systems more costly to build. Also, the release of some of these organic working fluid vapors into the atmosphere might negate their role and worth in carbon mitigation.

6.2.2 Thermoelectric Generator

Like with photovoltaic cells, we often want electrical work as a our final output. In a very similar manner as the photovoltaic effect, the *thermoelectric* or *Seebeck* effect enables a temperature gradient applied between the p-n junction - the interface between two dissimilarly doped semiconductors - and the

outer ends of each semiconductor to develop an electrical potential across those ends. Note that this is partially what enables a potential difference to develop across a PV cell, but in this case, only conductive sensible thermal energy is supplied. A device that uses this phenomenon to generate electricity directly from a thermal gradient is called a *thermoelectric generator* (TEG), and typically only has an efficiency of around 5-8%, largely due to resistive losses. Despite this low efficiency, however, their compact nature and the fact that they are *solid state* - i.e. have no moving parts - makes them useful in many applications[10]. A TEG can be operated in reverse as a heat pump by supplying current to generate a thermal gradient. Such a system is called a *Peltier* cooler.

6.3 Energy Storage

Despite the significant quantity of renewable energy sources available on average, in particular those forms that are derived from solar irradiance directly, many are only available intermittently. In a fixed location on Earth, for example, the sun only shines bright enough to extract substantial electrical work for 6-8 hours a day, and wind energy may be even less predictable. As a result, the degree to which renewables are available is characterized by a *capacity factor* - the average fraction of time they are able to supply usable energy. For solar and wind at the grid scale, this capacity factor is around 20-35%. Nuclear has a capacity factor near 100% to avoid the previously discussed issues with meltdowns. The energy demand, however, may drop at times, but never completely to zero for many regions - cities in particular - and thus is not compatible with low-capacity-factor energy sources on their own. To mitigate this issue, renewables must generate excess power when they can and store the extra energy for when their output cannot meet demand. Here, we will discuss several key energy storage technologies.

6.3.1 Electrochemical Energy Storage

Perhaps the most ubiquitous form of energy storage that modern humans interact with on a daily basis is electrochemical energy storage - *batteries* that store and release *electrical* potential energy via *electro*chemical reactions. Zooming in to the atomic level, individual atoms and atomic compounds are made up of

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[10]The radioisotope thermoelectric generator (RTG) on the NASA Curiosity Mars Rover converts thermal energy released from its decaying plutonium fuel source to electricity directly using an array of TEGs.

electrons, protons, and neutrons such that in their neutral state, the negative and positive charges of the electrons and protons respectively balance out exactly. Some atoms, however, have a stronger affinity for electrons than others based on their atomic structure. Thus, when certain pairs of dissimilar atoms - typically metals - are placed in close proximity, electrons can travel between them. This makes one more negative than the other, creating an *electric field*, and if we can physically separate the dissimilar metals, an *electrical potential*, or *voltage* difference is established. Mathematically, this this potential difference, $\Delta\Phi$, is given as

$$\Delta\Phi = \Phi_2 - \Phi_1 \tag{6.36}$$

$$= \int_1^2 -\vec{E} \cdot d\vec{l} \tag{6.37}$$

which is the *dot product* of the electric field along the path of separation. We will not show this here, but it is important to note that this potential is a state property and therefore is independent of the path of separation. Also like with entropy, we typically choose a reference value against which we can compare these potentials.

On its own, Φ has units of Volts in SI units which is equivalent to energy per *charge*, or Joules per Coulomb. From this, we can see directly that if we have a system that moves a charge through an electric field such that its electrical potential changes, the potential energy of the system will change as well. Consequently,

$$\Delta U_e = U_2 - U_1 \tag{6.38}$$

$$= q(\Phi_2 - \Phi_1) \tag{6.39}$$

where q is the charge. Energy stored in this way can be released in a *circuit* by establishing an electrical potential difference and allowing electrons or other charge carriers to move from high to low potential. The movement of these charge carriers is called *current*. This energy release at the atomic level is simply a force applied by the electric field on the charge over some distance and is thus exactly equal to our previous definition of work. For this reason, the change in potential is often called the *electromotive force* or *EMF*. We can therefore include the work done by moving an electrical charge through a potential difference in our First Law definition:

$$dU = dQ - dW_{mechanical} - dW_{electrical} \qquad (6.40)$$
$$= dQ - P\,dV - q\,d\Phi \qquad (6.41)$$

While we will not discuss electromagnetism in much greater detail in this text, we will see how the laws of thermodynamics enable us to predict the energy storage capability of various combinations of dissimilar atoms or compounds. As usual we will look at the steady state equilibrium conditions of the system, this time for a typical battery *cell* in which two dissimilar metals with different electron affinities are used to create a potential difference.

Daniell Cell

A simple battery cell configuration is the *Daniell Cell* in which zinc and copper, two metals with different electron affinities, are used to drive current through a circuit and do electrical work. Fig. 6.17 shows a typical cell in which the zinc and copper *electrodes* are placed in separate *electrolyte* solutions containing water and some dissolved salts of each element - zinc sulfate ($ZnSO_4$) and copper sulfate ($CuSO_4$), for example. Zinc atoms have a lower affinity for electrons than copper atoms, and thus when connected by a conductor, electrons will move from the zinc electrode, called the *anode* to the copper electrode, called the *cathode*.

At the anode, zinc is *oxidized* and loses two electrons by the following oxidation reaction:

$$Zn \rightleftharpoons Zn^{2+} + 2\,e^- \qquad (6.42)$$

where Zn^{2+} indicates that the zinc has lost two electrons and thus has a positive charge with a magnitude twice that of a single electron. We call the new charged atoms *ions*. Similarly, on the cathode side, copper ions dissolved in the solution each gain two electrons from the zinc to form neutral cooper by the following reduction reaction:

$$Cu^{2+} + 2\,e^- \rightleftharpoons Cu \qquad (6.43)$$

All the while this is occurring, positively and negatively charged salts travel in opposite directions towards the cathode and anode respectively via a salt
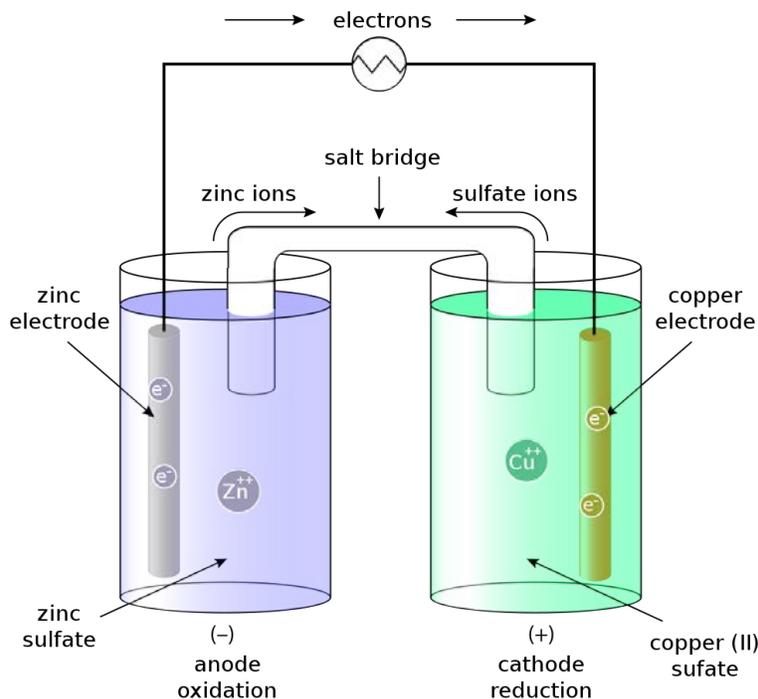
Figure 6.17: Simple electrochemical or galvanic battery cell called a *Daniell Cell* that uses zinc and copper electrodes to drive current through a circuit until the zinc is fully depleted [source]. **Image courtesy of Rehua on Wikimedia. License CC BY.**

bridge, which is a simple tube or absorbent paper sheet containing some electrolyte. This allows the reactions to proceed while zinc is removed from the anode and copper ions precipitate onto the copper electrode.

We know that in equilibrium, the molar change in Gibbs Free Energy, dg, must be zero for each reaction. Recall that for a chemical reaction, we have the general Gibbs-Duhem expression for the change in Gibbs Free Energy per mole:

$$dg = -s\,dT + v\,dP + \sum_i \mu_i\,dN_i \qquad (6.44)$$

or for constant pressure and temperature processes,

$$dg = \sum_i \mu_i\,dN_i \qquad (6.45)$$

For electrochemical reactions, we must add an additional term to also account for the change in electrical potential energy associated with a change in concentration of a particular species, dN_i,

$$dg = \sum_i (\mu_i + q_i \Phi) \, dN_i \tag{6.46}$$

where

$$q_i = z_i F \tag{6.47}$$

Here, z_i is the charge of the species (e.g. $+2$ for Zn^{2+}), and F is the Faraday constant[11]. Note that the right-hand side in parentheses for Eq.6.46 is defined as the electrochemical potential for species, i, denoted as η_i.

For the Daniell Cell used here, we can safely assume that reactions all happen at constant temperature and pressure, allowing us establish the equilibrium condition for each reaction using Eq. 6.46. First for the zinc oxidation reaction, we have

$$dg_{Zn^{2+}} + dg_{Zn} = 0 \tag{6.48}$$

$$(\eta \, dN_i)_{Zn^{2+}} + (\eta \, dN_i)_{Zn} = 0 \tag{6.49}$$

where from conservation of mass, we know

$$dN_{Zn^{2+}} + dN_{Zn} = 0 \tag{6.50}$$

$$\Rightarrow dN_{Zn^{2+}} = -dN_{Zn} \tag{6.51}$$

and thus

$$\eta_{Zn^{2+}} = \eta_{Zn} \tag{6.52}$$

$$\mu_{Zn^{2+}} + 2F\Phi_a = \mu_{Zn} \tag{6.53}$$

where Φ_a is the electrical potential of the zinc anode.

Similarly for the copper reduction reaction,

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[11]Equal to 96485.33... C/mol and is equivalent to Avogadro's number times the charge of a single electron.

$$\mu_{\text{Cu}^{2+}} + 2F\Phi_c = \mu_{\text{Cu}} \tag{6.54}$$

where Φ_c is the electrical potential of the copper cathode, which is referenced to the same arbitrary reference potential as Φ_a for the anode. The cell potential at equilibrium can then be found by taking the difference Eqs. 6.53 and 6.54 to find $\Phi_a - \Phi_c$, giving us:

$$2F(\Phi_a - \Phi_c) = (\mu_{\text{Zn}} - \mu_{\text{Cu}}) + (\mu_{\text{Cu}^{2+}} - \mu_{\text{Zn}^{2+}}) \tag{6.55}$$

$$\Rightarrow \Phi_a - \Phi_c = \frac{1}{2F} \left[(\mu_{\text{Zn}} - \mu_{\text{Zn}^{2+}}) + (\mu_{\text{Cu}^{2+}} - \mu_{\text{Cu}}) \right] \tag{6.56}$$

$$= \frac{-\Delta g_{overall}}{2F} = \text{EMF} \tag{6.57}$$

In its most general form, Eq. 6.57 is given as

$$\text{EMF} = \frac{-\Delta g_{overall}}{zF} \tag{6.58}$$

and is called the *Nernst Equation*. In this analysis, at equilibrium, this electrical potential difference or EMF is called the open-circuit voltage. In reality, once current starts flowing this voltage will drop due to resistance and other losses. To compute the open-circuit voltage, however, we can go back to our expression for the chemical potential of an ideal mixture, which gives

$$\mu_i = \mu_i^+(T) + RT \left[\ln \left(\frac{P}{P_0} \right) + \ln X_i \right] \tag{6.59}$$

which at constant pressure is simply

$$\mu_i = \mu_i^+(T) + RT \ln X_i \tag{6.60}$$

for a single species. The overall change in Gibbs Free Energy is given as

$$dg_{overall} = \sum_i \mu_i \, dN_i \tag{6.61}$$

$$= \sum_i \left(\mu_i^+(T)\nu_i + RT\nu_i \ln X_i \right) \tag{6.62}$$

$$= \sum_i \mu_i^+(T)\nu_i + RT \ln \left(\prod_i X_i^{\nu_i} \right) \tag{6.63}$$

where ν_i is the stoichiometric coefficient of species i[12]. This equation is usually valid for low concentrations. For non-ideal mixtures, we need to utilize the activity coefficient as previously discussed, which gives us

$$dg_{overall} = \sum_i \mu_i^+(T)\nu_i + RT \ln \left(\prod_i (\gamma_i X_i)^{\nu_i} \right) \tag{6.64}$$

$$= \sum_i \mu_i^+(T)\nu_i + RT \ln \left(\prod_i (a_i)^{\nu_i} \right) \tag{6.65}$$

$$\tag{6.66}$$

where a_i is the *activity* of the species.

Putting this all together, we get that the open circuit EMF is

$$\text{EMF} = \frac{-\Delta g_{overall}}{zF} \tag{6.67}$$

$$= \frac{-\sum_i \mu_i^+(T)\nu_i}{zF} - \frac{RT}{zF} \ln \left(\prod_i a_i^{\nu_i} \right) \tag{6.68}$$

$$= \text{EMF}^\circ(T) - \frac{RT}{zF} \ln \left(\prod_i a_i^{\nu_i} \right) \tag{6.69}$$

where $\text{EMF}^\circ(T)$ is the standard cell potential at a given temperature and is derived from experimental measurements.

For our zinc-copper Daniell Cell, we have the total reaction:

$$\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu} \tag{6.70}$$

for which the standard cell potentials for the zinc and copper *half* reactions are given at standard temperature as -0.763 V and 0.337 V respectively. The total standard cell potential is therefore $0.337 - (-0.763) = 1.1V$, and thus the actual EMF is given by

$$\text{EMF} = 1.1 \text{ V} - \frac{RT}{2F} \ln \left(\frac{a_{\text{Zn}^{2+}} \cdot a_{\text{Cu}}}{a_{\text{Zn}} \cdot a_{\text{Cu}^{2+}}} \right) \tag{6.71}$$

---

[12]recall that the products have negative stoichiometric coefficients.

for pure solids, the activity is equal to 1 and thus we can simplify this further as

$$\text{EMF} = 1.1 \text{ V} - \frac{RT}{2F} \ln \left(\frac{a_{\text{Zn}^{2+}}}{a_{\text{Cu}^{2+}}} \right) \tag{6.72}$$

where again the activity is typically a function of both the composition and temperature of the mixture and must be taken from experimental data. Note that this type of electrochemical cell is generally called a *Galvanic Cell*.

Rechargeable Electrochemical Batteries

What was implicit in our analysis of the simple Daniell Cell - and is true for all Galvanic cells - was that the stored energy is actually in the fact that the zinc starts out as a pure elemental electrode and that there are already Cu^{2+} ions in solution on the cathode side. The energy extracted as current initially went into reducing the zinc and liberating copper ions so that the reduction-oxidation reaction could later take place, much like our combustion reactions from Chapter 3, which were also reduction-oxidation reactions. Over the life of the electrochemical cell, electrons can only be transported as long as there is pure reduced zinc on the anode and there are Cu^{2+} ions in solution, and as the battery operates, more and more zinc dissolves into solution and copper ions reattach to the copper electrode.

In the Daniell Cell analyzed here, the two half reactions are reversible in theory. If instead a reverse voltage is applied, electrons will flow from the cathode to the anode, causing the reverse reactions to occur; however, in practice, for this type of battery, it is difficult to get the zinc to precipitate back onto the anode with out forming *dendrites* - long spindly formations that dramatically decrease the performance of the cell and can even cause short a short circuit between the anode and cathode. Consequently, this type of battery is not considered to be *rechargeable* in that the potential energy cannot be appreciably restored by simply reversing the direction of the current. Such a battery is typically called a *primary battery.*

Conversely, a *secondary* or rechargeable battery is one in which the chemistry can be reversed successfully by running the cell in reverse. Most alkaline batteries can be recharged several times before their performance degrades to the point where the cell is no longer usable. A major innovation came in the 1970's when it was discovered that cathodes made from lithium cobalt dioxide (LiCoO_2) were stable enough to undergo hundreds of recharge cycles and exhibit high energy densities. In the years since, *Li-ion* batteries have
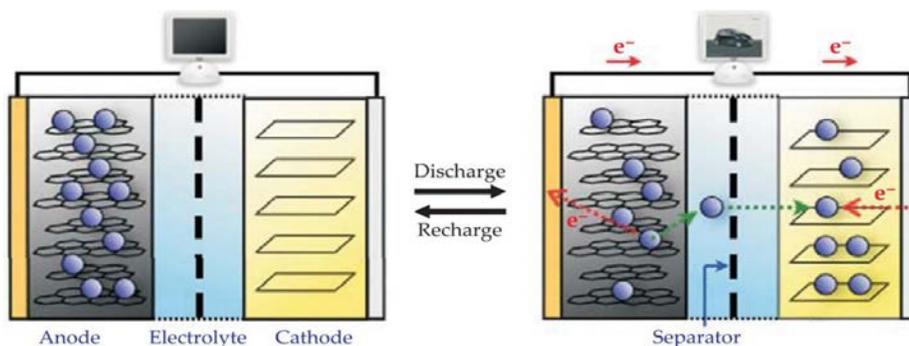
Figure 6.18: Li-ion battery architecture that uses a $LiCoO_2$ cathode and graphite anode.

emerged as the leading electrochemical-based energy storage technologies. In these cells, the charge carrier is lithium, which during discharge is the result of the following oxidation reaction on a graphite-lithium anode:

$$C_6Li \longrightarrow 6\,C_{gr} + Li^+ + e^- \tag{6.73}$$
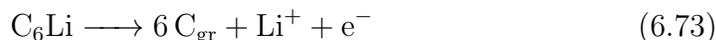
and subsequent reduction reaction in the cathode:

$$CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2 \tag{6.74}$$

State of the art Li-ion batteries can achieve specific energies and energy densities up to 265 Wh/kg and 700 Wh/L respectively.

6.3.2 Thermal Energy Storage

Another leading strategy for energy storage involves storing energy as heat - either in the latent heat of a *phase change material* (PCM) or as sensible heat. In either case, excess electrical or mechanical work generated by some energy conversion process is dissipated as thermal energy, which is then stored and later extracted using a heat engine, PV cells, or TEGs depending on the temperature of the available heat. As discussed earlier, the stored thermal energy can also be used directly as heat as well.

Because thermal energy has the tendency to spread out and diffuse irreversibly by the Second Law of Thermodynamics, it is inevitable that some

energy will "leak out" of any heat storage system. Also, we know well by now that there are limitations on the First Law efficiencies of each of these various energy conversion processes. It is therefore important to define the concept of a *round-trip* efficiency, which is ratio of how much energy we get out in the form we want to the amount of energy we put in originally. If we only need thermal energy as our output, the round-trip efficiency is given as

$$\eta_{round-trip} = \frac{Q_{out}}{Q_{in}} \qquad (6.75)$$

$$= \frac{Q_{in} - Q_{lost}}{Q_{in}} \qquad (6.76)$$

where Q_{lost} is the thermal energy lost to the environment during the storage period. If instead we need the energy back out as electrical or mechanical work, we must then also apply the First Law efficiency of whatever energy conversion process is used. For this case,

$$\eta_{round-trip} = \eta_{conversion} \left(\frac{Q_{in} - Q_{lost}}{Q_{in}} \right) \qquad (6.77)$$

The keys to a high round-trip efficiency are therefore to increase the efficiency of the energy conversion process and limit the lost heat. For the former, there are thermodynamic limits that place upper bounds on $\eta_{conversion}$. For heat engines in particular, we know that the higher the temperature at which the heat is stored, the higher the efficiency. Unfortunately, the amount of heat lost is also proportional to temperature, with higher temperatures leading to more heat loss over the same storage period, as we would expect. Physically, conductive heat transfer obeys *Fourier's Law*, which gives the heat flux, $\dot{q}$, in units of power per unit area - W/m^2 in SI units - as

$$\dot{q} = -k\nabla T \qquad (6.78)$$

where ∇ T is the spatial *gradient* of temperature. In one dimension, this equation is equal to

$$\dot{q} = -k\frac{dT}{dx} \qquad (6.79)$$

which shows us that a greater difference in temperature across the same distance will lead to a higher heat flux. In general, heat will be lost to conduction,

thermal radiation, and *convection*[13]. The heat flux from our storage system at temperature T_s to the environment at T_a can be approximated as

$$\dot{Q}_{lost} = hA(T_s - T_a) \tag{6.80}$$

where h is an empirical *heat transfer coefficient* with units of W/m²-K and A is the surface area over which the heat transfer occurs. The total heat lost over a storage period τ is then

$$Q_{lost} = \int_0^\tau hA(T_s - T_a)dt \tag{6.81}$$

where T_s, T_a, and even h, may change over the storage period.

In practice, h can be reduced by adding various types of insulation to the storage system, but can never be brought to 0. Thus a trade-off emerges between needing high temperatures for efficient energy conversion but also low enough temperatures or sufficient insulation to reduce losses. For latent heat storage, the primary benefit is that thermal energy can be stored at *constant temperature*, as we know from our analysis of phase changes from earlier. This helps to reduce losses in the case where the energy is needed back out as work. For these applications, substances with high melting points are typically used. Various salts or even silicon, which have melting points around 800 °C and 1,400 °C respectively, are common choices. In practice, however, these materials are often heated well past their melting points, adding thermal energy as *sensible heat*, which follows our usual expression for internal energy

$$Q_{stored} = mc\Delta T \tag{6.82}$$

where m and c are the storage material mass and specific heat capacity respectively.

6.3.3 Other Forms

Finally, in terms of energy storage, there are numerous other technologies that are being explored at the grid-scale, though we will not go into too much detail here.

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[13]conduction to a fluid
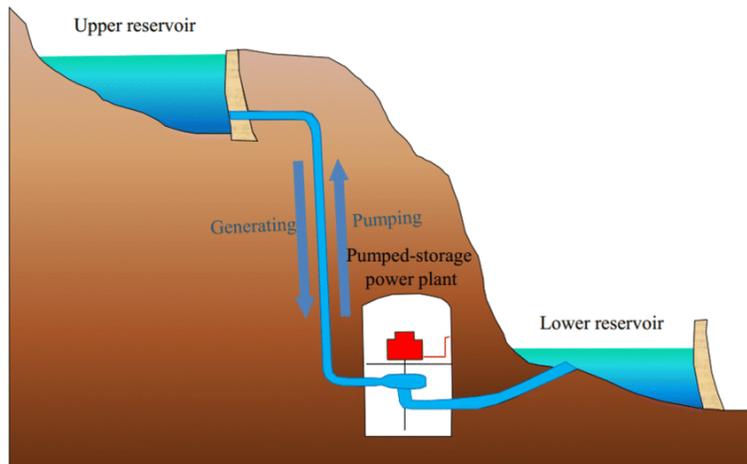
Figure 6.19: Schematic of a pumped-hydro storage system. Excess electricity is used to pump water from a lower reservoir to a higher one and then when energy is needed, the water flows back through the pump in the opposite direction to generate electrical power.

Pumped-Hydro

First, there are number of promising gravity-based storage technologies. For instance, *pumped-hydro storage* is basically a hydro-electric dam that can also run in reverse. As discussed earlier, hydro-power benefits from the natural water cycle using solar energy to transport water from a lower to a higher geographic region; however, this flow of energy is subject to natural weather patterns, which may be unpredictable. Pumped-hydro removes some of this uncertainty by using excess renewable electricity to pump water from a lower to a higher reservoir as shown in Fig. 6.19. Then when electricity demand exceeds that which can be produced by the renewable sources, water is released from the upper reservoir and flows the opposite direction through the pump to generate electricity. This is enabled by the fact that electric motors can operate in reverse to generate current from an input of mechanical work. It is believed that there is enough natural change in elevation throughout across the Earth to meet most of the world's energy storage needs. Presently, there are political and economic hurdles to implementing these systems.

Compressed-Air Energy Storage

Another leading energy storage technology is *compressed-air energy storage* (CAES), where excess mechanical or electrical work is used to run a compressor to compress air to high pressures. Here the energy is stored both as PV work and thermal energy. In this paradigm, the gas can be compressed adiabatically or isothermally, and either stored isochorically or isobarically. In all combinations, the theoretical round-trip efficiency is 100%, but in practical systems, irreversibility cannot be completely avoided, as the gas will heat up substantially during the compression process. In the adiabatic case, the final temperature after compression, T_2, is given as

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} \tag{6.83}$$

if we assume constant volume gas storage - which in practice can be achieved by compressing gas in a naturally occurring cavern, porous rock bed, or human-made tank - we can compute the work per unit mass from the First Law as

$$w_{c,s} = -(u_2 - u_1) \tag{6.84}$$
$$= -c_v(T_2 - T_a) \tag{6.85}$$
$$= c_v T_a (1 - \frac{T_2}{T_a}) \tag{6.86}$$
$$= c_v T_a \left[1 - \left(\frac{P_2}{P_a} \right)^{\frac{\gamma-1}{\gamma}} \right] \tag{6.87}$$

which also assumes no other losses. As discussed in Chapter 5, the real compressor will have some isentropic efficiency, η_c^{II}, that increases the work required by a factor of $1/\eta_c^{II}$ and thus:

$$w_c = \frac{c_v T_a}{\eta_c^{II}} \left[1 - \left(\frac{P_2}{P_a} \right)^{\frac{\gamma-1}{\gamma}} \right] \tag{6.88}$$

When energy is needed, this compressed air is released, and is expanded through a turbine to extract work. Due to the symmetry of the problem, we can compute the turbine work as

$$w_{t,s} = -(u_3 - u_2) \tag{6.89}$$

$$= -c_v(T_a - T_2) \tag{6.90}$$

$$= -c_v T_a (1 - \frac{T_2}{T_a}) \tag{6.91}$$

$$= -c_v T_a \left[1 - \left(\frac{P_2}{P_a} \right)^{\frac{\gamma-1}{\gamma}} \right] \tag{6.92}$$

for the ideal case and

$$w_t = \eta_t^{II} c_v T_a \left[1 - \left(\frac{P_2}{P_a} \right)^{\frac{\gamma-1}{\gamma}} \right] \tag{6.93}$$

for the real case, where η_t^{II} is the isentropic efficiency of the turbine. The round-trip efficiency is then

$$\eta_{round-trip} = \left| \frac{w_{out}}{w_{in}} \right| \tag{6.94}$$

$$= \left| \frac{w_t}{w_c} \right| \tag{6.95}$$

$$= \eta_t^{II} \eta_c^{II} \tag{6.96}$$

as we would expect.

In the isothermal case, we can determine the round-trip efficiency by a similar process. Looking at the First Law for the compression case, we have

$$\Delta u = q_{out} - w_{c,s} \tag{6.97}$$

$$\Rightarrow w_{c,s} = q_{out} - \cancelto{0}{\Delta u} \tag{6.98}$$

where we know $\Delta u = c_v \Delta T = 0$ for an isothermal process. Also, intuitively we know that in order for the gas to maintain the same temperature throughout the process, heat must be transferred from the gas to its surroundings. To determine the magnitude of this heat transfer, we look tp the Second Law:

$$\Delta s = \frac{q_{out}}{T_a} + \Delta s_{gen} \tag{6.99}$$

$$c_p \ln \cancelto{0}{\frac{V_2}{V_1}} + c_v \ln \frac{P_2}{P_a} = \frac{q_{out}}{T_a} + \Delta s_{gen} \tag{6.100}$$

$$\Rightarrow q_{out} = T_a \left(c_v \ln \frac{P_2}{P_1} - \Delta s_{gen} \right) \tag{6.101}$$

For the ideal case, $\Delta s_{gen} = 0$, giving us

$$w_{c,s} = c_v T_a \ln \frac{P_2}{P_a} \tag{6.102}$$

which by comparison to the adiabatic case, is considerably less work for the same pressure difference. We can lump all of the inefficiencies for this process together again as an isentropic efficiency, giving us the actual work of compression as

$$w_c = \frac{c_v T_a}{\eta_c^{II}} \tag{6.103}$$

By symmetry, the expansion process must also absorb the same amount of heat, giving us the ideal work extracted as

$$w_{t,s} = c_v T_a \ln \frac{P_a}{P_2} \tag{6.104}$$

and the real work as

$$w_t = \eta_t^{II} c_v T_a \ln \frac{P_a}{P_2} \tag{6.105}$$

giving us the same round-trip efficiency as with the adiabatic case,

$$\eta_{round-trip} = \eta_t^{II} \eta_c^{II} \tag{6.106}$$

Ideally, the isothermal process is preferred as it requires less work to achieve the same pressure ratio and there is no potential for heat loss during the storage
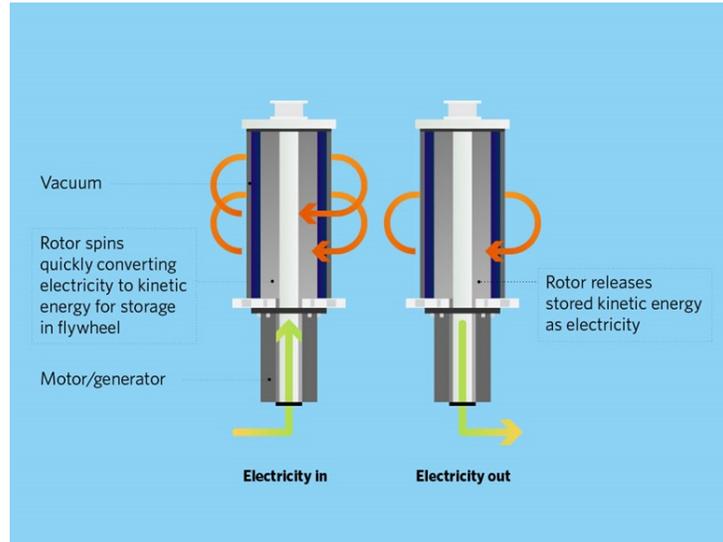
Figure 6.20: Basic inertial energy storage mechanism using a rotating flywheel to store energy as rotational kinetic energy [IESO].

period as the gas is at the same temperature as the environment; however, in practice it is difficult to achieve isothermal compression and requires multiple stages where the gas is cooled irreversibly in between. Thus, CAES systems typically operate closer to the adiabatic regime. Also, while we assumed constant volume processes here, constant pressure processes are also favored in the ideal case, as they allow for work to be extracted over the total expansion of the gas. This requires an expandable reservoir, though, which can add complexity and cost to a large storage project. In many cases, natural caverns already exist that form an ideal storage reservoir for the compressed air.

Flywheels

The final energy storage system we will discuss briefly here is *inertial* energy storage, in which energy is stored as macroscopic kinetic energy. One common approach is to use excess electricity to spin a motor attached to a mass with a large moment of inertia to high angular velocities, allowing energy to be stored as

$$E_{flywheel} = \frac{1}{2}I\omega^2 \qquad (6.107)$$

where I is the moment of inertia and ω is the angular velocity. The mass is then electrically decoupled from the motor, and the mass's kinetic energy is held roughly constant. When energy is needed back out, the spinning mass couples back to electric motor, generating electrical work. As shown in Fig. 6.20, this type of energy storage mechanism is typically placed in a vacuum with magnetic couplings, resulting in very little frictional losses or dissipation throughout the energy storage cycle. The state-of-the-art flywheel energy storage systems can achieve round-trip efficienies above 85%.

6.4 Summary

The main issue with burning fossil fuels for energy from a climate change perspective is that the CO_2 combustion products are being added to the atmosphere at a much greater rate than they are naturally removed. Given the comparatively long timescales required for forming coal, oil, and natural gas, these energy sources are considered non-*renewable*. Fortunately, there exist abundant *renewable* energy sources that can supply global human energy demands without emitting CO_2 and other greenhouse gases and further contributing to climate change. Sources like solar, wind, geothermal, and tidal energy together supply significantly more power on average than we consume, and thus they are playing a crucial role in slowing greenhouse gas emissions. In this chapter, we looked a several of these sources from a thermodynamics perspective, as well as some technologies used in the conversion of low temperature renewable thermal energy to work. Finally, because renewables, while abundant, typically provide power intermittently, new and efficient energy storage systems are required for bridging the gaps between demand and power generation capacity. To that end, we analyzed electrochemical, thermal, gravitational, and inertial storage.

It is clear from a thermodynamics perspective that our global energy needs can be met many times over with renewable energy sources, coupled with adequate energy storage; however, from a geopolitics and socioeconomics perspective, this transition from fossil fuels to carbon neutral energy infrastructure cannot occur instantaneously. Consequently, additional technologies will be necessary to mitigate the climate crisis while this transition is carried out in the background. This is where we are going next.

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