Chapter 1
Introduction: Why Thermodynamics?

1.1 Energy and Work in Our World

Mechanical and electrical work is what drives our daily lives: cars, trucks, planes, trains, ships—in short, all transport—require motors which are either based on combustion of fuel or on electric energy. Our home and work environments are unthinkable without the many devices that are powered by electricity: light, microwave and stove, freezer and refrigerator, television and radio, DVD and bluray, CD and MP3 player, smartphone and telephone landline, computer and printer, washer and dryer, air conditioning and (sometimes) heat, power drill and lawn mower; the list goes on. Hospitals and factories are filled to the rim with mechanical and electronic devices and robots that are driven by electrical energy.

Electricity, however, is mainly obtained by converting mechanical work into electrical work in a generator: our lifestyle requires an endless supply of mechanical work.

For most of its history, humankind was only able to harvest mechanical work as nature provided it. Wind and water wheels were used not only to mill grain, but also for other purposes, most importantly for pumping irrigation water.[1] But else, there was little, and an abundance of tasks had to be done by human labor: farming, e.g., harvesting with a scythe, and weaving with a loom come to mind immediately.

Heat, as obtained from combustion of wood, fat, oil or coal, however, was used for cooking, lighting and heating, and other tasks unrelated to mechanical work, most importantly probably the smelting of metals.

The industrial revolution was triggered in the 18th century by the invention of *heat engines*, that is engines that convert heat into work. In particular the development of the *steam engine* by engineers like James Watt led to the lifestyle we enjoy. Now a wide array of heat engines is available. The original

[1] Today, wind turbines and large hydropower dams harvest the same natural powers to directly produce electricity.

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piston steam engines are replaced by steam turbines, while piston engines such as the Diesel and Otto engines are omnipresent on our streets and in ships, gas turbines drive aircraft and run in power plants.

For all engines, the heat is typically created by the burning of a fuel, such as coal, natural gas, oil, etc., or from nuclear power. The fuel is costly, and scarce, and therefore one will aim to make heat engines as efficient as possible. Moreover, combustion of fuels releases carbon dioxide into the atmosphere, which impacts global climate. More efficient use of fuels can at least slow down the rate at which carbon dioxide is added to the atmosphere, and hence high efficiencies have more than pecuniary value.

Thermodynamics was developed out of the desire to understand the limits of heat engine efficiency. Modern power plants run on intricate improvements on the original steam engine process that result from the deeper understanding of thermodynamic processes. Early steam engines had efficiencies of heat to work conversion of only a few percent, while modern combined cycle gas turbine/steam power plants exhibit efficiencies of up to 60%. Moreover, thermodynamic consideration can establish absolute upper bounds on efficiencies for processes, answering questions such as: how much work can be obtained at best from a heat source at a given temperature? or: what is the maximum work that could be obtained from a given amount of fuel? Only comparing actual performance against these theoretical limits can give adequate measures of efficiency. Of course, these questions and the answers will be discussed throughout this book.

Since its beginnings with the industrial revolution, thermodynamics has developed into a science that explains a wide array of natural and technical phenomena. Thermodynamic laws govern a host of processes: heat to work conversion in heat engines, and the inverse, i.e., the work to heat conversion in freezers, refrigerators and air conditioning systems; mixing and separation; transport through membranes (osmosis); chemical reactions and combustion, and so on. All of these will be discussed in this text.

In short, a good understanding of thermodynamics is indispensable in a wide range of fields, in particular mechanical and chemical engineering, chemistry, physics, and life sciences.

1.2 Mechanical and Thermodynamical Forces

Newton's laws of motion describe how a system reacts to an applied force: it moves. For instance, a weight on a coiled-up thread can be used to bring a shaft to rotation. When the shaft is connected to a generator, electricity is produced: the potential energy of the weight is transformed into electrical work. We see that a force, here gravity acting on the weight, can be used to generate mechanical work, here the rotation of the shaft, which then can be transformed again, here into electrical work. As long as the mechanical and electrical systems used are frictionless and resistance free, there is no loss, that is the electrical work produced is equal to the mechanical work done by the weight.

But, of course, there is friction and ohmic resistance, and some of the input work is required to overcome these. Hence, in a system with friction, the amount of electrical work provided is less than the work done by the weight. So where has that work gone? Thermodynamics gives the answer: due to friction and resistance, the system becomes warmer than its environment, and then heat flows into the environment: some of the work is converted to heat. While mechanics can describe friction losses, and electrodynamics can describe ohmic resistance, a full account of the system requires a thermodynamic description, entailing quantities like *temperature* and *heat*, which do not appear in mechanics and electrodynamics.

We all have some idea of what temperature is, since we have a sense for hot and cold. Also, we have the experience that when we put a cold and a hot body in contact, the cold body will become warmer and the warm body will become colder, until they have the same temperature. Just think of a soft drink originally at room temperature and ice: the ice will warm and melt, and the drink will become cooler … and a bit watery. Or think of a hot cup of coffee left on a table: After sufficiently long time the coffee assumes the temperature of the room around—it has cooled down—while the air in the room has become just a tiny bit warmer. Our iced soft drink, when forgotten on the table, will eventually warm up to the room temperature. In both cases, thermal energy is redistributed between the subsystems we looked at—soft drink, ice, coffee, air in the room. The associated temperature change is also linked to the size of the system: soft drink and ice both experience sensible changes in temperature and state; also the coffee's temperature changes noticeably, while it would require a rather sensitive thermometer to measure the temperature change of the air in the room.

Hot and cold drinks are just an example for a fundamental observation: heat goes from hot to cold in the desire to equilibrate temperature. In analogy to mechanics, where a force causes movement of its point of application, we can say that the temperature difference is a *thermodynamic force* that causes heat to flow. And just as a mechanical force can drive a generator to produce electricity, the thermodynamic force can be used to generate mechanical work, and electricity. This, in fact, is what a heat engine does.

The tendency to equilibrate into a homogeneous state is not observed only for temperature but also for other quantities. For instance, a droplet of ink added to a glass of water will distribute until, after some time, the ink concentration is homogeneous. This desire to mix evenly is driven by another thermodynamic force, which is related to the difference in concentration. Careful analysis will show that the driving force is the difference in a quantity known as the *chemical potential.* Also this force can be harvested for work, e.g. using osmosis, where freshwater is drawn into saltwater through semi-permeable membranes that allow only water, but not salt, to pass.

There are other examples for nature's desire to equilibrate, for instance in chemical reactions. The amounts of reactants and reaction products will assume an equilibrium state that depends on the actual conditions in the reactor, such as pressure and temperature. Any equilibration process can be described by a thermodynamic force, and can be used—at least in principle—to provide work.

Processes opposite to equilibration move against the thermodynamic forces, and hence work must be provided to force these processes to happen. A refrigerator cools only a small part of the kitchen, by forcing heat from the inside to the outside: (electrical) work is required to drive the compressor in the refrigerator. Separation processes require work, or other forms of energy, as well. Using the same semi-permeable membrane as above, one can produce freshwater from saltwater by pressing the latter against the membrane. This requires high pressures, and consumes work.

Chemically fabricated materials are everywhere in our lives from clothing—fleece has replaced wool—to medication. About one percent of the world's energy consumption is used to produce ammonia (NH_3) which is the base product for nitrogen fertilizers and explosives. Widespread availability of fertilizer, together with modern machines—driven by heat engines—for the year-round farm work have increased yield from fields largely, while at the same time the relative number of people working in farming has—in the first world—declined dramatically. For all chemical processes the goal is to run the reactors such that the yield is high. This requires perfect understanding of the thermodynamic forces and equilibria, so that one can set the conditions, e.g., pressure and temperature, accordingly.

1.3 Systems, Balance Laws, Property Relations

In order to describe thermal processes accurately, we require a number of equations and relations to describe the behavior of the *thermal system* under consideration, and the details of the materials contained in the system.

The previous paragraph in fact points to the first requirement of any thermodynamic analysis, which is to chose a well defined system to be described, e.g., the system could be an entire power plant, or just the steam turbine within. In any case, the system boundary must be well defined so that all transport of material, energy etc. across the system boundary is well understood.

The processes within a system are described by *balance laws*, equations that account for all changes within the system as well as the transport across the system boundary. Balance laws are often written as rate equations, where the change of the amount of the balanced quantity over time is equated to causes for change, such as flow over the boundary, or creation/destruction inside the system.

The simplest balance law is the *conservation law for mass*, which states that mass cannot be created or destroyed. Hence, the mass inside the system boundaries can change only due to transfer of mass in or out over the boundaries. A *closed system* is defined as having no mass transfer over the boundaries, accordingly the mass in a closed system is constant. In an *open system* mass can enter or leave; this can lead to changing amount of mass within the system, for instance when a container is filled, or, when the inflow is balanced by the outflow, to an exchange of the material in the system, while the mass in the system is constant.

The *conservation laws for energy* states that energy cannot be created or destroyed. To emphasize its central importance, it is known as the *First Law of Thermodynamics.* Energy exists in different forms; familiar from mechanics are *kinetic* and *potential energy*, and thermodynamics adds *internal* (also called *thermal*) *energy.* The first law describes the conversion between the different forms of energy, and the transport of energy in form of heat and work. While the first law describes conversion from work to heat and vice versa, it cannot distinguish between possible and impossible processes.

Indeed, thermodynamic processes are restricted in many ways, e.g., heat will by itself go from hot to cold and not vice versa, or a mixture will not spontaneously separate. These restrictions are formulated in the *Second Law of Thermodynamics.* The second law introduces a new quantity, the *entropy*, which can only be created, but not destroyed. Accordingly, the second law is a balance law for entropy that describes the change of entropy in the system due to transport across the boundary, and creation inside the system. Since we have no sense for entropy, this quantity is somewhat non-intuitive, however, the second law is seen at work quite easily, for instance in all equilibration processes such as those discussed above. Processes in which entropy is created are called *irreversible*, and any creation of entropy can be related to a loss in work. The second law has far ranging consequences, including the restriction of the *efficiency* of heat engines to values below unity, that is, *heat cannot be fully converted into work.*

As just stated, we have no sense for entropy. But then, we have no sense for energy as well, and our sense for temperature is rather inexact. To fill the thermodynamic laws with life, the quantities appearing in them, most importantly energy and entropy, must be related to measurable quantities.

With temperature playing a prominent role in thermodynamics, temperature and its measurement must be clearly defined, which is done by means of the *Zeroth Law of Thermodynamics*, which states that two bodies in equilibrium have the same temperature. The assigned number (*zero*) indicates that this law now is introduced before the first and second laws, but historically its importance for a sound development of thermodynamic theory was recognized only after these were named.

Measurable quantities are length (and thus area and volume), time (and thus velocity and acceleration), mass, pressure (or force), temperature, and concentration. For specific systems the thermodynamic laws must be furnished with *property relations* that describe the physical behavior of the materials contained in the system, by relating measurable quantities to each other as well as to those that cannot be measured directly (energy, entropy . . .). Property relations are laid down in equations or in tables, they result from careful measurements and evaluation of these by means of the thermodynamic laws.

1.4 Thermodynamics as Engineering Science

Typically, scientists and engineers ask different questions. With some simplification, one might say that a scientist asks *Why does this happen?*, while an engineer asks *How can I use it?* But then, the boundaries between science and engineering are rather fluent, and there is significant overlap. For instance, both disciplines will be interested in the basic laws—in form of equations—that describe the observed phenomena. For the scientist this is part of understanding and describing nature, while for the engineer the basic laws are tools to model and improve engineering devices. It is probably fair to say that the deeper an engineer understands the laws of nature, the more use she/he can make of them. Deeper understanding will lead to new ideas that might not be obvious at the first look.

As stated earlier, thermodynamics was developed out of an engineering desire, namely to improve the efficiencies of heat engines. This need resulted in the thermodynamic laws, which were found on purely phenomenological grounds, that is by observation and conclusion. As will be seen, thermal energy and entropy arise as necessary, and rather helpful, quantities, which appear in their respective laws (1st and 2nd). The laws describe work and heat exchange, and the trend to equilibrium, but they do not answer the questions *What is energy? What is entropy?* Indeed, for engineering applications the answer to these questions is not relevant, as long as property relations for energy and entropy can be found from measurements, as is the case.

Nevertheless, a deeper understanding of these quantities can be obtained by looking at the microscopic description of matter, that is on the atomic or molecular level. Thermal energy can be related to microscopic kinetic and potential energies, so that concepts from mechanics can be transferred to some degree.

Entropy can be related to the number of microscopic realizations of the same macroscopic state, as will be discussed for rather simple model examples. The trend to equilibrium as expressed in the second law is then simply a motion of the system towards macroscopic states that have a larger number of microscopic realizations. The final equilibrium state has the largest number of realizations, and thus is—by far—most likely. Often one finds explanations of entropy as a measure for "disorder", but this might be misleading wording, unless a careful definition of "disorder" is provided.

Even somewhat superficial arguments on microscopic behavior can yield deeper insight into entropy, and thermodynamic processes. Hence, the introductory chapter on entropy and the chapters on reacting and non-reacting mixtures contain some descriptions on the microscopic level. Naturally, we can just scratch the surface. The reader might study these sections for some insight—for deeper understanding, we must refer to the relevant scientific literature.

As might become clear from the above, the microscopic description of entropy relies on ideas of statistics. The proper understanding of matter on the microscopic level is subject of *Statistical Mechanics*, a branch of physics which for instance can be used to find property relations.

1.5 Thermodynamic Analysis

After the introduction and general discussion of the basic laws of thermodynamics and the property relations, the study of thermodynamics turns to the thermodynamic analysis of a wide variety of systems.

The system considered, and the goal of the analysis, depends on the field of study. This text focuses on engineering applications of thermodynamics, where the aim is to understand the working principles, and to evaluate the performance of thermodynamic systems such as power plants, refrigerators, chemical reactors and so on. Deep understanding of system behavior from thermodynamic analysis will lead to performance enhancement by proper setting of available parameters, redesign for improved efficiency, replacement by more efficient alternatives, and, possibly, to development of completely new system configurations.

Thermodynamic analysis of a system entails some or all of the following:

- Introductory discussion of the system under consideration. What is the purpose of the system, how is it achieved?
- General discussion of the working principles of the system.
- Clear identification of the system. Decomposition into subsystems for easier evaluation.
- Material considerations. Are there limiting values for system parameters, e.g. maximum temperatures and pressures, that cannot be exceeded?
- Determination of all relevant physical data (pressure, temperature, energy, entropy and so on) at all relevant locations in the system, and its subsystems.
- Computation of all heat and work exchanges for the system, and its subsystems.
- Evaluation of system performance, as expressed through meaningfully defined efficiency measures, both for subsystems and the overall system.
- Analysis of system configuration and performance. Which controllable parameters must be changed, and how, to improve or optimize the system?
- Second law analysis: Identification of irreversible processes in the system. Determination of entropy generation and associated work loss, both within the system and in the exchange between system and its surroundings.

Which processes have the largest losses? Can the system be modified to reduce the loss?
- General analysis. Is the system as evaluated suitable for the chosen purpose? What are the alternative systems, or system configurations? Which system/configuration should be preferred?

1.6 Applications

Before we enter the technical part of our studies of thermodynamics, for a quick overview, we present a list of the engineering applications that will be discussed in the following chapters:

- Hydrostatic and barometric pressure laws.
- Efficiency limits for heat engines, refrigerators and heat pumps.
- Perpetual motion engines.
- Internal combustion engines: Otto, Diesel, Atkinson.
- Simple open systems: compressor, pump, turbine, throttle, nozzle, diffuser.
- Heat exchangers: co- and counter-flow closed heat exchangers, open heat exchangers
- Steam power plants: standard and reheat cycles, advanced cycles with open and closed feedwater heaters.
- Vapor refrigeration systems and heat pumps: standard cycles, advanced multi-stage cycles.
- Linde gas liquefaction process.
- Stirling and Ericsson engines.
- Multi-stage compressors.
- Gas turbine systems for power generation: standard cycle and multi-stage cycles.
- Combined cycle: gas turbine and steam cycle for high efficiency.
- Solar tower: updraft power plant.
- Air engines: standard air turbine and turbo-fan engines.
- Supersonic flows: rockets, ramjet and scramjet.
- Filling and discharge.
- Compressed air energy storage (CEAS): storing energy by compressing air into large caverns.
- Temperature change in throttling (Joule-Thomson coefficient).
- Thermodynamic equilibrium and phase equilibrium.
- Ice skating.
- Mixtures, heat and entropy of mixing.
- Psychrometrics: humidifying and de-humidifying for air conditioning, cooling towers.
- Mixing and separation.
- Osmosis.
- Desalination by reverse osmosis.
- Pressure retarded osmosis: power from mixing freshwater and saltwater.

- Gas separation and CO_2 removal: work requirement for carbon capture and storage.
- Two-phase mixtures: ideal and non-ideal mixtures, activity and fugacity, Raoult's law, phase diagrams.
- Distillation columns.
- Gas solubility: Henry's law, carbonized and nitrogenated drinks.
- Reacting mixtures: law of mass action and Le Chatelier principle.
- Haber-Bosch process for ammonia (NH_3) production.
- Combustion.
- Work potential of a fuel.
- Work losses in a steam power plant.
- Fuel cells: potential and power, losses caused by mass transfer, resistance, activation and crossover.
- Electrolyzers.