1

Introduction: A Brief History of Thermodynamics

COPYRIGHTED MATERIAL

In this chapter you will:

- Review the historical development of heat engines.
- Learn how thermodynamics grew out of efforts to improve the performance of heat engines.
- Gain an overview of concepts such as energy and entropy and the laws of thermodynamics.

1.1 What is Thermodynamics?

When earth's creatures were created, according to Greek legends, each received its own gift of speed or strength or courage. Some animals received wings to soar on, others claws to defend themselves, but finally, when it was the turn of humans, nothing remained. Prometheus saved mankind by stealing fire from the gods, making people far more powerful than any animal. Such myths – and similar stories exist in almost every society – trace the birth of human civilisation to the discovery of fire, which gave warmth, nourishment and the ability to craft objects out of stone and metal.

Fire alone would not have allowed humans to survive in the wilderness – they also needed tools. Life without sharp claws or fangs is possible if you can make knives and spearheads. Humans may not have the speed of a gazelle but they discovered wheels; levers and pulleys can lift heavier loads than any elephant. Tools improved slowly over time as wheelbarrows evolved into horse drawn carts and stones for grinding grain became windmills, but there were

Energy, Entropy and Engines: An Introduction to Thermodynamics, First Edition. Sanjeev Chandra.
© 2016 John Wiley & Sons, Ltd. Published 2016 by John Wiley & Sons, Ltd.
Companion website: www.wiley.com/go/chandraSol16

few gains made in the power used to drive them. Animals, water and wind were all harnessed to drive machines, but there is a limit to how effective any of these power sources are. Winds are unreliable, there are a finite number of sites with running water, and only a few horses can be hitched to a cart at one time. This lack of power sources limited how fast technology could evolve over most of human history. An ancient Egyptian, transported 30 centuries forward to medieval Europe, would have had little difficulty in recognising the machines used.

Then, a little over 300 years ago, fire was used as a power source for the first time. The first practical steam engine marked a turning point in human history, for it put enormous reserves of energy at our disposal. We are no longer restricted to capturing forces exerted by the elements or animals. Gases expand when heated and exert tremendous pressures that can be exploited to drive power plants, aircraft and automobiles. The only constraint on generating power is the amount of heat available, and the technology used to generate heat has advanced rapidly, whether it is by burning fuel, capturing solar radiation, or splitting atoms in nuclear reactions. Today, machines that use heat to produce work are everywhere.

As steam engines became more common, questions about them multiplied. What is the relation between heat and work? How much work can be obtained if a given amount of fuel is burned? Can the performance of engines be improved? Thermodynamics was the science that grew from efforts to answer these questions. The word itself is a combination of the Greek *therme*, meaning heat, and *dynamis*, meaning force, and thermodynamics is often defined as the science that studies the relationship between heat and work. Engineers struggling to understand how engines work formulated the principles of thermodynamics, but they have since been used in the study of all phenomena that involve changes in energy. Astrophysicists use the laws of thermodynamics to predict the fate of an exploding star, biologists apply them to the metabolism of animals and chemists rely on them to determine the products of chemical reactions.

1.2 Steam Engines

Using heat to produce motion is not a very novel achievement. As early as the first century a Greek inventor had designed a toy in which steam escaping from nozzles mounted on the surface of a metal sphere made it spin, but there seems to have been no practical application of this device. In subsequent centuries cannons became the most impressive illustrations of how objects could be transported by generating heat. But, no matter how spectacular the discharge of a cannon, it is difficult to harness it for any constructive purpose. For that we need a "heat engine", defined as a device that operates continuously, producing work as long as heat is supplied to it.

We can mark precisely the date when the first industrial heat engine was invented, for in 1698 the king of England was pleased to grant Thomas Savery a patent for a "fire engine" to be used "… for raising of water, and occasioning motion to all sorts of mill works …". Savery's machine did not resemble our typical image of a steam engine, for it had no furiously driving pistons or spinning flywheels. It consisted (see Figure 1.1) of a large chamber that was first filled with steam from a boiler, sealed and then sprayed with cold water to condense the steam in the vessel and create a partial vacuum that sucked water up from an underground mine. High-pressure steam was used to empty the chamber by pushing the water in it up to a

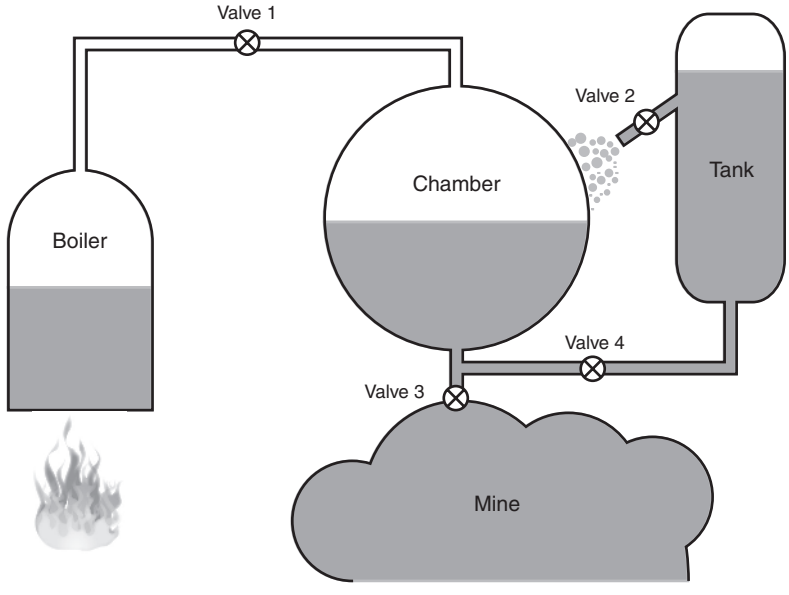


Figure 1.1 Savery Engine. Opening valve 1 fills the chamber with steam. Opening valve 2 douses the chamber with cold water, condensing the steam and creating a partial vacuum. Opening valve 3 sucks water into the evacuated chamber from the flooded mine. Opening valve 4 while filling the chamber with steam pushes water into the tank.

higher level. Valves controlling the flow of steam and water were operated manually and a good operator could complete several cycles in a minute.

Savery intended to sell his pumps to English coal mines where flooding was a frequent occurrence, so that water had to be drained by hand or horse driven pumps. Sadly, his pumps proved to be rather leaky so that it was hard to hold a very good vacuum in the chamber. Savery claimed that his engine could raise water by about 80 feet (24.4 m), which would have required steam pressures of almost three atmospheres. Frequent explosions of poorly made boilers were so common that high-pressure steam was viewed with fear and not used again for more than a century when manufacturing techniques had greatly improved.

Savery was unable to produce a commercially successful engine, but he proved that steam could be used to drive machines. By the time Savery's 14-year patent expired in 1712 Thomas Newcomen was ready with his design for a new engine, which looks far more recognisable to us as a steam engine (Figure 1.2). Newcomen had a piston moving back and forth in a cylindrical chamber, one side of which was connected to a boiler producing steam. When the chamber was filled with steam the piston rose up. Spraying water into the chamber condensed the steam, producing a partial vacuum so that atmospheric pressure forced the piston down. A beam connected to the piston oscillated as the piston moved up and down, which could be used to drive a pump or some other machine. This was an "atmospheric engine", in which work was done by the atmosphere pushing a piston against a vacuum. Steam pressure was never much higher than one atmosphere, minimising the hazard of explosions.

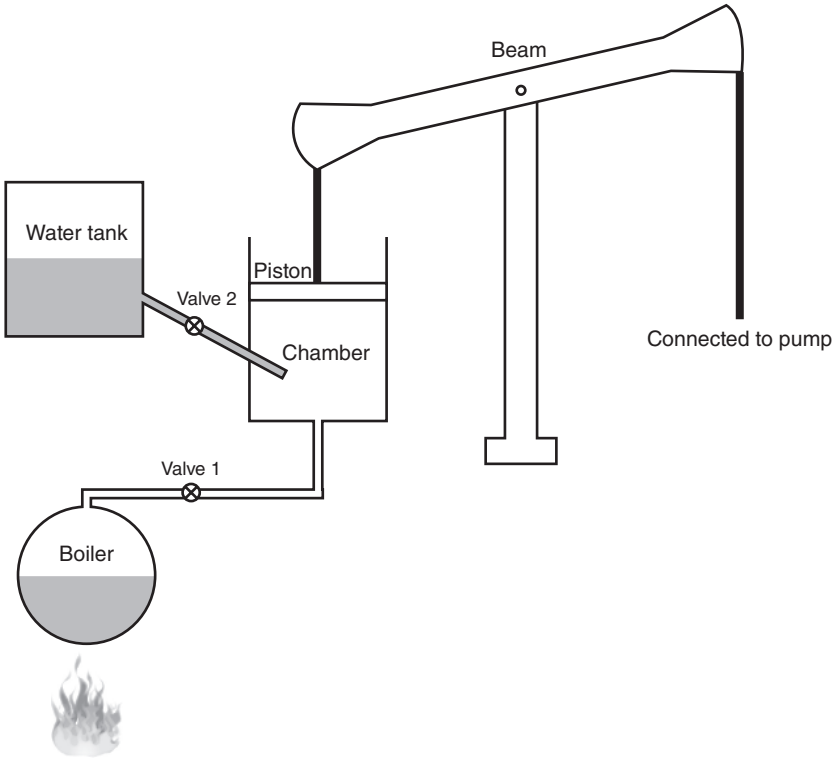


Figure 1.2 Newcomen Engine. Opening valve 1 sends steam into the chamber and raises the piston. Opening valve 2 sprays water into the chamber, condensing the steam so that atmospheric pressure forces the piston down. A beam connected to the piston oscillates up and down and drives the pump.

Newcomen's engine was an immense success and hundreds were built and sold. They were initially used to power pumps in coalmines but soon found new applications in textile mills and other factories. For over 50 years Newcomen's engines represented the most sophisticated technology available and sparked a remarkable technical and social transformation that changed human history. For the first time machines could work non-stop without depending on beasts of burden or being subject to the vagaries of weather. Any factory had access to as much power as it needed, no matter where it was located. The steam engine gave birth to the industrial revolution and created the modern world.

Newcomen's engines were a tremendous accomplishment but consumed enormous amounts of coal to generate steam, most of which was wasted. At the start of each cycle, when steam entered the cylinder, much of its energy went into heating the walls of the cylinder, only to have to cool them down again when the steam was condensed with a water spray. While engines were confined to coalmines this was not of great concern since fuel was practically free, but when they began to be used in factories far from fuel supplies operating costs became a serious problem.

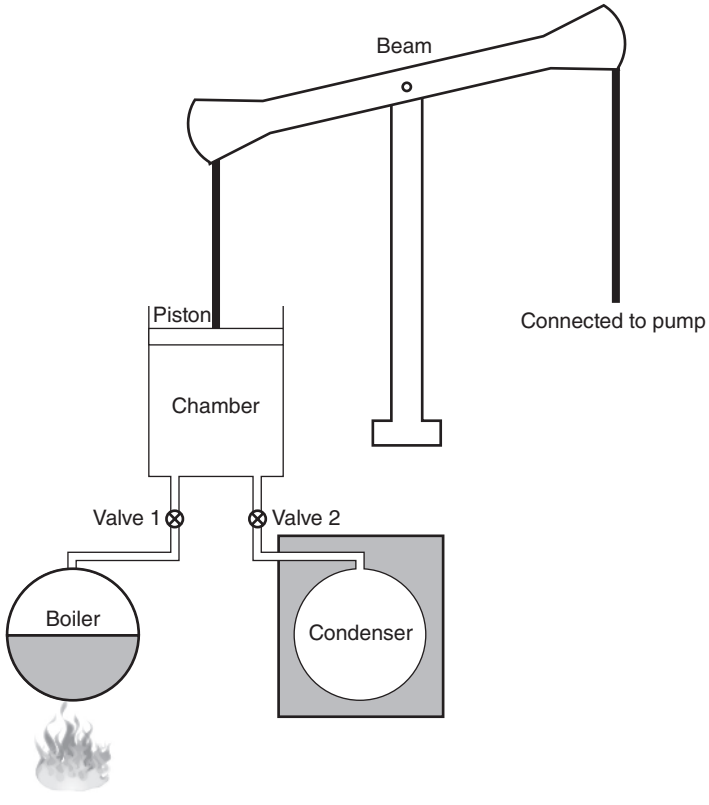


Figure 1.3 Watt's engine with an external condenser. Opening valve 1 allows steam from the boiler to fill the chamber and raises the piston. Opening valve 2 lets steam from the chamber escape into the condenser, creating a vacuum under the piston so that atmospheric pressure pushes the piston down.

James Watt, a young instrument maker at the University of Glasgow, proposed a solution. Watt had been assigned the job of fixing a model of a Newcomen engine used for laboratory demonstrations. He found that the model worked as designed, but consumed all the steam supplied simply to heat the cylinder wall. After much thought he solved the problem by adding an external chamber in which steam was condensed (Figure 1.3). In 1769 Watt obtained a patent for the external condenser, entitled a "new method for lessening the consumption of steam and fuel in fire engines". The new engines were so much more efficient than the older Newcomen engines that it became feasible to use them in many new industrial applications.

Many brilliant inventors have pioneered new technologies, only to see others reap the profits. Watt escaped this fate for he had the good fortune of entering into partnership with Matthew Boulton, an extremely shrewd businessman and manufacturer. For decades the firm of Boulton and Watt held the most important patents related to steam engines, enforced them vigorously and dominated the steam engine manufacturing industry. They produced atmospheric engines that used the pressure of the atmosphere to drive their pistons; steam was used

only to produce a vacuum. Watt strongly opposed the use of high-pressure steam to drive engines, firmly convinced that they were too dangerous, and even tried to get the British parliament to pass a law banning high-pressure steam. Even without the law, his control of patents on the external condenser and several other technologies essential to steam engines ensured that he could block any new development that he did not agree with. Watt's fear of high-pressure engines was well founded in his experience of boiler explosions in the early days of steam, but manufacturing techniques were also improving rapidly. In 1776 John Wilkinson invented a new type of lathe that made it possible to bore cylinders up to 18 inches (46 cm) in diameter with great precision. Wilkinson had designed his machines to produce better cannon barrels, but they also proved eminently suitable for making engine cylinders with piston seals strong enough to withstand high pressures.

James Watt's patent on the external condenser finally expired in 1800 and the field of engine design was again open to new developments. That same year, Richard Trevithick built a high-pressure steam engine to operate a pump in a Cornish mine. In his engine, steam at more than twice atmospheric pressure pushed against the piston to deliver power and was then released into the air instead of being condensed. The sound of steam being vented led to the engines being popularly known as "puffers". Once it was demonstrated that high-pressure engines could be safely built and run, their advantages became immediately obvious. A relatively small engine could deliver more power than a much larger atmospheric engine and, even better, it had no need for a heavy condenser. Such a light engine could be used to power a vehicle and by 1804 Trevithick had built a locomotive that could move 25 tons (25.4 t) at a speed of 3.7 miles / h (6 km / h). This was a remarkable machine for no one had ever seen a self-propelled vehicle before, but it was not a commercial success since it frequently broke down and the iron rails available at that time could not withstand the weight of the locomotives for long. The now elderly James Watt launched virulent attacks, railing that Trevithick "deserved hanging for bringing into use the high-pressure engine".

George Stephenson finally solved the technical problems related to both engines and rails when he built his locomotive in 1813 and was operating a commercial train service by the time Trevithick died in poverty in 1833. Stephenson is now acclaimed as the inventor of the locomotive while Trevithick is rarely remembered, but Trevithick's firm belief that high-pressure engines could be safely operated and would prove more efficient was vindicated as operating pressures steadily increased.

It is frequently said that the great age of steam is over, and it is certainly true that there are not many steam locomotives running today. However, steam is used to produce electricity in power plants in every part of the world. In a modern steam power plant water is pumped into boilers where it is heated as it flows through tubes (Figure 1.4). Hot gases flow across the outer surfaces of the boiler tubes, heating the water until it emerges as high-pressure steam. The heat source is most often a burning fuel, but can also be a nuclear reaction or a renewable source such as sunlight. The steam is fed into a turbine, jetting out of nozzles at velocities greater than the speed of sound, and impinges on turbine blades projecting from a rotating shaft. The turbine shaft spins and when connected to an electric generator produces electricity. Low-pressure steam emerging from the turbine passes through a condenser, where it flows through tubes that are cooled by water running over them. Water condensing in the tubes is collected and pumped back into the boiler to complete the cycle.

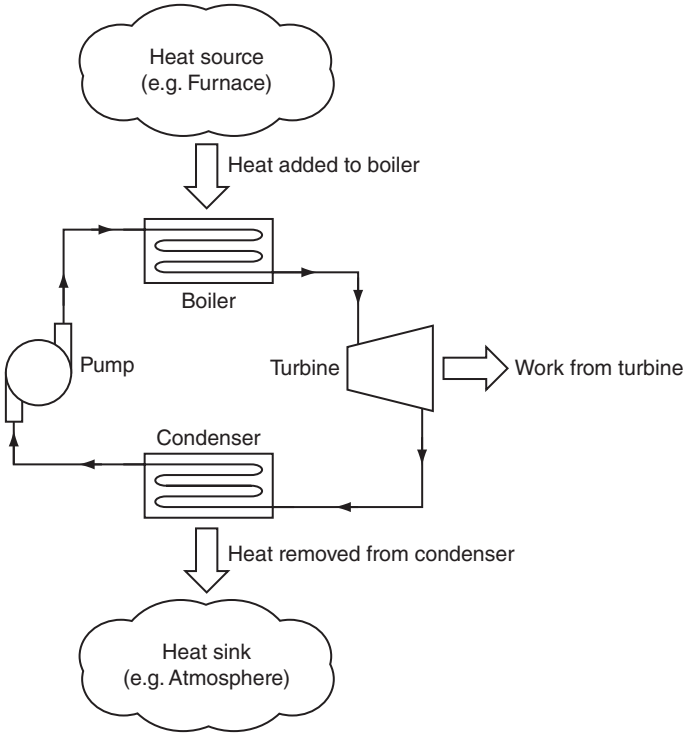


Figure 1.4 Steam power cycle.

1.3 Heat Engines

The first question a mine owner thinking of installing Newcomen's steam engine probably asked was "How much does this cost to run?" Methods of describing the performance of heat engines are almost as old as engines themselves. Operators using an engine for pumping water out of a mine defined the "duty" of an engine as the pounds of water raised one foot in height when one bushel (about 80 lbs; 36 kg) of coal was burned. Early Newcomen engines had a duty of 4.7 million ft.lb. / bushel which increased to 9.0 million ft.lb. / bushel with gradual improvements in design and construction.

Figures for duty were helpful in mines, but of no use when engines began to be used in textile mills for turning looms. Engines were typically replacing horses and for marketing purposes it made sense to compare the capacity of engines with the ability of a horse to lift a weight by a given height in a given length of time. One foot-pound (ft.lb.) was defined as the work required for raising a 1 lb weight by 1 ft. James Watt fixed one horsepower at 33 000 ft.lb. per minute. The unit still survives today, even though it would be a rare buyer who cares about comparing engine performance with that of a horse.

The horsepower of an engine tells us about its output – the rate at which it can do work – but nothing about the input, how much heat has to be supplied to it. We need a more general way of looking at heat engines. *A heat engine is any continuously operating device to which we*

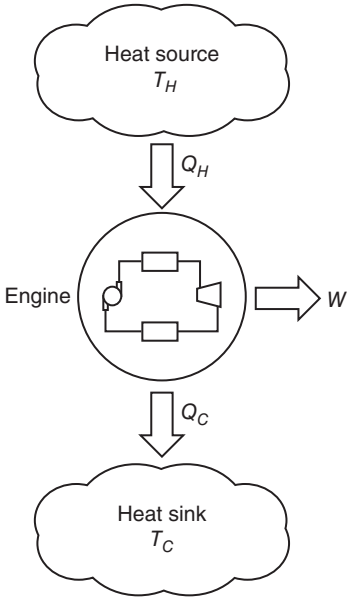


Figure 1.5 A schematic representation of a heat engine.

input heat and from which we extract work. This is a broad enough definition to encompass everything from Savery's engine to a modern nuclear power plant. We can represent a heat engine with a diagram such as Figure 1.5, in which heat (Q_H) from a high temperature (T_H) source (a coal furnace or nuclear reactor) is supplied to the engine. The engine does work (W) and loses heat (Q_C) to a low temperature (T_C) heat sink (the atmosphere or a river).

The question we would like to answer is: for a given heat input (Q_H) what is the maximum work output (W) that can be achieved? But how do we compare work with heat? What is the link between them? In the eighteenth century, there did not seem to be any obvious connection. In the era of James Watt, work was measured in ft.lbs. and heat in British Thermal Units (BTUs), defined as the amount of heat required to heat 1 lb of water by 1 °F (approx. 0.45 kg, 0.6 °C). Relating the two seems like comparing apples and oranges. But asking this question was the first step towards developing the science of thermodynamics.

1.4 Heat, Work and Energy

When Newcomen and Watt were designing their engines, the scientists of the day could offer them little assistance. There was still no clear understanding of what heat was. The prevailing theory, supported by the great French chemist Antoine Lavoisier, was that heat was a weightless, invisible fluid known as "caloric" that flowed from high temperatures to low temperatures. Most physical phenomena associated with heating an object could be explained with this theory. As caloric flowed into an object its temperature rose. Caloric seeping into the interstices between the atoms of an object being heated made it expand. Everybody had a

maximum amount of caloric that it could contain, its "heat capacity". When this limit was reached in a liquid it was "saturated" with caloric, at which point it changed to vapour. Rubbing two objects together squeezed caloric out of them and produced heat. Caloric theory has disappeared from textbooks, but we still use phrases such as "heat flow", "heat capacity" and "saturated liquid", evidence of the dominant role that it once played in science.

A fundamentally new way of thinking about heat was developed by three men who were not academic scientists, but amateurs with little formal training. Their lack of academic credentials allowed them to reject established wisdom, but it proved very difficult for them to get their ideas accepted, especially since they were directly contradicting Lavoisier, the most famous scientist of the era.

The first challenge to caloric theory came from Benjamin Thomson, an American born in the town of Concord, New Hampshire, which had formerly been known as Rumford. A loyalist during the American Revolution, he acted as a spy for the British, sending dispatches in an invisible ink of his own formulation. After the British surrender he left for England in 1776, where he found fame and fortune by inventing a stove that was efficient and smoke-free. He then entered the service of the Duke of Bavaria, rising to the rank of major general in charge of the defence of Munich. When offered a title of nobility he selected the name of his old New England hometown and called himself Count Rumford, the name by which he is remembered today. Rumford was in charge of manufacturing brass cannons that were bored out with a huge lathe, when he noted the heat generated by cutting tools rubbing against metal. He devised an experiment in which a very dull boring bit was used on a cannon submerged in water, whose temperature rose until it boiled. Rumford concluded that if heat could be generated without limit it "cannot possibly be a material substance" since it was impossible for caloric to be produced endlessly.

Rumford's presentation of his experiments was met mostly by incomprehension and indifference. Supporters of the caloric theory speculated that perhaps fresh caloric was continuously uncovered as the drill removed layers of metal. Even worse, Rumford had no alternate theory of heat to offer. He speculated vaguely that heat is a form of motion – but motion of what? Rumford had nothing more specific to add. For lack of any better ideas caloric theory continued to hold sway and Rumford's work was virtually ignored.

Inspiration sometimes strikes in the most unexpected places. The insight that had eluded generations of the best scientists in the world came from an odd source – a provincial German doctor. When the 26 year old Robert Julius Mayer signed on as a doctor on board a Dutch ship bound for Indonesia in 1840, he was looking for nothing more than some adventure before settling down to his small town medical practice, but the observations he made during the voyage diverted his life onto an unexpected path. When the ship was in tropical waters he observed that the blood of his patients was bright red, a sign of high oxygen concentration in the blood. Mayer knew that the human body is heated by oxidation of carbon in food to produce heat and he concluded that in a hot climate less heat is required and therefore less oxygen is used. This was an interesting observation, but hardly revolutionary. It was the astounding leap of intuition that followed that led Mayer to a radically new way of thinking about heat and work.

Mayer reasoned that the same metabolic processes that generate heat in the human body also allow it to do work, so somehow heat and work must be related. Mayer was familiar with Lavoisier's statement of the law of conservation of mass: during chemical reactions the

outward form of matter can change significantly – from liquid to vapour for example – but the total amount of mass remains the same. Perhaps there was a similar relation between heat and work – there was some underlying quantity that is conserved and cannot be destroyed, but appears in various forms. He was struggling for a term that would encompass both work and heat, what we now call energy, but the word did not have the same meaning at the time. Mayer called it "force". His 1842 paper concluded that this "force" was "indestructible and transformable", the earliest statement of a law of conservation of energy. He did no experiments but he gave an estimate for the mechanical equivalent of heat – the quantity of heat generated when a certain amount of work is done – purely from theoretical analysis of published data on temperature changes in gases as they are expanded or compressed.

Mayer's idea that heat and work were equivalent would eventually transform science, but it made little impact on the academic world when he first proposed it. Mayer's exposition was confused, he had little training in physics, and his mathematics was faulty. Most established researchers chose to simply ignore the paper. Deeply wounded by the rejection and facing family tragedies, Mayer despaired of receiving recognition and attempted suicide in 1850. He spent the next several years in institutions seeking help.

If Robert Mayer was an unlikely scientist, James Prescott Joule had been raised from birth for that role. The heir of a wealthy English brewer, he had been tutored at home by the famed chemist John Dalton. For the rest of his life Joule was to pursue both vocations, tending to the brewing business by day and pursuing his scientific pursuits as a gifted amateur. The two interests were not unrelated – brewing made him an expert at temperature measurements, indispensable in keeping vast brewing vats at controlled conditions. It also made him keenly aware of steam engines and the new technology of electric motors. In 1840, when he was just 22, his experiments led him to discover the relation between the heat released in a resistor and the current flowing through it, which is still known as Joule's law.

Unaware of Mayer's work on work and heat, Joule devised a simple experiment to measure the mechanical equivalent of heat. The apparatus he used was simple but very ingenious, consisting of a paddle wheel that rotated in a closed, well insulated container filled with water (Figure 1.6). A falling weight pulled a rope wrapped around the shaft of the paddle, making it rotate. The height of fall gave precisely the amount of mechanical work done in driving the paddle and a thermometer in the water measured the corresponding rise in temperature. After a series of tests, Joule calculated a value for the mechanical equivalent of heat that was within

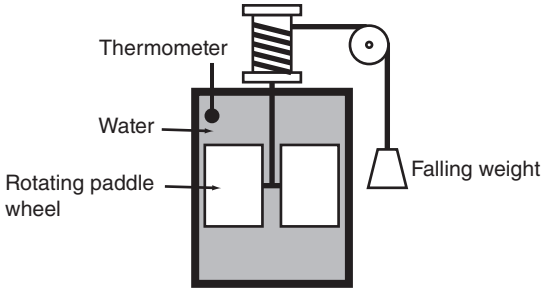


Figure 1.6 Joule's apparatus to determine the mechanical equivalent of work.

1% of modern measurements, an impressive feat of experimental research. But when Joule first presented his results in 1845 in Britain few found them noteworthy and his paper to the Royal Society was initially rejected.

Joule's work may have excited little comment initially, but he was not fated to face the total rejection that Mayer had. Attending his presentation was a young professor named William Thomson, who was later to become one of the most famous scientists in Britain and given the title of Lord Kelvin. Kelvin immediately grasped the importance of Joule's measurements and did much to publicise his work. Now it was time for the amateurs to make way for the professionals, and in 1847 a German professor, Hermann von Helmholtz, gave a talk to the Berlin Physical Society in which he used the phrase "conservation of energy" for the first time. In precise mathematical terms he showed that heat and work are both different forms of a fundamental property known as energy. He clearly stated the first law of thermodynamics, that energy can be transferred in the form of either work or heat, but it cannot be destroyed or created.

Helmholtz also made amends for an old injustice when he referred to the insights of both Mayer and Joule in his publications and recognised their pioneering work. By the time Mayer died in 1878 he had received many awards from the German government and the highest honour given by the British Royal Society. His greatest memorial, though, remains the principle of conservation of energy that is now one of the foundations of physics.

1.5 Energy and the First Law of Thermodynamics

Energy is a word that we are extremely familiar with in the modern world. We constantly monitor how much we use; we debate the price of it; we worry whether the world has enough. The concept of energy, though, is rather difficult to explain. In physics classes we define kinetic and potential energy and claim that these are related to chemical energy found in coal and electrical energy carried by copper wires. What makes all of these things the same?

A system is said to possess energy if it is capable of lifting a weight. When we raise a mass being pulled down by gravity we increase its potential energy, because if it is dropped it can lift another body to which it is tied by a rope passing over a pulley. A moving mass has kinetic energy: it is not difficult to devise a mechanism that uses its motion to lift another weight. A fuel contains energy in its chemical bonds, which can be released by burning it. Figure 1.7 shows a cylinder, one of whose walls is a movable piston, which contains a fuel gas. When the gas is ignited it heats and expands, lifting the piston. The motion of the piston can be used to do work – this is how a car engine works.

Energy can also be extracted in the form of heat. If a moving projectile hits a wall it comes to rest and all its kinetic energy is released as heat. Instead of letting the gas in Figure 1.7 expand and do work, we can lock the piston in place and let the gas cool. In both instances we have extracted energy from the cylinder, in the first case as work and in the second as heat. Work and heat are both measured using the same units, fittingly called joules.

The conservation of energy principle, known as the First Law of Thermodynamics, states that energy can neither be created nor destroyed. In a continuously operating engine the energy supplied must equal the energy leaving. Energy is added to the engine as heat (Q_H) and leaves

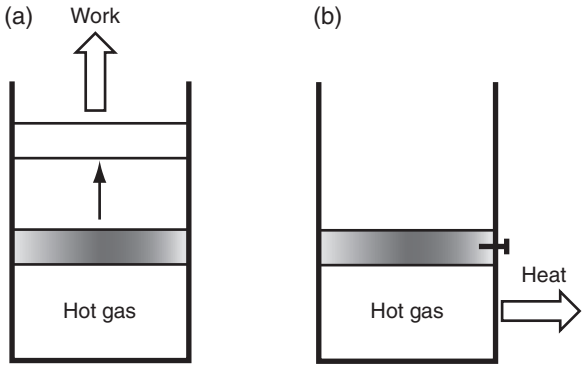


Figure 1.7 Energy extracted from a cylinder containing hot gas: (a) work is done as the gas expands and the piston is raised, (b) heat is removed from the cylinder while the piston is locked in place.

it both as work (W) and waste heat (Q_C). We can write an energy balance:

$$Q_H = W + Q_C. \tag{1.1}$$

We can now return to our original question – how do we describe the performance of an engine? If work and heat are both forms of energy, with the same units, we can calculate their ratio and define the thermal efficiency of an engine:

$$\eta_{th} = \frac{W}{Q_H}, \tag{1.2}$$

or, substituting Equation (1.1) into Equation (1.2),

$$\eta_{th} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}. \tag{1.3}$$

The thermal efficiency is a simple measure of the performance of an engine that tells us what fraction of the energy we supply as heat is recovered in the form of work

A calculation of the efficiency of a Newcomen Engine gives $\eta_{th} = 0.34\%$. Almost all the heat generated by burning coal was lost to the surroundings and went into heating up the chamber. James Watt, by providing an external condenser, increased efficiency more than 10-fold, to about 4%. This may not sound like a lot, but it was enough to power the industrial revolution and reshape the world. Further improvements increased engine efficiency to about 15% by the middle of the nineteenth century.

So how efficient are modern heat engines, the products of two centuries of research and development? The answer is surprising: not very. A typical steam power plant has an overall thermal efficiency of $\eta_{th} = 30\%$. Approximately two-thirds of the heat generated by burning an expensive fuel such as natural gas or oil is wasted, with only one-third converted to useful work.

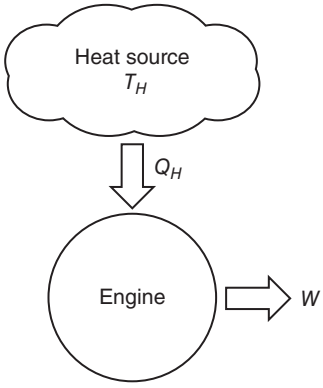


Figure 1.8 An engine with 100% efficiency.

Why are engine efficiencies so low? Could we increase them significantly through smarter engineering? It is quite easy to think of how we could get $\eta_{th} = 100\%$. If we build an engine in which there is no heat loss so $Q_C = 0$, like the one shown in Figure 1.8, then $\eta_{th} = 100\%$. Is it possible to develop an engine like this? If not, what is the highest efficiency that is achievable?

1.6 The Second Law of Thermodynamics

What is the maximum efficiency that a heat engine can have? This was a question raised almost 200 years ago by a young French engineer, Sadi Carnot. It was much more than an abstract puzzle for Carnot – whoever found the answer, he was convinced, would help his country achieve global supremacy.

Sadi Carnot was born in a family close to the centre of power in revolutionary France. His father, Lazare Carnot, was a brilliant engineer who was an expert on water driven turbines and also served as minister of war in Napoleon's cabinet. Sadi Carnot was tutored in science, mathematics and languages by his father and enrolled in the École Polytechnique in Paris where he was trained by some of the finest mathematicians and scientists in the world. He joined the army as a military engineer but Napoleon's defeat in 1815 left Carnot with little employment, giving him time to develop his interest in steam power. Resumption of trade with Britain gave him a chance to see the new engines developed by Watt and he realised that French technology had fallen far behind. Even worse, in his view, men with little scientific training had been trying to improve engines in a laborious process of trial-and-error. Carnot had in mind a far more ambitious undertaking: he would discover the theoretical principles that governed the operation of all engines and use these to design the most efficient engine possible.

For decades engineers had laboured to improve the performance of steam engines. Better lubrication, improved manufacturing tolerances, higher operating pressures had all helped to slowly edge efficiencies upwards. Carnot envisioned a much greater leap of the imagination. Let us take all engineering improvements as given, so that we have the perfect engine, frictionless, not leaking any steam and losing no heat to the surroundings. What would be the efficiency of this marvellous machine?

Carnot published the results of his study in 1824 in a book entitled *Reflections on the Motive Power of Fire.* In it he focused on the considerable loss of heat from an operating engine to its surroundings. Was there any way of completely eliminating this heat loss? Carnot's answer was no, there was no possibility of building a heat engine that did not entail heat rejection, and therefore an engine could never achieve 100% efficiency. But why was this? Carnot argued by analogy. Just as a water wheel needs water flowing continuously through it to operate, so an engine needs to have caloric flowing through it. If the outlet of a water wheel is blocked water will accumulate and soon stop the wheel from turning, so will caloric accumulate in an engine and stop it. Carnot was not satisfied with this explanation but, given the current status of knowledge about heat, it was the best that he could come up with. In spite of the flaws in reasoning his fundamental insight – that a heat engine cannot operate without losing heat – was correct and was later recognised as the second law of thermodynamics, which was actually discovered before the first.

Carnot's book was the only one that he ever published. In June 1832 a cholera epidemic swept through Paris and he fell ill and died at the age of only 36 years. Notes discovered in his papers, which were not understood until they were examined decades after his death, showed that he was preparing to abandon caloric theory and conduct experiments almost identical to those done by Joule 20 years later. Given a little more time Carnot would probably have discovered both the first and second laws of thermodynamics.

Carnot's reasoning may have been based on a false theory, but his conclusion was correct: an engine must lose heat to the surroundings to operate. Equally surprising was another deduction from Carnot's analysis – the efficiency of an ideal engine depended only on the temperatures of the heat source and heat sink it operated between. This implied that once the temperature of the boiler and the condenser were fixed, so was the engine efficiency. The working fluid in the engine, whether air or steam, made no difference. This was a truly remarkable result, but it had little impact at the time. Few practicing engineers read Carnot's book, viewing it as extremely abstract. Lay readers, for whom Carnot wrote the book, did not understand its significance.

By the middle of the nineteenth century the technology of steam engines was well developed but the science to explain them was still rudimentary. Caloric theory was on its way out and the idea of conservation of energy was beginning to be accepted. Carnot's book was out of print and almost forgotten. But all the pieces required to develop a comprehensive theory of thermodynamics were in place, waiting for someone to put them together.

Rudolf Clausius was a brilliant theoretical physicist who served as professor in most of the leading universities in Germany and Switzerland. In 1850 he published a paper that established the modern science of thermodynamics. He had before him the work of Helmholtz on the conservation of energy and, with a clear understanding of energy, he could revisit the work of Carnot and put it on a sound theoretical footing, explaining why a heat engine must continuously reject heat.

The first law tells us that transferring Q_H joules of heat from a source at temperature T_H to an engine increases its energy by an amount Q_H. Clausius postulated that heat transfer also makes another, previously undefined, property of the engine increase by an amount Q_H / T_H. He named this property "entropy", from the Greek word for transformation, deliberately choosing a name similar to "energy" to emphasise the relation between the two properties.

Adding or removing energy in the form of heat to any system always changes its entropy. When the engine loses Q_C joules of heat to a sink at temperature T_C its energy decreases by Q_C and its entropy by Q_C / T_C.

According to the first law the net change in energy (ΔE) of an engine must be zero after it has completed a heat addition and removal cycle. Rearranging Equation (1.1),

$$\Delta E = Q_H - W - Q_C = 0. \tag{1.4}$$

Clausius's work led to the development of the second law of thermodynamics which stated that over a cycle the net change in entropy (ΔS) of the engine must also be zero. Stated mathematically,

$$\Delta S = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0. \tag{1.5}$$

Rearranging Equation (1.5) and substituting into Equation (1.3) gives

$$\eta_{th} = 1 - \frac{T_C}{T_H}. \tag{1.6}$$

The second law of thermodynamics leads to the same conclusion that Carnot had reached earlier – that the efficiency of an engine depends only on the temperatures of the heat source and sink.

But what is the physical meaning of the ratio Q / T? We often combine other seemingly unrelated properties: for example, mass times velocity gives momentum. But whereas it is easy to understand the physical significance of momentum – being hit by a flying ball gives a quick appreciation of it – classical thermodynamics offered no easy insight into the meaning of entropy. It is useful here to draw a parallel with energy, another concept that we use very frequently but that is hard to visualise. We lift a weight or heat up a gas and say that energy has increased, but we have no direct way of measuring this change. Instead we measure other properties such as the elevation of the weight or the temperature of the gas and use these to calculate changes in energy. Similarly, we can calculate changes in entropy of a gas by measuring its temperature and pressure and developing mathematical equations that tell us how entropy depends on these properties.

1.7 Entropy

But we are still left with that nagging question: what does entropy mean? It is a word that is used quite frequently in ordinary language, often as a synonym for "chaos" or "disorder". An Internet search for "entropy" yields links to art galleries and rock bands among others. What does any of this have to do with engines?

The nineteenth century saw, for the first time, the use of atomic theory in physics. The idea that matter was composed of atoms had been around since ancient times, but it was an idea

that was difficult to prove or disprove, or to apply to any practical problem. Several scientists had proposed treating gases as a mass of molecules in motion, but nobody could conceive a method of applying the laws of mechanics to the unimaginably large number of molecules present in even a tiny volume of gas. The English physicist James Clerk Maxwell showed in 1866 how to solve what had appeared to be an insurmountable problem. When dealing with large populations it is difficult to predict the behaviour of any individual element, but probability theory can calculate average values very accurately. Assuming that the motion of each molecule in a gas is random, Maxwell showed how to use statistical theory to predict the average energy of molecules, while noting ruefully that probability was generally associated with "… gambling, dicing and wagering, and therefore highly immoral …". His results showed that the temperature of a gas is a measure of its molecular velocity: the hotter a gas, the faster its molecules travel. Summing the energy of all the molecules gives the total energy stored in the gas. Raising the temperature of a gas therefore increases its energy.

Maxwell's work linked energy, which had been considered a macroscopic property of a substance, to its molecular state. Perhaps entropy, which is also a macroscopic property, could also be interpreted in the same way?

Ludwig Boltzmann was a professor of physics at the University of Graz in Austria who crossed the last major hurdle in developing a science of statistical thermodynamics when he gave a molecular interpretation of entropy in 1871. He showed that the properties of a substance depend not only on how much energy it has, but also how that energy is distributed among its molecules. We can illustrate this idea by imagining a container filled with gas in which all molecules have exactly the same, low, value of energy. A few, very fast-moving molecules are introduced into one corner of the container, which is then sealed and left undisturbed. As the high-energy molecules collide with slower moving ones, some will accelerate and others decelerate until eventually there is an equilibrium distribution of velocities, with a few molecules moving slowly, a few very fast and the remainder with a range of velocities varying between the two extremes. Boltzmann related the entropy of the gas to the energy distribution of molecules. The gas in its initial state, with a few molecules possessing most of the energy, has low entropy. As energy is transferred from one molecule to another and spreads out in space entropy increases. Entropy is therefore a measure of how well the energy of a system is distributed among its molecules.

The molecular definition of entropy gives us new insight into this property. If a small amount of hot gas is injected into a large volume of cold gas and the mixture left isolated, energy diffuses out from the region where it was initially concentrated as molecules collide and exchange energy. Macroscopically we would observe this as a transfer of heat that produces an increase in entropy until the gas reaches equilibrium with the same temperature everywhere. However, the converse is never seen. If a gas is at equilibrium its molecules never rearrange themselves spontaneously so that all the energy in the system is confined to a small region. The entropy of an isolated system always increases until it reaches equilibrium and can never decrease. This is an observation with profound consequences, since it implies an asymmetry in nature: in an isolated system some processes only proceed in one direction and cannot be reversed.

Today the principles of thermodynamics are applied in every field of science and technology. Using the same fundamental theories mechanical engineers calculate the efficiency of

energy conversion processes, chemical engineers analyse the products of chemical reactions, materials scientists predict the structure of alloys, biologists investigate the functioning of living cells and astronomers study the entire universe. The laws of thermodynamics that we will study in the following pages have been used in ways that pioneers such as Carnot, Joule, Maxwell and Boltzmann could never have imagined.

Further Reading

1. H. C. Von Baeyer (**1999**) Warmth Disperses and Time Passes: The History of Heat, Modern Library Paperbacks, London.
2. M. Goldstein, I. F. Goldstein (**1995**) The Refrigerator and the Universe: Understanding the Laws of Energy, Harvard University Press, Harvard.
3. P. Atkins (**2010**) The Laws of Thermodynamics: A Very Short Introduction, Oxford University Press, Oxford.
4. D. S. L. Cardwell (**1971**) From Watt to Clausius – The Rise of Thermodynamics in the Early Industrial Age, Cornell University Press, Cornell.