

A Very Brief History of Thermodynamics

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‘Thermodynamics is the only physical theory of a general nature of which I am convinced that it will never be overthrown.’ Albert Einstein

Heat and Work

As its name implies thermodynamics is the science underlying heat and work. These terms have been known since early times, but energy, which brings them together, was not recognised and formally defined until well into the 19th century.

The potential for converting heat to work was known in ancient times. There is a famous drawing of a machine invented by Hero of Alexandria, a first century mathematician, in which the steam emerging from vents of a heated vessel makes the vessel rotate. Leonardo da Vinci drew a design for a steam driven canon. The first commercial advances were made in the late 17th century when several devices were tested for raising water from mines by steam pressure, and in the early 18th century Thomas Newcomen invented a safe and efficient pump based on the vacuum produced by condensing steam. James Watt deduced that too much energy was used in Newcomen’s pumps by raising the temperature of the chamber after each steam condensation, and he and Mathew Boulton made an improved steam engine in which the steam chamber was kept at an elevated temperature throughout the operation, with condensation occurring in a separate low temperature chamber. Steam produced mechanical power was being extensively used for manufacture and locomotion from the beginning of the 19th century.

The scientific underpinning of steam-powered engineering had two major hurdles to overcome. The first of these was to understand the nature of heat, and the second was the recognition that heat and work are different manifestations of a wider concept, which we call energy.

The modern view that heat is a manifestation of the motion of the atoms and molecules that make up matter was supported by many philosophers and scientists in the 17th century. Most notably, Francis Bacon wrote in 1620 “...the very essence of heat, or the substantial self of heat, is motion and nothing else”. It is rather surprising therefore that the alternative idea that heat was a fluid lasted for many years. Its origins probably go back to the Greek idea that fire was one of the four elements (with earth, air and water). Even Robert Boyle, a champion of the so-called mechanical philosophy that matter consists of particles in motion, proposed that the increase in the weight of metals after they were heated in air was due to their combination with the materials of fire.

The first quantitative measurements of heat by calorimetry were made by Joseph Black on melting and vaporization. His researches appeared in a book 'Lectures on the elements of chemistry', published after his death in 1803. However, Black himself assumed that heat was a substance by adopting the view that when a material is heated some heat matter is added to it, and when it is cooled that matter is taken away. He concluded that it was this 'matter' that led to the expansion of bodies when heated. Although we now reject the heat as a fluid model, some of its language is still with us as we talk about heat flowing from hotter to colder bodies.

The word calorique (caloric) was introduced by Guyton de Morveau in 1787, and adopted by Lavoisier, who, in his 'Traite elementaire de chemie' (1789), listed it along with 23 authentic elements, to represent the 'imponderable fluid' of heat. By placing it amongst his elements Lavoisier implied that it could not be created or destroyed, it just moved from one body to another. This assumption was finally overturned by the famous canon boring experiments of Benjamin Thompson, later to be Count Rumford. In 1798 he observed that the amount of heat produced by friction in boring a canon was greater for a blunt instrument than it was for a sharp instrument. Moreover, the quantity of heat and the quantity of borings were roughly in inverse proportions. He also established that the shavings had the same weight and heat capacity as the original metal. He concluded that heat was not a fluid being released from the material but was a result of the conversion of mechanical work into heat; he even made a rough estimate of the mechanical equivalent of heat.

**Rumford's experiments were carried out on a specially constructed brass canon barrel, which was insulated against loss of heat, and he used a blunt drill bit. The front of the barrel was immersed in a tank full of water. He wrote : "... at 2 hours and 30 minutes it actually boiled."*

Energy

Reasonably accurate values for the mechanical equivalent of heat were first obtained by James Prescott Joule around 1843. He examined the heat produced by both electrical and mechanical means, and was convinced that the various forms of energy could be converted one into another. By measuring the heat produced in water by a paddle wheel he deduced that 772 foot-pounds of mechanical work was equivalent to the heat required to raise one pound of water by 1°F. In modern units this would make 1cal=4.15J, the current value being 1cal=4.184J.

- *Joule deduced the mechanical equivalent of heat by both electrical and mechanical means. However, the rise in temperature produced by his famous paddle wheel experiment is very small, and a modern attempt at Cambridge failed to reproduce his result; but Joule claimed to be able to detect 1/200 of a degree Fahrenheit on his thermometer.*

- *One joule of energy is that required to raise a pound of water by 9 inches, or to raise its temperature by 0.001F*

The equivalence of all forms of energy also received support from biological studies. Lavoisier and Laplace had shown that the ratio of heat evolved to the quantity of carbon dioxide produced was roughly the same from a guinea pig as from the burning of a candle, and in 1842, Robert Mayer, a German physician, speculated about the link in humans between food consumption, heat produced and work done, and concluded that all were different manifestations of an indestructible quantity, which he called force, but meant energy. Not surprisingly Mayer and Joule later became involved in a priority dispute over who first proposed the conservation of energy, but perhaps both should give way to Friedrich Mohr who wrote in 1837, "Besides the fifty four chemical elements, there exists in nature only one agent more, and this is called force (he meant energy); it can under suitable conditions appear as motion, cohesion, electricity, light, heat, and magnetism. Heat is thus not a particular kind of matter, but an oscillatory motion of the smallest parts of bodies".

The work of Carnot and Clapeyron.

That thermodynamics had its foundations in engineering is most strikingly shown by the work of Sadi Carnot, a French engineer. In his book 'Reflections on the Motive Force of Fire' (1824), he drew a comparison between the work that could be extracted from a water wheel, and that which could be obtained from a steam engine. In the first case the work depends on the amount of water that passes and the height through which it drops, and for the second, he said that the motive force of a steam engine depends on the quantity of caloric employed and the difference in temperatures between the heat source and the heat sink. He believed that heat was a fluid until close to his death in 1832, and perhaps he would not have arrived at his conclusions without it; if heat reflected mechanical motion of the atoms the analogy between a water wheel and a steam engine would be far from obvious.

Carnot introduced two ideas in his analysis of heat engines, which were to play an important part in later thermodynamic theory. The first of these was the idea of a cycle, a process which occurred through several stages but which led finally back to the same point (the same conditions of temperature, volume and pressure). The second was the idea that one could go around this cycle in a reversible manner; reversibility being a succession of slow changes such that equilibrium in the system was maintained at all times. Carnot deduced that the maximum amount of work that could be extracted from an engine was when it was operating reversibly, and the efficiency of such an engine, defined as the ratio of the work done (w), to the heat supplied (q_h), depended only on the two temperatures between which it operated.

Carnot's conclusions were not well known until they were taken up by Clapeyron, another engineer. He examined cycles associated with changes in pressure and

volume and represented them by pressure-volume diagrams. He deduced that the area within such a diagram for a complete cycle represented the work done. He developed Carnot's ideas on the efficiency of an engine by proving that for the ideal reversible cycle operating between a heat source providing heat q_h , and a cold reservoir extracting heat ($-q_c$), the efficiency was given by

$$\text{Efficiency} = w/q_h = (q_h + q_c)/q_h \quad (1)$$

Note that by convention q is always heat added to the system so in the above equation q_c is negative.

Temperature.

Temperatures began to be measured quantitatively at the beginning of the 17th century; Galileo is credited with the first measurements with an air thermometer, which was based on the effect of temperature on the volume of a gas. Fahrenheit invented the mercury thermometer in 1724, and with three fixed points developed the temperature scale that bears his name. Celsius's scale was proposed in 1742.

Several people studied the dependence of gas volume on temperature, leading to what is known as Charles' law that the volume of a gas at constant pressure is proportional to the temperature, but this is only true if a constant equal to about 273 is added to the Celsius scale. A major step forward was made in 1848 by William Thomson (later Lord Kelvin) who proposed that an absolute temperature scale could be based on Carnot's theorem that the efficiency of an ideal engine depended only on the temperatures of the hot and cold reservoirs. The scale he defined, and which we now call degrees kelvin, was one for which engines operating between temperatures T and $T-1$, would have the same efficiency for all T .

'The relation between motive power and heat, as established by Carnot, is such that quantities of heat, and intervals of temperature, are involved as the sole elements in the expression for the amount of mechanical effort to be obtained through the agency of heat; and since we have, independently, a definite system for the measurement of quantities of heat, we are thus furnished with a measure for intervals according to which absolute differences of temperature may be estimated.'

'The characteristic property of the scale which I now propose is, that all degrees have the same value; that is, that a unit of heat descending from a body A at the temperature T of this scale, to a body B at the temperature $T-1$, would give out the same mechanical effect, whatever the number T . This may justly be termed an absolute scale, since its characteristic is quite independent of the physical properties of any specific substance'

In a later paper Kelvin and Joule studied the drop in temperature of gases flowing through a porous plug (the Joule-Thomson effect), and showed that the work that could be extracted for a 1° loss of temperature was proportional to temperature if

273.7° was added to the Celsius scale, which was approximately the same constant as that deduced from Charles's law; the accepted value today for the kelvin scale is 273.15.

The first law.

The law of the conservation of energy is the first law of thermodynamics. Such a law had long been proved for mechanical motion from Newton's laws, but its generalisation to all forms of energy was only slowly established and several people had claims to its origin. The works of Mayer and Joule have already been mentioned. William Grove published a book in 1846 'On the correlation of physical forces' in which the law is clearly stated, and Hermann Helmholtz in 1847 published 'Über die Enthaltung der Kraft' in which the law is dealt with very thoroughly. By the middle of the 19th century the principle of the conservation of energy was widely accepted.

The second law and entropy.

The second law of thermodynamics relates to spontaneous change. It stemmed from Carnot's ideas on cycles and his analysis of how best to convert heat to work. Kelvin's proposal for an absolute temperature scale was also important, but the main advance was made by Rudolph Clausius in 1850. He stated the second law in the form "A passage of heat from a colder to a hotter body cannot take place without compensation". Soon after (in 1851), Kelvin arrived at the same conclusion but expressed the law in a different form 'It is impossible to devise a continuously cycling engine that produces no effect other than the extraction of heat from a reservoir at one temperature and the performance of an equivalent amount of work'. Kelvin acknowledged the precedence of Clausius for this key law of science.

In 1854 Clausius gave a detailed analysis of the Carnot cycle in which he noted that for an ideal engine operating reversibly, the heat received at the hot reservoir divided by its temperature was equal to the heat given out at the cold reservoir divided by its temperature; both temperatures being in Kelvin's absolute scale. Noting the negative sign for the heat given out, this can be written

$$(q_h / T_u) + (q_c / T_c) = 0 \quad (2)$$

He further noted that if there were various temperature ranges in the cycle, all operated reversibly, then for the complete cycle one could write

$$\int (dq/T) = 0 \quad (3)$$

This puts the factor dq/T on the same footing as other quantities that are unchanged over a cycle, like volume and temperature, and indeed like the total energy, and in a

later paper (1865) he introduced the symbol S, which he called entropie (entropy), by the relationship

$$dS = dq/T \quad (4)$$

so that for a complete reversible cycle

$$\int dS = 0 \quad (5)$$

** Note that in all the above equations q is the heat added in a reversible cycle.*

In his 1854 paper Clausius also deduced that if the cycle is not carried out reversibly then

$$\int (dq/T) > 0 \quad (6)$$

and as a consequence he was later able to make his famous statement of the first two laws of thermodynamics “The energy of the universe is a constant; the entropy tends towards a maximum”. It is the second law that underpins the direction for spontaneous change, and the flow of systems to equilibrium. However, it is important to understand that when entropy is used as a measure for such changes it is the total entropy of a system and its surroundings that is involved.

Entropy and statistics

The first suggestion that the second law of thermodynamics had a statistical basis was made by James Clerk Maxwell who noted that to violate the second law for gases in two connected vessels one would have to put high velocity molecules in one vessel and low velocity molecules in the other, by the intervention of what became known as Maxwell’s Demon (but he ignored the entropy of the demon). The precise relationship between entropy and statistical quantities was made by Ludwig Boltzmann in a series of publications beginning in 1866. His first paper was titled, ‘On the mechanical meaning of the second law of thermodynamics’, but he reached this objective only in later publications. In 1868 Boltzmann extended Maxwell’s kinetic theory of gases and took the important step of saying that the total energy of the system should be distributed amongst the individual molecules in such a manner that all possible combinations are equally possible. He later examined the approach to equilibrium according to two ideas, the dissipation of energy and the increase in entropy, and this led in 1877 to one of the most famous equations of physics,

$$S = k \ln W \quad (7)$$

where k is Boltzmann's constant, and W is the number of possible configurations of the molecules which are consistent with the state of the system. The form of this equation is consistent with the fact that entropies are additive but probabilities (which determine W) are multiplicative. Note also that as W cannot be less than one, S is always positive.

Boltzmann did not put the equation in precisely this form but this is how his work was later interpreted by Planck.

Thermodynamic properties of systems.

We come finally to the relevance of thermodynamics to particular systems in which one is interested, rather than the totality of the system and its surroundings. A system may be thermally isolated or in thermal equilibrium with its surroundings, and it may be mechanically isolated or in mechanical equilibrium; there may, for example, be changes in temperature, pressure or volume accompanying other changes to the system. We need to know the implications of the first two laws of thermodynamics to systems in these different situations.

Several people made important contributions to the thermodynamics of systems in the 19th century, either by developing the theory themselves, or by writing some of the more obscure presentations in more understandable form. Josiah Willard Gibbs deduced most of what we know today in the 1870s, but published it using a complicated notation in an obscure journal (Transactions of the Connecticut Journal of Arts and Science). His work was clarified by translations into German by Ostwald in 1892, and into French by le Chatelier in 1899. Two other key figures were Helmholtz, who did much the same work as Gibbs, and van't Hoff.

Gibbs introduced two state functions that are important in interpreting the energies of systems at constant pressure and temperature. One of these H is now called the enthalpy, and the other, G called the Gibbs energy (earlier the Gibbs free energy). Gibbs showed that changes in H were given by the heat change in a process, and that the minimum of the function G is the equilibrium condition for such a system. G also measures the maximum work that can be extracted from a system at constant pressure and temperature.

It was Helmholtz who introduced the term free energy, and the function A which carries his name has the same role as G but for a system at constant temperature and volume.

Van't Hoff's main contribution was to the study of equilibria, and to the connection between equilibrium constants and the ratio of forward and backward rate constants. He deduced the temperature dependence of equilibrium constants in the form

$$(d \ln K)/dT = (\Delta H/RT^2) \quad (8)$$

and produced the equation giving the temperature dependence of rate constants which bears Arrhenius's name. Van't Hoff's contributions to the thermodynamics of solutions lead to his Nobel prize in 1901, the first year of the awards.

The third law.

Finally, we mention the development of the third law of thermodynamics. This was stated in 1913 by Max Planck as 'The entropy of each pure element or substance in a perfect crystalline state is zero at absolute zero'. This follows from the statistical view of entropy, because for a perfect crystal at absolute zero there is only one way of arranging the molecules in the lattice, and all molecules will be in their lowest energy state. However, the third law was first formulated by Walther Nernst in 1906 when it became known as the Nernst heat theorem. Nernst's contribution stemmed from the problem of deducing equilibrium constants from thermal data. The temperature dependence of the equilibrium constant depends only on enthalpy differences, according to equation (8), but integrating to get an absolute value for K requires one to determine a constant of integration. By examining the temperature dependence of the free energy Nernst deduced that entropy differences (ΔS) must become zero at absolute zero, and to be consistent with the statistical view of entropy it was decided to make the absolute values of entropies zero at absolute zero.

The End