Chapter 1

Thermodynamics: Founders and Flounderers

"..., you alwaies end ere you begin." W. Shakespeare, The Two Gentlemen of Verona. II, IV, 32

In 1875 when the seventeen-year old, Max Planck (1858 – 1947), applied to Professor Gustav Kirchhoff (1824 – 1887) of the University of Berlin to study physics with him, the eminent professor told him quite frankly, "Why do you want to come into physics? All is done and understood." Since Planck did not think he had enough talent for his other choice, a career in music, he went against the professor's advice and continued with physics.

At the University of Berlin, Planck fell in love with thermodynamics. It did not require any such abstract concepts as atoms and was built on solid experimental foundations derived from the practical problem of designing better steam engines. It was based on two seemingly innocuous postulates.

1. Energy is conserved. In other words, it is impossible to build an engine that does nothing but create energy. Stated another way, it is impossible to build what is called a perpetual motion machine of the first kind.

2. It is impossible to build an engine that does nothing but take heat from a source at one temperature and converts all of the heat into mechanical energy. This is called a perpetual motion machine of the second kind. As Lord Kelvin (1824 – 1907) phrased it in 1848, "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of

matter by cooling it below the temperature of the coldest of the surrounding objects."

A somewhat irreverent statement of the first two Laws of Thermodynamics is:
1) You can't win.
2) You can't even break even.

The laws of thermodynamics were derived from the practical observations found while designing better engines. Put into mathematical form they have far reaching consequences that extend beyond the phenomena they were intended to summarize. Among other processes, thermodynamics allows us to compute the maximum efficiency of any engine, from an internal combustion engine to a nuclear power plant. Of course real engines are even less efficient than these ideal ones in the theory, but the theory gave realistic goals to aim for.

At that time only a few physicists actually used what was considered the "abstract concept of atoms" in their calculations. Planck also wanted none of this abstract stuff; he wanted to do solid science. In that regard he would, as a mature scientist, applaud the (1892) statement by Heinrich Hertz (1857 – 1894) that, "The rigour of science requires that we distinguish well the undraped figure of nature herself from the gay-coloured vestments with which we clothe her at our pleasure." He would also, initially, disagree with the great Ludwig Boltzmann (1844 – 1906) who strongly advanced the notion of atoms and in 1895 had replied to Hertz, "But I think the predilection for nudity would be carried too far if we were to forego every hypothesis. Only we must not demand too much from hypotheses. ... Every hypothesis must derive indubitable results from mechanically well-defined assumptions by mathematically correct methods." Near the end of the nineteenth century atoms were far from accepted and definitely not yet 'in' as a valid scientific concept. On the other hand, thermodynamics was considered to be a solid science. This is understandable since it sprang from considering some very practical problems.

One of the inadvertent founders of thermodynamics was a most colourful character, Benjamin Thompson (1753 – 1814), an American. At the tender age of 19 he married a wealthy widow, age 33 and so could move in higher social circles. However, he was a staunch Empire Loyalist and his open support of the British crown soon forced him to abandon his wife and infant daughter and flee from Boston. After spying for the British forces he moved to England while the American revolution was still in progress. After this war ended he went to Germany where he served the Bavarian king as minister of war and in other offices. As a reward, the king gave him the title "Count Rumford".

Count Rumford performed his duties to the Bavarian king so well that to this day, in the city of Munich, there are two great monuments to him: a massive statue and a very famous park containing numerous beer gardens. The Bavarian king established the "Englisher Garten" at Count Rumford's suggestion. Later Rumford married the widow of the great chemist Antoine Lavoisier (1743 – 1794) who had been beheaded during the French Revolution.

While in Munich (1779 – 1799) Count Rumford assisted in the boring of cannons. The procedure used was to rigidly mount a huge brass cylinder and drive a gigantic drill rotated by the force of four horses into the cylinder. Rumford noticed that during the process workmen kept pouring buckets of water on the future cannon to keep everything from overheating. This aroused his curiosity. He used a dull drill and continued pouring water only to discover that he could bring the water to a boil and continue to do so as long as the work continued. This convinced him that heat was not a caloric fluid, as was currently believed, since there was no limit as to the amount of heat that could be extracted from a chunk of metal. Rumford drew the correct conclusion: the mechanical work of boring produced heat. He interpreted this to mean that work and heat are simply different forms of energy.

In 1842 a German physician, Julius Rupert Mayer (1814 – 1878) published an estimate of this "mechanical equivalent" of heat. On a trip to the tropics he had noticed, during blood letting, that human blood was much brighter there and concluded that this was because, due to the higher temperature, blood did not have to transport as much energy. So, like Rumford, he hypothesized that heat and energy were the same thing. Using available data on specific heats he computed this mechanical equivalent of heat and obtained a value in reasonable agreement with modern values.

A year later a brewer's son, James Prescott Joule (1818 – 1889), experienced in precise temperature measurements as required by his brewer's craft, and influenced by Rumford's experiments with cannons, set out and measured the mechanical equivalent of heat by various means. The present unit of energy, the joule, is named after him. The controversy over priority remains to this day. This was the beginning of the science of thermodynamics, a branch of physics that was firmly established by the researches of the nineteenth century.

Incidentally, beer has been important on more than one occasion in the history of physics. Donald A. Glaser (1926 –) invented the bubble chamber after watching bubbles rise in a glass of beer. This is an important tool in high energy physics experiments. Also, Carlsberg breweries funded the Carlsberg mansion in which Niels Bohr lived.

That energy is conserved had already been accepted by many savants. In 1775, the Paris Academy of Science announced, "The Academy has resolved, this year to examine no longer any solutions to the problems on the following subjects: The duplication of the cube, the trisection of the angle, the quadrature of the circle, or any machine claiming to be a perpetuum mobile." [1] This last item refers to conservation of energy.

The father of thermodynamics was a French engineer, Sadi Carnot (1796 – 1832). Always of a frail constitution, cholera deprived the world of his talents at an early age. He was not only one of the first to enunciate the law of the conservation of energy (First Law of Thermodynamics), but also formulated correctly the Second Law of Thermodynamics. It is therefore, not surprising that in France the law of conservation of energy (the First Law of Thermodynamics) is called "*le principe Carnot*". A later expert in thermodynamics, Max Planck, had this to say about Carnot. "He has unquestionably the merit of having given the first evaluation of the mechanical equivalent of heat." The reason for this statement is that Carnot described very detailedexperiments to measure the mechanical equivalent of heat.

The further development of thermodynamics included many famous individuals, but foremost among these was a Yale professor, J. Willard Gibbs (1839 – 1903), whose initial contract stipulated "without salary". It was only after Johns Hopkins University offered Gibbs a rather attractive position that Yale offered him a salary, about two-thirds of what Johns Hopkins had proposed. As one of his colleagues wrote to him to persuade him to stay at Yale, "Johns Hopkins can get on vastly better without you than we can. We can not." Gibbs remained at Yale.

Gibbs was very rigorous, even rigid, in his thinking and behaviour. According to one of his students, E. B. Wilson, Gibbs always lectured above the heads of his students and consistently refused to teach undergraduates at all. He knew his students did not follow him but did not alter his style on that account, having a definite idea how the subject should be presented. He once told Wilson that in all his years of teaching he had had only six

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[1] Histoire de lAccadémie des Sciences, Anneé 1775

students sufficiently prepared in mathematics to follow him.

Unlike modern physicists who frequently publish too often and too soon, Gibbs laboured for many years, until he had cast thermodynamics into a coherent and complete theory. He then published his entire work, as a book, which to this day is still one of the clearest expositions of this subject. Ironically, he was relatively unlauded in his own country, although much appreciated among scientific circles in Europe, especially Germany. Max Planck spoke of him thus, " whose name not only in America but in the whole world will ever be reckoned among the most renowned theoretical physicists of all times." Also Walther Nernst (whom we meet later) paid for a marble memorial to Gibbs, even though they had never met. Gibbs' writings were sufficient to inspire such admiration.

Gibbs also invented a notation which is a boon for every modern engineer: vector notation. This way of writing vectors allows great insight into and simplification of such diverse fields as electromagnetic theory and fluid mechanics.

There is one story that may illustrate to what extent J. Willard Gibbs was underestimated at his own university and why it took such a long time for him to be promoted to full professor. During a visit to Cambridge University, the president of Yale inquired about possible people to promote at Yale. The famous Scottish physicist, J. C. Maxwell immediately suggested Gibbs. At this time there was also a socially rather prominent individual, named Alan Gibbs, at Yale. Thus, the president replied with pleasure. "Oh, you mean Alan Gibbs."

"No! No!" answered Maxwell; "Willard Gibbs."

"Well, but he is a nobody. He just sits in his room and writes," came the president's disconsolate reply.

During the nineteenth century, as today, many philosophies abounded, but British empiricism dominated much of science. One of the results of this extreme empiricism was that the concept of atoms, which was already starting to prove itself very useful, was still considered to be bad science. The argument went along the following lines. Atoms are never observed and as unobservable quantities should be excluded from physical theories since the purpose of science is to describe the real world around us and not to speculate about unobservable entities. This was a Catch 22 situation because, before convincing evidence for atoms could be found, calculations had to be performed using atoms in order to determine how to best detect them. But this went contrary to accepted doctrine. One who had the courage to do just that was a tragic genius, Ludwig Boltzmann. The obstacles he faced were enormous.

Boltzmann was the younger colleague of Josef Loschmidt (1821 – 1895), the first person to calculate the size of a molecule by using the kinetic theory of gases. In fact, what is called Avogadro's number in the English speaking world is called Loschmidt's number in the German speaking world. Loschmidt also invented the markings for double and triple bonds of carbon and suggested the structural chemical formulas for a host of important molecules. His results were ignored for decades by the world's chemists.

Years later, Boltzmann visited Loschmidt after the latter's retirement and was shocked by the indigence of this great scientist. In Loschmidt's obituary he wrote, "This is how Vienna treats its great men."

Boltzmann went much further than his colleague and almost single-handedly created a new discipline, statistical mechanics, and in so doing unified the study of systems of atoms or molecules with thermodynamics. His main idea was that everything is made up of atoms and the very exact laws of thermodynamics result from the random collision of these atoms only because in all macroscopic phenomena the number of atoms involved is enormous.

To understand why this is so, consider flipping an unbiased coin. It is impossible to predict the result of a single toss. However, the prediction that, *on average*, one should get 50% heads gets better and better with the number of flips. In fact one can give a mathematical proof that the error in the prediction decreases like the reciprocal of the square root of the number of tosses. What this means is that for 100 tosses the fractional error is about 1/10, or 10%. For $10,000$ tosses about 1/100, or 1%, and for $1,000,000,000,000$ tosses the error is only about $1/1,000,000$ or $0.0,0001\%$. Even this error is large compared to the error involved with atoms since typically about $10^{24} = 1,000,000,000,000,000,000,000,000$ of them are involved so that the typical fractional error is of the order of $10^{-12} = 0.0,000,000,001\%$.

Of course the empiricists did not take Boltzmann's assaults on their beliefs lightly. He was severely criticized by many of his contemporaries not only for what he said but also most unfairly for "lacking elegance". To these remarks he replied, "Elegance is for shoemakers and tailors."

Some of the best minds of the last century grappled with Boltzmann's approach and found what appeared to be serious logical flaws. Again single-handedly (or better yet, single-mindedly) Boltzmann overcame all these difficulties and used the criticisms to improve and strengthen his theories so that his famous Boltzmann equation remains today, over a hundred years later, as the best description available for non-equilibrium systems.

One of the people who found a flaw in Boltzmann's work was Ernst Zermelo (1871 – 1956), a pure logician, after whom this flaw is called the Zermelo Recurrence Paradox. He showed that all systems eventually return (recur) to almost exactly the same state. Thus, Boltzmann's proof that systems tend to a state of equilibrium had to be wrong. Boltzmann was able to show that this apparent paradox was due to a failure on Zermelo's part to distinguish between logical and physical systems. True, all mathematical systems would eventually recur, but as Boltzmann showed, the recurrence time was much longer than even the age of the universe whereas the time to come to equilibrium was extremely short. Thus, Zermelo's proof, although logically quite correct, was totally irrelevant for physical systems.

As stated, Zermelo was a logician and while still only a Privatdozent (meaning that he had the right to teach without salary) at the University of Göttingen presented, according to Pauli, a rather irreverent version of the Russell's Paradox to one of his classes on mathematical logic. At the time the mathematics department was ruled by Felix Klein and Zermelo presented his class with the following problem. "All mathematicians in Göttingen belong to one of two classes. In the first class are those mathematicians who do what Felix Klein does, but what they dislike. In the second class are those mathematicians who do what they like, but what Felix Klein dislikes. To what class does Felix Klein belong?" According to Pauli none of the students was able to solve this problem. Zermelo then gloated, "Meine Herren, it's very simple. Felix Klein isn't a mathematician." Pauli finished the story with, "Zermelo was not offered a professorship at Göttingen."

By 1905 Zermelo had achieved some fame. He had worked on one of the famous 23 unsolved fundamental problems of mathematics, originally posed by David Hilbert, and gave a proof of what mathematicians call "the well ordering theorem". This was enough to bring his name to the attention of the mathematical world. In 1910 he accepted the chair of mathematics at Zürich, but resigned this position in 1916 due to poor health and returned to the Black Forest in Germany where he remained for ten years. In 1926 he was appointed Honorary Professor at Freiburg im Breisgau. He resigned this position in 1935 as a protest against Hitler's regime. In 1945 he requested to be reinstated and again became an Honorary Professor at Freiburg im Breisgau in 1946

Zermelo carried his logical analysis to extremes. He even analyzed everybody's statements. But he also had his slightly paranoid side. Once while he and several colleagues were at their mathemathische Stammtisch (literally "mathematical tribal table" that is, the table reserved for the regular mathematical guests) in the Schwarzen Bären in Göttingen, the meals were served and Zermelo looked around the table and pointing to one of the dishes protested. "There, of course, you have a much bigger portion and a much bigger slice than I have. They always treat me badly." Whereupon the plates were offered for exchange and the offer was graciously accepted.

Among these members of the Göttinger Stammtisch at the Schwarzen Bären was also the physicist M. Abraham. His contemporaries thought him to be very sarcastic and thus he cultivated many enemies which may explain why he was not promoted. On one occasion, after the Göttingen Academy of Sciences had accepted a paper which Abraham considered wrong, the author of this paper, a young man named Madelung, joined the Stammtisch and was introduced to Abraham. This fine gentleman greeted him with the words, "Hallo, you have cheated our learned Academy nicely by persuading them to publish your paper. I congratulate you." Actually Madelung's paper on the absorption of infrared radiation by crystals was correct.

Another eminent critic of Boltzmann's work was Henri Poincaré (1854 – 1912). The important point is that Boltzmann had to overcome tremendous opposition to have his work accepted as the great work that it was.

The strain of all this work, however, together with the fact that he was turning blind and suffering from severe depression caused this genius to finally release himself from suffering by ending his life. While on vacation near Trieste he had an argument with his wife. She and their daughter left the house to go for a walk and when she returned, found her husband dead at the age of sixty-two.

The city of Vienna, home of many great men unrecognized until after their death, has in one of its cemeteries a tombstone bearing the inscription

$$S = k \log W \quad .$$

Beneath it lie the remains of Ludwig Boltzmann who opened the door to our understanding of macroscopic physics on the basis of microscopic or atomic dynamics. Thanks to him, statistical mechanics was firmly established as a rigorous and powerful discipline and the concept of atoms became respectable among scientists. Incidentally, the equation on his tombstone is due to Planck, not Boltzmann; it is simply a direct consequence of Boltzmann's work. The constant k is also known as Boltzmann's constant but, was first introduced by Planck. When the latter was asked what he thought about the fact that this constant was not named after him he replied, "One constant is enough for me." The Boltzmann equation, which has withstood rigorous examination for more than a century, is not inscribed on Boltzmann's tomb.

In spite of the fact that Boltzmann suffered from depression much of his life and found it extremely difficult to lecture he has, through his writings, revealed a rather impish soul. His account of his 1905 visit to California which translates as *A German Professor's Trip to El Dorado* is filled with humour and it is difficult to believe that only a year later he took his life. In this account he voices his complaint about prohibition. Soon after his arrival in the New World he was treated to "an excellent dinner of fresh oysters". However, he was forced to drink something other than beer or wine, a procedure he considered barbarian. His main complaint about Berkeley also dealt with prohibition at that establishment, which forced him to drink water with the reaction that he had "to keep my clothes on all night to reach the toilet in time". Soon, however, he discovered the existence of an excellent wine merchant in nearby Oakland and thus was able to survive. His comment on America's "Noble Experiment" was, "The temperance movement is well on its way to giving the world a new species of hypocrisy."

Boltzmann however was not alone in advancing the notion of atoms. Hermann von Helmholtz in an address to the *Akademie der Wissenschaften zu Berlin*, in February, 1882 had this to say about the Second Law of Thermodynamics. "Unordered motion, in contrast, would be such that the motion of each individual particle need have no similarity to its neighbours. We have ample grounds to believe that heat-motion is of the latter kind, and one may in this sense characterize the magnitude of the entropy as the measure of the disorder."

In a similar manner James Clerk Maxwell (1831 – 1879) explained to Lord John William Strutt Rayleigh, Third Baron of Terling Place (1842 – 1919) how he regarded the validity of the Second Law as being very probable. "Moral: The Second Law of Thermodynamics has the same degree of truth as the statement that if you throw a tumblerful of water into the sea, you cannot get the same tumblerful out again."

At the end of the nineteenth century, Classical Mechanics, Thermodynamics, and Electromagnetic Theory seemed to be able to explain the entire physical world. So, it was not without cause that physicists thought that "all is done and understood". However, soon this was revealed as hubris. Although barely noticed, cracks were already beginning to show in this magnificent structure called physics. These cracks grew progressively larger until the whole structure crumbled, only to be replaced with a new edifice in which the old structure is still recognizable, but greatly changed and much richer in design.