Josiah Willard Gibbs

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The foundations of classical thermodynamics, as taught in textbooks today, were laid down in nearly complete form by Josiah Willard Gibbs more than a century ago. This article presents a portrait of Gibbs, a quiet and modest man who was responsible for some of the most important advances in the history of science.

Thermodynamics, the science of the interconversion of heat and work, originated from the necessity of designing efficient engines in the late 18th and early 19th centuries. Engines are machines that convert heat energy obtained by combustion of coal, wood or other types of fuel into useful work for running trains, ships, etc. The efficiency of an engine is determined by the amount of useful work obtained for a given amount of heat input. There are two laws related to the efficiency of an engine. The first law of thermodynamics states that heat and work are inter-convertible, and it is not possible to obtain more work than the amount of heat input into the machine. The formulation of this law can be traced back to the work of Leibniz, Dalton, Joule, Clausius, and a host of other scientists in the late 17th and early 18th century. The more subtle second law of thermodynamics states that it is not possible to convert all heat into work; all engines have to 'waste' some of the heat input by transferring it to a heat sink. The second law also established the minimum amount of heat that has to be wasted based on the absolute temperatures of the heat source and the heat sink. The formulation of the second law was pioneered by the French engineer Sadi Carnot in the beginning of the 19th century, who developed the 'Carnot Cycle' for the heat engine.

Today, thermodynamics is not confined to the inter-conversion of heat and work, but finds applications in a whole variety of disciplines including materials science, biology, information theory and economics. The credit for providing a broad statistical

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mechanical framework should go primarily to two scientists, J Willard Gibbs of the United States and Ludwig Boltzmann (see *Resonance*, Vol.6, Sept.2001) of Austria, in the late 19th century. Gibbs and Boltzmann were contemporaries whose dates of birth were separated by less than five years in the mid 19th century and who passed away within three years of each other at the beginning of the 20th century. However, their personalities could not have been more different. Boltzmann was a troubled soul who tragically committed suicide because his theories were not universally well received by his peers at that time. Gibbs led a quiet life and all by himself laid down the foundations of chemical thermodynamics and physical chemistry. In fact, the fundamental relations of thermodynamics are taught in college textbooks today in much the same form as they were derived by Gibbs more than a hundred years ago.

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Josiah Willard Gibbs was born in New Haven, Connecticut, USA, on February 11, 1839. His father, also named Josiah Willard Gibbs, was a Professor of Sacred Literature at Yale Divinity School, and an accomplished linguist. The elder Gibbs was an activist for the abolition of slavery, and played a small but key role in the 'Amistad' saga in 1841, where Africans captured for slavery aboard the Spanish ship *Amistad* were freed after a much publicised trial in the United States and were permitted to return to Africa. This was at a time when the issue of slavery was not yet settled in the United States; the Emancipation Proclamation was yet to be signed by Lincoln and the American Civil War was fought more than twenty years later.

The younger Gibbs grew up in the liberal and academic atmosphere at Yale, where he was to spend the rest of his life. He received his undergraduate degree from Yale University at the young age of 19, and he seems to have shown early indications of his capabilities, because he graduated at the top of his class in one of the best universities in the Unites States at the time, excelling in both mathematics and Latin. The second half of the 19th century was also the time when scientific advances of far-reaching consequence were being made in the great universities of Europe,

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such as Cambridge, Oxford, Paris, Vienna, and Berlin. However, colleges in the United States were considered to be primarily for teaching liberal arts and natural sciences at the undergraduate level. The top American universities were just starting instruction in applied sciences; Harvard established the Lawrence Scientific School in 1842, the Chandler Scientific School was started at Dartmouth in 1846, and the Sheffield Scientific School was founded in Yale in 1854. Graduate studies and facilities for advanced research were also initiated at the same time, and in 1861, Gibbs was the recipient of the first PhD in engineering in the United States. He carried out his doctoral research at the Sheffield Scientific School at Yale in what is now called applied mechanics, and the title of his thesis was 'On the Shape of Teeth in Spur Gearing'. He also worked on brakes for railway cars and governors for steam engines at the time and even patented his design of railway car brakes. The second half of the 19th century also saw the rise of the great American railroads, which were to unleash the economic potential of America by providing easy access to its natural resources and transform the United States into the new superpower. The first American railroad, about three miles long, was built in Massachusetts in 1826 and the first transcontinental railroad was built in 1869. So it is not surprising that the mechanics of engines and carriages was a subject of cutting edge research in the best American universities of the time. For Gibbs, the research for his thesis must also have provided him with a firm grounding in applied mathematics, especially in geometry, which would prove invaluable to him in his later academic endeavours.

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In 1866, three years after completing his doctorate, Gibbs traveled to Europe for further studies at the universities of Paris, Berlin and Heidelberg. He was probably attracted by the culture of scientific enquiry in Europe which was then witnessing the late stages of the scientific revolution, and important scientific and technological advances were being achieved in European Universities. He does not seem to have carried out research under the supervision of a professor, but restricted himself to attending lectures by the top European scientists of the time in order to improve his understanding of mathematics and physics. In Heidelberg, Gibbs interacted with the great German physicists Gustav Kirchoff and Hermann Helmholtz. Kirchoff was a versatile physicist with contributions in many areas including the law of conservation of charge that is used in electrical circuit theory, the equation for the thermal emission from black bodies, and the laws governing the spectral decomposition of radiation. Kirchoff's law for black body radiation, which was based on the principle of thermodynamic equilibrium, was formulated in 1862, just a few years before Gibbs visited Heidelberg. Helmholtz also had significant contributions in several areas, ranging from optics and ophthalmology to acoustics and electromagnetism. He had also worked on the principle of conservation of energy, and postulated that heat, light, mechanical energy, electricity and magnetism are all forms of the same energy. These interactions must have, doubtless, motivated Gibbs to take up further study in the field of thermodynamics upon his return to the United States in 1869, though electromagnetism and optics were the most active areas of interest in Europe at the time. Equally invaluable must have been his first-hand experience of the culture of advanced scientific research in the premier European universities at the time when a similar culture was yet to develop in the United States.

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Gibbs returned to Yale in 1869 and was appointed a Professor of Mathematical Physics in 1871. A lifelong bachelor, he lived the rest of his life in the house that his father built, a short walk from Yale University. He was looked after by his surviving sister later in life. His family's association with Yale University also continued. For example, one of his sisters' husbands was the librarian at Yale University. Despite his family's long association with Yale, he was not paid a salary upon his appointment as Professor and lived off the inheritance from his father. It was only in 1880 that a competing offer from Johns Hopkins University forced Yale to start paying a small salary. Though his personal life progressed in a calm and placid manner, the research that he proceeded to carry out could only be described as revolutionary.

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Gibbs published his first paper in 1873, two years after he was appointed as professor. His most important papers were published in the *Transactions of the Connecticut Academy of Arts and Sciences*, a rather obscure journal edited by his brother-in-law who was the librarian at Yale University. Since typesetting was expensive in those days, and his concise papers were longer and contained more equations than the average publication, funds had to be raised to cover the cost of publication. Contributions were forthcoming, thanks to the generosity of faculty at Yale and the businessmen in New Haven who would not have understood very much of the subject matter of the papers. Due to the publication in obscure journals, Gibbs' work did not receive wide recognition in Europe, until it was translated into German by Wilhelm Ostwald and into French by Henri Le Chatelier. Recognition in the United States came even later, possibly because there was insufficient emphasis on scientific teaching and research in the United States at that time. However, Gibbs' work was known among the eminent scientists in Europe at that time, because he personally sent copies of his papers to many of them.

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The two short papers Gibbs wrote in 1873 were on the graphical methods for the interpretation of thermodynamic variables. In the first of these, he represented the state of an object using two-dimensional diagrams, in which different combinations of pressure, volume, entropy, temperature and energy were used as coordinates. This was new, because engineers had only used pressure-volume representations for work cycles until then. Gibbs' use of entropy as one of the coordinates was also a breakthrough, because of all the thermodynamic quantities, entropy is the one which is most difficult to physically visualise and understand. The first paper also contained a geometric representation of the differential form of the second law of thermodynamics, which relates the change in free energy to the changes in entropy and volume, and also laid down the principle of maximisation of entropy for an isolated system. The second of these papers improved on the first one, and dealt with geometric representations in three dimensions, using entropy, volume and energy as the coordinates. The latter so impressed the British physicist James Clerk Maxwell that he constructed with his own hands a three dimensional model of the surface in Gibbs' paper and sent it to Gibbs.

From 1876 to1878, Gibbs wrote a series of papers collectively titled *On the Equilibrium of Heterogeneous Substances*, and published in two parts. This collection is a scientific achievement which has few parallels in the history of science simply because it comprehensively laid out the principles of a new area of study. It would not be an exaggeration to say that these principles are the first and last word in Classical Thermodynamics and there has been little modification and improvement of these principles in the century since. Until the work of Gibbs, the principles of thermodynamics had primarily been used for gases in heat and work cycles. The Gibbs formulation could be extended to all substances – liquid, gas or solids – provided there is no elastic strain energy due to lattice deformation. The 'Gibbs Phase Rule' for the co-existence of different phases at equilibrium was also contained here. This rule provided the means of calculating the number of independent thermodynamic properties which were necessary for completely specifying a system, and is one of the most widely used rules in classical thermodynamics.

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In *On the Equilibrium of Heterogeneous Substances*, Gibbs also defined what is now called the 'Gibbs free energy' as the maximum amount of useful work that can be extracted from a system in the absence of any volume change or heat interaction. This concept is not very useful for mechanical systems, because most engines involve heat interactions and volume changes of the working substance. However, this is of fundamental importance in chemical reactions. The Gibbs free energy per mole, also called chemical potential, determines whether a reaction will progress and to what extent. If the Gibbs free energies of elements in their standard states are assumed to be zero, then it can also be shown that the Gibbs free energy of a compound at a given temperature and pressure has a unique value, independent of the reaction pathway used to synthesize the compound. So the Gibbs free

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energy is essential for calculating the reaction 'equilibrium constant', which determines the extent to which a reaction will progress. Though it is now textbook material in physical chemistry, the implications of Gibbs' work was not immediately appreciated by chemists, in part because of the highly mathematical nature of the derivations.

Form 1880 onwards, Gibbs worked on vector calculus, which is the branch of calculus dealing with vector fields. A vector, such as the velocity of an object or the force of an object, has both magnitude and direction. Just as a 'scalar field' is a scalar which varies continuously in space, such as the temperature in a room, a 'vector field' is a vector that varies continuously in space, such as the velocity of the air in a room. The calculus for vector fields (differentiation and integration) is not a simple extension of the calculus for a one dimensional function ($y(x)$ as a function of x). Rather, vector calculus seeks to treat the vector as an object in itself, instead of separating it into components. Vector calculus provides the basic tools for all scientific areas which deal with continuously varying vector functions in multiple dimensions, from quantum mechanics to electrodynamics and fluid dynamics. Gibbs, and independently the British engineer Oliver Heaviside, provided the basic formulations of vector calculus based on earlier work by William Hamilton and Hermann Grassmann.

Gibbs later returned to the study of thermodynamics and wrote the classic text book *Elementary Principles in Statistical Mechanics*, which was published in 1901. In this, he introduced the now standard concept of 'ensemble', which is a collection of a large number of indistinguishable replicas of the system under consideration, which interact with each other, but which are isolated from the rest of the universe. The replicas could be in different microscopic states, as determined by the positions and momenta of the constituent molecules, for example, but the macroscopic state determined by the pressure, temperature and/or other thermodynamic variables are identical. Gibbs argued that the properties of the system, averaged over time, is identical to an average over all the members of the ensemble if the 'ergodic hypothesis'

Suggested Reading

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is valid. The ergodic hypothesis, which states that all the microstates of the system are sampled with equal probability, is applicable to most systems, with the exception of systems such as quenched glasses which are in metastable states. Thus, the ensemble averaging method provides us an easy way to calculate the thermodynamic properties of the system, without having to observe it for long periods of time. Gibbs also used this tool to obtain relationships between systems constrained in different ways, for example, to relate the properties of a system at constant volume and energy with those at constant temperature and pressure. Even today, the concept of ensemble is widely used for sampling in computer simulations of the thermodynamic properties of materials, and has subsequently found uses in other fields such as quantum theory.

Gibbs passed away in 1903, a year after his textbook on statistical mechanics was published. A year earlier, he received the Copley Medal of the Royal Society of the United Kingdom, which was the most prestigious honour at the time. (The first Nobel Prize was awarded in 1901, and it was only later that the prestige of the Nobel Prize grew to its present day levels.) In addition to his contributions to the world of science, Gibbs was also probably the first American scientist who made fundamental contributions. He heralded the advent of American dominance of science and technology, which continues to this day. Despite all his achievements, Gibbs was, by all accounts, a modest man, unencumbered by personal ambition. He led an unremarkable personal life at Yale University, and was always approachable and friendly. During his lifetime, his personal influence was largely restricted to a few talented students who were able to appreciate the scope of his work. In a sense, Gibbs was an unlikely harbinger of the American dominance of science that started around the time he passed away. He wrote the following words as a tribute to one of his senior colleagues: 'His true monument lies not in the shelves of libraries but in the thoughts of men, and in the history of more than one science.' No better tribute could be paid to Gibbs himself.

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