THE PHYSICS OF J. WILLARD GIBBS IN HIS TIME

A century and a half after his birth, Gibbs's work in thermodynamics and statistical mechanics stands out more clearly than ever. The historical origins of this work, however, remain hidden behind his austere and abstract presentation.

Martin J. Klein

Who was the "Mr. Josiah Willard Gibbs of New Haven" who was appointed professor of mathematical physics by the Yale Corporation on 13 July 1871?[1] He was born on 11 February 1839, the only son and the fourth of the five children of Mary Anna Van Cleve Gibbs and Josiah Willard Gibbs the elder, a distinguished philologist and professor of sacred literature at Yale. Although the elder Gibbs worked in a field of learning very different from his son's, there were common features in their approaches. What was said of the father could well have been said of the son: "Mr. Gibbs loved system, and was never satisifed until he had cast his material into the proper form. His essays on special topics are marked by the nicest logical arrangement."

The younger Gibbs graduated from Yale College in 1858, having won a series of prizes and scholarships for excellence in Latin and mathematics. He continued his studies in Yale's new graduate school and received his PhD in 1863, one of the first scholars to be awarded this degree by an American university. In view of the work Gibbs is known for, it is a little surprising to learn that his doctorate was earned in engineering and his dissertation bore the title "On the Forms of the Teeth of Wheels in Spur Gearing." But as Gibbs pointed out in his first paragraph, "the subject reduces to one of plane geometry," and the thesis is really an exercise in geometry and kinematics. The dissertation went unpublished until 1947, when the centennial year of Yale's Sheffield Scientific School provided the occasion for a little book on his early work in engineering. The editor's description of Gibbs's dissertation could apply to almost any of his later, more famous works: "If he has a natural friendliness for the niceties of geometrical reasoning, [the reader] will be rewarded with a sense of satisfaction akin to that felt upon completing, say, a book of Euclid; if he is not so endowed, he had perhaps better not trouble himself with the austerities of style and extreme economy (one might almost say parsimony) in the use of words that characterize the entire work."[2]

After receiving his doctorate Gibbs was appointed a tutor in Yale College, where he gave elementary instruction in Latin and natural philosophy (physics) for three years. Although he continued to work on engineering problems during this period, a paper he presented to the Connecticut Academy of Arts and Sciences in 1866 shows that Gibbs was already concerned with clarifying fundamental physical concepts. In August of that year Gibbs sailed for Europe, where he spent three years studying mathematics and physics. This would be his only extended absence from his native city. Gibbs spent a year each at the universities of Paris, Berlin and Heidelberg, attending a variety of lectures and reading widely in both mathematics and physics. He did not work as a research student with any of the scientists whose lectures he attended, a list that included Joseph Liouville, Leopold Kronecker, Heinrich Magnus, Hermann von Helmholtz and Gustave-Robert Kirchhoff. Nor is there any indication in the few notebooks that constitute the only record of his European studies that he had yet begun any research on his own or even decided what line he would try to follow in his later work. He was apparently satisfied to broaden and deepen the knowledge of mathematics and physics he had previously acquired, and to wait until after he returned home to choose the subjects of his own researches.

For two years after he came back to New Haven, Gibbs had no regular employment and his future was uncertain. He taught French to engineering students for a term, and he worked on an improved version of James Watt's governor for the steam engine. Gibbs was evidently able to manage adequately on the money he had

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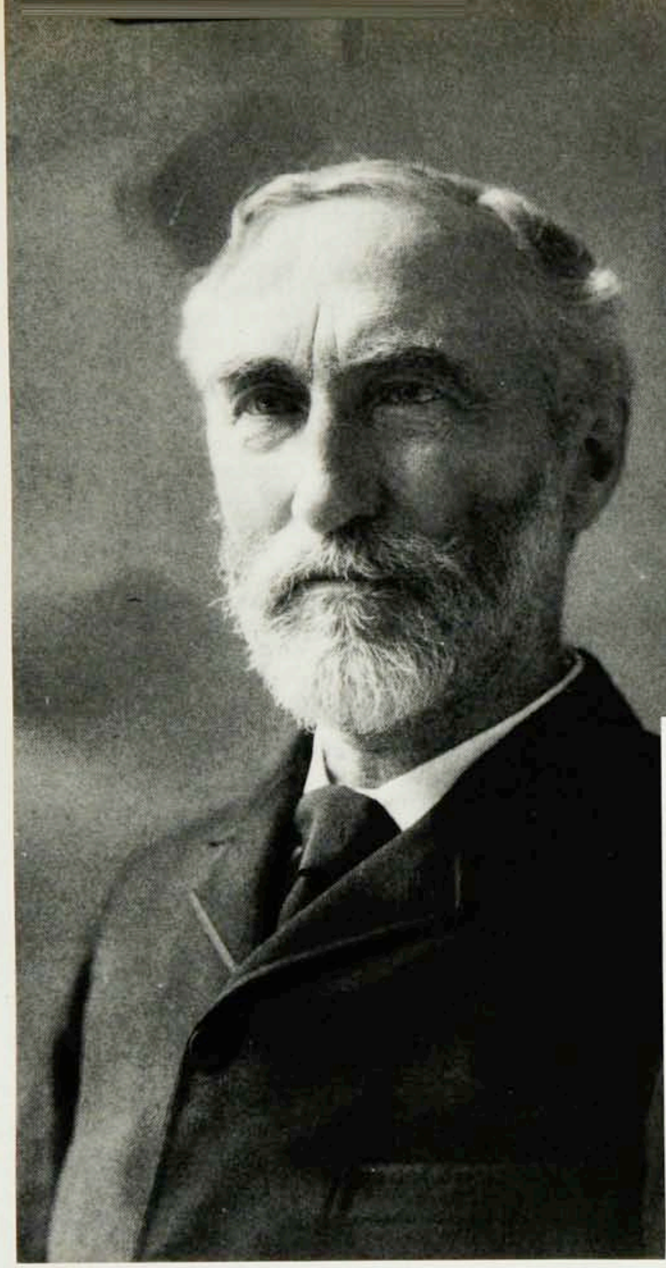
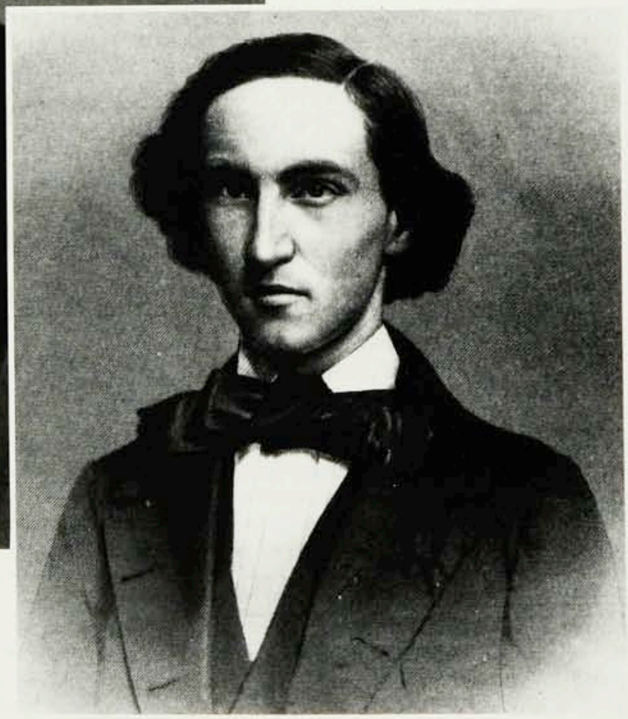




J. Willard Gibbs of New Haven, as a student (below) and late in his career (left). (Student photo from Burndy Library, courtesy of AIP Niels Bohr Library; adult photo from AIP Niels Bohr Library.)

inherited from his father. He never married, and continued to live in the family home, sharing it with his sisters Anna and Julia, and with Julia's growing family.

This fortunate state of financial independence must have been known within the Yale community when Gibbs was appointed to the newly created professorship of mathematical physics in 1871. This knowledge may help to explain why the official record of Gibbs's appointment includes the phrase "without salary." The new chair was unendowed, but in any case Gibbs's teaching duties would be light, since the appointment was in the small graduate department. An offer from Bowdoin College in 1873 that would have given him $1800 a year and his choice between chairs of mathematics and physics did not tempt him to leave New Haven. Only in 1880, when he was on the verge of accepting a professorship at the new and appealing Johns Hopkins University, a university devoted primarily to graduate study and research, did his own institution offer him a salary. Even though Yale offered only two-thirds of what Hopkins would have paid, the advantages of remaining in his familiar surroundings, of being at home, convinced Gibbs to stay. He must also have been influenced by his colleagues' warm reaction to the threat of losing him. "Johns Hopkins can get on vastly better without you than we can," James Dwight Dana wrote him, and then added, "*We can not*."

Gibbs's appointment to the chair of mathematical physics preceded his first published research by two years. This inversion of what we now take to be the normal order of events was not so extraordinary at the time. The 32-year-old Gibbs, with his brilliant college record, his doctoral degree, his demonstrated abilities as an engineer and his three years of postdoctoral study in Europe, had far more impressive qualifications for a professorship than most of his colleagues had had when they were appointed. Yale had every reason to express its confidence in Gibbs, who had, after all, been a member of this small academic community since his birth.

Fundamental thermodynamic equation

The new professor of mathematical physics published his first paper[3] in 1873. He had chosen thermodynamics as the subject of his research, and immediately demonstrated his mastery of that field. But why had Gibbs chosen thermodynamics? During his three years in Europe he had attended no lectures on the subject, nor had he listed in his notebooks any references on thermodynamics for future reading. Electromagnetism and optics drew more of his interest than anything else, judging by his notebook entries, and this is not surprising; they were certainly the most active areas for research in the 1860s. The first course he taught at Yale seems to confirm this predominant interest in physical optics. In the next academic year Gibbs lectured on potential theory, which hardly provided a natural step toward thermodynamics, even though he did use a text by Rudolf Clausius.

Gibbs's biographer and former student, Lynde Phelps Wheeler, conjectured that "the arousing of Gibbs's interest in thermodynamics is due at least as much to an interest in engineering applications of the subject as in its theoretical foundations." He points to Gibbs's work on the governor for the steam engine, which he dates to the early 1870s. Wheeler offers Gibbs's first paper in support of his interpretation, but Gibbs was never the sort of writer who tells his readers about the problems that prompted the work. He preferred a laconic, mathematician's style, making sure to say what was necessary for the logical structure of his argument but nothing more.

Gibbs began that first paper, "Graphical Methods in the Thermodynamics of Fluids," by remarking that although geometrical representations of thermodynamic propositions were in "general use" and had done "good service," they had not yet been developed with the "variety and generality of which they are capable." Such representations had been restricted to diagrams whose coordinate axes denoted volume and pressure, but he proposed to discuss a range of alternatives, "preferable . . . in many cases in respect of distinctness or of convenience." This modest beginning suggested that the paper to follow might break no new ground and that it would be of primarily didactic interest. But in the next few paragraphs, where he chose the basic variables and wrote down the equations that would underlie his argument, Gibbs quietly changed the direction of thermodynamics. In a few lines he arrived at what he named "the fundamental thermodynamic equation of the fluid,"

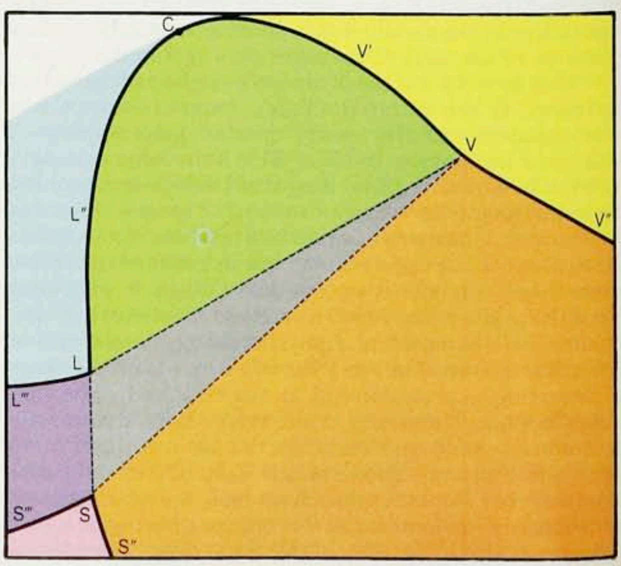
$$dU = T\,dS - P\,dV$$

The quantities involved are the temperature T, pressure P and volume V of the fluid, along with the fluid's internal energy U and entropy S. (I have not used Gibb's notation.) In 1873 this was by no means the standard way of developing thermodynamics. Even Clausius, who had formulated the second law in 1850, introduced the concept of entropy in 1854 and invented its characteristic name in 1865, never gave entropy a central place in his exposition of thermodynamics.[4] For Clausius and for his contemporaries thermodynamics was the study of the interplay between heat and work. For Gibbs, who eliminated heat and work from the foundations of the subject in favor of the state functions—energy and entropy—thermodynamics became the theory of the properties of matter at equilibrium.

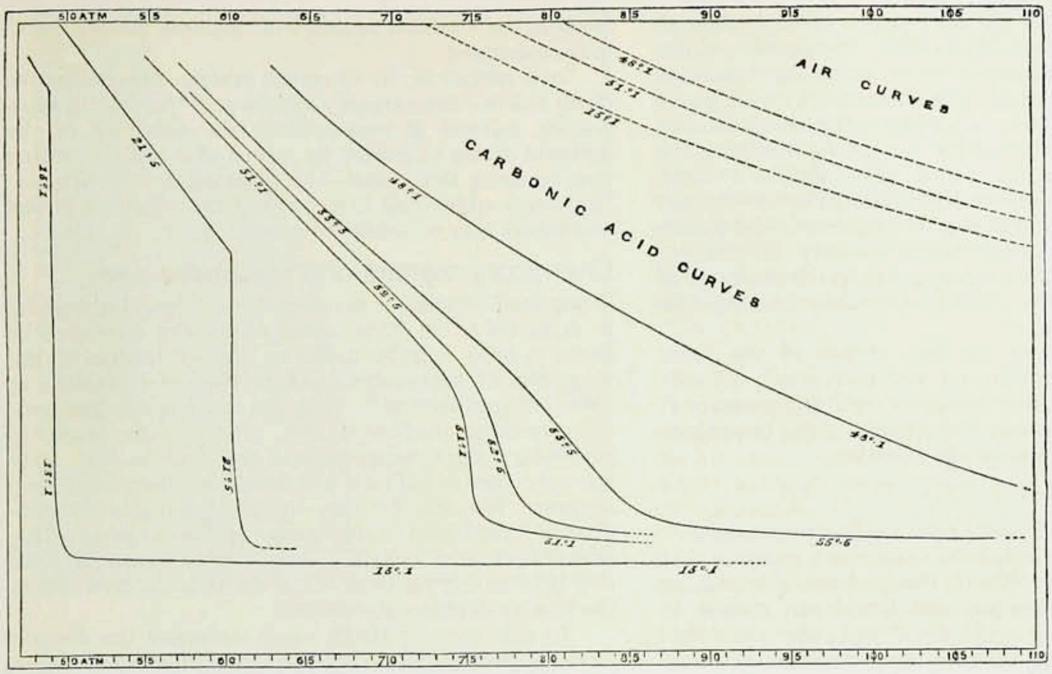
Gibbs wanted to find "a general graphical method which can exhibit at once all the thermodynamic properties of a fluid concerned in reversible processes." To this end he considered the general properties of any diagram in which the states of the fluid were mapped continuously on the points of a plane. The fluid's thermodynamic properties would then be expressed by the geometrical properties of the several families of curves connecting states of equal volume, of equal temperature, of equal entropy and so forth. He discussed the temperature–entropy diagram, in many ways closely analogous to the familiar pressure–volume diagram. It had obvious uses for the engineer's analysis of heat engines, but its real advantage was that it "makes the second law of thermodynamics so prominent, and gives it so clear and elementary an expression."

Most interesting to Gibbs was the entropy–volume diagram, whose "substantial advantages over any other method" he analyzed in some detail. Although less suited to applications in engineering, this diagram was the natural accompaniment of the fundamental equation that expressed energy as a function of entropy and volume. Among other things, Gibbs pointed out how well this diagram expressed the region of simultaneous coexistence of the vapor, liquid and solid phases of a substance. This "triple point" corresponds to a unique set of values of pressure and temperature, but it occupies the interior of a triangle in the entropy–volume plane.

As a natural aspect of his geometrical investigation,



'Surface of absolute stability' projected onto the entropy–volume plane, adapted from Gibbs's 1873 paper.[3] The points S, L and V together represent the solid–liquid–vapor triple point. Inside the triangle SLV these states coexist in an equilibrium mixture (gray). Between LL' and VV' is a liquid–vapor mixture (green), between SS'' and VV'' is a solid–vapor mixture (orange), and between SS''' and LL''' is a solid–liquid mixture (purple). Segments L''' LL', V' V V'' and S'' SS''' form the boundaries representing the stable states of liquid (blue), vapor (yellow) and solid (red), respectively. C is the critical point.



Pressure–volume curves for carbonic acid measured by Thomas Andrews and reported in his 1869 paper.[7] James Thomson argued that a minimum and maximum (rather than the straight horizontal lines that appear on the 31.1 °F, 21.5 °F and 13.1 °F isotherms) should exist for a given isotherm below the critical temperature.[9] The volume increases from bottom to top, and the pressure increases from left to right.

Gibbs examined those features of the families of curves representing thermodynamic properties that are independent of the choice of coordinates. Among these invariant features were the order of the curves of different kinds (isobars, isotherms, isentropics and so on) as they cross at any point, and the geometrical nature of these intersections, which could involve contacts of higher order.

But even after this sketch of the many fresh ideas in Gibbs's first paper, we are left with the question of what brought him to this study. Wheeler's suggestion of the importance of his engineering background can account at most for part for Gibbs's motivation. If we look at the literature of the time, we find a number of articles on thermodynamics appearing in the widely read *Philosophical Magazine* during 1872. They were largely devoted to the history, that is to say to the priorities, of the discovery of the second law. For all the lively, pointed and even angry words exchanged between Clausius and Peter Guthrie Tait (writing on behalf of William Thomson's claims), it seems likely that this controversy would have repelled rather than attracted Gibbs. It might have sent him to the library, however, to see what the shouting was all about.

One of the works discussed by Clausius in the article that touched off the controversy[5] was a little book by James Clerk Maxwell, his *Theory of Heat*,[6] published in 1871. It was Maxwell's neglect of his work that prompted Clausius to set the record straight by writing his own account of his earlier contributions. Gibbs might well have read Maxwell in any case, even without the priority dispute raging in the *Philosophical Magazine*. What Gibbs would have found in Maxwell's book, intended (according to the publisher) "for the use of artisans and of students in public and science schools," included Maxwell's discussion of recent developments that interested him in the area of heat. One such development was Thomas Andrews's recent (1869) discovery of the continuity of the two fluid states of matter—liquid and gas—and of the critical point above which these states were indistinguishable. Whether Gibbs learned of Andrews's work from Maxwell or by reading Andrews's paper in the *Philosophical Transactions of the Royal Society*[7] we do not know, but he certainly knew about it when he wrote his first paper. There is a footnote referring to Andrews at the place in the text where Gibbs discusses the possibility of a second-order contact between the isobar and the isotherm corresponding to a particular state of the fluid. It reads, "An example of this is doubtless to be found at the critical point of a fluid."

Andrews did not theorize at all about the implications of his discovery. His paper offered neither a thermodynamic analysis nor a kinetic–molecular explanation. It seems to me that Andrews's discovery—a new, unexpected and general feature of the behavior of matter, as yet totally unanalyzed—would have been just the sort of thing to capture Gibbs's attention as that promising new professor of mathematical physics sought for a suitable subject on which to work. (Edwin B. Wilson, Gibbs's student, remembered his teacher telling him that "one good use to which anybody might put a superior training in pure mathematics was to the study of problems set us by nature."[8])

Entropy and equilibrium

Gibbs's physical interests are much more apparent in his second paper, which appeared only a few months after the first. Although its title, "A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces," might suggest that Gibbs was merely extending his geometrical methods from two dimensions to three, one does not have to read very far to see that he was doing something quite different. His emphasis was now on the phenomena to be explained, rather than on the methods as such. The problem Gibbs treated was the characterization of the equilibrium state of a material system, a body that can be solid, liquid, gas or some combination of these according to the circumstances. This time Gibbs used only one way of representing the equilibrium states, namely the surface described by those states in the space whose coordinate axes are energy, entropy and volume; this surface represents the fundamental thermodynamic equation of the body. He proceeded to establish the relationships between the geometry of the surface and the conditions for thermodynamic equilibrium and its stability.

Gibbs showed that for two phases of the same substance to be in equilibrium with each other, not only must they share the same temperature T and pressure P, but the energies, entropies and volumes of the two phases (per unit mass) must satisfy the equation

$$U_2 - U_1 = T(S_2 - S_1) - P(V_2 - V_1)$$

where the subscripts 1 and 2 refer to the two phases.

This equation provided the answer to a question that had puzzled Maxwell: What is the condition determining the pressure at which gas and liquid can coexist in equilibrium? Maxwell originally thought that the difference in internal energy between the two phases must be a maximum at the pressure where they coexist. He soon changed his mind on reading Gibbs's second paper.

When Gibbs analyzed the conditions for the stability of thermodynamic equilibrium states in his second paper, he arrived at a new understanding of the significance of the critical point. The critical state not only indicated where the two fluid phases became one, it also marked the limit of the regions of instability associated with the two-phase system—both the "absolute instability" of the states like that of a supercooled gas and the "essential stability" of states on the rising part of the Thomson–van der Waals loop.[9] The critical point is the common limit of both regions of instability, though it is itself stable. Gibbs's analysis also led him to a series of new explicit conditions that must be fulfilled at the critical point and that can serve to characterize it.

These two early papers were published in the *Transactions of the Connecticut Academy of Arts and Sciences.* Although the Connecticut Academy, of which Gibbs had been a member since 1858, was a local society centered in New Haven, it had been in existence since 1799 and had developed a regular program for the exchange of its *Transactions* with comparable journals published by some 170 other learned societies around the world. Although Gibbs could expect his work to be circulated far and wide by this route, he also sent copies of his papers directly to an impressive list of scientists at home and abroad. We do not know how many of those 75 or so scientists who received Gibbs's first two papers read them, but we do know of one crucial reader: This was Maxwell, who learned the proper definition of entropy through Gibbs's papers. Maxwell had misused the term, following his friend Tait, in the first edition of the *Theory of Heat*, but corrected his error in later editions.[10] Maxwell talked about Gibbs's work to Cambridge colleagues in several fields and wrote about it to others, recommending it highly. He especially appreciated Gibbs's geometrical approach, since he too preferred geometrical to algebraic or analytical methods. The thermodynamic surface introduced in Gibbs's second paper fascinated Maxwell so much that he actually constructed such a surface showing the thermodynamic properties of water and sent a plaster cast of it to Gibbs. He even discussed the surface at considerable length in the 1875 edition of his book; whether this discussion met the needs of the intended audience of "artisans and students" may be doubted.

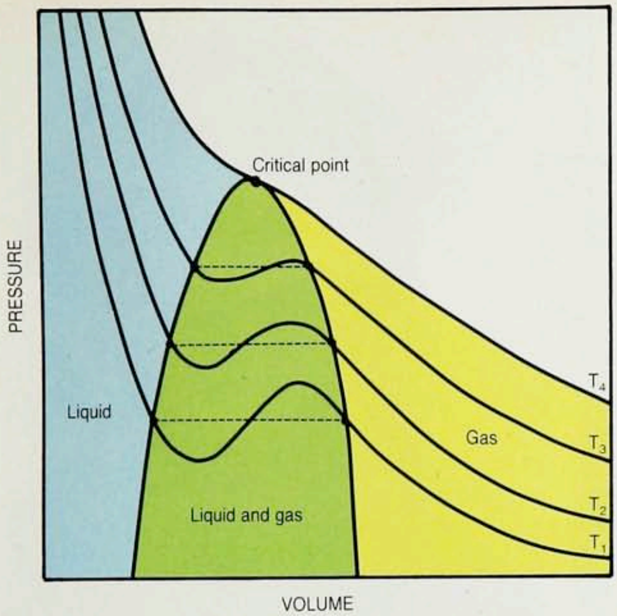
In a lecture to the Chemical Society, Maxwell spoke about Gibbs's "remarkably simple and thoroughly satisfactory method of representing the relations of the different states of matter by means of a model," adding that by using this model—the thermodynamic surface—"problems which had long resisted the efforts of myself and others may be solved at once."[11]

Chemical potential and the phase rule

When the Connecticut Academy held its regular meeting in June 1874, the 20 or so members who were present heard a brief talk by Gibbs on the application of the principles of thermodynamics to the determination of chemical equilibrium.[12] This was not just another ordinary evening in New Haven. Gibbs then gradually worked out the consequences of the ideas he could only have sketched in his talk, and developed them into a long memoir, "On the Equilibrium of Heterogeneous Substances," published in due course by the academy. This book-length work, which appeared in two parts, in 1876 and 1878, surely ranks as one of the true masterworks in the history of physical science.

In this memoir Gibbs vastly enlarged the domain encompassed by thermodynamics, treating chemical, elastic, surface and electrochemical phenomena by a single, unified method. Gibbs described the fundamental idea underlying the whole work in a lengthy abstract, published in the *American Journal of Science*, which reached a much broader audience than the academy's *Transactions*: "It is an inference naturally suggested by the general increase of entropy which accompanies the changes occurring in any isolated material system that when the entropy of the system has reached a maximum, the system will be in a state of equilibrium. Although this principle has by no means escaped the attention of physicists, its importance does not appear to have been duly appreciated. Little has been done to develop the principle as a foundation for the general theory of thermodynamic equilibrium." It was just that development which Gibbs set forth in his memoir.

The general criterion for equilibrium could be stated simply and precisely: "For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the systems which do not alter its energy, the variation of its entropy shall either vanish or be negative." But to work out the consequences of this general criterion, and to explore their implications allowing for the variety and complexity that thermodynamic systems can have, was a major undertaking. From the outset Gibbs introduced the chemical potentials, those intensive variables that must have the same values throughout a heterogeneous system in equilibrium and that function much like the temperature and pressure. From these conditions on the intensive variables Gibbs derived the phase rule, which specifies the number of independent variables (degrees of freedom) in a system of a certain number of coexistent phases having a specified number of chemical components. This phase rule later proved to be an invaluable guide to understanding a mass of experimental material, but Gibbs did not single it out for special mention in his memoir. As Pierre Duhem once remarked, it took "a remarkable perspicacity" on the part of J. D. van der Waals, who first saw its power, to perceive the phase rule "among the algebraic formulas where Gibbs had to some extent hidden it."[13] And Duhem wondered how many more such seeds that might have grown into whole programs of research "had remained sterile because no physicist or chemist had noticed them



Pressure–volume isotherms
($T_1 < T_2 < T_3 < T_4$), as illustrated in a modern textbook, show minima and maxima below the critical temperature—the temperature below which the volume changes discontinuously at the equilibrium, or phase-transition, pressure. (The dashed lines cut across the "loops" at the phase-transition pressures). At the critical temperature T_4 the transition between gas and liquid is smooth and continuous. (Adapted with permission from Herbert B. Callen, *Thermodynamics*, Wiley, New York, 1960, p. 158.)

under the algebraic shell that concealed them?"

Gibbs's spare and abstract style and his unwillingness to include a variety of examples and applications to particular experimental situations made his work very difficult for potential readers. As a consequence, the literature of the late 19th century contains many rediscoveries of results already published by Gibbs. Such major figures as Helmholtz and Max Planck independently developed their own thermodynamic methods for treating chemical problems, quite unaware of the treasures concealed in the third volume of the *Transactions of the Connecticut Academy*.

Gibbs wrote no other major works on thermodynamics, thinking that he had said all he needed to say—perhaps all that in principle could be said—on the subject. He limited himself to a few short papers elaborating several points in his long memoir. He shifted his attention to other issues in physics and mathematics, and he rejected all suggestions that he write a treatise on thermodynamics that would make his work more accessible. In 1892 Rayleigh wrote to Gibbs urging him to expand on his ideas, saying that the original memoir was "too condensed and too difficult for most, I might say all, readers." Gibbs's answer strikes an unexpected note: He now thought that his memoir seemed "too *long*" and showed a lack of a "sense of the value of time, of my own or others, when I wrote it."

Shortly before his death, however, Gibbs did agree to a republication of his writings on thermodynamics, to which he planned to add some new material in the form of supplementary chapters. Among the matters that Gibbs listed for inclusion in this supplement, two seem particularly appealing to me. Unfortunately we have only the bare titles, "On Similarity in Thermodynamics" and "On Entropy as Mixed-up-ness," and we shall never know what Gibbs planned to write on either subject. (One cannot help wondering if "entropy as mixed-up-ness" is related to the mixing process that Gibbs used in chapter XII of his *Statistical Mechanics* to discuss the irreversible increase of entropy.)

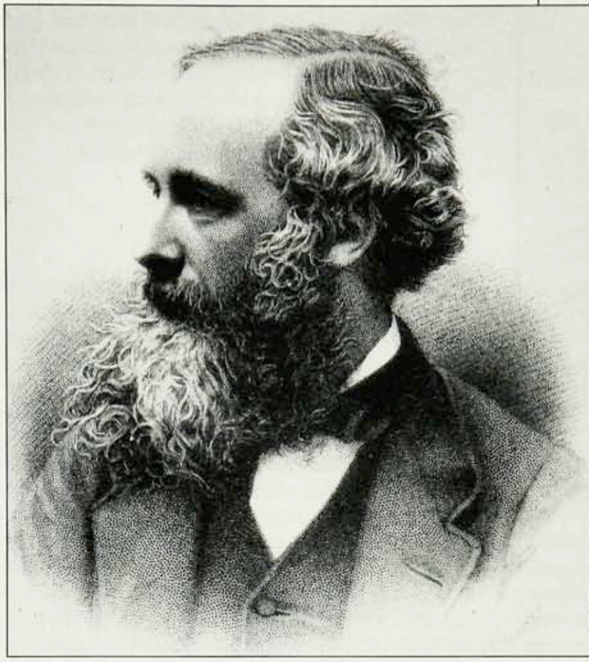
Statistical mechanics: Molecular concepts

I shall not even try to comment on the various subjects to which Gibbs devoted his attention in the decade after completing his thermodynamic studies. His vector analysis, his calculations of orbits and especially his investigations into the electromagnetic theory of light will have to go undiscussed here,[14] along with his new variational principle for mechanics and his famous note on the Fourier series. I do, however, want to say something about the development of Gibbs's ideas on statistical mechanics.

Gibbs's book, *Elementary Principles in Statistical Mechanics: Developed with Especial Reference to the Rational Foundation of Thermodynamics*, published in 1902 (Scribner's, New York) as one of the volumes in the Yale Bicentennial Series, stands alone among his works. It was his first and only treatment of the subject, with one minor exception, to be discussed shortly. Almost totally devoid of references to the literature, presenting the subject in a form quite different from that used by any other author, the book has some of the same quality—at once abstract and individual—as Paul A. M. Dirac's *The Principles of Quantum Mechanics*, published in 1930. But while Dirac's book was preceded by a series of the author's papers, Gibbs's appeared without any preparatory works that might have foreshadowed it. It must have been a genuine surprise to the scientific community, particularly since it would have seemed to some to represent not just a change of direction on Gibbs's part, but an actual reversal.

By this time Gibbs was widely known as one of the grand masters of thermodynamics. His work exemplified Maxwell's definition of thermodynamics as "the investigation of the dynamical and thermal properties of bodies, deduced entirely from what are called the First and Second Laws of Thermodynamics, without any hypothesis as to the molecular constitution of bodies."[11] The last phrase is the crucial one: Gibbs's work stood as the prime example of pure thermodynamics, unmarred by any appeal to hypotheses about the molecular structure of matter. The energeticists, who opposed and even scorned the use of molecular concepts, and especially the attempt to reduce thermodynamics to molecular mechanics, particularly valued Gibbs for having avoided these ideas in his work. Yet here he was in his new book discussing the principles of statistical mechanics and claiming, as his subtitle implied, that these principles could supply the "rational foundation of thermodynamics." Not only that, but according to the new Gibbs the laws of thermodynamics were only an "incomplete expression" of these more general principles. Did this apparent desertion of the thermodynamic camp really represent a sudden shift in Gibbs's basic outlook?

The answer to this question is certainly negative. Gibbs had not built molecular concepts into his papers on thermodynamics because he had "no need of that hypothesis," as Pierre-Simon Laplace is said to have remarked in a very different context. But when Gibbs thought he could clarify his discussion by referring to molecular behavior,



he had not hesitated to do so. These references are infrequent, but they do occur—in his treatment of the reaction carrying NO_2 into N_2O_4, for example, and in his mention of the "sphere of molecular action" when he introduced his analysis of the thermodynamics of capillarity. The discussion of the Gibbs paradox is the best known of the passages in "On the Equilibrium of Heterogeneous Substances" where molecules are mentioned. When two gases are allowed to mix at constant temperature and pressure, there is an increase of entropy. The amount of this increase is "independent of the degree of similarity or dissimilarity" between the two gases, unless they are identical—the same gas—in which case there is no entropy increase at all. Gibbs's discussion of this situation is explicitly molecular, and leaves no doubt that he had none of the objections to molecular arguments that some of his thermodynamic followers attributed to him.

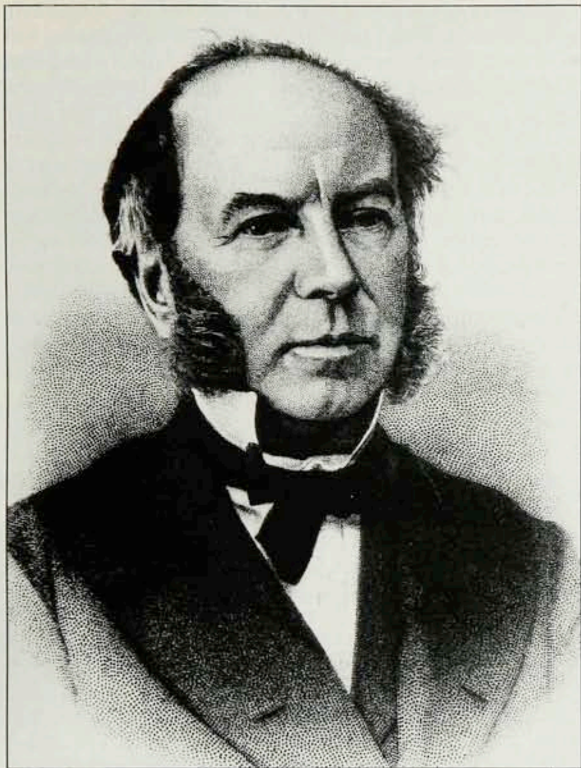
If we try to trace the development of Gibbs's ideas leading up to his book on statistical mechanics, we meet with only very limited success. The first sign of a statistical approach to the second law of thermodynamics in Gibbs's writings comes in the remarkable last sentence of his analysis of the Gibbs paradox. Because it is possible, in principle, for the ordinary molecular motions in a gas mixture to produce unmixing, with the corresponding decrease in entropy, one cannot exclude the possibility that this process will occur, unlikely as it may be. "In other words," Gibbs wrote, "the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability." This remark, so different in character from everything else in Gibbs's memoir, was apparently not developed at all.

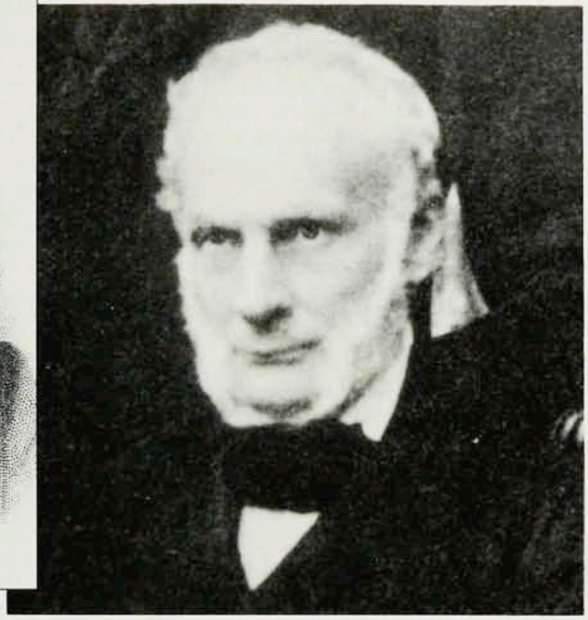
In 1884 Gibbs made one of his rare appearances at a meeting away from New Haven. He presented a paper in Philadelphia to the American Association for the Advancement of Science, "On the Fundamental Formula of Statistical Mechanics with Applications to Astronomy and Thermodynamics." Only the brief published abstract survives of this talk, but one can nevertheless draw some conclusions from it about the state of his thinking on the subject in at that time.

Gibbs had evidently studied the papers of Maxwell and Ludwig Boltzmann closely enough to decide that they had created a subject deserving a new name that would separate it from the limiting connotations of "the kinetic theory of gases." The new discipline treated bodies of arbitrary complexity moving according to the laws of mechanics, but it investigated their motions statistically. It considered, in Maxwell's words, "a large number of systems similar to each other in all respects except in the initial circumstances of the motion, which are supposed to vary from system to system," and it asked about "the *number* of these systems which at a given time are in a phase such that the variables which define it lie within given limits."[11] Gibbs coined the name "statistical mechanics" in his Philadelphia paper to denote the discipline based on such investigations.

The fundamental formula mentioned in his title described the evolution in time of the distribution function or phase density of a population of similar systems. Boltzmann had been discussing other versions of this equation since 1868, and had recently stressed its importance, as had Maxwell.[15] This equation is now generally known as Liouville's theorem, but Gibbs never called it that.

He must have gone on thinking about this statistical mechanics, for he listed it in 1888 among several possible topics for papers he was considering writing but nothing appeared in print until his 1902 treatise. He was already lecturing on it at Yale, where his courses on the subject bore various titles: "On the *A Priori* Deduction of Thermodynamic Principles from the Theory of Probabilities," "Theoretical Thermodynamics" and "Dynamics and Thermodynamics." From what we know about Gibbs's teaching, the very fact that he gave such courses implies that he had already carefully thought through the subject





Influences. Left to right: James Clerk Maxwell (1831–79), Ludwig Boltzmann (1844–1906), Thomas Andrews (1813–85) and Rudolph Clausius (1822–88) all did work that had an impact on Gibbs's efforts in thermodynamics and statistical mechanics. (Boltzmann photo from University of Venice, courtesy of AIP Niels Bohr Library; other photos from AIP Niels Bohr Library.)

and organized it to his own satisfaction. His student Henry Bumstead wrote that Gibbs "seldom, if ever, spoke of what he was doing until it was practically in its final and complete form."[16]

We find evidence of Gibbs's mastery of statistical mechanics in an unlikely place—the obituary notice for Clausius that he wrote in 1889. He compared Clausius's contributions to "molecular science" with those of Maxwell and Boltzmann: "In reading Clausius, we seem to be reading mechanics; in reading Maxwell, and in much of Boltzmann's most valuable work, we seem rather to be reading in the theory of probabilities." Gibbs recognized that "the larger manner in which Maxwell and Boltzmann proposed the problems of molecular science" allowed them to go further than Clausius. He nevertheless praised Clausius's "remarkable insight" and noted that his "hypothesis" about disgregation, which suffered from "the acknowledged want of a rigorous demonstration," had later found its justification in Boltzmann's work. No careful reader of Gibbs's obituary of Clausius could have doubted his active interest in the molecular approach to thermodynamics. There is, however, no indication that such careful readers actually existed.

By 1892 Gibbs was devoting much of his energy to writing up the results of his years of work. In the letter to Rayleigh referred to above, Gibbs wrote: "Just now I am trying to get ready for publication something on thermodynamics from the *a priori* point of view, or rather on 'Statistical Mechanics,' of which the principal interest would be in its application to thermodynamics—in the line therefore of the work of Maxwell and Boltzmann. I do not know that I shall have anything particularly new in substance, but shall be contented if I can so choose my standpoint (as seems to me possible) as to get a simpler view of the subject." Judging from Gibbs's extensive notes on statistical mechanics, some of which bear dates from about this time, he was working on a lengthy manuscript of more or less the size, structure and contents of the work that appeared in 1902. Lecture notes taken by a student in Gibbs's course for the academic year 1894–95 confirm that he had already worked out his own way of developing statistical mechanics and that he did not change it significantly over the years.

Equipartition and the irreversibility problem

One of the most remarkable things about Gibbs's book is that it reflects so little of the state of the subject at the time it was written. The two problems discussed with most urgency in the 1890s were the failures of the equipartition theorem and the difficulties and obscurities in Boltzmann's statistical explanation of irreversibility. The failure of the equipartition theorem to account for the specific heats of all the common gases had been recognized since Maxwell's first paper on the kinetic theory in 1860, and no real progress had been made despite many efforts to understand the difficulty.[17] Gibbs had no answer to this major unsolved problem either, but he was quite aware that it posed a serious threat to the status of the whole subject. His reaction was to set forth his statistical mechanics "as a branch of rational mechanics" and to give up "the attempt to frame hypotheses concerning the constitution of material bodies." "Difficulties of this kind," he wrote in his preface, "have deterred the author from attempting to explain the mysteries of nature, and have forced him to be contented with the more modest aim of deducing some of the more obvious propositions relating to the statistical branch of mechanics." In giving up the attempt to deal with the failures of equipartition, Gibbs may have sensed that the limits of that theorem could not be established within a theory that was "a branch of rational mechanics."

Gibbs could not avoid the question of the origin of irreversibility if he was going to supply the rational foundation for thermodynamics that the subtitle of his book promised. But he apparently decided at an early stage of his work that Boltzmann's methods for dealing with this question were not what he wanted. None of his research notes mention either Boltzmann's kinetic method, which made molecular collisions the basis of his *H*-theorem or the combinatorial method Boltzmann introduced in 1877. Nor did Gibbs comment on Boltzmann's papers of the 1890s, which elaborated and clarified his views on irreversibility. We are not even certain[17] that he read Boltzmann's *Lectures on Gas Theory* when they appeared in 1895 and 1898.

His own discussion of the irreversible approach to equilibrium is set forth the chapter XII entitled "On the Motion of Systems and Ensembles of Systems Through Long Periods of Time." Gibbs treated it as a mixing process in phase space, but his guarded language and the absence of equations in this chapter suggest that he may not have been completely satisfied with this analysis of irreversibility. At several places in his notes Gibbs asks himself questions like "What is the entropy of a system not in equilibrium?" Perhaps his uncertainty on this and related matters led to the delay in publishing the manuscript that he was working on in 1892. It is not impossible that the pressure to contribute to the Yale Bicentennial series propelled Gibbs into completing a book that he might otherwise have considered not quite ready to publish.

Serenity: Love of abstract truth

One sometimes still hears the story that Gibbs never received proper recognition during his lifetime. It is patently untrue. His name and work may have been quite unknown to the general educated public in this country and abroad, but how many knew of Maxwell or Carl Friedrich Gauss? Gibbs did receive almost every honor that the learned world could grant—election to the great academies of many lands, honorary degrees from universities in three countries, several prizes. He also received in good measure what he valued most, the respect and admiration of those colleagues everywhere whose own work put them in a position to appreciate his. In 1901 the Royal Society of London, which had elected Gibbs a foreign member in 1897, awarded him its Copley Medal, perhaps the highest distinction a scientist could receive at that time.

Among the personal qualities that impressed Gibbs's family and associates—his approachability, his lively sense of humor, his kindliness and sympathetic approach to students and colleagues alike, his readiness to give counsel and help—one seems to stand out, his serenity. He appears to have been a man utterly at home in his surroundings, a happy man; a friend even called him "the happiest man she ever knew."[1] While some of his notable contemporaries—Henry James, Charles Sanders Peirce, Henry Adams—found it impossible to come to comfortable terms with their American environment, Gibbs had no such problem. Yale and New Haven offered him what he needed.

In a famous section of his *Democracy in America*, Alexis de Tocqueville analyzed the reasons which he saw for the lack of attention paid to theoretical science in this country[18]: "Nothing is more necessary to the culture of the higher sciences or of the more elevated departments of science than meditation; and nothing is less suited to meditation than the structure of democratic society." However valid this generalization may or may not have been, it surely did not impose limits on Gibbs. He did find that needed opportunity for sustained thought, "that calm . . . necessary for the deeper combinations of the intellect," in de Tocqueville's phrase.

Nevertheless Gibbs might not have disagreed with de Tocqueville's generalization, and he actually formulated a similar one of his own. In writing about his late friend Hubert A. Newton, who had started as a mathematician but then turned to observational astronomy, Gibbs commented that this change of direction was probably due to "the influence of his environment." Gibbs thought it was to be expected "that the questions which nature forces on us are likely to get more attention in a new country and a bustling age, than those which a reflective mind puts to itself, and that the love of abstract truth which prompts to the construction of a system of doctrine, and the refined taste which is a critic of methods of demonstration, are matters of slow growth." The last part of Gibbs's sentence could be taken as a description of characteristic features of his own way of doing science, which was "part of the never-ending meditation."[19]

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The final text of this paper was completed while I was visiting professor of the history of science at Harvard University. The complete version of this article appears in Proceedings of the Gibbs Symposium, Yale University, May 15–17, 1989, *edited by D. G. Caldi and G. D. Mostow (1990); the reader is referred to that paper for a more detailed bibliography. This abridged version appears with the permission of the American Mathematical Society. I am grateful to the Yale University Library for permission to quote from the Gibbs Collection at the Beinecke Rare Book and Manuscript Library—the source for many of Gibbs's unpublished writings.*

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