

secondary factors. He did not accept particulate theories of heredity, and he rejected all theories based on unverifiable internal tendencies, such as the orthogenesis conceived by Teodor Eimer.

Giard created new biological terms, some of which became classic. He was also greatly interested in scientific societies and attempted to guide their activity. In 1878 he became editor of the *Bulletin scientifique du Nord*; ten years later this local journal became the *Bulletin scientifique de la France et de la Belgique*.

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ANDRÉE TÉTRY

GIBBS, JOSIAH WILLARD (b. New Haven, Connecticut, 11 February 1839; d. New Haven, 28 April 1903), *theoretical physics*.

Gibbs was the only son among the five children of Josiah Willard Gibbs and Mary Anna Van Cleve Gibbs. His father was a noted philologist, a graduate of Yale and professor of sacred literature there from 1826 until his death in 1861. The younger Gibbs grew up in New Haven and graduated from Yale College in 1858, having won a number of prizes in both Latin and mathematics. He continued at Yale as a student of engineering in the new graduate school, and in 1863 he received one of the first Ph.D. degrees granted in the United States. After serving as a tutor in Yale College for three years, giving elementary instruction in Latin and natural philosophy, Gibbs left New Haven for further study in Europe. By this time both his parents and two of his sisters were dead, and Gibbs traveled with his two surviving older sisters, Anna and Julia. He spent a year each at the universities of Paris, Berlin, and Heidelberg, attending lectures in mathematics and physics and reading widely in both fields. These European studies, rather than his earlier engineering education, provided the foundation for his subsequent career.

Gibbs returned to New Haven in June 1869. He never again left America and rarely left even New Haven except for his annual summer holidays in northern New England and a very occasional journey to lecture or attend a meeting. Gibbs never married and lived all his life in the house in which he had grown up, less than a block away from the college

buildings, sharing it with Anna, Julia, and Julia's family. In July 1871, two years before he published his first scientific paper, Gibbs was appointed professor of mathematical physics at Yale. He held this position without salary for the first nine years, living on his inherited income. It was during this time that he wrote the memoirs on thermodynamics that constitute his greatest contribution to science. Gibbs had no problem about declining a paid appointment at Bowdoin College in 1873, but he was seriously tempted to leave Yale in 1880, when he was invited to join the faculty of the new Johns Hopkins University at Baltimore. Only then did Yale provide a salary for Gibbs, as tangible evidence of the esteem in which he was held by his colleagues and of his importance to the university, but this salary was still only two-thirds of what Johns Hopkins had offered him. Gibbs stayed on at Yale nevertheless and continued teaching there until his death, after a brief illness, in the spring of 1903.

Gibbs's first published paper did not appear until he was thirty-four years old, and it displays his unique mastery of thermodynamics. If there are even earlier signs of Gibbs's intellectual power, they must be sought in his previous engineering work. His doctoral thesis, "On the Form of the Teeth of Wheels in Spur Gearing," certainly shows Gibbs's unusually strong geometrical ability. He generally preferred "the niceties of geometrical reasoning" to analytical methods in his later work, and this is true in his thesis. The style of this early work also shows the same "austerity," the same "extreme economy (one might almost say parsimony) in the use of words,"¹ that made his later memoirs so difficult to read. Some of his engineering work, such as the design of an improved railway car brake, for which he received a patent in 1866, is hard to relate to the concerns of the future master of theoretical physics—but this is not true of all of it. After his return from Europe, Gibbs designed a new form of governor for steam engines by suitable mounting of a second pair of massive balls on the simple Watt governor. This new arrangement was planned to increase the responsiveness of the system to a change in the engine's running speed. Although Gibbs went no further with this invention than having a model of it built in the department workshop, it is interesting nevertheless: the problems of dynamic equilibrium and stability of this particular mechanical device foreshadow the related questions of equilibrium and stability that he would soon raise and answer for general thermodynamic systems.

When Gibbs first turned his attention to thermodynamics in the early 1870's, that science had already

achieved a certain level of maturity. Rudolf Clausius had taken the essential step in 1850, when he argued that two laws and not just one are needed as the basis of a theory of heat. Only a year before that, William Thomson had been writing about the "very perplexing question," and the associated "innumerable" and "insuperable" difficulties, of choosing *the* correct axiom for the theory.² Should one hold fast to Carnot's postulate (that heat must pass from a hot body to a colder one when work is done in a cyclic process), even though Carnot's results seemed to depend on his use of the caloric theory of heat? Or should one accept the interconvertibility of heat and work, since James Joule's new experimental evidence clearly favored the mechanical theory of heat? Clausius showed that, despite the apparent need to choose one law or the other, both were necessary and both could be maintained without contradiction. One had only to drop Carnot's inessential requirement that heat itself be conserved. This change did have one major implication. The proof of Carnot's theorem (that the maximum motive power of heat depends solely on the temperatures between which the heat is transferred) now had to appeal to a new axiom: that heat "everywhere exhibits the tendency to annul temperature differences, and therefore to pass from a *warmer* body to a *colder* one."³ Clausius' memoir demonstrated how one could develop a thermodynamics starting with both the equivalence of heat and work and his new axiom. These two laws of thermodynamics were restated in slightly different form a year later by Thomson, who proceeded to apply them to a variety of physical problems, including thermoelectricity.

Clausius tried as hard as he could to find the essence of the second law of thermodynamics, since he felt unable at first to "recognize . . . , with sufficient clearness, the real nature of the theorem."⁴ This search led finally in 1865 to his most concise and ultimately most fruitful formulation of the two laws, the formulation Gibbs later used as the motto of his greatest work: "The energy of the universe is constant. The entropy of the universe tends to a maximum."⁵ The two basic quantities, internal energy and entropy, were, in effect, defined by the two laws of thermodynamics. The internal energy U is that function of the state of the system whose differential is given by the equation expressing the first law,

$$dU = \delta Q + \delta W, \quad (1)$$

where δQ and δW are, respectively, the heat added to the system and the external work done on the system in an infinitesimal process. For a simple fluid the work δW is given by the equation

$$\delta W = -PdV, \quad (2)$$

where P is the pressure on the system and V is its volume. Neither the heat δQ nor the work δW is the differential of a function of state, and the inexactness or nonintegrability of these differentials is indicated by the symbol δ , whose use for this purpose goes back to Carl Neumann's lectures in the early 1870's.⁶ The entropy S is that state function whose differential is given by the equation

$$dS = \frac{\delta Q}{T}, \quad (3)$$

valid for reversible processes, where T is the absolute temperature. For irreversible processes equation (3) is replaced by the inequality

$$dS > \frac{\delta Q}{T}. \quad (4)$$

The power and importance of the entropy concept were certainly not evident to Clausius' contemporaries upon the publication of his 1865 paper. Clausius himself considered it to be a summarizing concept and thought that the true physical significance of the second law was better expressed in terms of the disgregation, a concept he sought to interpret mechanically. Entropy plays no particular role in the thermodynamics texts by Georg Krebs (1874) and Carl Neumann (1875). The word was picked up by Peter Guthrie Tait in his *Sketch of Thermodynamics* (1868), but he completely changed its meaning, using it to denote available energy rather than the quantity Clausius had intended. Tait's misinterpretation was taken up and repeated by James Clerk Maxwell in his *Theory of Heat* (1871). The confusion and uncertainty about the thermodynamic significance of entropy were only aggravated by the bitter priority disputes between Clausius and Tait (on behalf of Thomson) that raged in the early 1870's. The basic structure of modern thermodynamics was implicitly present in the work of both Clausius and Thomson, but it was certainly not clearly visible to most writers on the subject.

It was in this context that Gibbs's first scientific paper, "Graphical Methods in the Thermodynamics of Fluids," appeared in 1873. His mastery and his quiet assurance in this paper are as remarkable as his scientific insight. Gibbs assumed from the outset that entropy is one of the essential concepts to be used in treating a thermodynamic system, along with energy, temperature, pressure, and volume. He immediately combined the first three equations given above to obtain the form

$$dU = TdS - PdV, \quad (5)$$

a relation that contains only the state variables of the system, the process-dependent heat and work having been eliminated. As Gibbs pointed out, an equation expressing the internal energy of the system in terms of its entropy and volume could appropriately be called its fundamental equation; for equation (5) would then allow one to determine the two equations of state, expressing temperature and pressure as functions of the pair, volume and entropy. These remarks were the starting point for Gibbs's later work, but in this first paper he limited himself to a discussion of what could be done with geometrical representations of thermodynamic relationships in two dimensions.

James Watt's indicator diagram, in which pressure and volume are plotted on the two coordinate axes, had been in use for thermodynamic purposes since Émile Clapeyron's memoir of 1834. But Gibbs showed how other choices for the coordinate variables would produce representations even more useful for thermodynamic purposes; the temperature-entropy diagram, for example, had many advantages in the study of cyclic processes. The form of the basic equation (5), expressing both laws of thermodynamics, suggested that the volume-entropy diagram might be best suited for general thermodynamic considerations, and Gibbs discussed it in more detail. He also showed how some of the interrelations among the curves describing, respectively, states of equal pressure, equal temperature, equal energy, and equal entropy were independent of how the thermodynamic diagram was constructed and followed directly from the stability of equilibrium states.

In his second paper, which appeared later in 1873, Gibbs extended his geometrical discussion to three dimensions by analyzing the properties of the surface representing the fundamental thermodynamic equation of a pure substance. The thermodynamic relationships could be brought out most clearly by constructing the surface using entropy, energy, and volume as the three orthogonal coordinates. Gibbs pointed out that, as a consequence of equation (5), the temperature and pressure of the body in any state was determined by the plane tangent to the surface at the corresponding point, since one has the equations

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad (6a)$$

and

$$-P = \left(\frac{\partial U}{\partial V} \right)_S. \quad (6b)$$

This way of representing the thermodynamic properties of a body in thermodynamic equilibrium could

be used just as well when different parts of the body were in different states (for example, a mixture of liquid and gas or of two different crystalline forms of the same pure substance). Gibbs showed how one could use the thermodynamic surface to discuss the coexistence of the various phases (liquid, solid, and gas) of a pure substance and the stability of these states under given conditions of temperature and pressure. One feature of particular interest was the critical point—the state at which liquid and gas become identical—a phenomenon discovered experimentally in carbon dioxide by Thomas Andrews only a few years earlier.

These early papers, as well as Gibbs's major memoir on thermodynamics that soon followed them, appeared in the *Transactions of the Connecticut Academy of Arts and Sciences*, a new and relatively obscure journal whose nonlocal circulation consisted largely of exchanges with other learned societies, including some 140 outside the United States. Gibbs did not count on finding his potential readers among those who checked the contents of the *Transactions*; he sent copies of his papers to an impressive list of scientists in many countries, a list that probably included all those he thought might really read and understand his work.⁷ One of them was James Clerk Maxwell, who proved to be Gibbs's most enthusiastic and most influential reader. He immediately accepted Gibbs's clarification of what Clausius had intended by the term "entropy," correcting the error in his own *Theory of Heat* accordingly and informing Tait about his mistake.

Maxwell found Gibbs's use of geometric rather than algebraic arguments particularly attractive, since he too preferred geometric insight to calculations, even when others found algebraic procedures decidedly simpler. He was sufficiently impressed by Gibbs's paper on the thermodynamic surface to include a discussion of this subject in the fourth edition of *Theory of Heat* (1875) and actually to construct a model of the thermodynamic surface for water, which he sent to Gibbs. He talked about Gibbs's work to his colleagues at Cambridge and recommended it to his friends. "Read Prof. J. Willard Gibbs on the surface whose coordinates are Volume Entropy and Energy," he wrote to Tait, and then added for the benefit of his rather chauvinistic friend, "He has more sense than any German."⁸ Maxwell even started to generalize Gibbs's thermodynamics of a pure substance to include the case of heterogeneous mixtures. This proved to be quite unnecessary and was dropped when he received a set of galley proofs of Gibbs's new memoir containing this generalization and a great deal more.

"On the Equilibrium of Heterogeneous Substances" contains Gibbs's major contributions to thermodynamics. In this single memoir of some 300 pages he vastly extended the domain covered by thermodynamics, including chemical, elastic, surface, electromagnetic, and electrochemical phenomena in a single system. The basic idea had been foreshadowed in his two earlier papers, in which Gibbs had directed his attention to the properties characterizing the equilibrium states of simple systems rather than to the heat and work exchanged in particular kinds of processes. In the abstract of his memoir that Gibbs published in the *American Journal of Science* in 1878, he began by stating the simple but profound idea underlying his work:

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.⁹

Gibbs formulated the criterion for thermodynamic equilibrium in two alternative and equivalent ways. "For the equilibrium of any isolated system it is necessary and sufficient that in all possible variations of the state of the system which do not alter its energy [entropy], the variation of its entropy [energy] shall either vanish or be negative [positive]."¹⁰ The bracketed form immediately indicates that thermodynamic equilibrium is a natural generalization of mechanical equilibrium, both being characterized by minimum energy under appropriate conditions. The consequences of this criterion could then be worked out as soon as the energy of the system was expressed in terms of the proper variables. Gibbs's first and probably most significant application of this approach was to the problem of chemical equilibrium. The result of his work was described by Wilhelm Ostwald as determining the form and content of chemistry for a century to come, and by Henri Le Chatelier as comparable in its importance for chemistry with that of Antoine Lavoisier.

The simplest case is that of a homogeneous phase—a liquid or gas, for example—containing n independent chemical species S_1, \dots, S_n whose masses m_1, \dots, m_n can be varied. Gibbs modified the basic equation (5) to include the change of internal energy due to a change in the mass of any of the chemical components by writing it in the form

$$dU = TdS - PdV + \sum_{i=1}^n \mu_i dm_i. \quad (7)$$

Here dm_i is the change in mass (conveniently expressed as the number of moles) and the new quantity μ_i is the (chemical) potential of the i th chemical species. The chemical potential is related to the energy by the equation

$$\mu_i = \left(\frac{\partial U}{\partial m_i} \right)_{s,v,m_j'} \quad (8)$$

where the subscript m_j' means that μ_i represents the rate of change of energy with respect to the mass of the i th component in this phase, the masses of all other components being held constant along with entropy and volume.

In a heterogeneous system composed of several homogeneous phases the fundamental equilibrium condition leads to the requirement that temperature, pressure, and the chemical potential of each independent chemical component must have the same values throughout the system. From these general conditions Gibbs derived the phase rule, that cornerstone of physical chemistry, which specifies the number of independent variations δ in a system of r coexistent phases having n independent chemical components:

$$\delta = n + 2 - r. \quad (9)$$

Gibbs also showed how to obtain the specific conditions for equilibrium when chemical reactions could take place in the system. Instead of one's attention being restricted to a set of independent chemical components, all the relevant chemical species are considered. Suppose, for example, that a reaction of the type

$$\sum_j a_j A_j = 0 \quad (10)$$

can occur; here the a_j 's are integers, the stoichiometric coefficients, and the A_j 's stand for the chemical symbols of the reacting substances. (An illustration would be the reaction $\text{H}_2 + \text{Cl}_2 - 2 \text{HCl} = 0$, where $a_1 = 1$, $a_2 = 1$, $a_3 = -2$ and the corresponding A_j are respectively H_2 , Cl_2 , and HCl .) The equilibrium condition that Gibbs derived for such a reaction has the simple form

$$\sum_j a_j \mu_j = 0, \quad (11)$$

obtained by replacing the chemical symbols A_j with the chemical potential μ_j of the corresponding substance in the reaction equation (10). Since the potentials could in principle be determined from experi-

mental data, the equilibrium conditions were really established by equation (11).

The requirement that the energy have a minimum and not just a stationary value at equilibrium was used by Gibbs to explore the stability of equilibrium states. This stability depends ultimately on the second law of thermodynamics and manifests itself in the unique sign of certain properties of all substances; the heat capacity at constant volume, for example, must be positive, and the isothermal derivative of pressure with respect to volume must be negative for any substance. The most interesting aspect of Gibbs's investigation of stability was his theory of critical phases, those situations where the distinction between coexistent phases vanishes and the stability is of a lower order than that usually found.

Gibbs's memoir showed how the general theory of thermodynamic equilibrium could be applied to phenomena as varied as the dissolving of a crystal in a liquid, the temperature dependence of the electromotive force of an electrochemical cell, and the heat absorbed when the surface of discontinuity between two fluids is increased. But even more important than the particular results he obtained was his introduction of the general method and concepts with which all applications of thermodynamics could be handled.

Although Maxwell responded immediately to Gibbs's work and influenced a number of his English colleagues to apply Gibbs's results if not his methods, it took a little longer for Continental scientists to appreciate Gibbs. Such figures as Hermann von Helmholtz and Max Planck independently developed thermodynamic methods for chemical and electrochemical problems in the 1880's, quite unaware of Gibbs's prior work. This situation changed gradually—Ludwig Boltzmann referred to Gibbs in 1883—but it was Wilhelm Ostwald's German translation of Gibbs's papers in 1892 that made his ideas more readily available to German chemists.

Gibbs wrote no other major works on thermodynamics itself, restricting himself to a few small applications and developments of his extensive memoir. He rejected all suggestions that he write a treatise that would make his ideas easier to grasp. Even Lord Rayleigh thought the original paper "too condensed and too difficult for most, I might say all, readers."¹¹ Gibbs responded by saying that in his own view the memoir was instead "too long" and showed a lack of "sense of the value of time, of [his] own or others, when [he] wrote it."¹²

During the 1880's Gibbs seems to have concentrated on optics and particularly on Maxwell's electromagnetic theory of light. He was giving lectures

on Maxwell's theory at Yale at least as early as 1885, and he published a series of papers in the *American Journal of Science* on double refraction and dispersion, that is, on the behavior of light as it passes through material media. Two aspects of Gibbs's optical work are of more than technical interest. He emphasized that a theory of dispersion requires one to treat the local irregularities of the electric displacement due to the atomic constitution of the medium. Since he was writing before H. A. Lorentz's theory of electrons (the first version of which did not appear until 1892), Gibbs had to make assumptions of a different kind from those of later theories, and he missed the essential contribution of the atomic structure of the medium—the frequency dependence of the dielectric constant. In the last two papers of this series, published in 1888 and 1889, Gibbs appeared as a defender of the electromagnetic theory of light against the latest versions of purely mechanical theories. These were based on special elastic ethers still being proposed by William Thomson. Gibbs showed that although such theories might account for the phenomena, they required rather artificial assumptions as to internal forces, while Maxwell's theory was "not obliged to invent hypotheses."¹³

Gibbs's reading of Maxwell's *Treatise on Electricity and Magnetism* led him to a study of quaternions, since Maxwell had used the quaternion notation to a limited extent in that work. Gibbs decided, however, that quaternions did not really provide the mathematical language appropriate for theoretical physics, and he worked out a simpler and more straightforward vector analysis. He wrote a pamphlet on this subject which he had printed in 1881 and 1884 for private distribution to his classes and to selected correspondents. No real publication of Gibbs's version of vector analysis took place until 1901, when his student Edwin B. Wilson prepared a textbook of the subject based on Gibbs's lectures. In 1891 Gibbs defended his use of vectors rather than quaternions against an attack by Tait, who was the great exponent of—and crusader for—William Rowan Hamilton's quaternions. Gibbs more than held his own in the ensuing controversy over quaternions, debating both Tait and his disciples in the pages of *Nature*, on minor matters of notation and on the "deeper question of notions underlying that of notations."¹⁴

During the 1890's the classic goal of the physicist—the explanation of natural phenomena in mechanical terms—was seriously questioned and sharply criticized. Among the most outspoken critics were such men as Ernst Mach, Pierre Duhem, and Wilhelm Ostwald, who rejected the concept of atomism along with that of mechanism. One of the spokesmen for

the group who called themselves energeticists was Georg Helm, who in 1898 wrote a treatise on the historical development of energetics. In his book Helm claimed Gibbs as a fellow energeticist, pointing to Gibbs's writings on thermodynamics as a sign that he was free of any prejudice in favor of atomistic mechanical explanations. To Helm, Gibbs's thinking proceeded directly from the two laws of thermodynamics "without any hankering or yearning after mechanics"; his writings were "not decked out with molecular theories."¹⁵ While it is true that Gibbs's papers on thermodynamics were based only on the two laws and required no assumptions about the molecular structure of matter, it is equally true that Gibbs believed in and constructed a (statistical) mechanical explanation of thermodynamics itself. He certainly did not share the scientific values of the energeticists.

Gibbs had carefully studied the writings of Maxwell and Boltzmann on the kinetic theory of gases. This is evident from his obituary notice of Clausius, written in 1889, in which he commented perceptively on a peculiar feature of Clausius' work in this field. Clausius never really accepted the statistical point of view. "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."¹⁶ Maxwell had introduced statistical methods in his first paper on gases in 1860 and had emphasized the essentially statistical nature of the second law of thermodynamics with the help of the "Maxwell demon." Boltzmann then developed all the essential features of a theoretical explanation of the second law based on a combination of mechanics and the laws of probability applied to a large assemblage of molecules in a gas. Gibbs had already paid his own respects to this fundamental insight in his memoir on heterogeneous equilibrium, when he argued that "the impossibility of an uncompensated decrease of entropy seems to be reduced to improbability."¹⁷

During the academic year 1889–1890 Gibbs announced "A short course on the a priori Deduction of Thermodynamic Principles from the Theory of Probabilities,"¹⁸ a subject on which he lectured repeatedly during the 1890's. He referred to this subject in a letter to Lord Rayleigh in 1892:

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.¹⁹

In fact Gibbs did not publish anything more than a very brief abstract on this subject (1884) until 1902, when his book *Elementary Principles in Statistical Mechanics Developed With Special Reference to the Rational Foundation of Thermodynamics* appeared as one of the Yale Bicentennial series.

Gibbs thought of his book as offering a more general approach to statistical mechanics than that used by Boltzmann or Maxwell. Individual results previously obtained by others could now assume their proper places in the logical structure Gibbs gave to the subject. He considered an ensemble of systems, that is, a large number of replicas of the physical system of interest—which might be anything from a molecule to a sample of gas or a crystal. The replicas were all identical in structure but differed in the values of their coordinates and momenta. The ensemble was then characterized by its probability density ρ in phase space, where $\rho dq_1 \cdots dq_N dp_1 \cdots dp_N$ is the fractional number of systems in the ensemble whose coordinates $\{q_j\}$ and momenta $\{p_j\}$ lie in the intervals $\{q_j, q_j + dq_j\}$ and $\{p_j, p_j + dp_j\}$, respectively, at time t . The phase point representing any individual system moves with time, and so the probability density ρ at any point in the $2N$ -dimensional phase space varies in a way determined by the mechanical equations of motion of the system.

If the average behavior of a system in the ensemble was to describe the behavior of the actual physical system, then a physical system in equilibrium had to be described by a stationary ensemble, one whose probability density ρ was constant in time. Gibbs analyzed several such stationary ensembles but found the one he called “canonical” to be most useful. In a canonical ensemble the probability density ρ is given by the equation

$$\rho(q_1 \cdots p_N) = \exp\{(\psi - E)/\Theta\}, \quad (12)$$

where $E(q_1 \cdots p_N)$ is the energy of the system having coordinates and momenta $q_1 \cdots p_N$, and ψ , Θ are constants in phase space. Gibbs showed that the energy of such an ensemble has a sharply peaked distribution, if the systems have many degrees of freedom; only a very small fraction of the systems in the canonical ensemble have energies appreciably different from the average.

The principal theme of Gibbs’s book is the analogy, as he describes it, between the average behavior of a canonical ensemble of systems and the behavior of a physical system obeying the laws of thermo-

dynamics. When this analogy is worked out, the modulus Θ of the canonical distribution is proportional to the absolute temperature, with a universal proportionality constant k ,

$$\Theta = kT. \quad (13)$$

The average energy \bar{E} , where \bar{E} satisfies the equation

$$\bar{E} = \frac{\int E \rho dq_1 \cdots dp_N}{\int \rho dq_1 \cdots dp_N}, \quad (14)$$

is identified with the thermodynamic internal energy U . The second parameter of the distribution, ψ , is fixed by the condition that ρ is a probability density, so one has the equation

$$\psi = -\Theta \ln \{\int \exp(-E/\Theta) dq_1 \cdots dp_N\} \quad (15)$$

and ψ is also related to the energy U (or \bar{E}) and the entropy S by the equation

$$\psi = U - TS, \quad (16)$$

a result Gibbs obtained by analyzing the meanings of heat and work in the ensemble.

Gibbs was very much aware of the gaps in his statistical mechanics. He had supplied a “rational foundation” for thermodynamics in statistical mechanics to the extent that thermodynamic systems could be treated as if they were conservative mechanical systems with a finite number of degrees of freedom. He could not incorporate the phenomena of radiation that were of so much interest at the turn of the century, nor could he surmount the long-standing difficulties associated with the theorem of the equipartition of energy. For these reasons he disclaimed any attempts “to explain the mysteries of nature” and put his work forward as the statistical “branch of rational mechanics.”²⁰ He was also dissatisfied with the effort he had made in the twelfth chapter of his book to explain the irreversibility of nature embodied in the second law. His argument in this chapter was almost completely verbal rather than mathematical, and his statements were carefully qualified. Gibbs’s manuscript notes suggest that he was still struggling with the problem of irreversibility and the nature of the entropy of systems not in equilibrium.

Despite these difficulties Gibbs’s work in statistical mechanics constituted a major advance. His methods were more general and more readily applicable than Boltzmann’s and eventually came to dominate the whole field. Gibbs did not live to see the real successes of statistical mechanics, for his fatal illness came within a year of the publication of his book.

NOTES

1. Everett O. Waters, "Commentary Upon the Gibbs Monograph 'On the Form of the Teeth of Wheels in Spur Gearing,'" in L. P. Wheeler, E. O. Waters, and S. W. Dudley, eds., *The Early Work of Willard Gibbs in Applied Mechanics* (New York, 1947), p. 43.
2. William Thomson, "An Account of Carnot's Theory of the Motive Power of Heat," in *Transactions of the Royal Society of Edinburgh*, **16** (1849), 541.
3. Rudolf Clausius, "On the Moving Force of Heat and the Laws of Heat Which May Be Deduced Therefrom," in *Annalen der Physik*, **79** (1850), 368, 500. Trans. into English by T. Archer Hirst as *The Mechanical Theory of Heat* (London, 1867), p. 45.
4. Clausius, "On a Modified Form of the Second Fundamental Theorem in the Mechanical Theory of Heat," in *Annalen der Physik*, **93** (1854), 481. Translation, *The Mechanical Theory of Heat*, p. 111.
5. Clausius, "On Several Convenient Forms of the Fundamental Equations of the Mechanical Theory of Heat," in *Annalen der Physik*, **125** (1865), 353. Translation, *The Mechanical Theory of Heat*, p. 365.
6. Carl Neumann, *Vorlesungen über die mechanische Theorie der Wärme* (Leipzig, 1875), p. ix.
7. The list is reprinted as app. IV in Lynde Phelps Wheeler, *Josiah Willard Gibbs* (New Haven, 1952).
8. James Clerk Maxwell to Peter Guthrie Tait, 13 Oct. 1874.
9. Gibbs, abstract of "Equilibrium of Heterogeneous Substances," in *American Journal of Science*, 3rd ser., **16** (1878), 441; *Scientific Papers*, I, 354.
10. *Ibid.*
11. Lord Rayleigh to J. W. Gibbs, 5 June 1892.
12. Gibbs to Lord Rayleigh, 27 June 1892.
13. Gibbs, "A Comparison of the Electric Theory of Light and Sir William Thomson's Theory of a Quasi-Labile Ether," in *American Journal of Science*, 3rd ser., **37** (1889), 144; *Scientific Papers*, II, 246.
14. Gibbs, "On the Role of Quaternions in the Algebra of Vectors," in *Nature*, **43** (1891), 511; *Scientific Papers*, II, 155.
15. Georg Helm, *Die Energetik* (Leipzig, 1898), p. 146.
16. Gibbs, "Rudolf Julius Emanuel Clausius," in *Proceedings of the American Academy of Arts and Sciences*, **16** (1889), 458; *Scientific Papers*, II, 265.
17. Gibbs, "On the Equilibrium of Heterogeneous Substances," in *Transactions of the Connecticut Academy of Arts and Sciences*, **3** (1875-1878), 108, 343; *Scientific Papers*, I, 167.
18. Henry A. Bumstead to Edwin B. Wilson, 22 Dec. 1915.
19. Gibbs to Lord Rayleigh, 27 June 1892.
20. Gibbs, *Elementary Principles in Statistical Mechanics* (New Haven, 1902), pp. ix-x.

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GIBBS, (OLIVER) WOLCOTT (b. New York, N.Y., 21 February 1822; d. Newport, Rhode Island, 9 December 1908), *chemistry*.

Gibbs's career epitomizes much of the development of chemistry in America. He received his M.D. in 1845 from the College of Physicians and Surgeons with a dissertation on chemical classification. He then studied in Germany and France and, while in Berlin, was particularly influenced by Heinrich Rose. After fourteen years (1849-1863) teaching elementary students at what is now City College of the City University of New York, he became Rumford professor at Harvard in 1863. Until 1871, when the Lawrence Scientific School's laboratory was combined with the Harvard College laboratory, Gibbs trained a good number of professional chemists by the German practice of research as a method of teaching.

Gibbs had neither laboratory nor chemistry students from 1871 until his retirement in 1887. He did, however, lecture in the physics department on heat and spectroscopy. Publicly, this was ascribed to economy; privately, it was explained by some as President Charles Eliot's revenge for not getting the