The History and Legacy of Josiah Willard Gibbs

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On February 11, 1839, Josiah Willard Gibbs Jr. was born the only son of Josiah Willard Gibbs Sr., a Professor at Yale University in sacred literature. The Gibbs family was abundant with academics and professors, notably Samuel Willard (1640-1707), who served as president of Harvard University from 1701 until his death in 1707 [18]. J. Willard Gibbs Jr attended Yale University and obtained his PhD in engineering in 1863, the first doctorate in engineering awarded in the United States; his dissertation covered the geometric analysis of the design of gears. After his graduation, he remained at Yale and tutored Latin for two years and natural philosophy during his third year [18].

Dr. Willard Gibbs then traveled to Europe, along with his four sisters, to continue their education. They spent the winter of 1866-67 in Paris, a year in Berlin, and the remaining year in Heidelberg. During this time, Gibbs was inspired by the works and lectures of Gustav Kirchoff and Hermann Von Helmholtz, both of whom made notable contributions to mathematical physics. In 1871, Gibbs was appointed Professor of Mathematical Physics at Yale University and was soon after appointed chair before his first publication. At the end of the year 1873, he had published "Graphical Methods in the Thermodynamics of Fluids" and "A Method of Geometrical Representation of the Thermodynamic Properties of Substances by Means of Surfaces." Both publications led to the creation of the three-dimensional model of Gibbs' thermodynamic surface by James Clerk Maxwell [18]. The following has been said of Gibbs' first publications: "The first two papers of this series… are themselves very remarkable and valuable contributions to the theory of thermodynamics… it is difficult to see how without them, the third could be written," [24, p. 188]. Both publications were exceptional in the world of thermodynamics and contributed to the theoretical concepts of physics, mathematics, and chemistry.

In his first publication, "Graphical Methods," Gibbs defines "Quantities and Relations which are to be represented by the Diagram," as follows, where v represents the volume; p, the pressure; t, the absolute temperature; ϵ, the energy; and η, the entropy (or spontaneity) of a given body in any state. Furthermore, he defines W, the work done; and H, the heat received, "by the body in passing from one state to another," [10, p. 1]. He proceeds to define the following differential equations for the state of the body for the given thermodynamics of a fluid.

$$d\epsilon = dH - dW \tag{1}$$

$$dW = pdv \tag{2}$$

$$dH = td\eta \tag{3}$$

$$d\epsilon = td\eta - pdv \tag{4}$$

He states: "... if we associate a particular point in a plane with every separate state, of which the body is capable… the points associated with states of equal volume will form lines, which may be called *lines of equal volume*… These lines we may also call isometric, isopiestic, isothermal, isodynamic, isentropic, and if necessary use these words as substantive," [10, pp. 1-2]. He then defines the *path* of the body as points in which the body passes to form a line, and that with every change in the body, it yields a result of change in the path and so "... a certain amount of work done, W, and of heat received, H…" which he represents mathematically as follows from equations (2) and (3).

$$W = \int p dv \tag{5}$$

$$H = \int t d\eta \tag{6}$$

Thus, the integration is completed from the beginning to the end of the path. He elaborates on cases such as if there is no change in the path, a circuit, or if the direction of the path is reversed.

If there is no change in the path, the resulting value of the integral is zero; furthermore, if the direction of the path is reversed, the sign of the resulting integral will be negative [10, pp. 1-5].

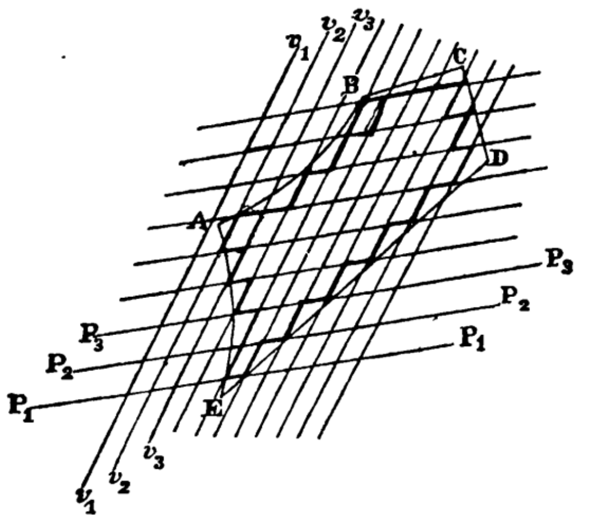

Fig. 1.

Figure 1: Graphical Representation of volume and pressure for a system [10].

Notably, Gibbs proves that the ratio of the included area to the work or heat of the circuit is independent of the shape of the circuit, shown by Figure 1. Let n be a natural number, where each v_n represents an infinite number of isometrics of equal differences in volume for all n, denoted dv. Each p_n depicts an infinite number of isopiestics of equal differences in pressure for all n, denoted by dp. Lastly, he defines the ratio of the area for one small quadrilateral in relation to the remaining different quadrilaterals; typified by γ, which is treated as a scalar coefficient. He proceeds, "But the area of this figure is approximately the same as that of the given circuit… Therefore, the area of the given circuit has to the work done or heat received in that circuit this ratio γ, which is independent of the shape of the circuit," [10, pp. 1-5]. This concludes his proof. He proceeds: "If we write δW and δH for the work and heat of an infinitesimal circuit, and δA for the area included, the relations of these quantities are thus expressed $\delta W = \delta H = \frac{1}{\gamma}\delta A$,". Furthermore, he describes the summations for the work and heat of the infinitesimal circuit, which calculates the limits of the circuit:

$$W_S = \Sigma^{[S,v'',p_0,v']} \frac{1}{\gamma} \delta A \tag{7}$$

$$H_S = \Sigma^{[S,\eta'',t_0,\eta']} \frac{1}{\gamma} \delta A \tag{8}$$

In the above equations, W_S and H_S depict the work and heat of any given path S [10, pp. 6-7]. In order to calculate the work and heat at a specific state, equations (5) and (6) are used.

The impact of this research was quickly noticed by James Clerk Maxwell, who had significant contributions to mathematical physics and thermodynamics. Within Maxwell's *Theory of Heat*, the section on Mechanical and Thermal Analogies cites "Professor J. Willard Gibbs, of Yale College, U.S., to whom we are indebted for a careful examination of the different methods of representing thermodynamic relations by plane diagrams, has introduced an exceedingly valuable method of studying the properties of a substance by means of a surface," [19, pp. 194-195]. Maxwell's inspiration from Gibbs' research led to the famous three-dimensional thermodynamic model (see Image 1). Unfortunately, as Maxwell passed away in 1879, their collaboration had only begun and yielded minimal but monumental scientific discoveries.

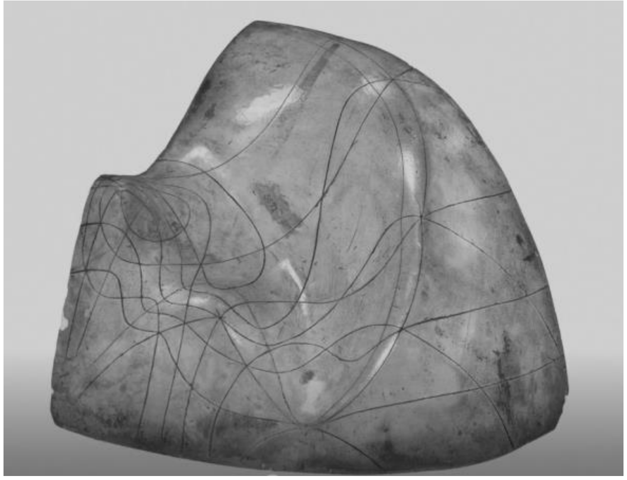

Image 1: Professor Frederick E. Beach's Historical Copy from 1909 of the Maxwell-Gibbs thermodynamic surface model [17].

In addition to his notable accomplishments in thermodynamics, Gibbs also discovered vector analysis, which led to the development of modern vectors used in mathematical physics. Prior to Gibbs' contributions, William Rowan Hamilton (1805-1865) had published over 100 works on physics and quaternion algebra. Quaternions, defined as members of noncommutative division algebras, were famously scratched on a bridge along the Royal Canal by Hamilton on October 16, 1843 [23, 3, p. 638]. Hamilton spent the remaining 20 years of his life dedicated to quaternions and their applications, publishing the great *Lectures on Quaternions*, a massive work which was said to be incredibly difficult to understand by mathematicians and physicists alike.

Gibbs, having studied Hamilton's methods for quaternion mechanics, and read *Lectures on Quaternions*, developed the representation of physical quantities based on the vector format of Hamilton's quaternion studies,

$$u = b\boldsymbol{i} + c\boldsymbol{j} + d\boldsymbol{k}$$

Gibbs denoted his discovery, "vector analysis", and introduced the now common and standard methods of multiplication for vectors:

> Namely, the scalar or dot product of v and $v' = b'\boldsymbol{i} + c'\boldsymbol{j} + d'\boldsymbol{k}$, defined by
>
> $$v \cdot v' = bb' + cc' + dd',$$
>
> and the vector or cross product given by
>
> $$v \times v' = (cd' - c'd)\boldsymbol{i} + (db' - b'd)\boldsymbol{j} + (bc' - b'c)\boldsymbol{k}.$$
>
> Despite the spirited advocacy of Hamilton's devoted followers, the vector analysis of Gibbs eventually prevailed, replacing the quaternions for the practical purposes of physics and engineering [3, pp. 638-639].

This significant mathematical discovery shaped the idea of linear algebras and vectors used in all physical sciences and applications: it simplified the robust methods of Hamilton and led to the findings of Arthur Cayley and Joseph Sylvester, who contributed to matrix algebras and matrix theory.

Much of Gibbs' work was shared during his lectures and remained unpublished. His work in vector analysis was published in 1901, not by Gibbs, instead by former student, Dr. Edwin Bidwell Wilson. Gibbs states in the preface of *Vector Analysis*,

> As, however, the years passed without my finding the leisure to meet this want [*Vector Analysis*] ... I was very glad to have one of the hearers of my course on Vector Analysis in the year 1899-1900 undertake the preparation of a text-book on the subject. I have not desired that Dr. Wilson should aim simply at the reproduction of my lectures, but rather that he should use his own judgment in all respects for the production of a text-book… [12].

Additionally, the discovery of the Gibbs phenomenon was first published by Henry Wilbraham in 1848 and fifty years later, in 1899, Gibbs rediscovered this phenomenon in a footnote given in his publication, *Fourier's Series* in the Nature publication journal in 1898. His footnote states,

> I should like to correct a careless error which I made in describing the limiting form of the family of curves represented by the equation
>
> $$y = 2[sin(x) - \frac{1}{2}sin(2x) \ldots \pm \frac{1}{n}sin(nx)]$$
>
> as a zigzag line consisting of alternate inclined and vertical portions. The inclined portions were correctly given, but the vertical portions, which are bisected by the axis of X, extend beyond the points where they meet the inclined portions, their total lengths being expressed by four times the definite integral
>
> $$\int_0^\pi \frac{sin(u)}{u} du$$ [9, p. 606].

Today, this phenomenon is known as the Gibbs-Wilbraham or Gibbs phenomenon and describes an overestimation of the convergence of partial sums within certain Fourier series [15, pp. 1-3]. This overshoot is also known as "ringing" and occurs near simple jump discontinuities (See Figure 2). It reflects oscillator behavior on the edges of the discontinuities for a periodic signal, which is proportional to the height of the discontinuity [21]. While the phenomenon was published prior to Gibbs' discoveries, it does show his independent findings and his corrections to his discoveries in the Fourier Series.

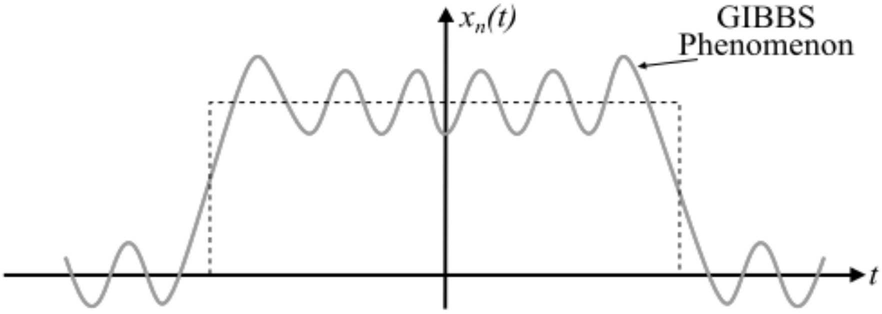

Figure 2: Gibbs Phenomenon [21].

Gibbs is notably credited for his mathematical discoveries, though additionally, his extensive knowledge in physics and engineering resulted in remarkable advancements in chemistry. Three years after the publication of Gibbs' first two papers, he published two parts of his research, "On the Equilibrium of Heterogeneous Substances" in 1875 and 1878, which laid the foundation for the majority of physical chemistry today [5]. The following can be said regarding Gibbs' third publication: "... which is generally, and probably rightly, considered his most important contribution to physical science…" [24, pp. 1-2]. Like Gibbs' first two publications, "On the Equilibrium," was crucial in the fields of thermodynamics as well as chemical equilibrium. Gibbs pioneered the field of physical chemistry and specifically introduced the concept of the "phase rule", defined as follows:

> The Gibbs phase rule $p + n = c + 1$ gives the relationship between the number of phases p and components c in a given alloy under equilibrium conditions at constant pressure, where n is the number of thermodynamic degrees of freedom in the system [4].

An example of Gibbs' phase rule is that a one-component system with one phase (solid, liquid, or gas) will have two degrees of freedom and can therefore have any temperature and pressure (within limits) attained. For a one component system with two phases, say liquid and gaseous, only one degree of freedom can exist with one correlating pressure for each temperature [2].

Continuing the discoveries within "On the Equilibrium," Gibbs discussed the free energies of heterogeneous substances, leading to what is now commonly known as 'Gibbs' free energy.' This change in the measurement of work required in the system is based on the heat content or enthalpy, the spontaneity or entropy, and the temperature which will represent the change in favorability of natural reaction, denoted as follows,

$$\Delta G = \Delta H - T\Delta S$$

Where ΔG represents the change in free energy in Joules, ΔH represents the change in enthalpy in Joules per mol, T represents the temperature in Kelvin, and ΔS represents the change in entropy in Joules per Kelvin. When the system is at equilibrium, ΔG is minimized and at constant temperature and pressure. For a spontaneous reaction to occur, ΔG must be negative. Furthermore, the standard Gibbs free energy change is defined as:

$$\Delta G^\circ = -RTln(K_p)$$

Where R represents the gas constant (8.3145 J per mol Kelvin), T represents the temperature in Kelvin, and K_p denotes the kinetic equilibrium constant for the system, achieved by the concentrations of the products and reactants, which remains unitless. Both equations are fundamental in chemistry in regard to equilibrium and thermodynamics and are often taught in the foundations of chemistry education.

As Gibbs' career progressed, his research continued in thermodynamics and equilibrium, as well as quantum and statistical mechanics alongside Ludwig Boltzmann and James Clerk Maxwell. Published in 1902, "Elementary Principles of Statistical Mechanics" combines thermodynamic theory with the physics of any given system based on that of all systems. He states in the preface:

> We may imagine a great number of systems of the same nature, but differing in the configurations and velocities which they have at a given instant… And here we may set the problem, not to follow a particular system through its succession of configurations, but to determine how the whole number of systems will be distributed among the various conceivable configurations and velocities at any required time… [8]

His research in statistical mechanics is often compared to that of Boltzmann, who developed the appropriately named Boltzmann mechanics. Today, Gibbsian statistical mechanics (GSM) is most widely used for statistical analysis of working physicists. In contrast, Boltzmann's methods of statistical mechanics are limited to dilute and classical gasses: real gasses at high temperatures in which, "(1) the interaction between the atoms is ignored and (2) the atoms are treated as classical particles," [20, p. 1]. Furthermore, "A system may be characterized as dilute based on the 'average' spacing between its molecules,

$$\delta \sim \sqrt[3]{\frac{1}{n}} \text{ or } \frac{\delta}{\sigma} \sim \sqrt[3]{\frac{1}{n\sigma^3}}$$

where n is the number density (number of atoms per unit volume) and σ is the effective 'diameter' of the molecule (referring to, for example, a Lennard-Jones model)" [20, p. 2]. The following quotation describes Boltzmann statistical mechanics.

> Boltzmann's statistical method, the method of the most probable distribution, addresses a mathematical model. The model is an assembly of N_A weakly interacting systems… so that each system could be regarded as statistically independent [13].

We can denote the number of systems as N_A, and the number of physical particles as N. A formula of Boltzmann states that

$$\bar{n}_s = e^{-\alpha\beta\epsilon_s}$$

where $\bar{n}_s$ represents the expected number of systems in the state energy ϵ_s, α and β are Lagrange multipliers. Based on the limitations of Boltzmann's statistical methods, we would only be able to classify statistical mechanics for dilute classical gasses, and not for solids, liquids, dense gasses, or quantum systems [13].

Gibbsian statistical mechanics works similarly; however, it removes the limitations of Boltzmann's methods. We still consider the assembly of N_A systems, "however, the system is taken as the whole body under study. It is the solid, liquid or gas composed {itself} of many particles," [13]. We can then compute the expected number of systems, denoted by $\bar{N}_S$, where N designates that we are considering systems with many particles. The following can be said:

$$\bar{N}_S = e^{-\alpha\beta E_S}$$

where E_S is one of the possible energy states of the many-particle system. Based on this, we can calculate the average work, entropy, and free energy of the system as follows,

$$dW = -\frac{1}{N_A}\sum_S \bar{N}_S dE_S$$

$$S = k[log(Z) + \beta U]$$

$$G = U - TS$$

where k represents Boltzmann's constant, U is the internal energy of the system, dW is the average work done, S is the entropy, and G is the free energy of the system. Gibbsian statistical mechanics are so broad that it has been remarked: "... Gibbs' interpretation is also valid equally for quantum or classical particles in the system since we have said nothing about the statistics of the particles within the system," [13]. His work was applicable to quantum physics: "Gibbs devised a new mathematical framework for statistical mechanics which bridged the gap between classical and (as yet undiscovered) quantum physics, paving the way for the quantum world," [16]. In comparison to Boltzmann statistical mechanics, Gibbs removed the two limitations in Boltzmann mechanics: the system must be classically gaseous and dilute.

During his academic career, Josiah Willard Gibbs made enormous discoveries in the worlds of physics, mathematics, and chemistry. His theoretical pursuits did not go unnoticed: he was awarded the Rumford Prize of the American Academy of Arts and Sciences in 1880 for his research in thermodynamics, the British Royal Society's Copley Medal in 1901, awarded once annually and considered as prestigious as the Nobel Prize today, cited to Gibbs for being: "The first to apply the second law of thermodynamics to the exhaustive discussion of the relation between chemical, electrical, and thermal energy and capacity for external work," [16]. Josiah Willard Gibbs' achievements let him live comfortably for the remainder of his life until his death at age 64 in 1903, in New Haven, Connecticut. He and his two sisters never left their family home, permitting Gibbs to serve as a professor of mathematical physics at Yale University for 32 years.

Today, Gibbs' name is far from obscure in the pertinent fields in which he specialized. The Chicago section of the American Chemical Society presents one Willard Gibbs Award annually "to publicly recognize eminent chemists who, through years of application and devotion, have brought to the world developments that enable everyone to live more comfortably and to understand this world better," [1, pp. 1-4]. For over 100 years ACS has recognized and bestowed the Willard Gibbs award to notable chemists such as William Merriam Burton, Marie Curie, and Peter Debye for their contributions and dedication to chemistry. The Bronze Hall of Fame medal of Josiah Willard Gibbs is displayed at the Yale University Art Gallery, designed by sculptor Lee Lavirie. Rather interestingly, the United States Navy named an oceanic research ship the USNS Josiah Willard Gibbs in his honor [6]. Gibbs' discoveries in chemical equilibrium were primarily ignored for the first decade after publication but had a gargantuan impact on the modern world of industrial manufacturing and technologies. In his legacy, Gibbs' contributions led to the development of modern "plastics, drugs, dyes, and organic solvents," as well as continuing to impact the world of science from today to tomorrow, and for many years to come [4].

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