SCIENCE

VOL. LVIII AUGUST 24, 1923 No. 1495

CONTENTS

SCIENCE: A Weekly Journal devoted to the Advancement of Science, edited by J. McKeen Cattell and published every Friday by

THE SCIENCE PRESS

Lancaster, Pa. Garrison, N. Y.

New York City: Grand Central Terminal.

Annual Subscription, $6.00. Single Copies, 15 Cts.

SCIENCE is the official organ of the American Association for the Advancement of Science. Information regarding membership in the association may be secured from the office of the permanent secretary, in the Smithsonian Institution Building, Washington, D. C.

Entered as second-class matter July 18, 1923, at the Post Office at Lancaster, Pa., under the Act of March 3, 1879.

J. WILLARD GIBBS AND HIS CONTRIBUTION TO CHEMISTRY[1]

THOMAS CARLYLE expressed the thought that "great men are the inspired texts of that divine Book of Revelations whereof a chapter is completed from epoch to epoch, and by some named History." These words acquire singular significance when applied to him of whom it is my privilege to speak to-day. In a very real sense Josiah Willard Gibbs was one of the most "inspired texts" which adorn the pages of the history of science in America. Unfortunately the process of exegesis has proved both difficult and slow, so that Gibbs did not live to see himself fully understood nor the practical value of his discoveries appreciated.

Josiah Willard Gibbs was born in New Haven, Connecticut, February 11, 1839. He was the fourth child and only son of Josiah Willard Gibbs, professor of sacred literature in Yale Divinity School, and of his wife, Mary Anna, daughter of Dr. Van Cleve, of Princeton, New Jersey. He was descended from Robert Gibbs, the fourth son of Sir Henry Gibbs, of Honington, Warwickshire, who came to this country and settled in Boston in 1658. Henry Gibbs, one of the grandsons of Robert Gibbs, married, in 1747, Katharine, the daughter of Hon. Josiah Willard, secretary of the province of Massachusetts. No fewer than six of the descendants of this couple have borne the name Josiah Willard Gibbs. The father of the subject of this sketch was regarded by his contemporaries as a man of unusual erudition. He was remarkable for his extreme modesty and for the conscientious and painstaking accuracy which characterized all of his published work. One of his colleagues in commenting on his uncompleted translation of Gesenius's Hebrew Lexicon wrote, "But with his unwonted thoroughness he could not leave a word until he had made the article upon it perfect, sifting what the author had written by independent investigations of his own." Thus, not only through inheritance but also by precept and example, the son acquired those habits of thoroughness which marked all of his life-work.

Willard Gibbs was prepared for college at the Hopkins Grammar School, New Haven, and entered Yale in 1854. His brilliance as a student is attested

[1] Presented before the historical section of the American Chemical Society at the New Haven meeting, April 6, 1923.

by the fact that during his undergraduate career he was awarded several prizes for excellence in Latin and mathematics. After his graduation in 1858 he continued his studies in New Haven until 1863, when he received the degree of doctor of philosophy and was appointed a tutor in the college for a term of three years. During the first years of his appointment he taught Latin, and in the third year physics, in both of which subjects he had earned distinction as an undergraduate. In 1866 he went to Europe, spending the winter in Paris, and the following year in Berlin where he attended the lectures of Magnus and other notable teachers of physics and mathematics. After spending the winter of 1868–69 in Heidelberg, where Helmholtz and Kirchoff were then lecturing, he returned to his home in New Haven. Two years later he was appointed professor of mathematical physics in Yale College, a position which he filled with distinction until the time of his death, April 28, 1903.

Professor Gibbs was most widely known for his contributions to the science of thermodynamics, and in all of the standard treatises on this subject his name repeatedly occurs. It is probably true that no one ever displayed greater originality in method of treatment or discovered a larger number of important thermodynamical principles than did Gibbs.

In 1873, when thirty-four years of age, he published in the Transactions of the Connecticut Academy[2] his first paper, entitled "Graphical methods in the thermodynamics of fluids." In this paper the reader will be impressed with the author's inclination to employ geometrical illustrations in preference to mechanical models as aids to the imagination. Gibbs recognized the fact that such models seldom fully correspond with the phenomena they are intended to represent and accordingly sought geometrical illustrations of his equations. In this endeavor he probably has had few if any equals. The late Professor Bumstead in commenting on his skill in this direction wrote as follows:

With this inclination, it is probable that he made much use of the volume-pressure diagram, the only one which, up to that time, had been used extensively. To those who are acquainted with the completeness of his investigation of any subject which interested him, it is not surprising that his first published paper should have been a careful study of all the different diagrams which seemed to have any chance of being useful. Of the new diagrams which he first described in this paper, the simplest, in some respects, is that in which entropy and temperature are taken as coordinates; in this, as in the familiar volume-pressure diagram, the work or heat of any cycle is proportional to its area in any part of the plane; for many purposes it is far more perspicuous than the older diagram, and it has found most important applications in the study of the steam engine. The diagram, however, to which Professor Gibbs gave most attention was the volume-entropy diagram, which presents many advantages when the properties of bodies are to be studied, rather than the work they do or the heat they give out. The chief reason for this superiority is that volume and entropy are both proportional to the quantity of substance, while pressure and temperature are not; the representation of coexistent states is thus especially clear, and for many purposes the gain in this direction more than counterbalances the loss due to the variability of the scale of work and heat. No diagram of constant scale can, for example, adequately represent the triple state where solid, liquid and vapor are all present; nor, without confusion, can it represent the states of a substance which, like water, has a maximum density; in these cases the volume-entropy diagram is superior in distinctness and convenience.

His second paper, entitled "A method of geometrical representation of the thermodynamic properties of substances,"[3] attracted the attention of physicists throughout the world. He here selects volume, entropy and energy as the three coordinate axes and proceeds to develop the properties of the resulting thermodynamic surface, the geometrical conditions for equilibrium, the criteria for its stability and the conditions for coexistent states, as well as those for the critical state. The importance of this work was quickly recognized by James Clerk Maxwell who, towards the end of his life, constructed a model of such a surface with his own hands and presented a cast of it to Professor Gibbs.

These two papers demonstrated to the world Gibbs's extraordinary powers in the domain of mathematical physics, and presaged the appearance of his most celebrated contribution to scientific literature, entitled "On the equilibrium of heterogeneous substances."[4] This paper, which won for him universal fame, was published in two parts in the Transactions of the Connecticut Academy, the first part appearing in 1876 and the second part in 1878. The author here applied the principles of thermodynamics to the conditions of equilibrium between substances differing not only in chemical properties, but also in physical state. The few attempts which had been made prior to the work of Gibbs to bring chemical action within the scope of the fundamental laws of thermodynamics had proven only partially successful. No broad generalizations, connecting thermal energy and chemical energy, similar to the relations which were known to obtain in the case of mechanical energy, had been established. It was Willard Gibbs who supplied the stroke of genius necessary to the solution of the problem. Not only did he blaze the trail, but in this masterly pub-

[2] Trans. Conn. Acad., 2, 309, (1873).

[3] Trans. Conn. Acad., 2, 382 (1873).

[4] Trans. Conn. Acad., 3, 108 (1876); 3, 343 (1878).

lication he carried the study of the relations between thermal energy and the energy of chemical reaction to a degree of completeness which rivals that of the older theory dealing with mechanical energy. It should be borne in mind that this older theory had to do with a far less complicated subject. As one of his biographers wrote:

The older theory was the work of a number of men whose mathematical deductions were constantly being checked by experiment and who had the stimulus of mutual suggestions from each other's work. Professor Gibbs worked alone in a field in which he had no rivals and no helpers; he published practically all that he had to say upon the subject in a single paper of great length; and there were scarcely any experiments to which he could look for confirmation or suggestion as to his theoretical conclusions. Yet his very numerous results were correct, were of the highest importance, and were extremely general in application. Many things which had been mysteries, and concerning which our ignorance had been confessed by such vague terms as "affinity" or "catalytic action," were in this paper shown to be simple and direct consequences of the two laws of thermodynamics. Relations between facts and laws of chemical action were stated *a priori* which have since been verified by laborious and exact experiments; in fact there is little exaggeration, if any, in the statement that this paper contains, so far as general principles are concerned, practically the whole of the science which is now called physical chemistry and which had scarcely been begun when it was written. Considered merely as an intellectual *tour de force,* there are very few chapters in the history of science which can be compared with this; as an example of scientific prediction it is probably without a rival in the number and complexity of the relations discovered by *a priori* reasoning, in a science essentially experimental.

Notwithstanding the importance of this paper, it was a number of years before its value to the science of chemistry was fully appreciated. The cause of this delay was, in large measure, due to the fact that the author expressed his generalizations in terms of mathematics of which the average chemist of forty years ago was blissfully ignorant.

In 1892 the paper was translated into German by Ostwald and seven years later Le Chatelier translated it into French. In the preface to the German edition, the translator writes:

The importance of the thermodynamic papers of Willard Gibbs can best be indicated by the fact that in them is contained, explicitly or implicitly, a large part of the discoveries which have since been made by various investigators in the domain of chemical and physical equilibrium and which have led to so notable a development in this field. . . . The contents of this work are to-day of immediate importance and by no means of merely historical value. For of the almost boundless wealth of results which it contains, or to which it points the way, only a small part has up to the present time been made fruitful. Untouched treasures of the greatest variety and of the greatest importance both to the theoretical and to the experimental investigator still lie within its pages.

Le Chatelier, in the foreword to the French edition, reminds his readers that

To Professor Willard Gibbs belongs the honor of having created by the systematic use of thermodynamic methods a new branch of chemistry, the importance of which, daily increasing, has now become comparable to that of the gravimetric chemistry created by Lavoisier.

While it obviously lies beyond the scope of this paper to attempt an outline of this remarkable piece of work, it should be pointed out that many of its theorems have served as guides for experimental investigations of fundamental importance, while others have served to classify and explain, in a thoroughly satisfactory manner, the results of numerous researches. No one who is familiar with modern physical chemistry can study this paper without being profoundly impressed by the remarkable clearness with which Gibbs formulated many of its fundamental theorems, despite the fact that so little experimental data was available.

Thus, in his treatment of binary mixtures in which one of the components was assumed to be present in relatively small amount, he deduced the law of dilute solutions which, as is well known, was subsequently derived by Van't Hoff from the experimental data of Pfeffer and Traube.

One also finds a derivation of the exact relationship which obtains between the chemical energy transformed and the maximum electrical energy developed in a reversible galvanic cell. Gibbs clearly pointed out that the total thermal energy of the chemical reaction occurring within a galvanic cell is never completely transformed into electrical energy, unless the temperature coefficient of electromotive force is zero. This same relationship was independently discovered by Helmholtz about four years after the publication of Gibbs's paper; in consequence of this fact its mathematical formulation is commonly known as the "Gibbs-Helmholtz equation."

It was Gibbs who first pointed out, that at the surfaces of dispersed systems, a different concentration is to be expected from that which obtains in the body of the dispersoid. While he did not know or employ the modern concept of dispersed systems, his deductions were of such a general character that they may be applied to the special field of colloids.

Another generalization of interest to the chemist which was first clearly stated in this paper deals with the direction of change of vapor pressure which occurs in the distillation of a mixture of changing composition. This generalization, sometimes referred to as the Gibbs-Konowalow rule, states that a liquid mixture corresponding to a minimum or maximum of vapor pressure at any specified temperature has the same composition as the vapor with which it is in equilibrium.

By far the most important principle enunciated in this wonderfully comprehensive paper, however, is that commonly known as the "phase rule." The Dutch physical chemist, Roozeboom, was the first to recognize the value of this principle in connection with the study of heterogeneous systems, and it is to him that we owe the familiar simplified statement of the theorem as well as numerous illustrations of its applications. The phase rule, as is well known, defines the conditions of equilibrium in a heterogeneous system by the relation between the number of coexisting phases and the number of components constituting the system. It may be briefly stated as follows: A system will be in equilibrium when the number of degrees of freedom is equal to the number of components less the number of phases increased by 2. It may be of interest to mention that Gibbs was the first to employ the term "phase" to signify a discrete portion of matter in which the smallest visible particles are all exactly alike, and which is, therefore, separated in space from every other homogeneous, but dissimilar portion of matter.

The importance of the phase rule in the realm of theoretical chemistry is to-day fully recognized. It has furnished a valuable basis for the classification of closely allied chemical compounds and has proven a trustworthy guide, both in the discovery of new substances as well as in the determination of the range of their stability. Its practical importance is attested by the fact that it forms the basis of modern metallography. The variation of the engineering properties, such as tensile strength, ductility, etc., with varying concentration and varying thermal treatment, can only be satisfactorily elucidated with the phase rule as a guide. The application of the phase rule to the metallurgy of iron and steel furnishes one of the most striking illustrations of its value. The phase rule has proven of inestimable value in connection with the interesting investigations upon minerals and rocks which have been in progress for some years at the Geophysical Laboratory in Washington, while in the ceramic arts and in the manufacture of glass it is destined to play an increasingly important rôle.

In 1879, Gibbs published a paper, "On the vapor-densities of peroxide of nitrogen, formic acid, acetic acid and perchloride of phosphorus,"[5] and a few years later he wrote a series of letters to the secretary of the electrolysis committee of the British Association on "Electrochemical thermodynamics."[6] These papers, together with those previously mentioned, comprise all of his contributions which have a direct bearing upon the science of chemistry.

Besides Gibbs's remarkable achievements in the domain of mathematical physics, he won equally great distinction in the realm of pure mathematics. In his lectures on mathematical physics he became aware of the need for a vector algebra by means of which the complex space relations, so frequently encountered in the study of the theory of electricity and magnetism, could be adequately expressed. To meet this requirement he developed a system of vector analysis for the use of his students. This was at first printed in pamphlet form, but subsequently Professor Gibbs, somewhat reluctantly, consented to its formal publication.

Between the years 1882 and 1889 he published five papers dealing with the electromagnetic theory of light which are regarded by physicists as remarkable for the entire absence of special hypotheses as to the connection between matter and ether.

Professor Gibbs's last work, entitled, "The elementary principles of statistical mechanics," published in 1902, is a masterly exposition of the methods available for the study of systems endowed with several degrees of freedom. This work is said to have opened new vistas to students of mathematical physics.

At the time of his death, in 1903, Professor Gibbs was engaged in the preparation of some additional chapters on heterogeneous equilibrium for a collected edition of his contributions to thermodynamics.

He was the recipient of many honors from learned societies and universities both at home and abroad. Among the societies and academies of which he was a member, or a correspondent, may be mentioned the Connecticut Academy of Arts and Sciences, the National Academy of Sciences, the American Academy of Arts and Sciences, the Royal Institution of Great Britain, the Cambridge Philosophical Society, the Royal Society of London, the Royal Prussian Academy of Berlin, the French Institute, the Physical Society of London, the Bavarian Academy of Sciences and the American Mathematical Society. He received honorary degrees from Williams College, and from the universities of Erlangen, Princeton and Christiania. In 1881 he was awarded the Rumford Medal from the American Academy of Boston, and in 1901 the Copley Medal from the Royal Society of London.

In 1910 a medal was founded in his honor by the Chicago Section of the American Chemical Society to be awarded annually for the best paper or address presented before the section.

[5] *Am. Jour. Sci.* [3], 18, 277, 371 (1879).

[6] Rep. Brit. Assoc. for 1886, p. 388; for 1888, p. 343.

As a teacher, Professor Gibbs is said to have possessed great originality and to have inspired all who came under the spell of his genius. In his classroom there were often revealed

Rich stones from out the labyrinthine cave
Of research, pearls from Time's profoundest wave
And many a jewel brave, of brilliant ray,
Dug in the far obscure Cathay
Of meditation deep . . .

The late Professor Bumstead, who was among those privileged to study under him, writes:

Although long intervals sometimes elapsed between his publications, his habits of work were steady and systematic; but he worked alone and, apparently, without need of the stimulus of personal conversation upon the subject, or of criticism from others, which is often helpful even when the critic is intellectually an inferior. So far from publishing partial results, he seldom, if ever, spoke of what he was doing until it was practically in its final and complete form. This was his chief limitation as a teacher of advanced students; he did not take them into his confidence with regard to his current work, and even when he lectured upon a subject in advance of its publication, the work was really complete except for a few finishing touches. Thus, his students were deprived of the advantage of seeing his great structures in the process of building, of helping in the details, and of being in such ways encouraged to make for themselves attempts similar in character, however small their scale. But on the other hand, they owe him a debt of gratitude for an introduction to the profounder regions of natural philosophy such as they could have obtained from few other living teachers. Always carefully prepared, his lectures were marked by the same great qualities as his published papers and were, in addition, enriched by many apt and simple illustrations which can never be forgotten by those who heard them. . . . No student could come in contact with this serene and impartial mind without feeling profoundly its influence in all his future studies of nature.

As a man Professor Gibbs was singularly retiring. With the exception of those few years spent as a student in Europe, he lived quietly during the academic year in New Haven and passed his summer vacations among the mountains of New Hampshire. He never married but made his home with his sister and her family. Professor Gibbs was unfeignedly modest with regard to his achievements, so much so, in fact, that those who were nearest to him believe that he failed to realize his remarkable mental endowments. He never permitted the importance of his scientific work to interfere with the most trivial duties as an official of the college, and he was ever ready to give generously of his time to those of his students who came to him for advice or assistance. In looking through some of his correspondence recently, a member of his family was particularly impressed by the patience he displayed in endeavoring to help those who were victims of some scientific delusion. In several instances he carried on lengthy correspondence with such people, even though they might not be open to conviction, in the effort to point out where their fallacies lay. Ex-president Hadley said of him, "his plain way of seeing straight where other people's preconceived ideas compelled them to see crooked was characteristic of the man and of his work from beginning to end." In a review of his collected papers which appeared in the *Nation,* the opinion was expressed that "Josiah Willard Gibbs advanced science the world over more than it has ever been given to any other American researcher to do," while one who knew him intimately said of him, "the greatness of his intellectual achievements will never overshadow the beauty and the dignity of his life."

Wherever he be flown, whatever vest
The being hath put on which lately here
So many-friended was, so full of cheer
To make men feel the Seeker's noble zest,
We have not lost him all; he is not gone
To the dumb herd of them that wholly die;
The beauty of his better self lives on
In minds he touched with fire, in many an eye
He trained to Truth's exact severity.

FREDERICK H. GETMAN
STAMFORD, CONNECTICUT

MEDICAL RESEARCH

MANY of the less reputable characters of history have found charitable interpreters in our time. M. Anatole France, for example, put the case for Gallio in a very favorable light. But Gallio's contemporary, Simon, alleged to have been a sorcerer but perhaps only a psycho-pathologist with a *flair* for promising therapeutic improvements, remains proverbially infamous. Yet, on the evidence, it seems that Simon was treated a little harshly. He appears to have made to the Apostles a proposition which would surely have seemed neither novel nor heinous to the Academic Registrars of the schools of Athens or Pergamos. One wonders what Peter would have said if Simon the magician, instead of merely offering the Apostles a fee for a course of lectures, had invited them, for a substantial consideration, to devote their entire energies to research into one problem of psycho-pathology named by himself. This at least is certain, that any such proposal in the twentieth century would be welcomed by a large majority of the general public and an important minority of the medical profession as a praiseworthy, public-spirited action to which the offensive word "simony" could not possibly be applicable.