

THE TROUBLE WITH THERMODYNAMICS

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There is an anecdote attributed to the famous German theoretical physicist, Arnold Sommerfeld (Figure 1), dealing with the problem of how one learns the rudiments of thermodynamics (1):

Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two points. The third time you go through it, you know you don't understand it, but by that time you are so used to the subject, it doesn't bother you anymore.

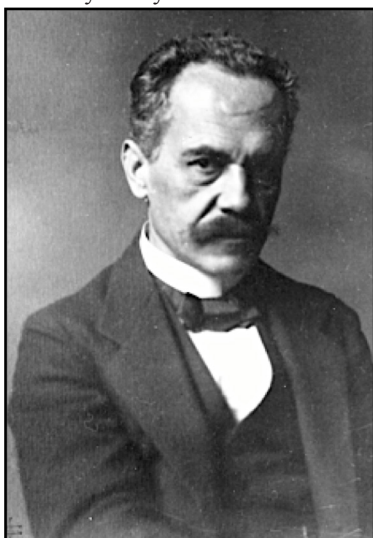


Figure 1. Arnold Sommerfeld (1868-1951). All figures are courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati.

The equally famous German physical chemist, Wilhelm Ostwald (Figure 2), tended to agree (2):

... thermodynamics, like Sleeping Beauty, was surrounded by hedgerows bristling with impenetrable mathematical thorns ... I can still remember the inner struggle I underwent as I tried to grasp thermodynamics, as it was called then, or energetics as I now refer to it today.



Figure 2. Wilhelm Ostwald (1852-1932)

Less diplomatic was the comment of Louis Kahlenberg of the University of Wisconsin (Figure 3), who, despite having received his Ph.D. under Ostwald at Leipzig, became a determined opponent of both the ionic

theory of dissociation and the use of thermodynamics or “thermodihumbug,” as he called it, in chemistry (3):

Thermodynamics is all right for studying steam engines. It is the greatest humbug ever to go up.

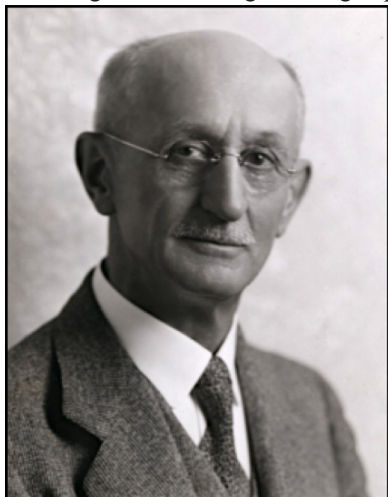


Figure 3. Louis Kahlenberg (1870-1941)

The Trouble with Entropy and the Second Law

Much of the problem with mastering thermodynamics seems to have centered on the concept of entropy increase and the second law, which Kahlenberg dismissed with the comment that (3):

The second law of thermodynamics simply means that water won't flow up hill.

Ostwald also admitted to having difficulties with the law (2):

How often back then did I take long walks alone so as to have a chance to think undisturbed about the second law ... It was at that time extremely difficult to realize what Clausius' law of the increase of entropy or William Thomson's law of the dissipation of energy had to do with the calculation of the latent heat of vaporization from the temperature coefficients of steam pressure.

Though thermodynamics was a brain child of the steam engine, many engineers had trouble, like the chemists, with the entropy concept. Thus the British engineer, James Swinburne (Figure 4), lamented in 1903 that (4):

As a young man I tried to read thermodynamics, but I always came up against entropy as a brick wall that stopped my further progress. I found the ordinary mathematical explanation, of course, but no sort of physical idea underlying it. No author seemed even to try and give any physical idea. Having in those days great respect for textbooks, I concluded that the

physical meaning must be so obvious that it needs no explanation and that I was especially stupid in that particular subject ... After a few years I would tackle the subject again, and always I was brought up dead by the idea of entropy. I asked other people, but I never met anyone who could tell me, and I met one—an engineer—who admitted he did not know.



Figure 4. James Swinburne (1858-1958)

Indeed, some engineers went so far as to either ignore or even deny the validity of the second law. Thus in 1879, Henry T. Eddy (Figure 5), the first Professor of Engineering at the University of Cincinnati, invoked three, rather than two, basic laws of thermodynamics in his textbook on the subject, not one of which mentioned entropy increase, even though Clausius was quoted throughout the text on other subjects (5). As far as I can determine from his rather confusing presentation, Eddy seems to have thought that Carnot's cycle was the second law, even though it only applies to ideally reversible heat engines and thus does not involve the net entropy increase demanded by Clausius' version of the second law.

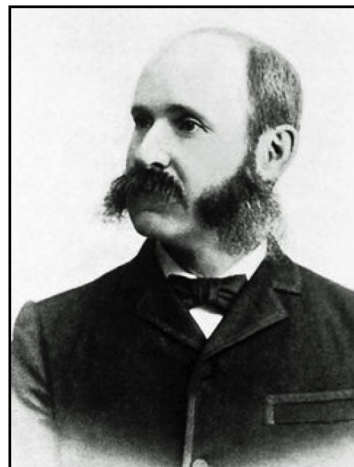


Figure 5. Henry Turner Eddy (1844--1921)

Even more explicit was Sidney A. Reeve, Professor of Steam-Engineering and Hydraulics at the Worcester Polytechnic Institute, who, in his 1903 monograph, *The Thermodynamics of Heat-Engines*, referred to “the so-called law of the dissipation of energy,” followed by his personal paraphrase of Clausius’ second law (6):

The entropy of the world tends to a maximum and the temperature to a minimum.

which, in turn, was followed by the alternative:

The total entropy and the average temperature of the universe remain constant.

Reeve expressed doubts that either of these statements was true. His reason was his belief that entropy applied only to heat energy and since heat was but one of many kinds of energy, it was doubtful that it applied to the universe as a whole. This was further coupled to his belief that entropy was simply the capacity factor for heat energy, just as mass was for gravitational energy and electrical charge was for electrical energy, and that it, like the latter two, was conserved. He even went beyond Eddy’s three laws of thermodynamics and postulated four laws, the third and fourth of which dealt with various temperature-entropy cycles, of which the third was again Carnot’s idealized cycle.

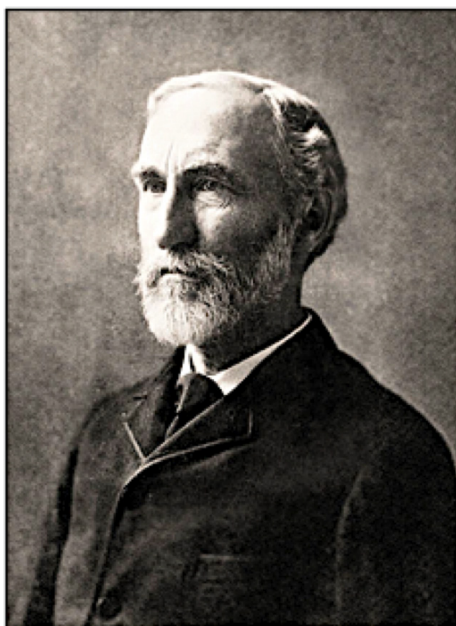


Figure 6. Josiah Willard Gibbs (1839-1903)

The Trouble with Gibbs

Yet another difficulty, at least for the average chemist with limited mathematical training, was the extensive use of mathematics in most treatises on thermodynamics—those “hedgerows bristling with impenetrable mathematical thorns,” that Ostwald had mentioned. Nowhere was this more obvious than in the reception accorded the work of the American physicist, Josiah Willard Gibbs (Figure 6), whose memoir “On the Equilibrium of Heterogeneous Substances,” published in installments in the Proceedings of the Connecticut Academy of Arts and Sciences in the period 1876-1878, is now considered one of the most significant scientific papers published in the 19th century (7).

Not only were problems created by Gibbs’ choice of an obscure journal in which to publish his epic memoir, but also by his dense mathematical presentation of his results. This is confirmed by Ostwald’s first encounter with Gibbs’ work (2):

Gibbs, for his part, had so successfully buried the results of his monumental research in the inaccessible journal of a provincial scientific academy that it required no small effort (in which I was involved) to bring them back into the light of the scientific record ... I managed, not without considerable difficulty, to obtain these papers and study them ... I found them hard to read, but recognized, without any doubt, their great importance.

To solve these difficulties, Ostwald decided to publish a German translation of Gibbs’ memoir (2, 8):

I found no better way to get to the heart of the matter than to translate the publications word for word. They certainly couldn’t be summarized because they were written in such a condensed form. I thought that by bringing out a German edition. I could do my part to rescue these long overlooked treasures and make them available as common currency ...

The dense nature of Gibbs’ work was also noted by the famous British physicist, Lord Rayleigh (Figure 7), when in 1892 he wrote to Gibbs (9):

Have you ever thought of bringing out a new edition of, or a treatise founded upon, your “Equilibrium of Heterogeneous Substances?” The original, though now attracting attention, is too condensed and too difficult for most, I might say all readers.

to which Gibbs replied:

I thank you very much for your kind interest in my “Equilibrium of Heterogeneous Substances.” I myself had come to the conclusion that the fault was that it was too long. I do not think I had any sense of the value of time, of my own or others, when I wrote it.

In fact, in 1878 Gibbs had already published a condensation of his memoir (10) and in 1919 a French condensation would also appear (11).

Even more shocking was the correspondence between Rayleigh and Lord Kelvin (Figure 7), one of the founders of the second law of thermodynamics, in which Kelvin admitted that he could find nothing of value in Gibbs’ memoir (9):

I feel very doubtful as to the merit of Willard Gibbs' applications of the "Second Law of Thermodynamics" ... Do you attribute merit to them?

Followed in a later letter by his final conclusion that:

I find no light for either chemistry or thermodynamics in Willard Gibbs.

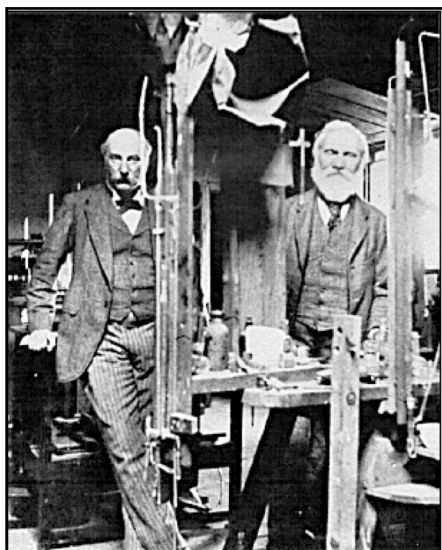


Figure 7. Right: Lord Rayleigh (1842-1919). Left: Lord Kelvin (1824-1907).

Perhaps the best summary of both the impact and problems produced by Gibbs was given by Wilder D. Bancroft (Figure 8), Professor of Physical Chemistry at Cornell, founder of the *Journal of Physical Chemistry*, and, like Kahlenberg, a former student of Ostwald (12):

The famous monograph on equilibrium in heterogeneous systems by J. Willard Gibbs is in some respects one of the most remarkable scientific articles that has ever been written. Gibbs was possessed of marvelous and apparently unerring insight, but the gift of expression was denied to him. It is not too much to say that Gibbs wrote in hieroglyphics and that a great part of his manuscript is still undeciphered. We know now that we can find in it the chemical potential, the phase rule, and the theory of osmotic pressure; the theory of electromotive forces, the Donnan equilibrium, and the theory of emulsification. We feel certain that some day we shall find in it theories in regard to all sorts of other things; but we do not know when we shall find them. It used to be popular to ascribe the negligible influence which Gibbs then had on the development of physical chemistry to the fact that his monograph was published in the Transactions of the Connecticut Academy, but this fiction cannot be maintained. Everyone knows about Gibbs now; but the only way that one can find anything new in Gibbs is to discover it independently and then look it up in Gibbs.



Figure 8. Wilder D. Bancroft (1867-1953)

The Trouble with Ideality

A final difficulty was the gradual recognition that most of the laws of the newly emerging discipline of physical chemistry, such as the determination of equilibrium constants, the depression of solution freezing points and the elevation of boiling points, the Nernst equation, and the calculation of osmotic pressures, were rigorously true only for highly diluted solutions, causing one writer to define the field as "the chemistry of slightly impure water" or, as Bancroft preferred, the study of "slightly polluted water."

As usual, Kahlenberg was less diplomatic when he stated in his lecture notes that (3):

Infinitely diluted solutions = Infinitely concentrated humbug

Nor was Bancroft impressed by G. N. Lewis' attempt to deal with this problem via his introduction of such concepts as fugacity and activity. Indeed, he would satirize the latter concept with the observation that (13):

We can always make the experimental data agree with the theoretical values by multiplying the data by the ratio of the theoretical values to the experimental values.

leading to his infamous final characterization (13):

We might remember Mrs. Eddy and G. N. Lewis as the Gold Dust Twins of Christian and Physical Science. Mrs. Eddy eliminates sickness but admits error. Lewis admits sickness but eliminates error.

Or as the historian, John Servos, has phrased it (14),

Lewis' distinction between concentrations and activities was simply a fig leaf concealing physical chemists' ignorance.

References and Notes

1. S. W. Angrist and L. G. Hepler, *Order and Chaos: Laws of Energy and Entropy*, Basic Books, New York 1967, p 215. The quote is attributed to Sommerfeld with a disclaimer that it could be apocryphal.
2. R. S. Jack, F. Scholz, Eds., *Wilhelm Ostwald: The Autobiography*, Springer: Cham, Switzerland, 2017, pp 94, 179. This translation of W. Ostwald, *Lebenslinien*, 3 Vols, Kassing & Co. Berlin, 1926-1927, is reviewed later in this issue, *Bull. Hist. Chem.*, **2022**, 47(3), 330-332.
3. Quoted in R. E. Oesper, *The Human Side of Scientists*, University Publications. University of Cincinnati: Cincinnati OH, 1975, pp 106-107. Anecdotes from Kahlenberg's lecture notes provided by Aaron Ihde of the University of Wisconsin.
4. J. Swinburne, *Entropy or Thermodynamics from an Engineer's Standpoint and the Reversibility of Thermodynamics*, Dutton: New York, NY, 1903.
5. H. T. Eddy, *Thermodynamics*, Van Nostrand, New York, NY, 1879.
6. S. A. Reeve, *The Thermodynamics of Heat-Engines*, Macmillan, New York, NY, 1903, pp 35-36. I could not locate a photo of Reeve.
7. J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances," *Trans. Conn. Acad. Arts Sci.*, **1876**, 3, 108-248, 1878, 343-524. Also available as *The Scientific Papers of Josiah Willard Gibbs*, Vol. 1, Dover, New York, NY, 1961.
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13. W. D. Bancroft, "How to Ripen Time," *J. Phys. Chem.*, **1931**, 35, 1904-1921.
14. J. W. Servos, *Physical Chemistry from Ostwald to Pauling: The Making of a Science in America*, Princeton University Press: Princeton, NJ, 1990, p. 311. The author would like to thank the reviewer for bringing this quote to his attention.

About the Author

William B. Jensen is professor emeritus of chemistry at the University of Cincinnati, where he was Oesper Professor of the History of Chemistry and Chemical Education and curator of the Oesper Collections in the History of Chemistry. He was founding editor of the *Bulletin for the History of Chemistry*.

Chemistry and Inuit Life and Culture

Chem 13 News, published by the University of Waterloo (Ontario, Canada) devoted a special issue in Fall 2022 to chemistry and Inuit life and culture. Its twelve wonderful pieces from Chaim Christiana Andersen, Rosalina Naqitarvik and Geoff Rayner-Canham on the chemistry behind the traditional knowledge of the Inuit People are accessible online at <https://uwaterloo.ca/chem13-news-magazine/fall-2022-special-edition/feature/chemistry-and-inuit-life-and-culture>.