

# VI

## The Quantification of 20th-Century Chemical Thermodynamics

A Tribute to “Thermodynamics and the Free Energy of Chemical Substances”

### 1. Introduction

Most chemists would count themselves as lucky to have written a book now considered to be a chemical classic, but to have written two such books in widely different areas of chemistry and to have published both in the same year is, I believe, almost unprecedented (1). Indeed, it is an accomplishment which, to the best of my knowledge, has been achieved by only one person – the American chemist, Gilbert Newton Lewis (figure 1) – who in 1923 not only published *Valence and the Structure of Atoms and Molecules*, describing his seminal contributions to the electronic theory of bonding, but also his classic monograph *Thermodynamics and the Free Energy of Chemical Substances* (figure 2), which he coauthored with Merle Randall and which laid the foundations for the quantification of modern thermodynamics (2). I have already described the first of these books in the morning session of this symposium, and it is the second of these books which forms the subject of this afternoon’s presentation.

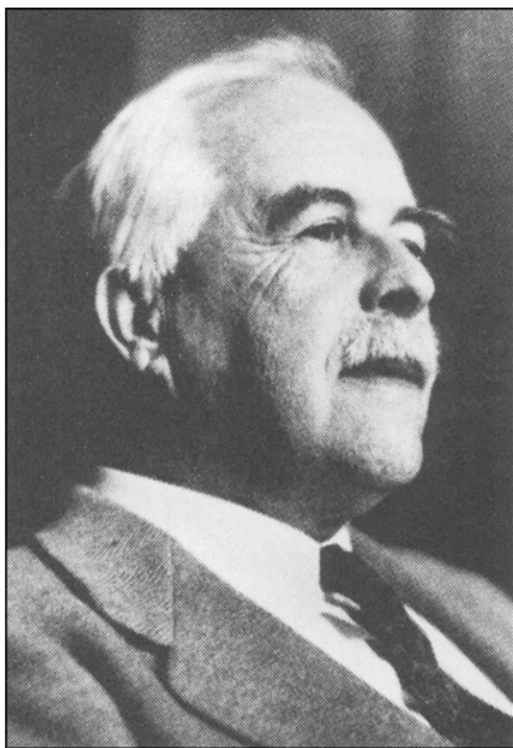


Figure 1. Gilbert Newton Lewis (1875-1946) in later life.

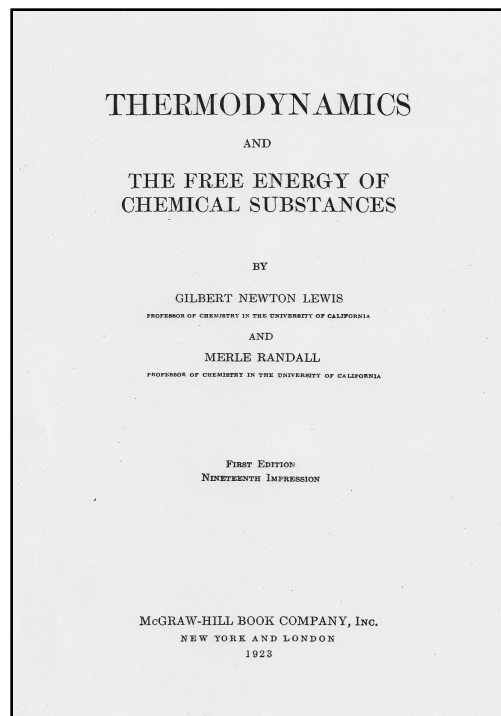


Figure 2. The title page to the first edition of *Thermodynamics and the Free Energy of Chemical Substances*.

### 2. The Authors

Since I have already summarized the life of Lewis when discussing *Valence* in this morning’s session, I will not bore you with a repetition of the facts, but will instead say a little about his coauthor, Merle Randall. Born in 1888, Randall received both his B.S. (1907) and M.S. (1909) degrees in chemistry from the University of Missouri, followed by a Ph.D. from MIT in 1912 for the thesis, *Studies in Free Energy*, based on work done under the supervision of Lewis.

When Lewis departed for Berkeley later that year, Randall went with him, initially serving as his private assistant. In 1917 he was officially appointed to the position of Assistant Professor of Chemistry at Berkeley, where he continued to teach and do research on thermodynamics until his retirement in 1944. Until his death in 1950, he was involved with J. M. Ritchie in the production of the notorious battery additive AD-X2 which eventually led to a major scandal at the National Bureau of Standards. In addition to his collaboration

with Lewis, he also published a textbook of physical chemistry in 1942 (3).

### 3. The Book

*Thermodynamics* was published by McGraw-Hill of New York in 1923 using the same characteristic brown cover and black and gold spine label that would later become the hallmark of its "International Chemical Series." The book, in sharp contrast to Lewis's much shorter monograph on *Valence*, was 653 pages in length and consisted of 42 chapters and four appendices. It was the culmination of a research program undertaken by Lewis in 1899 which was directed at the clarification and quantification of chemical thermodynamics as summarized in a 55-item bibliography of the publications of Lewis and his students appended to the book.

### 4. The Context

In chapter 1 Lewis noted that the development of chemical thermodynamics was characterized by three distinct periods:

1. The establishment of the basic laws of thermodynamics (1842-1865).
2. The application of these laws to the theory of chemical affinity and equilibrium (1873-1905).
3. The quantification of chemical thermodynamics via a fusion of theory with experimental data (1905-1923).

The first of these periods began with the enunciation of the first law of thermodynamics by Mayer (1842), Joule (1843), and Helmholtz (1847) in the 1840s and the equally important enunciation of the second law by Clausius (1850) and Kelvin (1852) in the 1850s. It was completed in 1865 when Clausius explicitly reformulated the second law in terms of his famous entropy function.

The second period began with the first application of the entropy function to the phenomenon of chemical equilibrium by Horstmann in 1873, followed by its application to heterogeneous phase equilibria, the introduction of the phase rule, and the introduction of both the chemical potential and free-energy functions by Gibbs in the period 1874-1878. Of equal importance was the further elaboration of the *Arbeit* and free energy concepts by Helmholtz (1882) in the 1880s and the translation of Gibbs' work into both German (Ostwald 1892) and French (Le Chatelier 1899) in the 1890s.

This stage was also characterized by the publication of several monographs explicitly devoted to the theory of chemical thermodynamics, the most important of which are summarized in the following table:

**Table 1. Early monographs dealing with the theory of chemical thermodynamics.**

| Date | Author     | Title   | Approach           |
|------|------------|---|--------------------|
| 1884 | van't Hoff | <i>Etudes de dynamique chimique</i>                             | Arbeit or affinity |
| 1885 | Liveing    | <i>Chemical Equilibrium the Result of Dissipation of Energy</i> | energy dissipation |
| 1886 | Duhem      | <i>Le potentiel thermodynamique</i>                             | chemical potential |
| 1893 | Nernst     | <i>Theoretische Chemie</i>                                      | Arbeit or affinity |
| 1893 | van Laar   | <i>Die Thermodynamik in der Chemie</i>                          | total entropy      |
| 1897 | Planck     | <i>Vorlesung über Thermodynamik</i>                             | total entropy      |
| 1906 | van Laar   | <i>Sechs Vorträge über das thermodynamische Potential</i>       | chemical potential |

The foundations of the third period were actually laid nearly a half century before the formal development of thermodynamics itself with the first measurements of heats of combustion by Lavoisier and Laplace (1783) and with the extensive measurements of heats of reaction and specific heats within context of the caloric theory during the period 1840-1854 by such thermochemists as Hess, Andrews, and the French team of Favre & Silbermann, leading to the enunciation of the law of constant heat summation by Hess in 1840. These results were translated into the context of the first law of thermodynamics and greatly augmented by the work of Thomsen (1882-1884), and Berthelot (1879, 1897) during the last half of the 19th century.

Thus, by the turn of the 20th century there already existed an extensive data bank of quantitative enthalpy values. However, this remained largely localized in a separate literature dealing with thermochemistry rather than with chemical thermodynamics proper, and the books listed in Table 1 remained primarily theoretical, rather than practical, in their orientation, in large part because that theory showed that what was important in

determining the chemical affinity of a reaction was not just the enthalpy of the reaction, but its ability to perform useful work, whether measured in terms of *Arbeit*, energy dissipation, total entropy change, chemical potential or free energy. What was needed before this enthalpy data could be fully exploited by the newer field of chemical thermodynamics was an equally comprehensive collection of either free-energy or entropy values.

As a consequence the true quantification of chemical thermodynamics, as distinct from the more traditional field of thermochemistry, did not really begin until the enunciation of the third law of thermodynamics by Walther Nernst (figure 3) in 1906, though important anticipations of this approach were made by Richards and especially by Haber (1905). Starting around 1905-1906, one sees the appearance of an increasing number of German monographs (Table 2) devoted to this subject, though not formulated in terms of  $\Delta S$  and  $\Delta G$ , as we might think today, but rather in terms of evaluating the reaction isochor directly in terms of thermochemical data alone and within the context of the *Arbeit* or Helmholtz free-energy function (*A*).

**Table 2. Early monographs dealing with the quantification of chemical thermodynamics.**

| Date | Author    | Title   | Approach  |
|------|-----------|---|-----------|
| 1905 | Haber     | <i>Thermodynamik technischer Gasreaktionen</i>                                  | A isochor |
| 1906 | Nernst    | <i>Experimental and Theoretical Applications of Thermodynamics to Chemistry</i> | A isochor |
| 1908 | Sachur    | <i>Die chemische Affinität und ihre Messung</i>                                 | A isochor |
| 1912 | Pollitzer | <i>Die Berechnung chemischer Affinitäten nach dem Nernstschen Wärmestates</i>   | A isochor |
| 1918 | Nernst    | <i>Die theoretischen und experimentellen Grundlagen des neuen Wärmestates</i>   | A isochor |

Lewis clearly conceived of his book as belonging to this third phase and, in particular, as an extension of the work of the German chemist, Fritz Haber (figure 4), whom he singled out for special praise (4):

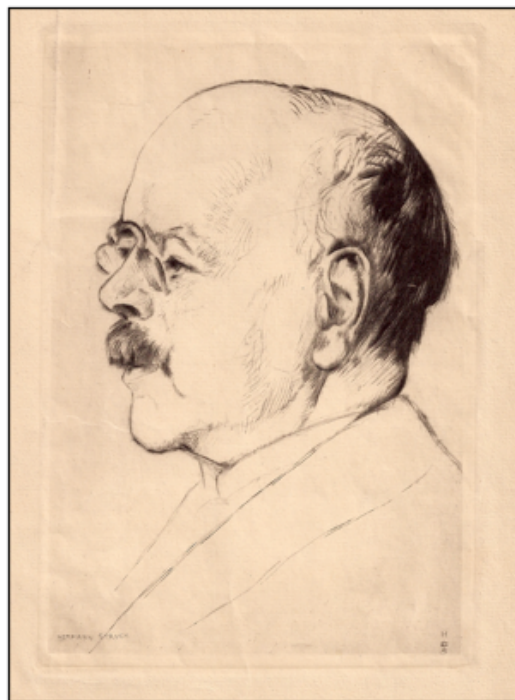


Figure 3. Walther Nernst (1864-1941).

*The first systematic study of all the thermodynamic data necessary for the calculation of the free energy changes in a group of important reactions was published in Germany by Haber. This book, "Thermodynamik der technischen Gas Reaktionen," is a model of accuracy and of critical insight.*

In keeping with this self-evaluation, Lewis originally intended that his book should merely be a summary of the free-energy data that he and his associates had collected over the previous quarter of a century:

*We [originally] proposed merely to collect, for the practical use of the chemist and the chemical engineer, the data which we have obtained, or which we have assembled from the work of other investigators, pertaining to the great problem of chemical affinity.*

However, it was soon realized that it was also necessary to include a description of the methods used to obtain the data:

*But then we were convinced that mere reference tables would hardly render full service without some description of the methods by which they were obtained ... we have been forced to develop a variety of special methods chemical, algebraic, arithmetical and graphical – and it is our hope that a full presentation of these*



Figure 4. Fritz Haber (1868-1934).

*methods may spare other workers in this field much of the arduous labor which we ourselves have spent.*

And lastly, it became apparent that these purely technical aspects were best appreciated if they were first prefaced by an introductory overview of the underlying principles of thermodynamics:

*Finally, these methods themselves require a fuller understanding of the underlying principles of thermodynamics than most elementary treatises afford... Partly for this reason, and partly perhaps because of a temptation to present in a somewhat novel manner the basic principles of thermodynamics, we devote the first part of our book to a presentation of the elements of thermodynamic theory.*

In keeping with this plan, Chapters 1-26 of the final book dealt with theory and chapters 27-42 with methods and data.

## 5. Innovations

The best way of appreciating the unique features of the Lewis-Randall text is through a comparison with the earlier textbook and monograph literature listed in Tables 1 and 2, and especially with the American text,

*Thermodynamics and Chemistry*, by F. H. MacDougall of the University of Minnesota, which was published in 1921, only two years before the Lewis-Randall text.

Though the early works by Duhem (1886) and van Laar (1906) made explicit use of the Gibbs chemical potential, it is apparent from Tables 1 and 2, that they were the exception rather than the rule and that most previous writers on chemical thermodynamics preferred instead to use the so-called *Arbeit* or affinity functions derived from the work of Helmholtz in which the role of entropy was implicit rather than explicit. This may come as something of a surprise to the modern chemist, but, in fact, in the period 1876-1923, Gibbs was far better known for his enunciation of the phase rule than for his free-energy function.

The manner in which the role of entropy was made implicit rather than explicit may be seen in the approaches favored by van't Hoff and Nernst, which dominated the chemical literature in the period between 1884 and 1922. Thus van't Hoff preferred to write the *Arbeit* equation in a form that was analogous to the classical Carnot equation for calculating the efficiency of a steam engine:

$$A = Q[(T_{eq} - T)/T_{eq}]$$

in which  $\Delta S$  appeared only as  $Q/T_{eq}$ , whereas Nernst always used the temperature dependency of the *Arbeit*,  $(dA/dT)$ , in place of  $-\Delta S$  when writing the equation for Helmholtz free energy:

$$A = U + T(dA/dT) = Q + T(dA/dT)$$

In keeping with these preferences, an informal survey of 17 physical chemistry texts published during this period showed that 11 or 65% did not list entropy as a index entry, whereas 5 of the remaining 6, though listing it once, devoted little more than a paragraph to the subject. Likewise, the 1921 text by MacDougall has only three index entries for free energy, two of which refer to Helmholtz free energy and only one to Gibbs free energy.

In sharp contrast, the Lewis-Randall text is firmly and unambiguously based on the Gibbs free-energy function (symbolized as  $\Delta F$  rather than as  $\Delta G$ ) and formulated in terms of explicit enthalpy and entropy terms:

$$\Delta F = \Delta H^\circ - T\Delta S^\circ + RT \ln Q$$

Other important innovations may be briefly enumerated as follows:

1. The Lewis-Randall text makes extensive use of

partial molal properties in discussing the thermodynamics of solutions, whereas this topic is missing from the MacDougall text.

2. The Lewis-Randall text extends the concept of standard states ( $\Delta X^\circ$  vs  $\Delta X$ ) beyond the Nernst equation ( $E^\circ$  vs  $E$ ) so as to also include the free energy, enthalpy and entropy functions. The MacDougall text does not.

3. Building on the thermochemical tradition of Berthelot (1879, 1897) and Nauman (1882), the Lewis-Randall text essentially perfects our current suffix conventions for indicating physical states (e.g.  $\text{CO}_2(\text{g})$ ,  $\text{H}_2\text{O}(\text{l})$   $\text{Fe}(\text{s})$ ). The MacDougall text does not.

4. The Lewis-Randall text deals with the issue of nonideality through the introduction of such concepts as fugacity (1901), activity (1907), and ionic strength (1921). The MacDougall text mentions activity but neither fugacity nor ionic strength.

5. In sharp contrast to the Lewis-Randall text, the Haber-Nernst tradition deals with the quantification of affinity in terms of a power expansion of the temperature dependency of either the *Arbeit* function or the integrated van't Hoff isochore:

$$\ln K = Q_0/RT + (\Sigma \nu \alpha/R) \ln T + (\Sigma \nu \beta/R) T + \dots I/R$$

rather than in terms of explicit tabulations of  $\Delta F^\circ$ ,  $\Delta H^\circ$  and  $S^\circ$  values.

6. The Lewis-Randall text contains a table of  $S^\circ$  values at 298 K for 75 elements and a table of  $\Delta F^\circ$  values at 298 K for 140 ions and compounds. The MacDougall text contains no entropy or free energy data, only tables of heats of formation and various phase diagrams – a topic that is completely missing from the Lewis-Randall text.

Points 5 and 6 represent the most defining feature of the Lewis-Randall text and are what distinguish it from all of its predecessors. Whereas the primary contact with experimental data, if any, for most thermodynamic texts written in the period 1884-1922 was via the phase rule and various phase diagrams, for the Lewis-Randall text this contact was made for the first time via the use of tabulated free energy and entropy values.

## 6. Prose Style

As with many of his papers and reviews, Lewis dic-

tated *Thermodynamics* to his coauthor and, not unexpectedly, like his monograph on *Valence*, it contains many superb examples of the “Lewis style” in technical writing, of which I have time to quote only a few representative examples:

1. On the quality of the thermodynamic literature:

*We have seen “cyclical processes” limping about eccentric and not quite completed cycles, we have seen the exact laws of thermodynamics uncritically joined to assumptions comprising half truths or no truth at all, and worst of all we have seen ill-begotten equations supported by bad data.*

2. On the question of thermodynamic nomenclature:

*We presume that every author regards his own as the best of all possible notations. While we may privately be victims of some such hallucination, all that we care to claim publicly is that our system of nomenclature and notation is one which has gradually developed through many years of practical work and the teaching of many types of students, and that it has proved satisfactory.*

3. On the intended uses of the book:

*Our work is not a textbook in the ordinary sense of the term. A textbook is a sort of table d’hote to which anyone may sit down and satisfy his hunger for information with no thought of the complex agricultural processes which gave rise to the raw materials, nor of the mills which converted these raw materials into food-stuffs, nor of the arts of cookery responsible for the well-prepared meal which has been set before him. It has not been our desire to offer such a repast to the reader.*

4. And, most famous of all, the opening paragraphs of the book’s preface:

*There are ancient cathedrals which, apart from their consecrated purpose, inspire solemnity and awe. Even the curious visitor speaks of serious things, with hushed voice, and as each whisper reverberates through the vaulted nave, the returning echo seems to bear a message of mystery. The labor of generations of architects and artisans has been forgotten, the scaffolding erected for their toil has been removed, their mistakes have been erased or have become hidden by the dust of centuries. Seeing only the perfection of the completed whole, we are impressed as if by some supernatural agency. But sometimes we enter such an*

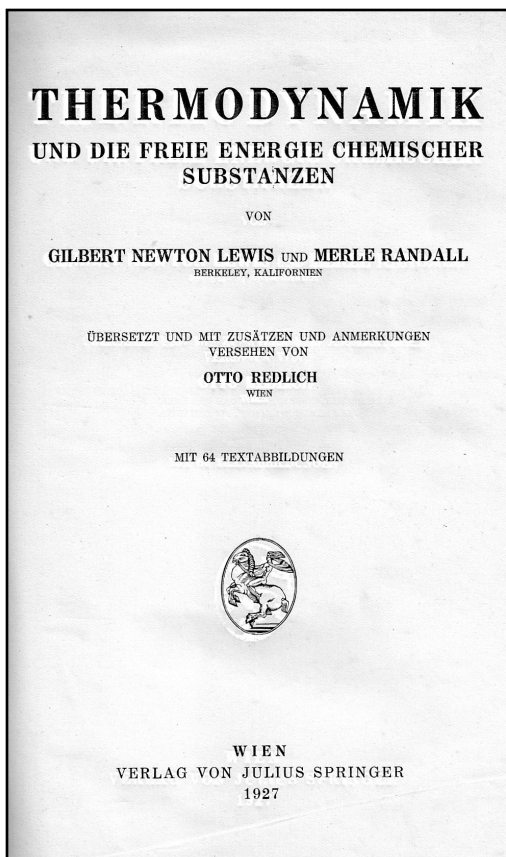


Figure 5. The title page to the 1927 German translation.

*edifice that is still partly under construction; then the sound of hammers, the reck of tobacco, the trivial jests bandied from workman to workman, enable us to realize that these great structures are but the result of giving to ordinary human effort a direction and a purpose.*

*Science has its cathedrals, built by the efforts of a few architects and of many workers. In these loftier monuments of scientific thought a tradition has arisen whereby the friendly usages of colloquial speech give way to a certain severity and formality. While this may sometimes promote precise thinking, it more often results in the intimidation of the neophyte. Therefore we have attempted, when conducting the reader through the classic edifice of thermodynamics, into the workshops where construction is now in progress, to temper the customary severity of the science in so far as is compatible with clarity of thought.*

## 7. The Legacy

In 1927 Springer Verlag published a German translation by Otto Redlich of the Lewis-Randall text (figure 5), and Lachman has also hinted at an unauthorized Russian translation, though I have been unable to con-

firm this (5, 6). In addition, in 1961, after remaining in print and active use for almost four decades, the original book was finally updated and revised by Kenneth Pitzer and Leo Brewer (both Berkeley doctorates and faculty members) and published as a second edition (figure 6) as part of the “McGraw-Hill Series in Advanced Chemistry” (7). But the legacy of the Lewis-Randall text is reflected in more than just translations and new editions. It is also reflected in the many additional contributions made by the faculty and students at Berkeley to the quantification program first envisioned by Lewis in 1899 and of which the Lewis-Randall text was merely the fountainhead.

Thus by 1930 Randall was able to contribute 81 pages of enthalpy, entropy, and free-energy data to the seventh volume of the *International Critical Tables* (8) – a significant increase over the tables given in 1923 – and by 1938 Wendell Latimer (figure 7), who was also a Berkeley doctorate and faculty member, was able to list free-energy values for 531 species in the first edition of his monograph, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions* (9).

Building on the 1936 monograph, *The Thermochemistry of the Chemical Substances* by Francis Bi-

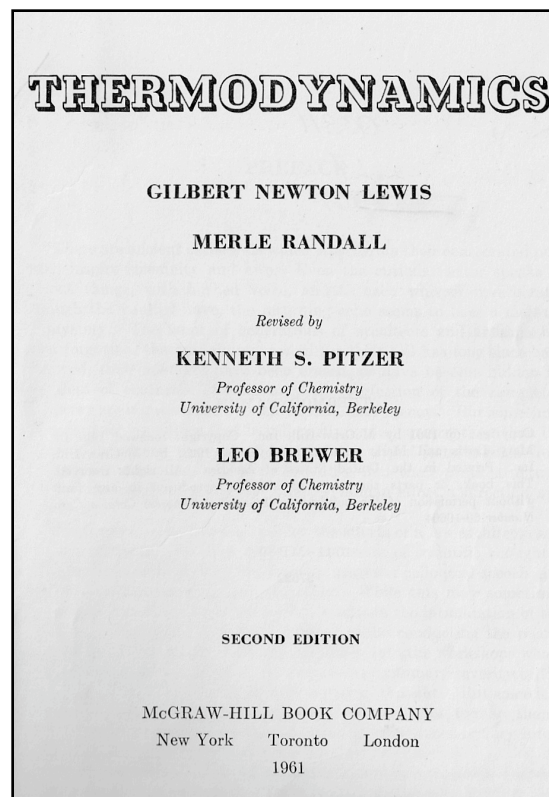


Figure 6. The second edition of the Lewis and Randall text as revised by Kenneth Pitzer and Leo Brewer and published by McGraw-Hill in 1961.



Figure 6. A young Wendall Latimer (1893-1955).

chowsky and Frederick Rossini (a Berkeley graduate and student of Randall) (10), the National Bureau of Standards undertook a program in 1940 to collect and collate thermodynamic data, the results of which were distributed after the Second World War in the form of loose-leaf tables (later known as the JANAF tables). In 1952 Rossini (figure 7) and associates published a revised, single volume, edition of these tables under the title, *Selected Values of Chemical Thermodynamic Properties*, which contained more than 1160 pages of enthalpy, free-energy, entropy and heat capacity data (11).

Today vast stores of thermodynamic data are available at the touch of a computer key board and we give little thought to the many workers who contributed to their measurement, compilation, and critical assessment. Indeed, in many ways we have reached the state predicted by Lewis almost 80 years ago:

*... we realize that the time may arrive when handbooks of thermodynamic data will be placed in the hands of the craftsman, that he may follow a recipe, or substitute numerical values in a formula of origin unknown to him.*

Substitute “student” for “craftsman,” and we have a perfect description of our current state of affairs.

In a 1928 letter to James Partington relative to his

possible nomination for a Nobel Prize, Lewis summarized his own achievements as follows (3):

*While I have flirted with many problems, I was for many years pretty loyal to the main task which I had set for myself, namely, to weave together the abstract equations of thermodynamics and the concrete data of chemistry into a single science. This is the part of my work in which I feel the greatest pride, partly because of its utility, and partly because it required a considerable degree of experimental skill ... That part of my work therefore which has given me the greatest amount of personal satisfaction was the study of the free energy of formation of the most important compounds and, in particular, the electrode potentials of the elements.*

Indeed, the data collection and formatting program undertaken by Lewis and his associates over a century ago so permeates our current thermodynamic thinking that we may, with considerable justification, characterize our present approach as the Gibbs-Lewis formulation of chemical thermodynamics.

## 8. References and Notes

1. An invited lecture given at a symposium organized by the Bolton Society on classic 20th-century chemistry textbooks held at the 230th National Meeting of the ACS in Washington, DC, on 29 August 2005.



Figure 7. Frederick Dominic Rossini (1899-1990).

2. G. N. Lewis, M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill: New York, NY, 1923.
3. W. L. Jolly, *From Retorts to Lasers: The Story of Chemistry at Berkeley*, College of Chemistry, University of California: Berkeley, 1987, pp. 99-101.
4. Specific quotes from reference 2, pp. vii, viii, ix, xi, 2, 5.
5. G. N. Lewis, M. Randall, *Thermodynamik und die freie Energie chemischer Substanzen*, Springer: Wein, 1927.
6. A. Lachman, *Borderland of the Unknown: The Life Story of Gilbert Newton Lewis*, Pageant Press: New York, NY, 1955.
7. G. N. Lewis, M. Randall, K. Pitzer, L. Brewer, *Thermodynamics*, 2nd. ed., McGraw-Hill: New York, NY, 1961.
8. M. Randall, "Free Energy of Chemical Substances, Activity Coefficients, Partial Molal Quantities, and Related Quantities," in E. W. Washburn, Ed., *International Critical Tables of Numerical Data, Physics, Chemistry, and Technology*, Vol. 7, McGraw-Hill: New York, NY, 1930, pp. 224-313.

9. W. Latimer, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, Prentice-Hall: New York, NY, 1938.
10. F. R. Bichowsky, F. D. Rossini, *The Thermochemistry of Chemical Substances*, Reinhold: New York, NY, 1936.
11. F. D. Rossini, D. D. Wagman, W. H. Evans, S. Levine, I. Jaffe, *Selected Values of Chemical Thermodynamic Properties*, NBS Circular 500, U. S. Government Printing Office: Washington, DC., 1952.

### Update

I have only recently become aware of the 1996 study by Helge Kragh and Stephen Weininger ("Sooner Silence than Confusion: The Tortuous Entry of Entropy into Chemistry," *Hist. Stud. Phy. Bio. Sci.*, **1997**, 27, 91-130) which provides an even more detailed context for the emergence of Lewis' textbook and independently reaches many of the same conclusions as I have in this and other papers dealing with the history of chemical thermodynamics.