

George Downing Liveing and the Early History of Chemical Thermodynamics

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Though the history of thermodynamics, as it relates to both engineering and physics, is well documented in both the journal and monograph literature (1-3), the same is not equally true of the history of its specific applications to the field of chemistry (4). In an attempt to fill this lacuna, the author has recently published English translations and commentaries on the work of both the Austrian chemist and physicist, Leopold Pfaundler, who was the first to apply the newly emerging kinetic theory of gases to chemical rates and equilibria in 1867 (5-6), and the German chemist, August Horstmann, who was the first to apply Clausius' entropy function to the rationalization of chemical equilibria in 1873 (7-8). In keeping with this program, the present paper is concerned with a distinctive British attempt to base the early teaching of chemical thermodynamics on the use of William Thomson's concept of energy dissipation rather than on Rudolf Clausius' more familiar entropy function, as reflected in the pioneering contributions of the British chemist, George Downing Liveing (9-10).

Energy Dissipation versus Entropy Increase

The first English-language textbook on thermodynamics (figure 1) was published by the Scottish physicist, Peter Guthrie Tait (figure 2), in 1868 under the title *Sketch of Thermodynamics* (11). In actual fact, this small volume of only 128 pages consisted primarily of a slightly revised reprint of two popular articles on heat and energy that Tait had published four years earlier in the *North British Review*, plus an additional, far more mathematical, chapter on thermodynamics proper, and was intended for classroom use by his students at the University of Edinburgh.

In his first two chapters Tait had adopted a largely historical approach and, as a result, had managed to ignite two historical debates over issues of priority (12). The first of these involved the law of the conservation of energy and the relative merits of the contributions of the German physician, Robert Mayer, versus those of the Englishman, James Joule, with Tait, not surprisingly, coming down decisively in favor of Joule. This

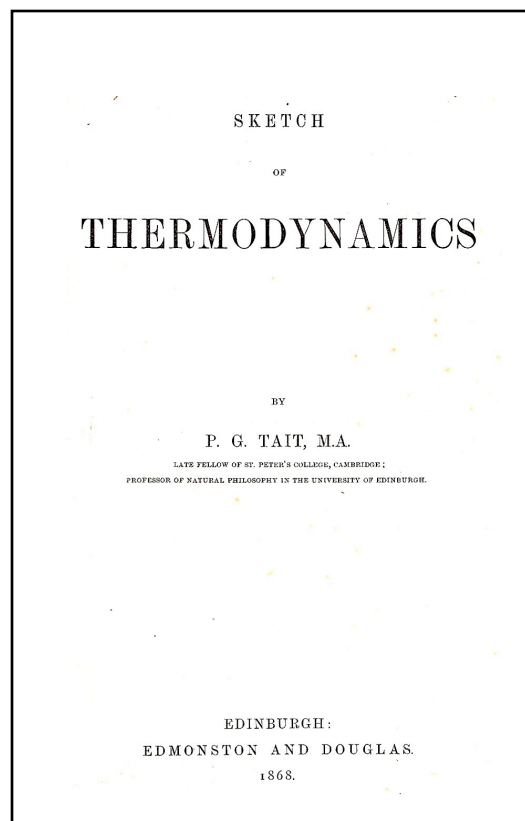


Figure 1. Title page of Tait's 1868 monograph on thermodynamics.

would elicit a defense of the claims of Mayer by both Hermann von Helmholtz and John Tyndall and, if I am to judge from a spirited conversation I had with a visiting British physicist some years ago, this debate is still going strong among determined Anglophiles.

The second debate involved the relative merits of two competing formulations of the second law of thermodynamics. The first of these, by Tait's colleague and frequent collaborator, William Thomson or Lord Kelvin (figure 3), was first formulated in 1852 and was based on the concept that in all spontaneously occurring natural processes a certain portion of the useful energy was necessarily irreversibly dissipated or de-



Figure 2. An etching of Peter Guthrie Tait (1831-1901) lecturing on the subject of electrostatics.

graded into isothermal heat, leading to the further conclusion that the universe, once its reserve of available energy was exhausted, would undergo a so-called “heat death” (13):

1. *There is at present in the material world a universal tendency to the dissipation of mechanical energy.*
2. *Any restoration of mechanical energy, without more than an equivalent of dissipation, is impossible in inanimate material processes, and is probably never effected by means of organized matter, either endowed with vegetable life or subject to the will of an animated creature.*
3. *Within a finite period of time past the earth must have been, and within a finite period of time to come the earth must again be, unfit for the habitation of man as at present constituted, unless operations have been, or are to be performed, which are impossible under the laws to which the known operations going on at present in the material world are subject.*

Though, in his original formulation, Thomson had made reference only to the dissipation of mechanical energy, by 1864 Tait had generalized this to include all forms of useful energy, whether mechanical, chemical, electrical or gravitational, and had enshrined it as one of the three underlying principles of the science of energy (11):

The Theory of Energy, as at present developed, contemplates its Conservation, Transformation, and Dissipation.

The second approach was due to the German physicist, Rudolf Clausius. In his 1850 memoir on heat, Clausius had reconciled Carnot’s original theory of heat engines with the newly emerging principle of the conservation of energy and the mutual interconversion of heat and work. In so doing, he had shown that only a portion of the heat passing through the temperature gradient of a heat engine was converted into work, with the remainder being ejected as waste heat at the lower temperature. It was only in 1854 that Clausius reformulated his results using the ratio of heat to absolute temperature or Q/T as a convenient quantitative measure of what he called the system’s “equivalence value of transformation,” and only in 1865 that he finally gave this ratio the name of *entropy* and assigned it a distinct symbol (S), leading to his often quoted summary of our currently accepted versions of the two laws of thermodynamics, as distinct from Tait’s earlier three principles of energy (14):



Figure 3. William Thomson (1824-1907) as he appeared in 1852, the year he proposed the principle of energy dissipation.

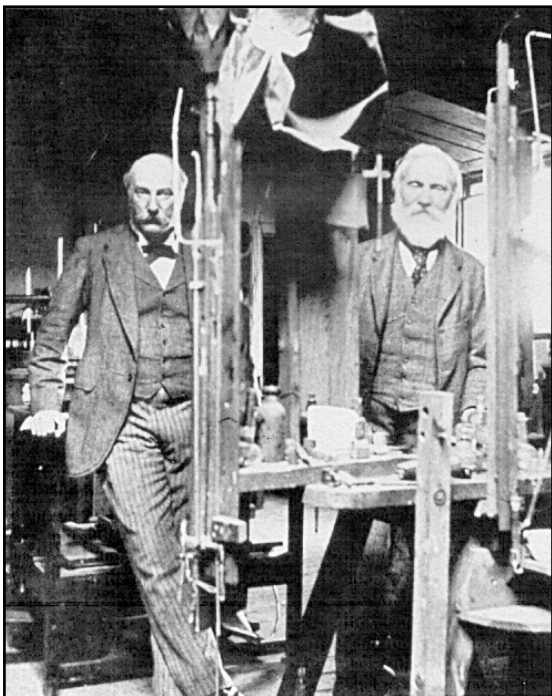


Figure 4. Lord Rayleigh (left) and Lord Kelvin (right) consulting in later life in Rayleigh's private laboratory.

*Die Energie der Welt ist constant.
Die Entropie der Welt strebt einem Maximum zu.*

Perhaps the best overall evaluation of the relative merits of these two contributions was given by Horstmann, who had studied under Clausius, in his famous paper of 1873 on the application of the entropy concept to chemical equilibrium, in which he argued that, while Thomson was the first to qualitatively state the underlying physical basis of the second law of thermodynamics, it was Clausius who first gave it a proper mathematical formulation via his entropy function (7):

W. Thomson was the first to take note of one of the consequences of the mechanical theory of heat – namely that the entire world is continuously approaching, via the totality of all natural processes, a limiting state in which further change is impossible. Repose and death will then reign over all and the end of the world will have arrived. Clausius knew how to give this conclusion a mathematical form by constructing a quantity – the entropy – which increases during all natural changes but which cannot be decreased by any known force of nature. The limiting state is, therefore, reached when the entropy of the world is as large as possible.

As might be expected, Tait, with his distinctly British bias, overwhelmingly favored Thomson's dissi-

pation approach over Clausius's entropy approach and would even go so far as to appropriate Clausius's term to describe the opposite of Thomson's concept. Tait, observed a later biographer, "was always ready to put on his armor and place lance in rest for the cause of British science" (15). Believing that the word entropy was Greek for "transformation capacity," Tait argued it should be used to describe the amount of available energy remaining in a system, rather than its loss. Once this energy was dissipated and the system no longer possessed the capacity for further change, its transformation capacity or entropy would be at a minimum rather than at a maximum, as argued by Clausius. Hence Tait proposed reversing both the sign and meaning of Clausius's original entropy function (11):

It is very desirable to have a word to express the "Availability" for work of the heat in a given magazine; a term for that possession, the opposite of which is called "Dissipation." Unfortunately the excellent word "Entropy," which Clausius has introduced in this connexion, is applied by him to the negative of the idea we most naturally wish to express. It would only confuse the student if we were to endeavor to invent another term for our purpose. But the necessity for some such term will be obvious from the beautiful examples which follow. And we have taken the liberty of using the term Entropy in this altered sense ... The entropy of the universe tends continually to zero.

Tait's rationale for this linguistic kidnapping was hardly convincing, since, despite his claim that inventing his own term would prove confusing to students, he had in fact already done so earlier in the paragraph when he chose to highlight the word "Availability." In addition, as we will soon see, his proposed revision of Clausius's terminology would have unfortunate consequences for the early development of chemical thermodynamics in Great Britain

Dissipation and Chemical Equilibrium

Though Tait mentioned chemical reactions in his treatise, most of his passing references had to do with their use in constructing voltaic cells and examples of the application of the conservation of energy. Little or nothing was said on the subject of dissipation and chemical equilibrium. Indeed, it was not until 1875 that this subject was finally raised by Lord Rayleigh (figure 4) in the course of a popular lecture delivered at the Royal Institution (16):

The chemical bearings of the theory of dissipation are very important, but have not hitherto received much

attention. A chemical transformation is impossible if its occurrence would involve the opposite of dissipation (for which there is no convenient word); but it is not true, on the other hand, that a transformation which would involve dissipation must necessarily take place. Otherwise, the existence of explosives like gunpowder would be impossible.

What is of particular interest in this quote is Rayleigh's explicit recognition of the importance in chemical phenomena of what is now called "kinetic metastability" – the realization that energy dissipation is a necessary, but not a sufficient, condition for a given chemical reaction to occur.

Rayleigh then went on to rather oddly argue that the supposed widespread absence of reversibility in chemical reactions had so far hampered the application of thermodynamics to chemistry – odd because reversible chemical reactions are quite common in gaseous and liquid solution systems, and, in any case, energy dissipation must accompany all spontaneous chemical reactions, reversible or otherwise (16):

The difficulty in applying thermodynamical principles to chemistry arises from the fact that chemical transformations cannot generally be supposed to take place in a reversible manner, even though unlimited time be allowed. Some progress has, however, recently been made, and the experiments of Debray on the influence of pressure on the evolution of carbonic anhydride [i.e. carbon dioxide] from chalk [i.e. calcium carbonate] throw considerable light on the matter.

He then concluded his lecture with a few remarks on the role of contraction and expansion in altering the degree of energy dissipation for a given chemical reaction.

It was not until 1882 that the relevance of such topics as energy conservation and dissipation, the mechanical theory of heat, and the kinetic theory of gases to the theory of chemical reactions were once again brought to the attention of the British scientific community – this time via an address on "Chemical Dynamics" given in Southampton at the August meeting of the British Association for the Advancement of Science (BAAS) by the Cambridge chemist, George Downing Liveing (figure 5), in his capacity as President of the Chemical Section of the Association (17):

If I were asked in what direction chemical science had of late been making the most important advances, I should reply that it was in the attempt to place the dynamics of chemistry on a satisfactory basis, to render

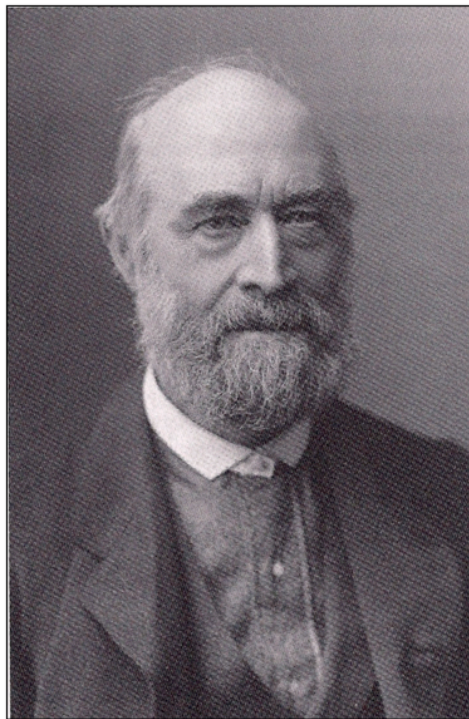


Figure 5. George Downing Liveing (1827-1924).

an account of the various phenomena of chemical action on the same mechanical principles as are acknowledged in other branches of physics.

Liveing then briefly summarized just what these universal mechanical principles were (17):

The kinetic theory of gases has analyzed for us the different motions of the molecules in a mass of matter and has facilitated the conception of the part which heat plays in chemical actions. Hence we have had of late several attempts to reduce to a form susceptible of mathematical calculation the problems of chemistry. Most of these attempts have proceeded on the well-known mechanical principle that the change of vis viva of a system, in passing from an initial to a final configuration, is independent of the intermediate stages through which it may have passed provided the external conditions are unaltered; and on the principle of the dissipation of energy, that is to say, on the condition that the state of the system, if it be a stable one, must be such that the energy run down in reaching it is a maximum.

Citing the recent work of Gibbs, Berthelot, Thomsen, and Deville as examples of this progress, Liveing then called attention to the almost negligible impact that this work had so far had on the average chemistry textbook (17):

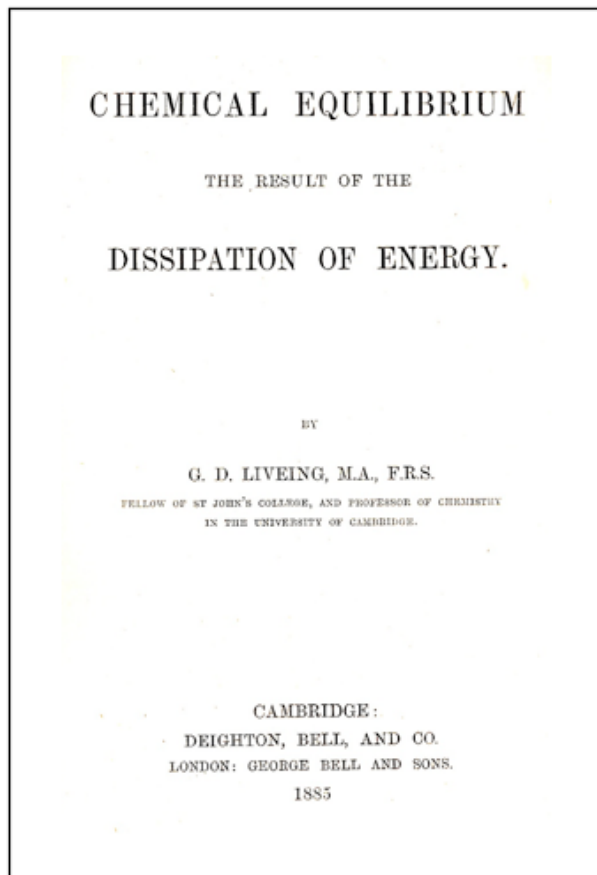


Figure 6. The title page of Liveing's 1885 monograph on chemical thermodynamics.

But how far can we say that mechanical principles are actually recognized as the true basis of rational chemistry? So far as I know no chemist denies that this is so, and yet how little do our textbooks, even the most recent and the most highly reputed, show the predominance of this idea! How very small a portion of such books is taken up with it, how much seems to utterly ignore it or to be couched in language antagonistic to it!

At this point Liveing diverged from his initial theme and spent the remainder of his address (indeed the majority) discussing recent advances in his research speciality of spectroscopy and their bearing on such issues as Prout's hypothesis and the unity of matter and the origins and renewal of the sun's ultimate source of energy.

This address appears to have been a resume of a course on chemical thermodynamics that Liveing had either already given, or was planning to give, to his students at Cambridge – the full contents of which were finally published three years later in the form of a small booklet (figure 6) of only 97 pages entitled, with

startling directness, *Chemical Equilibrium the Result of the Dissipation of Energy* (18). This is, to the best of my knowledge, the first English-language monograph to deal specifically with chemical thermodynamics, rather than with either thermochemistry or engineering thermodynamics, and the only such monograph to explicitly adopt an approach based on Thomson's energy dissipation principle rather than on Clausius's entropy function.

Unhappily, it is also very difficult reading for the modern chemist, not because it is crammed with complex mathematics or because it talks of energy dissipation rather than entropy changes, but for precisely the opposite reason. In actuality the book contains virtually no mathematical equations whatsoever and, though it describes a great many chemical reactions, it also contains very few balanced chemical equations. Likewise, though reference is made to various experimental set-ups, no figures of apparatus appear and, though each chapter addresses multiple topics, there are no section headers or numbered paragraphs to mark the passage from one subject to another. The modern reader, who takes for granted these conventions for summarizing and organizing technical material – conventions already widely used by the 1880s – will quickly discover that their absence, coupled with an almost total reliance on verbal description only, imposes a great burden on both one's memory and attention span.

The book is divided into six brief chapters and also contains a lithograph of typical line spectra and a photographic plate of three complex spectra. The first chapter, entitled "Introduction," verbally defines energy dissipation and discusses various mechanisms for the process, including heat conduction and variations in rarefaction and condensation due to changes of state (taken in the broad sense to also include both mixing and adsorption). It concludes with a summary of the criteria for establishing that energy dissipation has occurred:

1. The system can be returned to its initial state only through addition of available energy from an external source.
2. For small perturbations at least, the system returns to its final state of maximum dissipation when the external energy sources are removed.

The second chapter is entitled "Equilibrium in Dissociation," and attempts to dispel the older belief, based on the caloric theory, that heat is a repulsive force which acts in opposition to chemical affinity. The reason compounds eventually dissociate upon heating is not because the repulsion of the added heat finally

overwhelms the attractions of the internal bonds, nor because, in keeping with the newer mechanical theory of heat, the increasing violence of the intramolecular vibrations finally break the internal bonds. Rather it is because the net increase in the number of independently moving species formed upon dissociation is more able to effectively dissipate the system's internal kinetic energy.

The third chapter, entitled "Termination of Reactions," contains the only diagram in the booklet and depicts the gravitational potential of a rolling ball (figure 7). Though admittedly not a direct representation of the actual potential of a chemical reaction system, Liveing nevertheless uses this diagram as an analogy to describe the changes in the potential energy of several example chemical reactions, and thus it is arguably the first known example of the use of a potential energy surface to analyze chemical reactivity. Its primary use by Liveing was to discuss the issue of successive reactions.

As early as 1793 the French chemist, Antoine Fourcroy, had enunciated the principle that, if a set of reactants was able to form more than one alternative set of products, the least stable set was produced first and only subsequently converted into the more stable set (19). This same principle was repeated again by Gay-Lussac in 1842 (20) and again by Ostwald in 1897 under the guise of "the law of successive reactions" (21). In terms of Liveing's potential energy surface of 1885, the initial reactants are represented by position *A* and the successive products by positions *B*, *C*, and *D*. Whether the system stops at one of these local minima (*B* or *C*) or proceeds all the way to the true minimum (*D*) depends on how rapidly it dissipates its kinetic energy. If the dissipation is rapid, the system will stop at either *B* or *C* because it will lack sufficient kinetic energy to surmount the intervening potential energy maxima (*b* and *c*). If, however, it is slow, then the system may retain sufficient kinetic energy to surmount these barriers and will then proceed all the way to the true minimum (*D*).

In our modern terminology, points *a*, *b*, and *c* correspond to activation barriers, and in the first scenario *B* and *C* correspond to kinetically metastable products and *D* to the true thermodynamic product, whereas in the second scenario *B* and *C* correspond to reaction intermediates. However, not only did Liveing lack our modern terminology, he also failed to make a clear distinction between the kinetic and thermodynamic aspects of chemical reactivity, so his analysis is only partially correct by modern standards.

The final issue addressed by Liveing in this chapter was the question of whether a chemical reaction will proceed all the way to completion or will come to

equilibrium before completion. In Pfaundler's kinetic approach of 1867 equilibrium was the result of the dynamic equalization of the forward and reverse reaction rates, whereas in Horstmann's entropy approach of 1873 it was a consequence of the competitive demands of the reactants versus the products with respect to maximization of their individual entropies of dilution. Since he did not deal with the question of reaction rates, Liveing's rationale is, not surprisingly, most closely related to that of Horstmann. If gases are generated in a reaction, their accumulation in a closed container creates a pressure which can be used to perform useful work. Likewise, the increase in the concentrations of any dissolved products in a solution can also be used to perform useful work (e.g. in an electrochemical cell). The resulting accumulations of potential energy eventually limit the ability of the system to dissipate its kinetic energy and thus bring the reactions in question to equilibrium before completion. On the other hand, removal of the products from the system via precipitation, or by allowing any product gases to escape into the environment, has the opposite effect and allows the reactions in question to proceed to completion. Unfortunately, this purely verbal rationale via a series of special cases lacks the generality of Horstmann's approach and is further compounded by the absence of any mathematical expressions for equilibrium constants.

The fourth chapter is entitled "The Nascent State." This term was first introduced by Priestley in the 18th century and refers to the observation that gases chemically generated *in situ* within a reaction system are frequently far more reactive than when the same gases are bubbled into the reaction system from an external source. A remarkably large number of rationales have been offered for this phenomenon over

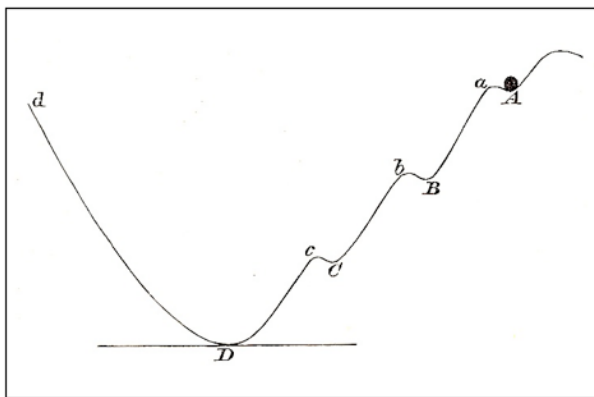


Figure 7. The 2D potential energy surface used by Liveing to illustrate the existence of metastable states (*A*, *B*, *C*) and activation barriers (*a*, *b*, *c*).

the years (22), the most popular of which was the hypothesis that chemically generated gases, such as hydrogen, were initially formed in a monoatomic state, whereas the fully formed gases from the external source were diatomic. The chapter is essentially an attack on this idea based on the argument that the initial formation of such high potential energy products as free atoms, without any corresponding mechanism for energy dissipation, is impossible.

Liveing's failure to properly distinguish between the kinetic and thermodynamic aspects of chemical reactions and his lack of an adequate vocabulary for this purpose are nowhere more apparent than in chapter five of his booklet entitled "The Passage from One State of Equilibrium to Another." The first part deals largely with the role of external energy sources in stimulating the passage of a reaction system from a high potential metastable state to a lower potential thermodynamically stable state, such as the role of light in initiating the violently explosive reaction between dihydrogen and dichlorine gas:



In other words, it deals with what we now call activation energy. This would have been an ideal topic for the potential energy diagram introduced in chapter three. But instead of referring this energy requirement back to the energy maxima in his earlier diagram, Liveing instead talks about these stimuli as "opening a new channel for energy dissipation." Also included among his examples are many that would today be classified as catalytic, though he does not employ this term.

The second part discusses the synthesis of metastable compounds or "explosives" from reactants of lower potential energy. Liveing suggests that this happens in one of two ways – either the reactants are first promoted to a higher potential, which lies above rather than below that of the desired products, via addition of external energy, as in the electrical excitation of dioxygen gas in the synthesis of metastable ozone:



or the high potential metastable product is formed along with a low potential energy by-product, such that the combined change leads to the required net energy dissipation, as in the synthesis of metastable nitrogen triiodide along with ammonium iodide as the thermodynamically stable by-product.



Again, though these arguments cry out for representation on his earlier potential energy surface, no use is made of it.

Just as the second chapter contained an attack on the outdated concept of heat as a repulsive force, so the sixth and final chapter, entitled "Theoretical View of the Nature of Chemical Combination," contains an attack on the Newtonian concept of chemical affinity as a specific force of interatomic attraction. Here Liveing extends the concept of energy dissipation from a macroscopic reaction system to an individual molecule, arguing that dissipation leads to an equalization of the kinetic energies of all of the atoms within a molecule. This, in turn, leads to a synchronization of their motions and it is this synchronization, rather than specific forces of attraction, which allow the atoms to move together as a single cohesive molecular unit (18):

The consideration of the conditions of chemical equilibrium points to the conclusion that chemical combination is not due to any bonds which have to be untied from one union before they can be tied together again in a new one, nor yet to any special forces of chemical affinity peculiar to each element and "satisfied," whatever that may mean, or disappearing in its combinations; but that it consists rather in a harmony of the motions of the combined atoms in virtue of which they move and vibrate together, and that such harmony is brought about by the general force of nature which compels to an equal distribution of energy throughout the universe.

The resulting complex of harmonized vibrations found in a typical molecule can change on heating, leading, in turn, to changes in atomic valence and spectra (whence the relevance of spectroscopy and the attached plates of spectra) and are probably best envisioned using William Thomson's vortex atom rather than the hard billiard-ball atoms of Dalton and the kinetic theory of gases, though Liveing provides no specific examples.

What these conclusions reveal is that Liveing had little sympathy for the entire 19th-century program of synthetic organic chemistry and its accompanying edifice of structural formulas, which he viewed as historical anachronisms based on outdated ideas concerning chemical affinity – a position that was much more explicit in his earlier BAAS address of 1882 (17):

Moreover, we still find in many of our textbooks the old statical notion of chemical combination stereotyped in pictures of molecules. I do not, of course, mean to accuse the distinguished inventors of graphic formulae of meaning to depict molecules, for I believe they would

agree with me in thinking that these diagrams do not any more nearly represent actual molecules than they represent the solar system; but unfortunately we cannot prevent beginners from regarding them as pictures, and molding their ideas upon them. They present something easily grasped by the infant mind, and schoolmasters are fond of them; but only those who have each year to combat a fresh crop of misconceptions, and false mechanical notions engendered by them, can be aware of how much they hinder, I won't say the advance, but the spread of real chemical science.

Nor was Liveing alone in these assumptions. As revealed by the work of McGucken, the Thomson vortex atom was something of a fad among spectroscopists of this period (23) and the idea that valence and chemical combination are really a consequence of synchronized atomic motions forms the climax of Lothar Meyer's 1892 textbook, *Outlines of Theoretical Chemistry* (24):

We have gradually receded from the idea of a static state of equilibrium of the atoms brought about by their powers of affinity, and we now consider the atoms, and the molecules which are built up of atoms, as particles in an active state of movement. Their relations to each other are essentially determined by the magnitude and form of their movements. Chemical theories grow more and more kinetic, and although, partly from habit and partly from want of a better expedient, the existence of an attractive force between atoms is frequently assumed in explaining chemical phenomena, this only happens in the conviction that this hypothetical affinity is merely an expression for the real, though imperfectly known, cause of the internal cohesion of chemical compounds.

Similar ideas concerning a kinetic interpretation of both chemical affinity and valence were still being advocated by the American chemist, Francis Venable, as late as 1904 (25).

Evaluation

By this point it should be apparent to the modern reader that Liveing's unique approach to chemical thermodynamics proved to be a dead end and that his booklet had no intellectual successors. Indeed, an argument can be made that it was already outdated by the time of its appearance. The ground-breaking work of both Horstmann (1873) and Gibbs (1874), which had already laid a proper mathematical foundation for chemical thermodynamics – couched explicitly in terms of Clausius's entropy function in the case of Horst-

mann and indirectly, via free-energy functions, in the case of Gibbs – were already more than a decade old by the time Liveing's book appeared, and Pfaundler's kinetic molecular rationale of both chemical rates and equilibria (1867) was even older.

Interestingly, in the preface to his booklet, Liveing revealed that he was well aware of the work of both Horstmann and Gibbs, though one suspects that he had mastered neither. His excuse for not employing Gibbs's approach was that it was too mathematical for the average student (an interesting claim given the supposed mathematical prowess of the typical Cambridge undergraduate), though much of the problem was really due to Gibbs's terse prose style and could have easily been compensated for by a good teacher.

Liveing's reason for rejecting the entropy approach of Horstmann is even more interesting (17):

I regret that I have been obliged to abandon in this essay the use of the very expressive word "entropy" coined by Clausius. I have done so because it has been used by Clerk Maxwell with a meaning different from that which Clausius intended to express by it, and as Clerk Maxwell's elementary treatises are in the hands of most students of chemistry, I did not wish to run the risk of a misunderstanding of the word.

What Liveing is referring to in this quote is James Clerk Maxwell's textbook, *Theory of Heat*, which was first published in 1871 and in many subsequent editions (26). In the first edition Maxwell had adopted Tait's earlier suggestion that the term entropy be used to denote the amount of available energy left in a system, rather than in the sense originally intended by Clausius. However, by 1875 Maxwell, as a result of having read Gibbs, had caught his mistake and had corrected it (27):

In former editions of this book the meaning of the term Entropy, as introduced by Clausius, was erroneously stated ... the book then proceeded to use the term as equivalent to the available energy; thus introducing great confusion into the language of thermodynamics. In this edition I have endeavored to use the word Entropy according to its original definition by Clausius.

Thus we find that the excuse cited by Liveing had actually been obviated more than a decade earlier.

There is no doubt that Maxwell's textbook was used at Cambridge. According to Liveing's successor as Professor of Chemistry, William Jackson Pope, Liveing himself had taught the course on heat before Maxwell's arrival at Cambridge as the Cavendish Professor of Physics in 1871 and had even played a role in

Maxwell's hiring (28). But by 1885 Maxwell's textbook had passed through at least eight editions and the idea that most Cambridge undergraduates were still using the first edition is either implausible or provides us with an unintended insight into the degree to which used textbooks were recycled by students of the period.

Ironically, the true predecessors of our current textbook tradition in chemical thermodynamics were making an appearance within the same time frame as Liveing's small booklet and include both Jacobus van't Hoff's 1884 monograph, *Études de dynamique chimique* (29) and Pierre Duhem's 1886 monograph, *Le potentiel thermodynamique et ses applications à la mécanique chimique et à l'étude des phénomènes électrique* (30). As suggested by its title, Duhem's approach was based on the use of Gibbs's chemical potential and was the first of a series of books on chemical thermodynamics that he would write over the next two decades, culminating in his 1902 textbook *Thermodynamique et chimie*, the only one to be translated into English (31).

Justly celebrated as the first modern monograph on chemical kinetics, van't Hoff's book also concluded with a section on chemical thermodynamics based on the concept of equilibrium as an equalization of the forward and reverse phenomenological reaction rates. Although heavily influenced by the work of Horstmann, whose writings on thermodynamics he would later edit (32, 33), van't Hoff unfortunately chose to abandon Horstmann's explicit use of the entropy function and opted instead for an approach based on *Arbeit* or useful work in which the role of entropy was implicit rather than explicit. His work was extremely influential in molding the teaching of chemical thermodynamics for the next 40 years but also condemned it to the use of such artificial devices as reversible cycles, osmotic-pressure membranes, and adiabatic pistons. Only with the publication in 1923 of the famous textbook of Lewis and Randall was this pseudo-engineering approach finally eclipsed and the subject once again returned to the purity of Gibbs (9).

A Modern Reconciliation

In modern terms, the entire hiatus prompted by Tait's ill advised attempt to redefine entropy can be summarized by the fundamental relationship:

$$G = -TS_T \quad [4]$$

where G is the Gibbs free-energy of the reaction system, S_T is the total entropy of both the reaction system and its surroundings, and T is the absolute temperature. Essentially G is identical to what Tait meant by "Availability" and, like it, tends to a minimum as one ap-

proaches equilibrium. This was the term that Tait wished to rename entropy – a proposal that entailed not only a change in the meaning and sign of S_T , as originally defined by Clausius, but also, taking T into account, a change in its fundamental physical dimensions as well (60). TS_T , on the other hand, when taken in Clausius's original sense, is a good measure of the total energy dissipation of the system at the temperature in question and tends to a maximum as one approaches equilibrium.

Unfortunately the term "dissipation," though having uses in modern engineering thermodynamics, seldom appears today in the literature on chemical thermodynamics. However, when used in Thomson's original sense, it has been argued that it is a far better interpretation of the physical meaning of entropy than either disorder or information (10, 34-35). Neither information nor disorder are true causal agents like energy, and entropy is essentially a descriptor for how the energy of a system is distributed. Modern quantum statistics teaches us that movement from a low entropy state to a high entropy state corresponds to a dilution or dissipation of the system's kinetic energy content over an ever greater number of accessible quantum levels. Though increased molecular disorder is frequently, though not invariably, an *indicator* that the system has acquired a greater capacity to disperse its energy, it is not entropy in and of itself. Likewise, the idea that entropy is linked with information is actually based on a formal mathematical isomorphism rather than on a true physical isomorphism, and opens the entire concept to the charge of being subjective (36-37). Had Tait chosen to equate Thomson's dissipation with Clausius's entropy, rather than with available energy, this entire unfortunate episode in the history of chemical thermodynamics might have been avoided.

Having outlined and evaluated Liveing's contributions to the teaching of chemical thermodynamics, it is only fitting that, in conclusion, something should also be said about his life and career in general.

Biographical Background

George Downing Liveing (figure 8) was born on 21 December 1827 in Nayland, a small English village on the Suffolk bank of the River Stour, the eldest son of Edward Liveing and Catherine Downing (28, 38-42). His father was a surgeon by profession and his mother the daughter of a London barrister. In 1845, at age 18, Liveing entered St. John's College of Cambridge University as a pensioner, where he would remain in various capacities until his death 79 years later on 26 December 1924 at age 97.

Matriculating at St. John's in 1846, Liveing was

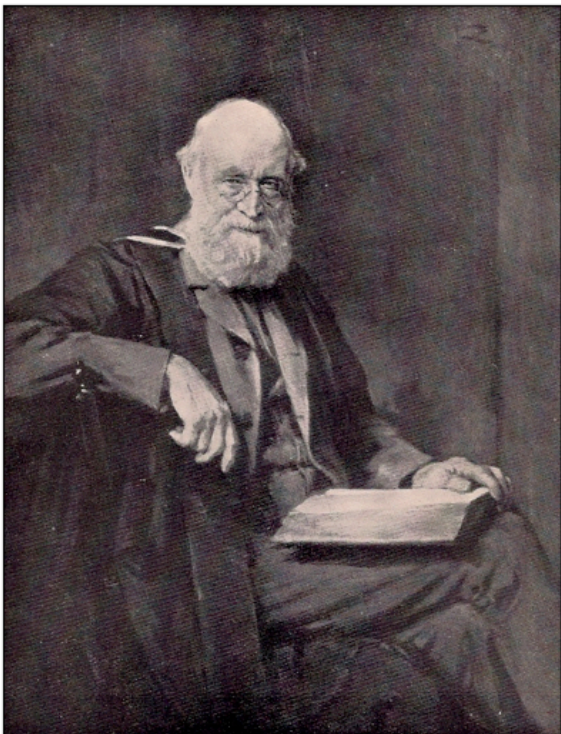


Figure 8. Liveing as he appeared in later life in the full tide of Cambridge honors.

awarded his B.A. in 1850 along with the position of 11th Wrangler in the Mathematical Tripos. Continuing on with postgraduate work at St. John's, he was awarded a first class with distinction in chemistry and mineralogy in the Natural Sciences Tripos of 1851, followed by work in the chemical laboratories of August Hofmann at the Royal College of Chemistry in London and Karl Rammelsberg in Berlin.

On his return from Berlin in 1852, he began teaching a practical course in chemistry for medical students in a primitive laboratory which he had outfitted at his own expense in a small cottage on the west side of Corn Exchange Street. However, in 1853 he received not only an M.A. from St. John's, but also appointment as a fellow of the college and an official lectureship in chemistry, along with a teaching laboratory which the College built for him behind New Court – the first of its kind at Cambridge.

By 1860 Liveing was able to supplement his position at St. John's through his appointment as Professor of Chemistry at the Staff College in Camberley and at the Royal Military College in Sanhurst, and in 1861 he was finally appointed as full Professor of Chemistry at Cambridge upon the death of the Reverend James Cummings, who had held the position since 1815. From this point on, he became involved in a continuous campaign to improve and expand the student labo-

ratory facilities at Cambridge.

One of several plans for a chemical laboratory proposed during this period, but subsequently rejected by Liveing, reveals just how leery and unfamiliar the University was with the requirements of experimental chemistry (39):

The laboratory is to be constructed underground and is to be capable of resisting violent explosions and to be as little flammable as possible.

And just how rare the opportunity for actual hands-on laboratory work was in these early years may be gaged from Lord Rayleigh's recollections of his experiences as a student at Cambridge in the 1860s, as later recounted by his son (43):

In 1867 he took a course of qualitative chemical analysis (test-tubing as it is now often called) under Professor Liveing. This was, I think, the only laboratory instruction of any kind which he could get at Cambridge. I have dwelt in detail on the difficulty he found in getting experimental instruction, because it was a subject he often spoke of in telling me of his early years of manhood. "It wasted three or four years of my life."

In 1888 Liveing's efforts finally paid off with the completion of the Pembroke Street University Laboratories, described at the time as "one of the finest facilities in the Kingdom." (41). But even then, as one biographer noted, Liveing's laboratory stipend was only (28):

... 100£ per annum, paid by the government and subject to a deduction of Treasury fees amounting to four guineas. As he has said himself, men in those days had to devote their means as well as their wits to the service of the University.

In keeping with this remark, Liveing was forced, until his retirement two decades later, to finance (28):

... the chemical laboratory as a private venture, and informed me that he declined to submit his accounts, when challenged in later years by the suggestion that he had been drawing a large revenue, because he was ashamed to disclose to his colleagues how large a sum he had thus contributed from his own resources.

The retirement in question finally came in 1908 at age 80, on which occasion Liveing was also awarded an honorary Sc.D. Elected a Fellow of the Royal Society in 1879, he was also a recipient of its Davy Medal in 1901, served as President of St John's College from 1911-1924, and as corresponding secretary to two

successive University Chancellors.

Liveing could be terse and abrupt with those who irritated him, either by invading the privacy of his personal work room or by violating the strict working rules of the new University Laboratories – attributes which won him the nickname of “Red Precipitate” among the undergraduates. As recalled by a former colleague (40):

Liveing had a great objection to being interrupted when at work in his private room in the Laboratory. One day I was asked by a man whether he could see the Professor and where was his private room. My reply was that the Professor did not see people except by appointment, but there was his room ... I could do no more than point to the door behind which the Professor worked and wait. I heard three taps on the door, a voice “Come in,” a louder voice “Get out!,” and a shutting of the door. I retreated with discretion. He was indeed extraordinarily terse in his conversation; not exactly abrupt or curt, but sometimes very monosyllabic. Like Captain Cuttle, he did not “waste language as some do.”

On the other hand, Liveing could also be “a very entertaining companion” when he chose to be and especially when one succeeded in tapping his remarkable memory of past events, which remained intact until the end (41):

He had a remarkable memory, talked freely of the men and events of the past, but would write no reminiscences. “I never look back,” he said, “I always look forward”

In a similar vein, Pope recalled after Liveing’s death in 1924 that (28):

In his conversation, always sprightly and vivacious, Liveing seemed often trying to translate our later knowledge into terms of the science of seventy years ago. As befitted one who belonged to the age when the collection of facts was the main objective of science, he was apprehensive as concerned the vast theoretical flights of modern physics and chemistry ... In talking with Liveing and hearing his statement of long obsolete chemical views, one began to realize the difference between the science of seventy years ago and that of today, and to speculate on what our survivors seventy years hence will think of the science of the future. At the same time, and although an authority on older chemical knowledge, Liveing always maintained an excellent appreciation of recent progress.

After all, as Pope emphasized, here was a man who had completed his chemical training (28):

... before Frankland had stated the doctrine of valency and before Kekulé had devised the structural formulae of the chemist. Liveing had been the personal friend of Dr. Whewell, the great Master of Trinity, W. H. Miller, the founder of our present system of crystallographic nomenclature, Adam Sedgwick, Sir Joseph Hooker, Michael Foster, Sir Gabriel Stokes, Sir George Airy, de Morgan and Charles Darwin; he had studied under Rammelsberg, Mitscherlich, Rose and Magnus. He once mentioned to me that he and Hooker, after some preliminary discussion, walked over to see Darwin for the purpose of hastening the publication of the “Origin of the Species,” which appeared in 1859.

Indeed, his life had encompassed so much scientific history, that he occasionally forgot that this was not equally true of his younger colleagues (28):

His memory of long-past events was remarkably clear until quite recently, but he sometimes forgot that others could not reach so far back into the past. A few months ago, while still in full mental vigor, he expressed surprise that I had not noticed the splendor of Donati’s comet of 1858 [Pope was born in 1870].

What was true of Liveing’s memory was equally true of his physical health, which also remained intact until the end. He seems to have been one of those lucky persons who take their personal good health as an unquestioned given and who remain puzzled as to why others do not display a similar resiliency (28):

Like many other men of robust health and great vitality, Liveing found it difficult to understand why his contemporaries dropped out and passed away. Declining health seemed to him as due to a lack of resolution. He was an enthusiastic gardener, and when well past his ninetieth birthday engaged in all the manual toil incidental to the care of a large garden.

He was also an avid walker in old age and would walk each day from his home in Maid’s Causeway to his laboratory in the Goldsmith’s metallurgical building, where he was working on a project related to his final publication on “The Recuperation of Energy in the Universe,” which he had read to the Cambridge Philosophical Society in May of 1923 (41):

In his old age, his tall bent figure as he made his daily journeys between his home and the College, was one of the most familiar in town.

And it was during one of these daily walks, in early October of 1924, that he was run down by a woman bicyclist – an accident which resulted in his death several months later from the resulting injuries, just five days after his 97th birthday.

Research Activities

During his extraordinarily long career Liveing published over 100 research papers and notes, although this output was not evenly distributed over time (44). For the first 25 years of his active career he published virtually nothing. Indeed, for the years prior to the date of his appointment in 1861 as Professor of Chemistry at Cambridge, the *Royal Society Catalogue of Papers* lists no publications whatsoever and, for the next 16 years, only four are given, all of them dealing with geology and all of them published in the Proceedings of the local Cambridge Philosophical Society. Here we should perhaps heed John Shorter's caution that in the 19th century (42):

Cambridge did not seek to produce people who intended to practice chemistry ... At Cambridge, chemistry was a part of a liberal education for those who cared to include it, with the exception of its ancillary role for medicine ... The aim of a Cambridge chemical education through the Tripos was to impart a knowledge of chemistry, not to train chemists.

As a consequence, there was little incentive to acquire a Professor of Chemistry with an already established research reputation and, in any case, for his first quarter century at Cambridge Liveing's time and energy were largely consumed in establishing the very laboratory facilities necessary for such work in the first place.

A radical change in Liveing's research prospects finally occurred in 1875 with the appointment of Sir James Dewar (figure 9) as the Jacksonian Professor of Physics at Cambridge. Though Liveing was nearly 16 years older than Dewar, the two men soon struck up a friendship that would last for nearly a half century and which would lead to the collaborative publication of more than 78 papers and notes dealing with the subject of spectroscopy. As later noted by Pope (28):

The close and intimate friendship which existed between Dewar and Liveing was very striking. Both men were of strong personality, but no two men could have presented a greater contrast in outlook, tastes, and all essential characteristics. Yet each held the other in profound esteem, and neither ever said a word in criticism of his colleague. Without this absolute loyalty, the happy collaboration of Liveing and Dewar could not

have persisted for nearly fifty years.

This collaboration would establish Liveing's reputation as a research chemist and lead to both his election to the Royal Society and his award of the Davy Medal mentioned earlier. After his retirement, he would edit much of it for inclusion in a volume of collected papers published by the Cambridge University Press in 1916 (45).

Most of this work belongs to what A. C. Chandler would later call the "acoustics" period of spectroscopy and consisted of the publication of raw spectral data with some qualitative classification and speculative interpretation of the results, but without the empirical mathematical equations that would characterize the later "series" period of spectroscopy nor the theoretical interpretations that would characterize the later "quantum" period (46, 47). Its most lasting contribution was the division by Liveing and Dewar of the lines in the spectra of the alkali metals into the classes of sharp, principal and diffuse – terms which, via a series of historical twists and turns, would eventually become enshrined in our current atomic orbital abbreviations of *s*, *p* and *d* (48).

Which Tradition?

With the exception of his BAAS address of 1882, five papers published in the late 1880s on the kinetic theory



Figure 9. James Dewar (1842-1923).

and some aspects of chemical reactions, solution formation and crystallization (49-53), and his final paper of 1923 on cosmology (54), little in Liveing's list of research publications would seem to be related to his small monograph on chemical thermodynamics, and it has been our assumption so far that this work evolved primarily out of his teaching duties at Cambridge and is best interpreted in light of two competing approaches to the second law. However, another interpretation is also possible.

Though at least one biographer claimed that Liveing's small booklet "attracted a great deal of attention" when first published (39), I have been able to locate only one book review, and that single review casts a very different light on the subject. Published in the *Chemical News*, it characterized the book as "evidently of a preliminary nature," dismissed its treatment of chemical equilibrium and dissipation of energy as of little interest except to the physicist and "physico-chemist," proceeded to focus solely on the final chapter containing Liveing's speculations on the nature of matter as the only part of interest to the "pure chemist," and concluded with the recommendation that (55):

All who are not content to accept the reputed "elements" as the ultimate facts will find this book worthy of careful study.

The author of the review was not listed, but given its emphasis, it is almost certain that it was the journal's editor, William Crookes, who was well known for his own spectroscopic studies and speculations on the ultimate nature and evolution of the chemical elements – speculations that would attract widespread attention the very next year as a result of his 1886 address as President of the Chemical Section of the BAAS (56). As shown by the pioneering studies of David Knight (57) and William Brock (58) in the 1960s, both Crookes's address of 1886 and Liveing's earlier address of 1882 are part of a long-lived debate among British chemists of the 19th century over the ontological status of both the atomic theory and the ultimate nature of Lavoisier's chemical elements – a debate in which Liveing's research specialty of chemical spectroscopy played a key role in the guise of Norman Lockyer's so-called "dissociation hypothesis" (59).

Nevertheless, while the reviewer's conclusion might have been applicable to Liveing's 1882 address, it is difficult to understand how he could have extracted such a message from Liveing's booklet of 1885, which contains nothing on either Prout's hypothesis or the ultimate nature of the chemical elements. Likewise, though one might surmise that Crookes may have found the principle of energy dissipation relevant to the

mechanism for the gradual cooling of the primeval *protyle* that he would postulate as the cause for the gradual evolutionary building-up of our present-day chemical elements – no mention of either Liveing or energy dissipation is to be found in Crookes's famous address of 1886. In short, the implied contention of the reviewer that Liveing's booklet is best viewed as part of a 19th-century tradition of spectroscopic speculation on the ultimate nature of the chemical elements, rather than as part of a tradition of the monographic literature devoted to the theory of chemical thermodynamics, is dubious at best, however consistent it may be with some of Liveing's other writings.

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60. A plot of G versus the extent of reaction parameter ξ would have a U shape with the equilibrium value of G occurring at the base of the U curve, where G has its minimum value. A plot of S_i versus ξ would have an inverted U shape with the equilibrium value of S_i occurring at the top of the inverted U. The S_i curve is transformed into the G curve by multiplying it by $-T$ so as to invert it and to give both curves the units of energy/(mole rx K). ΔG and ΔS_i actually refer to the slopes of these curves or to $dG/d\xi$ and $dS_i/d\xi$ respectively. Thus while G and S_i are at their minimum and maximum respectively at equilibrium, their slopes, ΔG and ΔS_i , are both equal to zero at these points. For a recent discussion of the confusions produced by using ΔX in place of $dX/d\xi$ in chemical thermodynamics, see J. Quílez, "First-Year University Chemistry Textbooks' Misrepresentations of Gibbs Energy," *J. Chem. Educ.*, **2012**, 89, 87-93.

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Update

For a more detailed account of Tait's attempts to replace entropy with dissipation, see E. E. Daub, "Entropy and Dissipation," *Hist. Stud. Phys. Sci.*, **1970**, 2, 321- 354.