AUGUST HORSTMANN AND THE ORIGINS OF CHEMICAL THERMODYNAMICS

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1. The Challenge. Arguably the single most recognizable equation of modern chemical thermodynamics is that connecting the free energy (ΔG) of a reaction at constant T and P to its standard enthalpy change ($\Delta H°$), standard entropy change ($\Delta S°$), and reaction quotient (Q):[1,2]

$$\Delta G = \Delta H° - T\Delta S° + RTlnQ \qquad [1]$$

which, in the limiting case of equilibrium ($\Delta G = 0$ and $Q_{eq} = K$), gives us the equally famous equation:

$$\Delta G° = \Delta H° - T\Delta S° = -RTlnK \qquad [2]$$

If asked when these relations were first recognized and by whom, most chemists would probably plead ignorance or perhaps guess, given that ΔG is now known as the Gibbs free-energy function, that they were first derived by the American physicist, Josiah Willard Gibbs.

In fact, as we will see, they were first derived in a different, but equivalent, form in 1873 by an obscure German chemist by name of August Friedrich Horstmann, who has all but disappeared from the modern textbook. But before examining Horstmann's contribution, it is necessary to provide a context for his work by briefly reviewing the early history of both thermochemistry and chemical thermodynamics. This history has been extensively documented by previous historians and is the subject of numerous monographs, several of which which are listed in the accompanying references. It is not our purpose here to repeat this history in detail, but merely to remind the reader of some significant names and dates in order to provide a chronological framework for our more detailed discussion of Horstmann.

2. The Thermochemical Context. As just suggested, it is necessary to distinguish between the older discipline of thermochemistry, which deals with heat alone, and the discipline of chemical thermodynamics proper, which deals with heat, work, and entropy. Indeed, the history of thermochemistry may, in turn, be further divided into what might be called the "caloric" phase and the "first law" phase.[3]

In the caloric phase heat was regarded as a subtle, imponderable (i.e., weightless) fluid which could chemically combine with atoms to form an external atmosphere which rendered them mutually repulsive.[4] As such, it worked in opposition to chemical affinity, which caused the atoms to mutually attract. Association reactions were assumed to be inherently exothermic because they decreased the atomic surface area available to bind caloric, thus setting some of it free as sensible heat. In contrast, dissociation reactions were assumed to be inherently endothermic since they increased the atomic surface area available to bind free heat as insensible combined caloric. No necessary relationship was postulated between heat release or absorption and the degree of chemical affinity. If anything, the preoccupation was compositional (i.e., measuring the caloric content or composition of various molecules) rather than dynamic.

The caloric phase began in 1784 with the work of Lavoisier and Laplace on heats of combustion. Its most productive practitioners were the French team of Pierre Favre and Johann Silbermann, who measured many heats of reaction, formation, and transition in the period 1841-1853, and its most important contribution was the law of constant heat summation, first proposed by the Swiss-Russian thermochemist, Germain Hess, in 1840.

As suggested by its name, the first law phase rested on the enunciation, in the period 1841-1847, of the first law of thermodynamics or the law of energy conservation - primarily by James Joule in England and by Robert Mayer and Hermann von Helmholtz in Germany – though there are many other claimants.[5] It was first extensively applied to chemical systems a decade later, where it was most closely associated with the work of Julius Thomsen in Denmark in the period 1850-1886 and that of Marcelin Berthelot in France in the period 1864-1897.[6, 7]

Based on the equivalence of heat and work, it postulated, in contrast to the caloric theory, a direct relationship between heat release and the degree of chemical affinity via the so-called "principle of maximum work," which assumed that the greater the heat release, the greater the decrease in the potential energy of the atoms, and the more stable the resulting molecule. Direct application required that a distinction be made between the heat release due to chemical change (ΔH_{chem}) and that due to the physical changes of state (ΔH_{phys}) which necessarily accompanied the reaction:

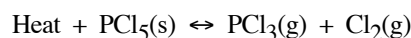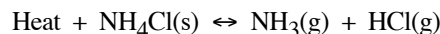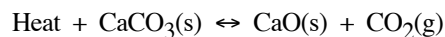$$\Delta H_{rx} = \Delta H_{chem} + \Delta H_{phy} \qquad [3]$$

a distinction which proved impossible in practice.

3. The Thermodynamic Context. The passage from thermochemistry to chemical thermodynamics proper is predicated on the enunciation of the second law by Rudolph Clausius in Germany in 1850 (using Q/T, not called entropy until 1865) and by William Thomson (Lord Kelvin) in Great Britain in 1852 (using the concept of energy dissipation).[2, 8] However, nearly two decades would pass before the second law was applied to chemical reactions.[9] Early contributions of note then came from

J. Moutier (1871) and H. Peslin (1871) in France, Lord Raleigh (1875) in Great Britain, J. W. Gibbs (1875-1878) in the United States, and, as we will soon see, from Horstmann in Germany (1869, 1873). The first monograph to deal with chemical thermodynamics proper was published in England by George Liveing in 1885, but was based on the qualitative concept of energy dissipation rather than on Clausius' quantitative entropy function.[10]

4. The Empirical Context. In addition to the above two conceptual threads we also have a final experimental thread based on the empirical concept of chemical equilibrium. First introduced by the French chemist, Claude Berthollet, in the period 1799-1803, the study of equilibrium reactions in solution was pioneered by, among others, L. F. Wilhemy (1850), J. H. Gladstone (1855), M. Berthelot and L. Péan de Saint-Gilles (1862), A. G. V. Harcourt and W. Essen (1864), and, most famously, by the Norwegian team of C. M. Guldberg and P. Waage (1864, 1867).[9, 11]

Empirical equilibrium studies entered a new phase (both literally and figuratively) when they were extended from solution reactions to gaseous dissociation reactions. Typical examples of this type of reaction include:

Heat $+$ $CaCO_3$(s) $\leftrightarrow$ CaO(s) $+$ CO_2(g)

Heat $+$ NH_4Cl(s) $\leftrightarrow$ NH_3(g) $+$ HCl(g)

Heat $+$ PCl_5(s) $\leftrightarrow$ PCl_3(g) $+$ Cl_2(g)

Though some important early results were obtained by G. Aime (1837) and W. R. Grove (1847), it was the extensive efforts of Henri Sainte-Claire Deville and his colleagues, H. J. Debray, and L. J. Troost, in France in the period 1857-1868 that really brought the experimental study of gaseous dissociation equilibria to the forefront by establishing important analogies between the pressure and temperature dependency of these equilibrium reactions and those observed for the vapor pressures of liquids.[12]

5. Rationalizing Gaseous Dissociation Equilibria. Various attempts to rationalize theoretically these experimental results began to appear in the late 1860s and the 1870s, some of which were based on the newly emerging kinetic-molecular theory of gases and others on the laws of thermodynamics. The most important qualitative kinetic-molecular rationale was given by the Austrian physicist, Leopold Pfaundler, in 1867 based on the temperature and pressure dependence of molecular collision frequencies, the formation of transient collision complexes, and the requirement of threshold reaction energies – ideas which anticipated much of the conceptual basis of modern chemical kinetics.[13]

Following the qualitative approach of Pfaundler, Horstmann initially attempted to develop a quantitative theory of dissociation using the kinetic theory of gases, but

abandoned these attempts because they appeared unable to explain the absence of a mass action effect in the case of pure solids.[14] Adopting an alternative thermodynamic approach instead, Horstmann first applied it to the thermal dissociation of ammonium chloride (the second reaction given in the previous section) in 1869.[15] Using the analogy with vapor pressures, he fit the data for the change in the dissociation pressure of ammonium chloride as a function of absolute temperature to an empirical equation first proposed by Biot for vapor pressures and then applied a rearrangement of the Clausius-Clapeyron equation:

$$(dP/dT) = \Delta H/(T\Delta V) \tag{4}$$

in order to calculate the corresponding heat of dissociation:

$$\Delta H = (T\Delta V)(dP/dT) \tag{5}$$

This was followed by three more papers on dissociation in period 1871-1872, again based on the application of both the differential and integrated forms of the Clausius-Clapeyron equation.[16]

In 1873, however, Horstmann returned to the subject once more in a paper entitled *Theorie der Dissociation*, in which he took an entirely new approach based on an explicit application of Clausius' new entropy function.[17] Here he formulated the equilibrium condition for dissociation as a direct function of having maximized the change in the total entropy (dS) of the isolated system with respect to the degree of reaction or dissociation (dx):

$$(dS/dx) = 0 \tag{6}$$

in which the total entropy production was given by the equation:

$$S = (Qx)/T + Z \tag{7}$$

where Q/T is the heat of reaction per mole (Q) divided by the absolute temperature (T), and Z is the change in the "disgregation" of chemical reactants and products. This latter quantity was first introduced by Clausius in 1862 and was his rationale for the underlying molecular basis for entropy increase - namely that it corresponded to a decrease in the degree of molecular aggregation and thus to a corresponding increase in the degree of molecular dispersion or disgregation.[18] Similarly, Horstmann's requirement that $(dS/dx) = 0$ at equilibrium was nothing less than a direct mathematical expression of Clausius' famous 1865 reformulation of the second law: "Die Entropie der Welt strebt einem Maximum zu."

However, application of these equations to actual chemical reactions required a further elaboration of equation 7, which Horstmann then proceeded to do on a case by case basis. This may be illustrated using his simplest case – the thermal dissocia-

tion of a solid reactant to produce a single solid product and an accompanying gaseous product:

Heat + AB(s) $\leftrightarrow$ A(s) + B(g)
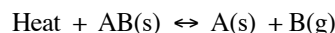
as exemplified by the thermal dissociation of calcium carbonate shown in the pervious section. Here the final equilibrium condition was given by the specific equation:

$$(dS/dx) = q/T - ARln(u/u_o) + C = 0 \qquad [8]$$

where q is the equilibrium value of Qx, A is the mechanical equivalent of heat, R is the universal gas constant, C is the change in the disgregation of the various reactants and products when in their standard states, and u/u_o is the ratio of the equilibrium molar volume (u) of the single gaseous product to that of its standard state (u_o).

In other words, the second term in this equation represents the manner in which the disgregation or entropy of a gaseous species varies as a function of its degree of dilution expressed as volume per mole (V/n). In deriving it, Horstmann made pioneering use of the ideal gas law written for the first time on a per mole, rather than a per gram, basis :

$$up = RT \qquad [9]$$

where u is the volume per mole of gas.[19] Molar volume (V/n) is, of course, inversely related to both molar concentration (n/V) and partial pressure (p) – the two variables usually employed when writing the reaction quotient.

In his third example, Horstmann derived the specific equilibrium conditions for the reaction of a gas with a solid to generate both a solid and gaseous product, as in the reaction of steam with hot iron to produce dihydrogen gas and iron oxide:

$H_2O(g) + Fe(s) \leftrightarrow H_2(g) + FeO(s)$
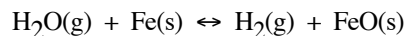
for which he obtained the specific result:

$$(dS/dx) = q/T + ARln(p_1/p_3) + C = 0 \qquad [10]$$

where p_1 and p_3 are the equilibrium pressures of the gaseous reactant and gaseous product respectively (note their inversion relative to u_1 and u_3), and the other symbols have the same meaning as previously.

Lastly, Horstmann applied his approach to the solution-phase double-displacement reaction:

$K_2SO_4(aq) + BaCO_3(s) \leftrightarrow K_2CO_3(aq) + BaSO_4(s)$
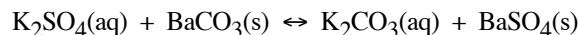
Using the data and symbolism of Guldberg and Waage, he showed that his approach led to Thomsen's conclusion that, at equilibrium, this reaction obeyed the relationship:

$$apq = p'q' \qquad [11]$$

where p and q are the equilibrium concentrations of the reactants, p' and q' are the equilibrium concentrations of the products, not to be confused with Horstmann's earlier use of the same symbols for other quantities (2). The letter a in this equation represents our modern equilibrium constant K, but only if, as Horstmann noted, the concentration dependence of the disgregation for the solute species obeyed a law similar to that for ideal gases and the values of q and q' for the insoluble barium carbonate and sulfate also remained constant. This first condition anticipated by more than a decade the later work of van't Hoff on the theory of dilute solutions and his famous analogy between osmotic pressure and the ideal gas law.[20]

In summary, we see that all of Horstmann's specific results at equilibrium can be generalized using the master equation:

$$(dS/dx) = q/T - ARlnK + C = 0 \qquad [12]$$

though he himself never took the final step of subsuming all of his specific concentration and/or pressure ratios for the gaseous- and solution-phase species at equilibrium under a single generalized symbol K.

6. A Comparison with the Modern Free-Energy Equation. To see the equivalence between Horstmann's result and our modern free-energy equation it is necessary to first divide the latter by $-T$:

$$-\Delta G/T = -\Delta H°/T + \Delta S° - RlnK = 0 \qquad [13]$$

and compare both this and equation 12 with a proper accounting of the resulting entropy changes:[21]

$$\Delta S_t = \Delta S_e + \Delta S_s \qquad [14]$$

where ΔS_s is the entropy change of the closed chemical reaction system, ΔS_e is the entropy change of the surrounding environment, and ΔS_t is the total entropy change for the resulting isolated system corresponding to their sum, whence it is apparent that:

$$\Delta S_t = -\Delta G/T = dS/dx \qquad [15]$$

$$\Delta S_e \ = \ -\Delta H°/T \ = \ q/T \qquad\qquad [16]$$

$$\Delta S_s \ = \ (\Delta S° \ - \ RlnK) \ = \ (C \ - \ ARlnK) \qquad\qquad [17]$$

The absence of a minus sign in front of q in equation 16 reflects a difference in sign conventions for heats of reaction, as formulated by Thomsen in the 19th century, and our modern conventions for enthalpy changes[6], whereas the presence of the minus sign in equation 15 accounts for why maximization of the total entropy corresponds to minimization of the free-energy and vice versa.

7. Who was Horstmann? Since the life of Horstmann (figures 1 and 2) has recently become the subject of an excellent biographical monograph by Alexander Kipnis, all that is required here is a brief outline of its bare essentials.[22]
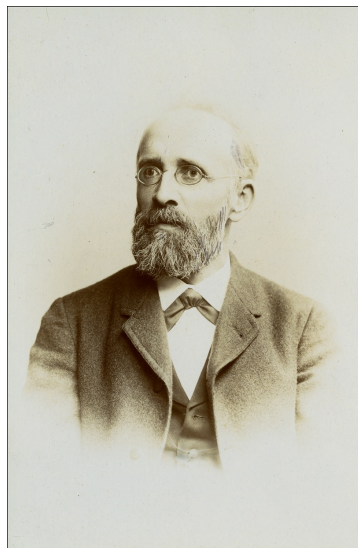

Figure 1. Typical portrait of Horstmann in middle age. (*Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati*).

August Friedrich Horstmann was born on 20 November 1842 in Mannheim Germany to a family of prosperous merchants. He entered the University of Heidelberg in 1862, where, despite the presence of such illuminaries of the future discipline of physical chemistry as Bunsen, Kopp, Kirchhoff and Helmholtz, he chose instead to study organic and theoretical chemistry in the private laboratory of Emil Erlenmeyer. Receiving his D. phil. in 1865, he did postdoctoral work under Rudoph Clausius at Zürich, where he learned thermodynamics, and under Hans Landolt at Bonn, where he learned the techniques for the experimental study of the vapor pressures of volatile liquids. Following a brief visit to Paris, where he met Regnault and Silbermann,

he returned once more to Heidelberg in 1867, where he presented a Habilitation thesis dealing with the relationship between the densities and molecular weights of vapors and was appointed as a Privatdozent. There he remained for the rest of his life, eventually becoming Professor of Theoretical Chemistry. He was 26 when he wrote his paper on the dissociation of ammonium chloride in 1869 and 30 when he wrote his definitive paper on the theory of dissociation in 1873. His productivity in later years was increasingly hampered by diminishing eyesight, and he was essentially blind when he died at age 86 on 10 October 1929.
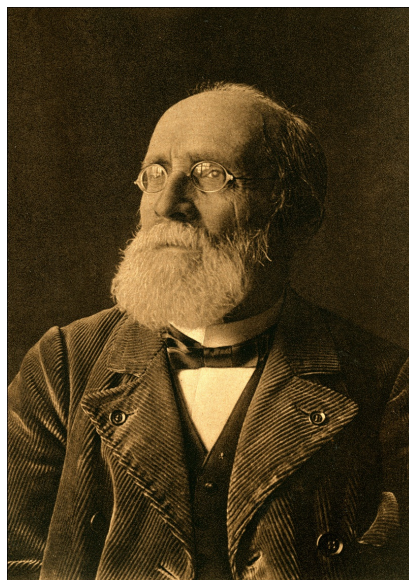

Figure 2. Typical portrait of Horstmann in old age. (*Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati*).

8. Why is He Forgotten? By the end of the 19th century, Horstmann's work was already being regularly mentioned in various histories of chemistry.[23] In 1903 his collected papers on the theory of dissociation were reprinted, under the editorship of van't Hoff, as part of Ostwald's series *Klassiker der exakten Wissenschaften*,[24] and he was accorded a 25-page obituary notice in the *Berichte* after his death in 1929, as well as numerous shorter notices in other journals.[25] Yet unlike Gibbs, for example, his name has all but vanished from the 20th- and 21st-century thermodynamics literature.

One important reason for this neglect is that Horstmann did little to propagate his explicit entropy approach to chemical equilibrium. Thus, in an important dictionary article on "Dissociation," which he wrote for the 1876 edition of Fehling's *Neues Handwörterbuch der Chemie*, he described Pfaundler's kinetic theory in detail, but dismissed the reference to his own work of 1873 with the comment that it was not

possible to describe in detail.[26] Though he published at least eight more papers on the theory of dissociation between 1876 and 1884, he made no further mention of his entropy equation, but rather reverted once more to the approach he had originally used in 1869 based on the Clausius-Clapeyron equation.[15, 16] Only in his 1885 text-book, *Theoretische Chemie,* did he once again make an explicit, albeit brief, mention of his entropy function.[27] However, this book never went beyond the first edition and, to the best of my knowledge, was never translated into other languages.

The reasons for this neglect were simple enough. All of the parameters in the Clausius-Clapeyron equation could be quantitatively evaluated using available experimental data, whereas the same was not true of the standard disgregation term (C) in Horstmann's entropy function. It would not be until the early decades of 20th century and the advent of the thermodynamic quantification program undertaken by G. N. Lewis and his associates at the University of California-Berkeley that both quantified entropy and free-energy data would become widely available.[28]

However, a far more important reason for this neglect was the fact that the 19th- and early 20th-century chemical community was extremely uncomfortable with the entropy concept, which is precisely why Horstmann's approach was so unique. Accustomed as we are today to a molecular interpretation of entropy as a measure of kinetic energy dispersion based on the quantum-statistical theory of thermodynamics, it is difficult for us to appreciate how little this physical point of view had permeated chemical and engineering circles by the end of the 19th century and how abstract the purely phenomenological definition found in typical textbooks of the period appeared to the average student of chemistry and engineering. As the engineer, James Swineburne, lamented in 1903:[29, 30]

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 seem 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.

Initially the free-energy function introduced by Gibbs in 1875, which also contained an explicit entropy term, fared little better.[31] French and German translations of Gibbs' epic memoir were made available by Ostwald and Le Chatelier in 1892 and 1899 respectively,[32, 33] but the succinctness and rigor of Gibbs' mathematical approach made his work largely inaccessible to the average chemist. Although he would become a virtual icon among physical chemists by the 1920s, this was, as Wilder D. Bancroft observed in 1926, largely a result of their having retrospec-

tively uncovered in his memoir ideas and concepts which they had discovered independently via a much less rigorous and more tortuous path:[34]

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.

While it is true that Planck had used an explicit total entropy function in his 1897 textbook on thermodynamics,[35] and both Duhem[36] and van Laar[37] had written early monographs arguing for the use of the Gibbs free-energy function (1886, 1906), most chemists of this period preferred instead to discuss the thermodynamics of chemical equilibrium in terms of the "Arbeit" or "Affinity" (*A*) functions and osmotic pressure analogs advocated in the influential writings of Nernst and van't Hoff. Though mathematically equivalent to the functions of Horstmann, Planck, and Gibbs, these approaches completely disguised the role of the entropy function in chemical reactions by making it implicit rather than explicit.

Thus Nernst preferred to use "the more intelligible" notion of maximum work (*A*) or Helmholtz free energy and always used its temperature coefficient, (dA/dT), rather than $-\Delta S°$ when writing his Arbeit function:[38]

$$-RTlnK \; = \; A \; = \; U + T(dA/dT) \tag{18}$$

Even more eclectic was van't Hoff, who preferred an approach formally analogous to the standard equation for the interconversion of heat and work in a steam engine!:[39]

$$-RTln\,K \; = \; A \; = \; Q(T_{eq} - T)/T_{eq} \tag{19}$$

where Q is the heat of reaction, T_{eq} is the equilibrium temperature for the reaction (i.e., the temperature at which $A = 0$), and T is the actual temperature at which the reaction is being run. At other times he preferred to use the gas law and his famous equation for osmotic pressure to calculate the work required convert the initial system into one at equilibrium via a series of expanding and contracting pistons and

selective osmotic membranes assembled in an imaginary device known as an "equilibrium box" (see figure 3) – which calls to mind the famously sarcastic comment by Lewis and Randall concerning so-called "cyclic processes limping about eccentric and not quite completed cycles."[28]

Figure 3. Typical example of a van't Hoff equilibrium box. (*Image courtesy of the Oesper Collections in the History of Chemistry, University of Cincinnati*).
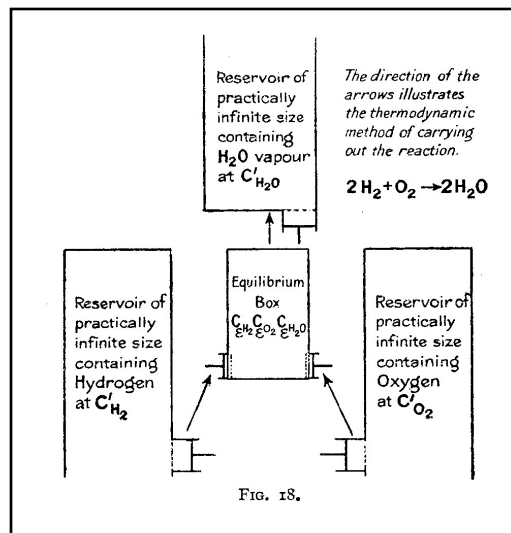
Indeed, an informal survey of introductory physical chemistry textbooks and chemical thermodynamics texts published between 1893 and 1933, showed that 70% preferred the "Arbeit" or work approach of Nernst and van't Hoff, 22% used either Gibbs or Helmholtz free energy with $\Delta S°$ explicitly given, 8% used neither, and 40% contained no index entry for entropy. It is, of course, the famous 1923 textbook of chemical thermodynamics by Lewis and Randall in the United States[28] and its advocacy by Hudleston in Great Britain[40] which are generally credited with having finally made ΔG and $\Delta S°$ an inherent part of every chemist's thinking.

A third and final reason for this neglect lies in the descriptions of Horstmann's contributions found in the average history of chemistry text, whether written during his lifetime[23] or subsequently.[41] Though all of these acknowledged his contributions to the theory of dissociation and often mentioned his use of the Clausius-Clapeyron equation, almost none of them, including the account of his life appearing in the prestigious *Dictionary of Scientific Biography*,[42] called explicit attention to his pioneering application of the *(dS/dx)* function to the theory of chemical equilibrium in general. An exception is the 1952 history by Eduard Farber, which was, in fact, responsible for first drawing the present author's attention to this subject.[43]

9. What Goes Around Comes Around. Given Horstmann's almost total disappearance from the 20th-century thermodynamics literature, it is somewhat ironic that several developments in this field during the past century strongly resonate with Horstmann's original approach:

1. The introduction by De Donder in 1920 of the extent of reaction parameter (ξ) and his replacement in certain situations of the ΔG symbol with the differential $dG/d\xi$ - a distinction which greatly clarifies the relationship between the ΔS_t and ΔG terms in equation 15 and Horstmann's own use of dS/dx:[44]

$$\Delta S_t = -\Delta G/T = -(dG/d\xi)/T = dS/d\xi \qquad [20]$$

This unfortunate dual usage of the Δ symbol was characterized by Bent in 1973 as "a weed in the garden of thermodynamics" and has since become a subject of some interest in the chemical education literature.[45]

2. The widespread use since the 1960s of a qualitative molecular disorder interpretation of entropy in introductory chemistry courses in order to address, like the original qualitative molecular disgregation interpretation of entropy used by Clausius and Horstmann, Swinburne's "missing physical basis" lament. Of course neither the disorder nor the disgregation interpretations of entropy are absolutely identical to the more sophisticated energy dispersion picture provided by modern statistical mechanics and, as Lambert has repeatedly pointed out, the disorder picture, in particular, can lead to a number of incorrect conclusions if pressed too far.[46]

3. The proposal by Rosenberg and Klotz in 1999 that ΔG be replaced by an explicit total entropy function, which they have called the "Planck function" in honor of Planck's use of such an approach in his textbook of 1897, and which they have also since incorporated into the most recent edition of their own popular thermodynamics text.[47, 48] They seem unaware that this approach was already used by van Laar in his thermodynamics text of 1893 and that he had already dubbed it the "Planck potential."[37] Of course, both terms are, as we have seen, historically inaccurate and a more appropriate name choice would be either the Horstmann function or, perhaps, the Horstmann-Planck potential. As any historian is aware, such historical misattributions are rampant in the textbook literature, where they function as perfect examples of Stigler's famous law of eponymy.[49] In addition, there are problems with interfacing this approach with the absolute rate theory of chemical kinetics, as it requires that activation barriers be replaced with entropy sinks.[50]

10. References and Notes

1. First presented at the 193rd National Meeting of the ACS in Denver, CO, 5-10 April 1987 and in revised form at the 236th National ACS Meeting in Philadelphia PA, 17-21

August 2008 as part of the Edelstein symposium in honor of Sir John Rowlinson.

2.   One of the difficulties in reading Horstmann is that his choice of symbols often conflicts with modern thermodynamic conventions. Thus the modern use of Q for reaction quotient will conflict with Horstmann's use of this letter to represent heat of reacton at constant T and P, now symbolized as ΔH. Likewise Horstmann often uses the same symbol to represent more than one quantity. Thus he uses q not only for standard heat of reaction ($\Delta H°$) but also, via Guldberg and Waage, to represent (along with q') the solution concentrations of various reactants and products, as well as p to represent not only partial pressure, but also (again via Guldberg and Waage) solution concentration, etc. Consequently the reader must always be aware of the immediate context in which a particular symbol is being used. It should also be noted that similar examples of context related redundancies also occur in modern thermodynamics, such as the continued use of Q for heat, when discussing Clausius' original formulation of the second law in terms of the quantity Q/T.

3.   L. Médard, H, Tachoire, *Histoire de la thermochimie*, Université de Provence: Aux-en-Provence, 1994.

4.   R. Fox, *The Caloric Theory of Gases from Lavoisier to Regnault*, Clarendon: Oxford, 1971.

5.   Y. Elkana, *The Discovery of the Conservation of Energy*, Harvard: Cambridge, MA, 1974.

6.   Thomsen's work is summarized in J. Thomsen, *Thermochemische Untersuchungen*, 4 Vols., Barth: Leipzig, 1882-1884.

7.   Berthelot's work is summarized in M. Berthelot, *Essai de méchanique chimique fondée sur la thermochimie*, 2 Vols., Dunod: Paris, 1879; and in M. Berthelot, *Thermochimie: données et lois numériques*, 2 Vols., Gauthier-Villars: Paris, 1897.

8.   D. S. Cardwell, *From Watt to Clausius: The Rise of Thermodynamics in the Early Industrial Age*, Cornell University Press: Ithaca, NY, 1971.

9.   M. Goupil, *Du flou au clair: histoire de l'affinité chimique*, Comité des Travaux Historiques et Scientifiques: Paris, 1991.

10. G. Liveing, *Chemical Equilibrium the Result of the Dissipation of Energy*, Deighton, Bell and Co.: Cambridge, 1885.

11. F. L. Holmes, "From Elective Affinities to Chemical Equilibrium: Berthollet's Law of Mass Action," *Chymia*, **1962**, *8*, 105-145.

12. The work of the Deville school is summaried in H. Sainte-Claire Deville, "Leçons sur la dissociation (18 Mars et 01 Avril 1864)," in Société chimique de Paris, *Leçons de chimie*, Hachette: Paris, 1866, pp. 255-378 , and H. Sainte-Claire Deville, "Leçons sur l'affinité (28 Févier et 06 Mars 1867);" *Ibid.*, 1869, pp. 1-85.

13. L. Pfaundler, "Beitrag zur chemischen Statik," *Ann. Physik*, **1867**, *131*, 55-85. See also E. W. Lund, "Activated Complex – A Centenarian?," *J. Chem. Educ.*, **1968**, *45*, 125-128.

14. A. Horstmann, "Zur Theorie der Dissociationserscheinungen," *Berichte*, **1868**, *1*, 210-215.

15. A. Horstmann, "Dampfspannung und Verdampfungswärme der Salmiaks," *Berichte*, **1869**, *2*, 137-140.

16. A complete bibliography of Horstmann's publications may be found in reference 22, pp. 185-188.

17.   A. Horstmann, "Theorie der Dissociation," *Ann. Chem. Pharm.*, **1873**, *170*, 192-210. An English translation appears in this issue on pages 76-82.

18.   R. Clausius, "On the Application of the Theorem of the Equivalence of Transformations to the Internal Work of a Mass of Matter," *Phil. Mag.*, **1862**, *24* [Series 4], 81-97 and 201-213.   Reprinted in R. Clausius, *The Mechanical Theory of Heat*, Van Voorst: London, 1867, pp. 215-266.

19.   Previously the gas law had been written using the volume per gram rather than per mole. Under these circumstances the value of R is no longer universal, but varies from gas to gas. Rather remarkably, many physics texts continued to use this specific approach to the gas law well into the 20th century. See W. B. Jensen, "The Universal Gas Constant R," *J. Chem. Educ.*, **2003**, *80*, 731-732.

20.   G. Bredig, Ed., *Die Gesetze des chemischen Gleichgewichtes für verdünnten, gasformigen oder gelösten Zustand von J. H. van't Hoff*, 2nd ed., Engelmann: Leipzig, 1913.

21.   I. Prigogine, R. Defay, *Chemical Thermodynamics*, Longmans, Green & Co: London, 1954.

22.   A. Kipnis, *August Friedrich Horstmann und die physikalische Chemie*, ERS Verlag: Berlin, 1997. This also contains a far more detailed discussion of the thermochemical and thermodynamic context of Horstmann's contributions than is given here. Unfortunately, aside from a few short entries in various biographical dictionaries (see reference 42), there is no full-length biographical account of Horstmann''s life available in English.

23.   See for example, E. von Meyer, *A History of Chemistry from the Earliest Times to the Present Day*, Macmillian: London, 1898, pp. 492, 521, 595; and A. Ladenburg, *Lectures on the History of the Development of Chemistry Since the Time of Lavoisier*, Alembic Club: Edinburgh, 1900, pp., 304, 316, 333.

24.   J. H. van't Hoff, Ed., *Abhandlungen zur Thermodynamik chemischer Vorgänge von August Horstmann*, Engelmann: Leipzig, 1903.

25.   M. Trautz, "August Horstmann," *Berichte*, **1930**, *63A*, 61-86. A complete list of other published obituaries and biographical sketches many be found in reference 22, p. 191.

26.   A. Horstmann, "Dissociation" in H. von Fehling, Ed., *Neues Handwörterbuch der Chemie*, Vol. 2, Vieweg: Braunschweig, 1875, pp. 988-1004.

27.   A. Horstmann, *Lehrbuch der physikalischen und theoretischen Chemie, II. Theoretische Chemie*, Vieweg: Braunschweig, 1885, pp. 712-721. This was volume 2 of the 3rd edition of multivolume series *Otto-Graham's Ausführliches Lehrbuch der Chemie*. Volume 1 on chemical physics was authored by A. Winkelmann.

28.   G. N. Lewis, M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, NY, 1923.

29.   J. Swinburne, *Entropy or Thermodynamics from an Engineer's Standpoint and the Reversibility of Thermodynamics*, Dutton: New York, NY, 1903.

30. Even as Swinburne wrote steps were being taken to provide accessible popular accounts for engineers of the statistical interpretation of entropy based largely on Planck's extension of Boltzmann's original work. See, for example, J. F. Klein, *Physical Significance of Entropy or of the Second Law*, Wiley: New York, NY, 1910.

31. J. W. Gibbs, "On the Equilibrium of Heterogeneous Substances," *Trans. Conn. Acad.*, **1875-1876**, *3*, 108-248; *Ibid.*, **1877-1878**, *3*, 343-524. Reprinted in *The Scientific Papers of Willard Gibbs*, Vol. 1, Longmans, Green & Co.: London, 1906, pp. 55-353.

32. J. W. Gibbs., *Thermodynamische Studien*, Veit: Leipzig, 1892.

33. J. W. Gibbs, *Équilibre des systèmes chimiques*, Carré et Naud: Paris, 1899.

34. W. D. Bancroft, "Physical Chemistry," in C. A Browne, Ed., *A Half Century of Chemistry in America, 1876-1926*, American Chemical Society: Easton, PA, 1926, pp. 89-110.

35. M. Planck, *Vorlesungen über Thermodynamik*, Veit: Leipzig, 1897. An English translation is available as M. Planck, *Treatise on Thermodynamics*, Longmans, Green Co: London, 1917.

36. P. Duhem, *Le potentiel thermodynamique et ses applications a la méchanique chimique et à l'étude des phénomènes électriques*, Hermann: Paris, 1886.

37. J. J. van Laar, *Sechs Vorträge über das thermodynamische Potential*, Vieweg: Braunschweig, 1906. Previously van Laar had favored the use of Planck's total entropy function. See J. J. van Laar, *Die Thermodynamik in der Chemie*, Engelmann: Leipzig, 1893 and J. J. van Laar, *Lehrbuch der mathematischen Chemie*, Barth: Leipzig, 1901.

38. W. Nernst, *Theoretical Chemistry From the Standpoint of Avogadro's Rule and Thermodynamics*, Macmillan: London, 1895, pp. 17-18, 42, 45, 90, 105, 136, 552, etc.

39. J. H. van't Hoff, *Etudes de dynamique chimique*, Muller: Amsterdam. 1884, pp. 178-179, 192, 195, 199, 202-209.

40. L. J. Hudleston, *Chemical Affinity*, Longmans, Green & Co: London, 1928.

41. See, for example, A. Ihde, *The Development of Modern Chemistry*, Harper & Row: New York, NY, 1965, p. 404-405, and J. Partington, *A History of Chemistry*, Vol. 4, Macmillan: London, 1964, p. 618.

42. O. J. Drennen, "August Friedrich Horstmann," in C. C. Gillispie, Ed., *Dictionary of Scientific Biography*, Vol. VI, Scribner's: New York, NY, 1972, pp. 519-520.

43. E. Farber, *The Evolution of Chemistry*, Ronald Press: New York, NY, 1952, pp. 211-212.

44. Th. de Donder, *Leçons de thermodynamique et de chimie*, Gauthier-Villars: Paris, 1920. A more accessible account may be found in Th. De Donder, P. van Rysselberghe, *Thermodynamic Theory of Affinity*, Stanford University Press: Palo Alto, CA, 1936.

45. H. A. Bent, "The First Law for Scientists, Citizens, Poets and Philosophers," *J. Chem. Educ.*, **1973**, *50*, 323-328. See also J. N. Spencer, "ΔG and $dG/d\xi$," *J. Chem. Educ.*, **1974**, *51*, 577-579 and R. S. Treptow, "Free Energy versus Extent of Reaction: Understanding the Difference Between ΔG and $dG/d\xi$," *J. Chem. Educ.*, **1996**, *73*, 51-54.

46. F. Lambert, "Shuffled Decks, and Disorderly Dorm Rooms - Examples of Entropy Increase? Nonsense!", *J. Chem. Educ.*, **1999**, *76*, 1385-1388; and F. Lambert, "Disorder - A Cracked Crutch for Supporting Entropy Discussions," *J. Chem. Educ.*, **2002**, *79*, 187-192.

47. R. M. Rosenberg, I. M. Kotz, "Spontaneity and The Equilibrium Constant: The Advantages of the Planck Function," *J. Chem. Educ.*, **1999**, *76*. 1448-1451.

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49. I. M. Kotz, R. M. Rosenberg, *Chemical Thermodynamics: Basic Concepts and Methods*, 7th ed., Wiley: Hoboken, NJ, 2008.

50.   W. B. Jensen, "Reaction Feasibility and the Planck Function," *J. Chem. Educ.*, **2000**, *77*, 1411.

11. Update

I have only recently (2015) become aware of the 1977 article by H. A. M. Snelders ("Dissociation, Darwinism and Entropy," *Janus*, **1977**, *64*, 51-75) which also discusses Horstmann's entropy treatment of dissociation reactions. Likewise for 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 slow entrance of entropy into the chemical literature and independently reaches many of the same conclusions as I have in this and other papers dealing with the history of chemical thermodynamics.

Lastly, in Section 9 I failed to point out the modern nature of Horstmann's molecular rationale for equilibrium based on his application of the disgregation concept to the case of dissociation reactions involving both gaseous reactants and gaseous products – namely that both the reactants and products are simultaneously attempting to increase their degree of disgregation or entropy of dilution, as we would say today. As the reaction proceeds, the reactants become increasingly dilute and thus their entropies of dilution increase, but at the same time the products become increasingly concentrated, so their entropies of dilution decrease. At some point these two entropy changes balance and the system comes to equilibrium before the reaction goes to completion. Though the insight that both the entropy maximum and the equilibrium state are due to the mixing of the various reactant and product gases can be found in a few modern textbooks (see for example, K. Denbigh, *The Principles of Chemical Thermodynamics*, Cambridge University Press: Cambridge, 1956, pp. 134-135), its true significance is often disguised by the misconception – due to the popular disorder interpretation of entropy – that mixing in and of itself always leads to an entropy increase. In fact, mixing will lead to an entropy increase only if the act of mixing also results in the two components undergoing mutual dilution. In other words, the entropy increase is due to the entropy of mutual dilution and not to the supposedly greater disorder of the mixture itself. See, E. F. Meyer, "Thermodynamics of 'Mixing' of Ideal Gases: A Persistent Pitfall," *J. Chem. Educ*, **1987**, *64*, 676.