Georg Helm's Chemical Energetics

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Abstract: This essay has three interrelated goals: first, to sketch the basic contours of Georg Helm's energetic theory; second, to describe his attempt in his *Grundzüge der mathematischen Chemie. Energetik der chemischen Erscheinungen* (1894) to apply that theory to the (then) burgeoning new field of physical chemistry. This is of some interest historically, since Helm's work is the most sophisticated attempt to develop the whole of physical chemistry mathematically from an energetic point of view. Nevertheless, it is seriously flawed technically. Moreover, that development is inconsistent with Helm's considered way of thinking about energy and energetic change. So a third goal of the essay is to explain his mature conception of the goal of energetics. I begin with a brief introduction to Helm and energetics, and end with some general conclusions about the success of Helm's *mathematische Chemie*.

Keywords: *energetics, Georg Helm, mathematics in chemistry, Wilhelm Ostwald, physical chemistry*.

1. Introduction

Georg Helm spent his entire professional life in his native Dresden. Born there in 1851, he was educated in mathematics and physics at the city's Polytechnical Institute, studying principally with Gustav Zeuner, and for three years at the Universities of Leipzig and Berlin, where he attended the lectures of Wilhelm Henkel, Karl Neumann and probably those of Helmholtz. He received his doctorate from Leipzig in 1881 for a dissertation, written under Neumann, on differential equations in mechanics.

For nearly fourteen years, beginning in 1874, Helm taught mathematics and physics at the Annenschule in Dresden, where he was instrumental in the reform of physics education. He left in 1888 to become extraordinary professor of analytical geometry, analytical mechanics, and mathematical physics at the Polytechnicum, remaining there until 1892 when he was appointed ordinary professor of these subjects at the newly founded Technische Hochschule. Helm retained this title for fifteen years, until 1906, when he

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was named professor of applied mathematics, a position he held until his retirement in 1919. He died in Dresden in 1923 after an academic career spanning half a century.

Helm's early research, reflecting the influence of Zeuner, Neumann, and the mathematician Gustav Schlömilch, was at the interface between mathematics and physics. It also reflected the wide range of his teaching responsibilities. He investigated problems in analytical mechanics and mathematical physics, including gravitational theory, as well as in the theory of probability. A widely used textbook, *Die Elemente der Mechanik und mathematischen Physik*, based on lectures at the Polytechnicum, was published in 1884. Later publications include papers on the electron theory and Einstein's special relativity principle and longer treatises on electrodynamics and the fundamental principles of higher mathematics. He is probably best known, however, for his systematic development and vigorous defense of energetics.[1]

Since the subject of energetics is likely unfamiliar to many contemporary readers, a bit of context may prove useful.[2] The great unsettled question of late nineteenth-century physics was the status of the mechanical world view. For more than two hundred years – from Descartes, Huygens, and Newton in the seventeenth century to Helmholtz, Hertz, and Boltzmann at the end of the nineteenth – physicists had usually sought mechanical explanations for natural phenomena. Indeed, as the nineteenth century drew to a close, Heinrich Hertz reaffirmed the classical goal of physical theory: "All physicists agree," he wrote, "that the problem of physics consists in tracing the phenomena of nature back to the simple laws of mechanics" (Hertz 1894, p. iii). But when these words appeared, there was in fact no longer general agreement among physicists about the nature of their project. Many doubted, and some explicitly denied, that mechanics was the most basic science; other candidates for that honor – thermodynamics and electromagnetic theory, in particular – were seriously considered; and comprehensive alternatives to the mechanical world view were proposed and vigorously debated throughout the 1890's and early 1900's.

Energetics was one of the alternatives. Tracing its origins to the founders of the law of energy conservation, especially Robert Mayer, and to the thermodynamic writings of Clausius, William Thomson and Gibbs, energetics was an attempt to unify all of natural science by means of the concept of energy and of laws describing energy in its various forms. The energeticists believed that scientists should abandon their efforts to understand the world in mechanical terms, and that they should give up atomism as well, in favor of a new world view based entirely on the transfers and transformations of energy.

The emergence of energetics was largely, if not entirely, a German phenomenon. Its main proponents were Helm and Wilhelm Ostwald, the professor of physical chemistry at Leipzig. Helm first urged the formulation of a 'general energetics' in his *Die Lehre von der Energie* (1887), which proposed an 'energy principle' (a law allegedly more general that the usual law of energy conservation) as its basis. An essay in 1890 sought to reduce mechanics to energetics by means of this principle, and another in 1892 was intended to do the same for electricity and magnetism. An exploratory note (Helm 1893) anticipated a book on the energetic development of physical chemistry (Helm 1894). These publications, plus more wide-spread interest in energetics, led to an invitation to address the 1895 Lübeck meeting of the German Association of Scientists and Physicians on the "current state of energetics" (1895a, b).

The heated debate at the Lübeck meeting proved to be a disaster for energetics and an unhappy occasion for Helm personally. It and he were apparently attacked from all sides (see Deltete 1999). Helm was offended and deeply hurt. The situation worsened when the physicists Ludwig Boltzmann and Max Planck quickly recorded their negative appraisals of energetics in the *Annalen der Physik* (Boltzmann 1896a; also b, c & 1898; Planck 1896). Given what he thought had happened to him in Lübeck – that he had been set up, lured into a trap – Helm was outraged. He responded with a vigorous reply (Helm 1896), as did Ostwald (1896), apparently his only Lübeck ally. And two and a half years later, Helm recounted the evolution of energetics, and his contribution to it, in a book-length history of the subject (Helm 1898, 2000; see Deltete 2000b for a 'reading guide' to Helm's book).

Helm's history is not the subject of this essay, but the conception of the task of energetics that he defended in it is, since it is inconsistent with his application of energetic theory to physical chemistry. Accordingly, I describe that conception (which I call his 'official position') in Section 2, and do so by contrasting it with Ostwald's very different conception. In Section 3, I sketch the basic contours of Helm's energetic theory, which is of some historical interest as a novel view of physical theory, before turning in Section 4 to his application of that theory to the (then) burgeoning new field of physical chemistry. Helm's 1894 book on physical chemistry, *Grundzüge der mathematischen Chemie. Energetik der chemischen Erscheinungen*, is also of historical interest, since it is the most sophisticated attempt to develop the entire field from an energetic point of view. Nevertheless, I argue in Section 4 that Helm's efforts here were seriously flawed. Sections 4 and 5 also reveal in some detail how his development of an energetic physical chemistry is inconsistent with his 'official position' on the goal of energetic theory. In Section 6, I draw some general conclusions about the nature and viability of Helm's project for a mathematical chemistry.

2. Helm on the Goal of Energetics

The conception of energetics that Helm sought to defend and promote in 1898 was one he attributed, in nascent form, to the physician Robert Mayer. That conception is perhaps best approached by contrasting his interpretation of Mayer with Ostwald's, since this approach has the added advantage of highlighting some fundamental differences between Ostwald's vision of a science of energy and Helm's own.

Helm and Ostwald included all of the pioneers of energy conservation among the founders of energetics, but they both accorded a special place of honor to Robert Mayer. Sometimes, their reasons for doing so coincided. Each admired the boldness and independence of Mayer's thought, his skeptical attitude toward prevalent molecular and mechanical hypotheses, and the way he steadfastly opposed any attempt to reduce heat to a form of mechanical energy. Above all, each praised Mayer's insight that all natural phenomena are really energy transformations and his vision of a unifying science of energy. But, at the same time, they disagreed fundamentally about the content of his insight and the meaning of his vision.

When Helm praised Mayer in 1898 for the clarity of his insight into a fundamental principle, it was for adumbrating the possibility of a science of energy that was a "pure system of relations", exemplifying a phenomenalism of the sort championed by Ernst Mach (Helm 2000, p. 80). Mayer had founded "a new world view," Helm claimed, that was both energetic and phenomenalist in orientation (*ibid*., p. 26). Like Mach, that is, Mayer was interested only in quantitatively describing and relating the data of experience – the phenomena. Eschewing any metaphysical references to underlying substances or causes, he was satisfied to show that "a relationship exists in consequence of which one phenomenon decreases in favor of another, or increases at its expense" (*ibid*., p. 84). But Mayer went beyond Mach in suggesting that all our experience, and so all phenomena, are the outcomes of energy relations. That was his "fundamental energetic idea" (*ibid*., p. 76).

This interpretation is fanciful, and, in any case, it conflicts with Helm's earlier assessment of Mayer (see Helm 1887, pp. 14-15). But that is not my concern here. Instead, I want only to clarify the view Helm attributed to Mayer in 1898, because then Helm clearly *did* think that a "pure system of relations can be achieved by means of energetics," and *this* was the "fundamental energetic idea" that *he* sought to develop, defend, and promote in his history of the subject (*e.g.*, Helm 2000, pp. 253, 263, 400-404). For reasons to be discussed shortly, I will call this Helm's 'official position' on the goal of energetics and collect its main features under one heading, which I shall call the 'Relations Thesis' (RT)

There are epistemological, methodological, and anti-metaphysical dimensions to RT. First, it claims that we can only know phenomena and changes in phenomena, all of which are energetic in character. Second, it claims, in consequence, that the goal of natural science is to describe and relate energy phenomena in the simplest and most unified manner possible. Accordingly, a general theory of energy, or energetics, will relate the phenomena in terms of simple, unifying principles, such as the law of intensity and the factorization principle, properly construed (see Section 3). Third, RT rejects all inferences to anything 'behind' or 'beneath' the phenomena, whether it be atoms or forms of energy. Specifically, it rejects all efforts to substantialize energy or to reify energetic changes in terms of 'migrations', 'transitions', 'transformations', 'conversions', or what have you.

According to RT, the concept of energy – like any other genuine physical concept – is empirical and relational, as is the law of its conservation. The energy law was essential to Helm's version of energetics as we shall see in the next section, even if it was not its basic principle; but for him that law only expressed empirically verified, quantitative correlations between different energetic phenomena. Unverifiable inferences to the existence of an indestructible substance underlying the phenomena were ruled out – dismissed as metaphysical speculation – as were any inferences beyond what has been empirically confirmed. "With the pronouncement 'The energy of the world is constant'", Helm remarked of Clausius' dictum, "the firm footing of the energy law is abandoned, according to which this law is nothing more than an empirical relation between measurable quantities that we find present in any natural process. And for this sacrifice, absolutely nothing is gained in returned but an empty saying." He then extended this conclusion to include Clausius' other well-known statement concerning the entropy of the world, that it "tends to a maximum", commenting that while both had no doubt encouraged a livelier study of energy and entropy than "sober claims that try to express the true importance of these concepts", they were, in fact, "nothing more than metaphysical aberrations" (*ibid*., p. 176).

RT thus expressed *all* there is to energetics; but to Helm, writing in 1898, that is all that is *needed and warranted*. And he portrayed Mayer as its first significant advocate:

> Mach has repeatedly and justifiably warned of the *mysticism* associated with the word 'transform' that has sometimes tried to make its way into energetics. But it emerges clearly from the above words [of Mayer] that, judged by his manner of thinking, the *founder* of energetics does not need this warning, although the way he expressed himself in his writings has given some of his followers occasion for misunderstanding. In the sense of its founder, energetics is a pure system of relations (*ein reines Beziehungstum*) and is not out to place a new absolute in the world. When changes occur, *this* definite mathematical relationship still exists between them – That is the guiding formula of energet-

> ics, and certainly it is the only formula of all true knowledge of nature. What goes beyond it is fiction. [*Ibid*., pp. 79-80]

Ostwald disagreed. In his view, Mayer's most important contribution to energetics was to have ascribed reality and substantiality to energy as well as matter. *That* was the 'essential insight' that Ostwald sought to promote and develop in his first writings of energetics, but obstacles had made this difficult. Sometimes Ostwald claimed that Mayer's insight had been obscured by subsequent developments of the energy concept, especially in thermodynamics, where he thought that energy often tended to be regarded more as an interesting mathematical function, comparable to the potential function in mechanics, than as a physical reality. Usually, however, he put the blame elsewhere: "One may undoubtedly explain this as a consequence of the rapidly spreading mechanistic conception of nature" (Ostwald 1887; see 1904, pp. 192-193), a way of thinking he found harder to overcome.

Whatever the reason, Ostwald initially only wanted to recover and underline the importance of Mayer's 'basic idea': that energy is as real and fundamental as matter. Within a few years, though, he was converted to the way of 'pure energetics' and began to defend in his writings the idea that *only* energy is substantial and real. "The more I reflected on the nature of energy," Ostwald wrote in 1891, "the clearer it became to me that matter is nothing but a complex of energy factors" (Ostwald 1891, p. 566). Given that realization, he concluded that a genuine energetics had to do more than treat energy as "a real substance and not just a mathematical abstraction" (*ibid*.); it had to acknowledge energy as the *ultimate* substance and the *only* reality.

Helm's RT was likely on Ostwald's mind, therefore, when he later reflected on the historical evolution of energetics. After proclaiming that his own development of the subject had not only opposed the "sterility of unbridled mechanism", but had also sought to remove energy from "the realm of mathematical abstraction and to view it as the real substance of the world", Ostwald then proceeded to criticize Helm's initiatives as "a retreat to a position even less progressive than Mayer's" (Ostwald 1926, vol. 2, pp. 157-158). For his own part, Helm clearly had large reservations about Ostwald's vision for energetics, but he confined them to correspondence (*e.g.*, Helm to Ostwald, 13 May 1893; Helm to Ostwald, 19 May 1895; in Ostwald 1961, pp. 75-76, 80-81). Still, there are many critical passages in his history that point in Ostwald's direction, even if Ostwald is not mentioned by name. Here is one example:

> I thus consider it […] to be the best thing about energetics that it is capable to a much greater degree than the old [mechanical] theories of adapting itself directly to our experiences; and I see in the attempts to attribute substantial existence to energy a dubious departure from the original clarity of Robert Mayer's views. There exists no absolute; only relations are accessible to our

> knowledge. Whenever the spirit of research has contentedly reclined on the sluggard's bed of any kind of absolute, it has immediately expired there. It may be a comfortable dream that our questioning can find rest in atoms, but it remains a dream! And it would be no less a dream if we wished to see in energy an absolute, instead of only the most striking expression up to now of the quantitative relations among the phenomena of nature. [Helm 2000, p. 401]

Helm's position on the status of energy was never as definite and consistent as these passages might suggest. In his writings on energetics, Helm vacillated between the ascetic phenomenalism of RT and some form of energetic realism, but two conclusion are reasonably secure. First, despite his explicit advocacy of RT (the 'official position') in 1898, he always spoke of the internal (or intrinsic) energy as if it were a substance. More precisely, he always attributed to a system, as a real possession, a definite internal energy, which was a function of its physical and chemical state (Helm 1887, pp. 50-51, 54, 56-57, 61-62; 1894, pp. 1, 58, 68-70, 113; 1898, pp. 226, 296-299). As late as 1894 in the *Grundzüge*, as we shall see in Section 4, Helm also seemed committed to another idea which I shall call the thesis of 'real presence' (Helm 1887, pp. 34-36, 42-44; 1894, pp.16, 24-28, 42-43, 58, 60, 70-73). The real presence thesis claims that the internal energy of a system can be divided into distinct components (mechanical energies, heat, chemical energies, and so on), each of which is physically present in the system. By 1895, however, he had rejected that thesis as physically unfounded, and, in fact, argued vigorously against it, insisting that a physical system no more possesses a definite amount of kinetic energy than it does of heat or volume energy. Thus in the report he prepared for the Lübeck meeting, Helm wrote:

> In general, one hesitates to ascribe forms of energy to a body as possessions, although this is often done. Strictly speaking, what a body possesses are its internal energy and the various [intensity and capacity factors], or the coordinates on which these [factors] depend. A form of energy, on the other hand, has reality only at the moment in which it passes from one body to another. Forms of energy as possessions of a body have only a mathematical meaning [Helm 1895a, p. xii].

So we may perhaps summarize the *Praxis* of Helm's history, in contrast to his official RT position, by saying that while he took for granted a substance view of internal energy, he opposed the thesis of real presence. That is, he treated the internal energy of a system as an undifferentiated 'something', but rejected the idea that it can be split up into physically distinct forms. Hence, his approval of P. G. Tait's criticism of Clausius: "We are quite ignorant of the condition of energy in bodies generally. We know how much goes in, and how much comes out, and we know whether at entrance or exit it is in the form of heat or work. But that is all" (Helm 2000, p. 172). The *appearance* of different forms of energy is a sign of internal energy in transition; however, such forms are not themselves really present in different amounts in the energy content of a body.

Ostwald evidently disagreed, but his own position is also difficult to reconstruct. From the early 1890's, when he first began to write in earnest on energetic theory, he officially subscribed to a view of matter's relation to energy that might be called the 'Composition Thesis'. On this view, 'material objects' (or 'bodies' or 'physical-chemical systems') are nothing more than energy complexes – spatially co-present and coupled clusters of energy. The Composition Thesis was undoubtedly central to Ostwald's conception of energetics; in fact, acceptance of it in some form or other constitutes much of what he later meant when he spoke of his conversion to "pure energetics" (Ostwald 1926, vol. 2, pp. 168-170). In his detailed discussions of energetic science, however, Ostwald employed a very different conception of matter's relation to energy. There he casually spoke of an object or system 'containing' (or 'possessing' or 'having') energy of certain kinds in certain amounts – as if a system were not the same as, but something in addition to, its energy content. In short, he assumed that objects or systems were 'containers' of energy. When he did so, moreover, he also usually just assumed, without comment, that every system contains definite amounts of distinct forms of energy (real presence) and that in each case the total energy content is given by the sum of the amounts of each form (really) present. This view, into which Ostwald slipped whenever he attempted to apply his energetic theory (see Deltete 2008 & 2010), might therefore be called the 'Containment Thesis'.

Gathering together these brief remarks, I may now quickly summarize the results of my comparison. In his 1898 history of energetics, Helm defended and promoted RT. This was his 'official position', and the one he thought has evolved, or was evolving, in the history of science. The scientific *Weltgeist* was moving in the direction of energetic phenomenalism. He ignored the fact that his own thought on the goal of energetics had changed (see Section 4) and that he continued to regard internal energy as both real and substantial. This looks like a version of what I have called the Containment Thesis; and it is, except that Helm, by 1895, opposed the thesis of real presence. By contrast, Ostwald embraced real presence, even when he denied that he was engaging in metaphysics (see Ostwald 1895). His 'official position' was what I have referred to as the Composition Thesis. For him, the scientific *Weltgeist* had moved, and continues to move, in the direction of energetic realism, that is, toward the recognition that energy is the only reality. He ignored the fact that his own applications of energetic theory were instead based on the Containment Thesis, in accordance with which material systems are at least as real as the energies they possess.

Certainly much more could be said about the contrasting views of Helm and Ostwald on the nature and goal of energetics, but enough has been said to put Helm's view in relief. From the standpoint of his RT official position, however, much of the language of the *Grundzüge*, which refers to 'transmissions' and 'diffusions' of distinct forms of energy, is at best misleading and at worst entirely misguided. That is, the application of Helm's energetic theory is at odds with his conception of the task of energetics. To better understand why, we first need to introduce that theory.

3. The Basics of Energetic Science in *Die Lehre* (1887)[3]

"From the standpoint of the energy idea, all changes or transformations in nature can be reduced to two kinds of change: they are in part *transfers* (*Übergänge*) of energy from one body to another, in part *transformations* (*Umformungen*) of energy from one form to another" (Helm 1887, pp. 50-51). Such transformations are all subject to the law of energy conservation, but that law says nothing about how changes occur and when. In fact, the energy law says little about the processes actually taking place in nature; it only states a condition that must be satisfied by any process if it is to occur, namely, that energy always be conserved (*ibid.*, pp. 51, 57-58).

What is needed, Helm thought, is some concept of 'tendency', analogous to vectorial forces in mechanics, that is able to specify which of all the possible changes compatible with the energy law actually occur. It is these *Übergangstendenzen* which determine when transfers of energy occur and, consequently, when transformations of energy may occur as well. In mechanics, where forces and pressures often account for energy changes, the idea of a tendency or striving to motion is especially clear in variational principles such as d'Alembert's Principle. But a special principle is needed in thermodynamics. That principle, that heat energy always spontaneously flows from higher to lower temperatures, formed the basis of Clausius' derivation of the second law of thermodynamics:

$$dQ \leq TdS \tag{1}$$

where Q, T, and S stand for absorbed heat, absolute temperature, and entropy, respectively, and where the inequality applies if the change is irreversible. If the energy law is now written in the form

$$dE = dQ + dA \tag{2}$$

where E represents internal energy (*Eigenenergie*) and A external work, these two results may be joined to yield

$$dE = TdS - pdV \quad (3)$$

the familiar differential form of the combined first and second laws of thermodynamics for reversible processes, or

$$dE \leq TdS - pdV \quad (4)$$

to include irreversible ones (*ibid.*, pp. 62-63).

Helm believed that this "perfected energy law" (*vervollkommnete Energiegesetz*) (*ibid.*, p. 52) clearly and concisely displayed the energy relations which characterize simple thermodynamic changes. If we ask why, he offers several reasons. First, it is an expression containing only the state variables of the system, the process dependent heat and work having been eliminated. Second, "the [internal] energy element […] appears as a sum of products" (*ibid.*). Finally, each of these products is resolvable into factors with analogous properties: S and V vary when the energy of the system changes, while p and T determine whether an energy change occurs at all (*ibid.*, pp. 53, 55, 61-62). Greatly impressed by the suggestiveness of these results, Helm was encouraged to undertake a general analysis of energy in its various forms.

The first main result of this analysis was the Factorization Principle, a defining feature of late nineteenth-century energetics. In Helm's version it asserts that the differential of every form of energy can be expressed in the form JdM, where J indicates the 'strength' or 'intensity' of the energy form, and M its 'amount' or 'magnitude' or 'quantity' (*ibid.*, p. 61). In the simple thermodynamic case described above, T and -p are the intensity factors of 'heat' energy and 'expansion' energy, respectively, and S and V their quantity (or, as he would later call them, capacity) factors (*ibid.*, pp. 59-60). Helm thought that the differentials of other forms of energy could be analyzed in the same way. For example, he wrote the differential of kinetic energy as $d(1/2mv^2) = v\,d(mv)$, where momentum (mv), the capacity factor, varies whenever kinetic energy is exchanged between two systems, and velocity (v), the intensity factor, must be different if they are to exchange that form of energy at all.

Each of the factors of an energy form thus has distinguishing features. The J's indicate the strength of a form's tendency to migrate from one place to another.[4] Energy transfers occur between two systems only when there exists a difference in intensity between them. Only then will energy of a given form pass from one to the other, and always from the higher to the lower intensity. The quantity, M, of an energy form in a system changes when it receives or gives off energy of the form in question. Moreover, these changes are supposed to take place in such a way that, in general, quantities released by one system are exactly balanced by quantities absorbed by other systems. In general, that is, the capacity factors of the various forms of energy are conserved. A conspicuous exception, of course, is entropy, the quantity factor of heat energy, which increases in irreversible processes; but irreversibility is apparently confined to thermal phenomena. Only heat has the peculiarity that its M factor is not conserved in many processes (*ibid.*, pp. 62-63).[5]

Armed with the Factorization Principle and his account of energy factors, Helm was ready to state a "general law of intensity" that would make his theory of energy "independent and free of propositions which hold true only for particular forms of energy". This law, a second major result of his *Lehre*, is expressed as follows: "*Any form of energy has the tendency to pass from places in which it is present in higher intensity to places of lower intensity*" (*ibid.*, p. 62). When joined with the energy law and the doctrine of energy forms and their factorization, that law determines the course of any natural process. One is first to ascertain what changes are *possible* by comparing the intensities of the energy forms of a system with those of its surroundings. Then, according to Helm, there follows for any virtual reversible change an equation of the form

$$dE = \sum JdM \qquad (5)$$

where the sum extends over all forms of energy involved in the change (*ibid.*, pp. 64-65). To include changes that are irreversible, (5) must be modified to read

$$dE \leq \sum JdM \qquad (6).$$

This is Helm's 'Energy Principle' (*Energieprinzip*), which allegedly stated more than the conservation of energy, and on which he hoped to base the whole of natural science.[6]

The basics of Helm's energetic theory may now be stated very briefly. All natural processes are transfers and transformations of energy in which the total energy is conserved. That energy, in turn, appears in different forms, each of whose differential admits of analysis into two factors: an intensity factor and a capacity factor, the former indicating the 'strength' of the energy form and the latter its 'amount'. Consequently, the energy transactions into which any system may enter with other systems depend on two parameters characterizing the 'state' of each energy form possessed by the participants. And those transactions themselves take place in accordance with two principles: the first, an intensity law, which governs the migration of energy, and a second principle requiring that the capacity factors of all forms of energy be conserved in any reversible change.

4. Energetics in *Die Grundzüge* (1894)

By 'mathematical chemistry' Helm meant that he intended to develop his subject in the same manner as he would a branch of mathematical, or theoretical, physics. He would show, that is, how "a few basic principles" could be so articulated as to yield "the results of recent investigations into the realm of general [read physical] chemistry" (Helm 1894, p. ii). The *Grundzüge* was therefore a theoretical work, whose aim was to collect together, to organize, and to unify a variety of physical-chemical findings within a single framework. Helm quickly indicated, moreover, that the central principle of that framework was his energy principle, which had played the same role in his earlier studies.

> That domain of the mathematical consideration of Nature, which in its beginnings was called physical chemistry, can, in its present state of development, be viewed from a general theoretical standpoint; and indeed, so viewed, it appears to be one of the clearest and most complete confirmations of the energy principle. [*Ibid.*, p. iii]

Helm admitted that certain parts of mathematical chemistry had been derived from other points of view – from molecular hypotheses of various sorts or from gas-theoretic analogies – with little or no reference to the energy principle, but he criticized these approaches as failing to promote the unifying goal of theoretical research. Instead, he urged an approach that was at once phenomenological and based on the study of energy, such as could be found, he thought, in "the theories of Gibbs":

> The return to Willard Gibbs and – so far as concepts are concerned with thermodynamics proper – to Horstmann, appears to me to be a purification of the scientific structure from ideas which have become unnecessary to it. In the light of a few fundamental concepts – held together by means of the energy principle – the whole [field of physical chemistry] attains a clarity and order, which is especially beneficial for a first introduction to the subject. [*Ibid.*, pp. iii-iv][7]

Helm's preface announced, in short, a theoretical study in "chemical energetics" ('*chemische Energetik*', *ibid.*, p. 4), whose goal was to bring the new field of physical chemistry within the mathematical framework of the science of energy.

An important part of Helm's work is devoted to articulating the energy principle, which serves as the central, unifying principle of his study. That principle was developed in stages as the investigation progressed, its scope gradually widening to include more forms of energy and more kinds of change. He first restricted his attention to those changes in which the internal energy of a body is altered only through gain or loss of heat or through increase or decrease of its volume, that is, to use his words, he attended only to processes involving changes in "heat energy" or "volume energy" (*ibid.*, part I). Retracing steps that I have already outlined in my discussion of his earlier work, he again reached

$$dE \leq TdS - pdV \tag{4}$$

his first version of the energy principle (*ibid.*, pp. 42-43). In this form the energy principle is said to govern any possible change, reversible or irreversible, involving only heat and volume energy. It indicates, for example, that the entropy of a system can never decrease during any possible change in which volume and energy are held constant, and that its energy, in turn, can never increase for any possible change in which entropy and volume remain constant. Moreover, analytical transformation of (4) yields a variety of expressions (such as what we should now call the enthalpy and the Gibbs and Helmholtz functions) applicable to changes in heat and volume energy in which temperature or pressure or both are held constant.

Helm's discussion of volume energy forms the basis for his discussion of other energy forms (1894, 14-18). It is the first form of energy that he considered in any detail and one soon realizes that, in this work if in no other, it has been accorded a sort of conceptual primacy. Helm used the results of his investigation of volume energy to determine the properties of other forms of energy, including not only heat, but electrical and chemical energy as well. We must, therefore, have a closer look at his discussion.

Helm appears to have accepted Ostwald's division of the so-called 'energies of position' (*Lagenenergien*) into distance, surface, and volume energy, but thought that the first two were relatively unimportant for his study. "On the other hand," he wrote,

> volume energy is of great importance in thermo-chemistry, because it can immediately be converted not only into kinetic energy, but also into heat. Fluids and gases, which, because of their simplicity, are the only bodies that are treated here, have the property that if no change takes place other than an increase in volume, their intrinsic energy decreases. And, indeed, the ratio of the energy decrease, $-dE_V$, to the volume increase, dV, in this case is given by the pressure, p, so that $-(dE_V/dV) = p$ and $dE_V = -pdV$. [*Ibid.*, p. 13]

To reveal the important features of volume energy, Helm asked his readers to consider the following arrangement (see Figure 1): A closed cylinder filled with a gas is divided into two parts, A and B, by a moveable piston, K. Assuming the A portion to have initial pressure p_1 and Volume V_1, and the B portion initial pressure p_2 and Volume V_2, Helm proposed to examine the changes in internal energy of the two gases when their volumes are changed. It seemed obvious to him that the internal energies of the gases change as a result of a change in their volume energies only if the pressures on the two sides of the piston are unequal. If, for example, we assume $p_1 > p_2$, then the volume energy of the gas in A decreases by $-p_2dV_2$, and the volume energy of the gas in B increases by p_1dV_1, where $dV_1 = -dV_2$ since the volume of the cylinder is constant. During the change, moreover, the greater pressure, p_1, decreases, while the lesser one, p_2, increases.

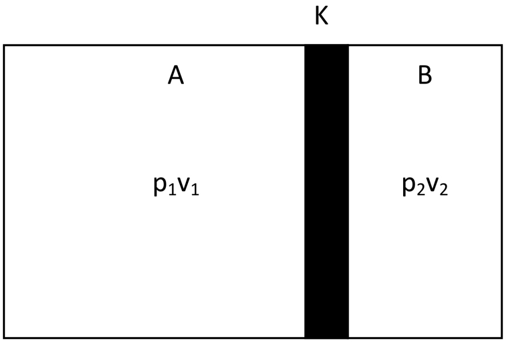

Figure 1: Illustration of changing 'volume energies' from Helm 1894, p. 24.

From this simple example Helm drew the following conclusions: First, that the volume of a body must be able to change for its internal energy to increase or decrease through a change in volume energy. In such a process, however, the sum of all the volumes involved in the change retains a fixed value – the constancy of quantity requirement of his earlier work. Second, that a change in the internal energy of a body through an increase or decrease of volume energy occurs only if there exists a difference in pressure between that body and others. This condition, a version of the earlier intensity law, he now expressed in the following way: "Every body shows a tendency, which increases with pressure, to diminish its pressure, so that, during any change, the greater pressure decreases, while the smaller one increases. Or briefly: Volume energy passes over from higher to lower pressures" ("*Oder kurz: die Volumenergie geht vom höheren Druck zum niederen über*", *ibid.*, p. 25).

This analysis has large problems. There is, first of all, Helm's tendency to substantialize volume energy, to regard it as migrating during changes of volume, and to treat it as a function of the state of a system – neither of which, I think, reflected his considered view. Since, moreover, the expression for volume energy, $-pdV$, can replace the differential work, dA, in equation (3) only for reversible processes, it is either inadmissible in formula (4) or the inequality, signifying irreversibility, in that formula is idle. Here, as elsewhere in his work on physical chemistry, Helm has conflated *internal* intensities (those exerted by a system on its surroundings) with *external* ones (those exerted by a system's surroundings on it), so that his expression for the energy principle does not apply to his example (see Section 4). Apparently unaware of these difficulties, however, Helm immediately generalized the conclusions drawn from that example, first to other changes of volume, and then to include other forms of energy.

Helm began by asserting, as he had done in his first work, that every form of energy can be analyzed into factors of intensity and quantity, but now volume energy served as the model for that analysis: "In general it can be shown that the change in internal energy, E, in any form can be represented as a product, JdM, where J has those properties that pressure has in volume energy, and M those which volume has in volume energy" (*ibid.*, p. 25). He then applied to heat energy the conclusions reached in his study of volume energy. Indeed, Helm sought to determine, by analogy, the properties of the former sort of energy from those of the latter. Here the central argument was designed to show that *since* volume, the quantity factor of volume energy, *increases* during irreversible change, entropy, the quantity factor of heat energy, may be expected to do as well (*ibid.*, pp. 26-8, esp. 28)!

That line of argument is astonishingly implausible. Not only does it conflict with Helm's own example, which presupposes that the total volume remains constant, but consistently applied, it requires the quantity factors of other forms of energy (such as mass and electrical charge) to increase in an irreversible process. Almost certainly, Helm would have rejected that implication; if pressed, in fact, he would likely have denied that volume behaves like entropy. (After all, the logic of the situation required him to argue that *since* volume is a conservative function, entropy *should* be as well.) Still, the later chapters of Helm's book *do* argue that the factors of other forms of energy behave analogously to those of volume energy.[8] I shall therefore look briefly at the two forms receiving the most attention, electrical energy and chemical energy.

A chapter devoted to the 'relations between heat and electrical energy' outlined an energetic theory of electrical current and the galvanic cell. The first result of Helm's investigation was another version of the energy principle, relating heat and electrical energy,

$$dE \leq TdS - \Delta d\varepsilon \qquad (7)$$

where Δ is the electromotive force between two plates of a capacitor, and $d\varepsilon$ represents the charge transferred between the plates. Of this result he remarked: "Now the equation [(7)] already stands, in its form and in the physical significance of its quantities, in such complete analogy with the equation [$dE = TdS - pdV = dQ + dA$] that the conclusions developed [for the latter] may, without further ado, be carried over to it" (*ibid.*, p. 60) But this assertion is misleading at best. Again Helm does not mention – does not even seem to notice – that the replacement of dA by $-\Delta d\varepsilon$ in (2) is permissible only if, as the equation in his remark suggests, the change being described is a reversible one. But then what meaning can be given to the inequality sign? Moreover, not all of the conclusions developed earlier apparently apply to electrical energy, for – in one place at least – Helm unequivocally asserts the conservation of electrical charge (*ibid.*, p. 60).

Things do not get any better. Helm is working toward his most general statement of the energy principle,

$$dE \leq JdM \tag{6}$$

but the same problems infect the remainder of its development. To further advance the theory of the galvanic cell, another form of energy is needed, which Helm called chemical energy, for electrolysis involve the chemical reaction of substances within the cell (*ibid.*, p. 64). Given his goal of elaborating a chemical energetics, it is not surprising that much of Helm's work – nearly two thirds of it, in fact – is devoted to explicating the concept of chemical energy and to surveying its various applications.

Helm introduced the idea of chemical energy by considering the simple case of a homogeneous phase of a substance – a liquid or gas, for example – containing several independent chemical components whose masses could be varied. Temporarily ignoring any change in electrical energy, he again modified the energy principle, this time to include the change in internal energy of the substance due to a change in the mass of any of the chemical components. Expression (4) now took the form

$$dE \leq TdS - pdV + \sum \pi_i dM_i \tag{8}$$

where dM_i gives the change in mass of the i^{th} chemical component and π_i represents what Gibbs had earlier called its chemical 'potential'. Helm preferred to refer to the factors π as chemical 'intensities', in part because he had already used the word 'potential' to designate other thermodynamic functions, but principally because he wished to stress the similarity between those quantities and pressure, temperature and electrical potential, which played analogous roles for other forms of energy (*ibid.*, p. 70). Indeed, he considered several general properties of the chemical intensities with the expressed intent of showing their similarity to the intensity factors of other forms of energy (*ibid.*, pp. 70-9, esp. 70-3), and then used them, and the variety of energy equations in which they appeared, to treat a wide range of subjects in physical chemistry. An impressive list of topics included: gas mixtures, mixtures of gases and liquids, saturated vapors, phase changes (especially changes in states of aggregation), freezing and boiling points, general conditions of chemical equilibrium, simple chemical reactions, mass action, reaction velocities, dilute solutions, heats of solution and dilution, osmotic pressure, electrolytic dissociation, and electrical conductivity.

All of these subjects – and more – were treated from a general energetic standpoint, which employed an appropriately formulated energy principle and stressed the similarity of the different forms of energy. One chapter, for example, developed a variety of results concerning osmotic pressure from energy equations for a solution and a solvent separated by a semi-permeable membrane (*ibid.*, pp. 106-111). Another generated equations, from an hypothesis concerning chemical intensity, for the diffusion of matter which was, he thought, "completely analogous with formulae for the *diffusion* of other forms of energy" (*ibid.*, pp. 111-117; on 113; my italics). Still others completed the theory, deferred earlier, of the reversible galvanic cell, by combining (6) and (7) to give an energetic account of the dissociation and conductivity of electrolytes (*ibid.*, pp. 64-69, 85-98). Helm's goal throughout was to show that the whole field of physical chemistry could be understood in terms of energy changes and unified by means of the energy principle.

The last part of Helm's *mathematische Chemie* examined the degrees of freedom exhibited in chemical phenomena (*ibid.*, pp. 124-135). It developed, among other relations, Gibbs's phase rule and the equilibrium conditions when chemical reactions may occur within a system (*ibid.*, pp. 126, 128-130). Here, as elsewhere, Helm followed closely the line of reasoning pursued by Gibbs in his famous memoir on heterogeneous equilibrium. In fact, while he brought together many of the important results in the field of physical chemistry in one of the subject's first introductory texts, Helm's discussions often simply summarize work by other researchers. As one reads his book, one wonders, moreover, what much of it has to do with energetics. Excepting certain passages, many of which have already been noted, it appears to have no obvious connection with the subject. The most plausible explanation is that Helm emphasized the power of thermodynamic reasoning in chemistry because he believed it to be energetic in character, and he described the thermodynamic writings of such physicists as Gibbs, Helmholtz, Duhem, Nernst, and Planck because he considered them contributions to a chemical energetics whose structure he had now given a systematic form.

5. Evaluating Helm's *Grundzüge*

Helm's text is remarkable in many ways. It was one of the first general introductions to physical chemistry, presenting results which, in the words of one reviewer, would otherwise have to be dug out of "many scattered and obscure papers" (Buckingham 1895-1896, p.154). But the real novelty of his work, as this and other reviewers soon pointed out, resided less in its particular results than in its general point of view and unifying intent. Helm's principal goal, as we have noted, was to bring the whole of mathematical chemistry within the theoretical umbrella of his conception of energetics. Did he succeed?

I think not, although I can only sketch some of the reasons here. The reasons are internal and technical, they are not social and political. Begin with Helm's equation

$$dE = TdS - pdV \tag{3}$$

for any infinitesimal reversible process between two equilibrium states. Helm then replaced (4) with

$$dE < TdS - pdV \tag{9}$$

for infinitesimal irreversible changes. What does this mean? If the changes Helm had in mind take place between two equilibrium states, then (3) holds *regardless* of whether they are reversible or irreversible; if, on the other hand, either the initial state or the final state, or both, are not states of equilibrium, then S has no thermodynamic meaning in (9) and neither, in most cases, do any of the Js and Ms. When this happens, in fact, the energies included in the sum of

$$dE < \sum JdM \tag{10}$$

cannot even be analyzed into the canonical JdM form. (See Boltzmann 1896a, pp. 59-60; 1898, p. 67). Hence Helm's "general energy principle"

$$dE \leq TdS + \sum JdM \tag{11}$$

or

$$dE \leq \sum JdM \tag{6}$$

is either redundant or meaningless.

Another technical problem concerns the inequality in

$$dE < TdS - pdV \qquad (9).$$

This is supposed to hold for infinitesimal *irreversible* changes. But then the pressure in the pdV term cannot be the internal pressure, p_i, of the system on its surroundings, since dA, the work term in the energy law

$$dE = dQ + dA \tag{2}$$

can be analyzed into $p_i dV$ form only for *reversible* changes, that is, for changes in which the internal pressure is equal to the external pressure, p_e, or pressure of the system's surroundings on it. And only if the internal pressure is a function of the thermodynamic state of the system, so that (but only for *reversible* processes) one may write familiar relations such as

$$dE = TdS + pdV \qquad (3).$$

The same line of argument may be extended to the other energetic intensities (temperature, *e.g.*) to show that Helm's general energy principle

$$dE \leq \sum JdM \qquad (6)$$

is inadmissible, since the Js cannot stand for the internal intensities of systems.

6. Conclusions

A final technical problem having to do with volume energy will lead to some concluding general remarks about Helm's development of energetics in the *Grundzüge*. As I noted earlier, volume energy is in this work the implausible model for understanding other forms of energy. Among the bizarre conclusions Helm reached is that the capacity factors of all forms of energy increase in irreversible change, since volume, the capacity factor of volume energy, does. The only factor for which this is the case is entropy. Moreover, volume energy is not a state function, any more than heat is, but Helm treats both in the *Grundzüge* as if they were. He also treats them as if they were moveable stuffs capable of migrating from one place to another, and all systems (except purely mechanical ones) as having definite amounts of each at any time.

However, none of this reflects what I think was Helm's considered view. Significantly, volume energy serves as a model for understanding other forms of energy only in the *Grundzüge,* and later (*cf.* Helm 1898) is not even recognized as a *form* of energy. I suspect that reflection and good sense made it clear to him that modeling the analysis of energy forms on volume energy was untenable. The view of energetic change that reflected Helm's mature position is developed in his *History of Energetics* (*ibid*.). That position is contained in what I earlier (Section 3) called the Relations Thesis (RT). Allow me here to remind readers of the main features of RT. Epistemologically, it claims that we can only know phenomena and changes in phenomena, all of which are energetic in character. Methodologically, it claims, in consequence, that the goal of natural science is to describe and relate energy phenomena in the simplest and most unified manner possible. Accordingly, a general theory of energy, or energetics, will relate the phenomena in terms of simple, unifying principles, such as the law of intensity and the factorization principle, properly construed. (Anti)-metaphysically, RT rejects all inferences to anything 'behind' or 'beneath' the phenomena, whether it be atoms or forms of energy. Specifically, it rejects all efforts to substantialize energy or to reify energetic changes in terms of 'migrations', 'transitions', 'transformations', 'conversions', or what have you. But from this standpoint much of the language of Helm's *Grundzüge,* which refers to 'transmissions' and 'diffusions' of distinct forms of energy, is at best misleading and at worst entirely misguided. I conclude that his admirable attempt to formulate a chemical energetics is not only beset with serious mathematical and physical problems, but is in conflict with his 'official', mature position on the goal of energetic science.

Notes

1 For biographical information on Helm, I have relied on Naetsch 1923 and Körber 1968. More details, as well as a fuller bibliography of Helm's writings, may be found in Deltete 2000b.

2 This summary is based on Deltete 1995b, 2000b, and 2003.

3 This section is based on Deltete 2005.

4 Transfers of energy (*Übergänge*) are explicitly said to be "migrations" of energy in Helm's 1887 (pp. 54, 61-62), and in Helm 1894 he often slips into talking about energy as if it were a migrating substance (*e.g.*, p. 113), contrary to RT.

5 Helm apparently thought of irreversibility as confined to phenomena accompanying the uncompensated flow of heat, but he had little to say about the subject in his first work on energetics (see Helm 1887, p. 64).

6 Unfortunately, in 1887 and later, Helm used a variety of expressions ('Energieprinzip', 'Energiesatz', and 'Energiegesetz') interchangeably to express the content of (6), and that variable usage likely perplexed many of his readers, who thought that he was trying to obtain more from the conservation than it in fact implies. See Deltete 1999 and 2000b.

7 For an introduction to Gibbs, see Deltete 2000a & 2011. For Gibbs' large influence on the energeticists, see Deltete 1995a,b, 2000b & 2011.

8 One example may suffice. "According to the energy principle, the equation $dE = dQ + dA$, which represents the change of internal energy that takes place with absorption of heat dQ and of volume energy dA, also holds if dA signifies another form of energy. Moreover, *all the consequences developed in earlier sections are also in effect if this other form of energy can be represented in manner corresponding to volume energy*, that is to $-pdV$. The way of considering natural processes known as energetics places the similarity of the different forms of energy in the foreground of interest, thereby permitting conclusions which have been developed in a limited domain of natural knowledge to be carried over to other domains. The energy of an electrical current may now be represented in a manner corresponding to volume energy [...]" (Helm 1894, p. 58, my italics; see also pp. 60, 70-73).

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