Thermodynamics in Wilhelm Ostwald's Physical Chemistry

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This essay focuses on the place of the second law of thermodynamics in Wilhelm Ostwald's physical chemistry. After a brief introduction to his energetic theory, which was supposed to be a generalization of thermodynamics, I contrast Ostwald's understanding of the second law, which ignored entropy and irreversibility, with Max Planck's, which emphasized both. I then consider how Ostwald sought to develop physical chemistry without any concern for irreversibility and little concern for entropy, and I argue that he was mistaken.

1. Introduction. Wilhelm Ostwald was professor of physical chemistry at the University of Leipzig from 1887 to 1905. He was awarded the Nobel Prize in Chemistry in 1909 for his work on catalysis and rates of chemical reaction. Ostwald sought to use parts of thermodynamics as a basis for an allegedly more general science of energetics.[1] He accepted the first law as the law of the conservation of energy. He did not (to my knowledge) ever refer to the third law and would not have accepted it in the now standard entropic form. Indeed, he minimized the importance of entropy in his formulation of energetic theory and, until later, the significance of irreversibility. I will therefore focus on the second law of thermodynamics. Section 2 offers a sketch of Ostwald's energetic theory. Section 3 contrasts Ostwald's view of thermodynamics in general, and of the second law in particular, with Max Planck's and discusses Ostwald's explanation of irreversibility. In section 4, I then explain and criticize aspects of Ostwald's chemical energetics. Finally, in section 5, I suggest a reason, based on his energetic theory, why Ostwald later paid more attention to irreversibility.

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1. Introductions to energetics may be found in Deltete (1995, 2003) and the translator-editor essay to Helm's 1898 book (Deltete 2000).

Philosophy of Science, 77 (December 2010) pp. 888–899. 0031-8248/2010/7705-0023$10.00
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https://doi.org/10.1086/656824 Published online by Cambridge University Press

2. Ostwald's Energetic Theory. As Ostwald once put it, he dared to "construct a world view exclusively from energetic material without using the concept of matter" (1902, 165–66).[2] The main features of that worldview are as follows. Every object or system is constituted of energy of different, distinct forms. Each form of energy, in turn, is resolvable into two factors, one indicating the intensity of the energy and the other its capacity. Since such factorization is a "universal characteristic of energy," Ostwald, like Helm, proposed a "Factorization Principle," calling it "the foundation of modern energetics" (1892, 368; 1893a, 44). In Ostwald's version, this principle took the form

$$E = ic, \tag{1}$$

where E represents some form of energy, i is the magnitude of its intensity, and c is its capacity factor.

Ostwald recognized a number of distinct forms of energy, two of which deserve mention. First, he admitted—indeed emphasized the importance of—"volume energy" as one of the "spatial" forms of mechanical energy and factored it as

$$E_v = pV, \tag{2}$$

where p is pressure and V is volume. He also recognized "heat energy" as a distinct form of energy. Initially, he factored it as $Q = Ts$, where T represents temperature and s specific heat. Later, he factored it as

$$Q = Tc, \tag{3}$$

where c stands for either heat capacity or entropy. (An important consequence of this factorization is that entropy has an official role in Ostwald's energetic theory only as the capacity factor of heat energy for isothermal changes.) Ignoring criticism that neither form of energy is a function of the state of the system, Ostwald insisted that every system has a definite amount of volume energy as part of its makeup and that all but purely mechanical systems have definite amounts of heat as well. The total energy composition of an object or system, in turn, is given by

$$E_T = \sum_n E = \sum_n ic, \tag{4}$$

where the sum extends over every form of energy present and n is greater than one.

To understand change, Ostwald directed his attention to the intensity factor of energy "that property upon which the motion or rest of energy, that is, everything which occurs, depends" (1892, 371). Energetic inten-

2. In the interest of brevity, I usually provide citations to Ostwald in the text only for quoted passages. More detailed citations may be found in Deltete (1996, 2007a, 2007b, 2008). For Georg Helm's early energetic theory, see Deltete (2005).

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sities are inherent tendencies of energy forms toward equilibration. Specifically, they are tendencies to pass over to regions of lower intensity, or to be transformed into other energies, unless prevented from doing so. Following Helm, Ostwald called this "essential and universal" fact about the behavior of energy the "intensity law" (1891/1892, 571; 1892, 367–68; 1893a, 46). This law says that intensity differences are a necessary condition of change (conversely, that equilibrium obtains when no differences are present) and that natural change never occurs from lower to higher intensity. To explain why the natural tendencies of energies are often prevented from being actualized, Ostwald introduced the notion of "compensated intensities." The basic idea here is that the intensity of one form of energy can balance the intensity of another, the resulting "quiet state" also being (some) state of equilibrium. This must be going on all the time, Ostwald reasoned, since bodies composed of several forms of energy exist as stable individuals. But the actual situation is more complex: the changes a body undergoes depend on the *relation* between the intensities of its energies and those of its surroundings. Ostwald concluded, therefore, that a system is in (some state of) equilibrium with its surroundings if and only if the corresponding sets of energetic intensities are mutually compensatory. Hence his *Gesetz des Geschehens*: "In order for something to happen it is necessary and sufficient that non-compensated differences of energy are present" (1893a, 48).

Ostwald expressed the conditions of energetic equilibrium in several other ways, two of which may be mentioned. In his first "Studien zur Energetik," he called this condition the "Principle of Virtual Energy Change" and stated it as follows: "In order for a system possessing any forms of energy to be in equilibrium, it is necessary and sufficient that, for any displacement of the system compatible with its state, the sum of the amounts of energy appearing and disappearing is equal to zero" (1891/1892, 567). Ostwald attempted no analytical formulation of this principle, but said that as far as he could determine, it "contains the entire theory of equilibrium, and permits equations of state of the briefest form to be found as soon as the nature of the system and the kinds of energies in it are given." In his second "Studien" a year later, Ostwald called one of his propositions expressing the condition for equilibrium the "Second Law of Energetics" and stated it for any possible change involving two forms of energy in this way: "If the conditions are such that, in the event of a virtual change of the correlative factors, just as much energy of type A vanishes on the one hand as must, on the other hand, come into being of type B by virtue of the assumed relationship, and vice versa, then the system is in a state of equilibrium" (1892, 377). This time, however, he provided an analytical formulation,

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$$\Delta A + \Delta B = 0, \tag{5}$$

and extended it to changes involving any number of forms of energy:

$$\sum \Delta E = 0. \tag{6}$$

The second law of energetics is allegedly a generalization of the second law of thermodynamics. The previous discussion, plus two additional items of background information, allow us to see what Ostwald had in mind. The first item is Ostwald's view of thermodynamics. He regarded it as essentially the study of the reciprocal transformations of heat and mechanical energy, with the laws of thermodynamics governing such transformations. The second item is his view of the second law. He regarded it as a law of energy, like the first, but a law confined to the behavior of heat. The proof of the second law depends on the characteristic behavior of heat energy, that it cannot by itself pass from a cold body to a warm one. But this assumption (the "Clausius Postulate") is merely a perspicuous instance of the more general intensity law governing the behavior of all forms of energy. The energetic essence and proof of the second law are, therefore, a simple matter. The Factorization Principle, equation (1), yields equation (3) for heat, which in turn yields the familiar $dQ = TdS$ on differentiation at constant temperature. This argument is intended to cut through all the mathematical difficulties that had earlier perplexed Ostwald. It is also likely the basis of his remarks to Arrhenius and Boltzmann that finally, after 8 years of reflection, he had grasped the content of the second law and that it has nothing to do with the dissipation of energy or the increase of entropy (1961, 9–10; 1969, 110).

3. Planck, Entropy, and Irreversibility. Planck emphatically disagreed. He began with Clausius's most fruitful analytical formulation of the second law:

$$dS \geq dQ/T, \tag{7}$$

where S is the entropy, Q is the heat added, and T is the absolute temperature, and where the equality holds for reversible processes and the inequality for irreversible ones. Planck then asked: How would entropy change with time as a system evolved *by itself*, in thermal and mechanical isolation from its environment? The answer given in his 1879 thesis *Über den zweiten Hauptsatz der mechanischen Wärmetheorie* was

$$S' - S \geq 0, \tag{8}$$

where S' is the entropy at a later time and S at an earlier time. This was Planck's version of the second law, which he thought was conceptually clearer, more general, and more fundamental than Clausius's. Just as the first law governs the behavior of energy over time, so the second governs

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that of entropy. But while the total energy of an isolated system remains constant, its entropy can only increase or, in the ideal limiting case, remain constant. The second law applied to "all processes occurring in nature, not just to thermal phenomena" (1879/1958, 3–4). It prohibited not only the spontaneous passage of heat from a lower to a higher temperature but any process that would decrease the entropy of an isolated system.

Papers published by Planck in the 8 years following his thesis refined this fundamental thermodynamic theory and applied it to various sorts of physical situations, including equilibrium, saturation, and changes of phase. The important insight he developed in these works was one that had already been exploited by Gibbs, namely, the idea that stable equilibrium in a system corresponds to its state of maximum entropy. Planck then turned his attention, in the years between 1887 and 1894, to the newly emerging field of physical chemistry, where he found further confirmation and additional applications for his theory. In a series of papers collected under the general heading "Über das Princip der Vemehrung der Entropie," he employed the entropy principle to solve problems of chemical affinity, spontaneity, and equilibrium and, in a final installment, applied the principle to a variety of electrochemical phenomena.

The contrast between Ostwald and Planck is striking:

> Ostwald: Thermodynamics is confined to the reciprocal transformations of heat and mechanical energy; it is just one "chapter" of the more comprehensive science of energetics. (1961, 9)
>
> Planck: Thermodynamics is a universal science, governing all but purely mechanical changes, which are ideal.
>
> Ostwald: The second law of thermodynamics is confined to the behavior of heat, and irreversibility is not part of it.
>
> Planck: The second law governs all natural processes, and irreversibility is its essence. (Planck 1893; Ostwald 1961, 45–57).
>
> Ostwald: The second law of energetics, which is based on the intensity law, is more general than the second law of thermodynamics, since it governs all natural "happening."
>
> Planck: The second law of thermodynamics does what the second law of energetics purports to do, and does it better, since the former ignores irreversibility and virtually ignores entropy. It is the real *Gesetz des Geschehens*.

Planck's position is (more or less) the accepted one today, but it was unusual at the time. Few other physicists and chemists accorded entropy the conceptual importance that he did. The likely reasons are worth pur-

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suing, but not here (see Kragh and Weininger 1996). Instead, we ask: If Ostwald did not think that the second law of thermodynamics had anything to do with the dissipation of energy or the increase of entropy, how did he explain irreversibility? Like many other physicists and chemists, he was often inclined to attribute it to the peculiarity of heat, in that it always has a tendency to flow from higher to lower temperatures. But every other energetic intensity also tends toward equilibrium when not prevented from doing so. In addition, as we have seen, Ostwald also thought it meaningful to speak of the "heat energy" of a system, so that temperature, the intensity factor of heat, can (at least sometimes) be compensated by the intensity factors of other forms of energy. These considerations led Ostwald (for a few years at least) to explain irreversibility in terms of a unique property of radiant energy: that it could not, allegedly, be coupled to other forms of energy, and so compensated by them, but always "follows unconditionally the general law of intensity," thereby destroying the intensity differences on which change of any sort depends. Moreover, the same thing happens whenever other forms of energy are converted into radiant energy: "moveable energy" (*bewegliche Energie*) is lost, and this explains irreversibility (1892, 385; 1893a, 1018–19). Between coupled forms of energy, movable energy is never lost; that is why the laws of thermodynamics, and their generalization in energetics, are confined to reversible processes.

I will not offer a critique of this strange view here (see Deltrete 2008) but will say a bit about coupling. After his conversion to "pure energetics" (1892), Ostwald's official view on the relation of energy to matter is what I have elsewhere called the Composition Thesis (1995, 140; 2008, 196–200). In this view, "material objects" (or "physical-chemical systems") are nothing more than energy complexes—spatially copresent and coupled clusters of energy. There is no material carrier or container. Energies are linked either naturally or via a "machine." Ostwald never explained how distinct forms of energy can be naturally coupled or what it means for them to be linked via a "machine." "Machine equations" (*Machinegleichungen*) may describe the transformation relations between different forms of energy, but they do not physically link the energies. And on the Composition Thesis, physical "machines" should themselves just be coupled clusters of energy, which does not help to explain how they succeed in linking other clusters. In trying to do science (especially chemistry) energetically, as we will see, Ostwald usually employed a quite different view of the relation between energy and matter. Then he usually spoke of an object or system "containing" ("having" or "possessing") certain kinds of energy in certain amounts (including, often, chemical energy), as if a system were not the same as, but something in addition to, its energy content. Then the distinct forms of energy are coupled (at least) in the

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sense that they are all "bound" to the same carrier (*Träger*) or contained in the same system. I have called this the Containment Thesis and do not seek to resolve the inconsistency between it and the Composition Thesis.

4. Chemical Energetics. I turn instead to a sketch of Ostwald's chemical energetics. The central conceptual element of a proper theory of chemical phenomena, not surprisingly, is the notion of chemical energy. The intensity factor of chemical energy is its (Gibbs) chemical potential, which corresponds (roughly) to the old concept of chemical affinity but is more precise. "The property of being conserved is possessed by the *amounts of material* (*Stoffmengen*) involved in chemical processes and they must therefore be regarded as the capacity factors of chemical energy" (1893b, 50). Ostwald variously called these "amounts of material" their "atomic" weights, or their "combining" or "equivalent" or "formula" weights, but he did not really think that the chemical capacities were weights. Nor did he think they were masses since, in his view, both are factors only of mechanical energy. Although proportional to mass and weight, chemical capacities are quantities of a special sort—or, rather, of many sorts, since he thought that there were as many of them as there are distinct chemical species. This peculiarity of chemical energy greatly complicates its study since in any change involving such energy, its two factors are mutually dependent. Differences in chemical potential therefore depend on both the nature and the amounts of the substances present and changes in chemical potential on the ways in which, as well as on the amounts by which, the substances constituting a chemical system are altered.

The term *Stoffmengen* is unfortunate since *Stoff* is substance, matter, or material in German, and Ostwald sought "eine Chemie ohne Stoff" (1893b, 50; 1895/1904, 63). Often he seems to think that a chemical capacity is just the symbol for a chemical element plus a numerical coefficient to indicate how many units of this element are being combined. Surely, though, it is not the symbols themselves that are reacting, but masses or weights of the chemical elements of which they are the symbols. Ostwald must have recognized this, but his insistence that mass and weight were the capacity factors only of mechanical energies made it impossible for him to allow them as capacity factors of chemical energy as well (1895/1904, 62–63).

So what are they? Far from treating the *Stoffmengen* that are supposed to be the capacities of a system for chemical energy as mere symbols, or even as factors of chemical energy, Ostwald treats them rather as *material stuffs* or substances in their own right, which have or contain or possess energy of their own! That is, despite Ostwald's professed allegiance to the Composition Thesis, his discussions of chemical energy are all couched in terms of the Containment Thesis. He viewed chemical systems as made

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up of various substances—chemical elements or compounds—and as containing various sorts of energy, chemical energy included. Chemical reactions, in turn, consist in energy exchanges or transformations (usually the latter) between the components of such systems, or between such systems and their surroundings, and are usually caused by the addition of new substances, which themselves have energy and therefore disrupt energy balances or remove energetic constraints. Most chemical processes consume chemical energy and reduce chemical potentials, creating other energies (usually heat) as by-products. This general point of view is not implausible in itself, but it is clearly not "eine Chemie ohne Stoffe."

As with other forms of energy, the intensity factor of chemical energy—its chemical potential—determines the occurrence and direction of chemical processes. If the chemical potentials of the substances of a system, or of two bordering systems, have the same value, then the substances or systems are in chemical equilibrium. Differences of chemical intensity may be compensated by differences in other energetic intensities. The occurrence of chemical reactions indicates (and always presupposes) the presence of differences of chemical potential between the substances or systems taking part in the reaction. But it is not correct to say that whenever the chemical potentials of two substances or systems are different, then they will automatically react chemically. Again, such differences may be compensated by differences of intensity of other energies.

The formal developments of these ideas are infrequent and filled with problems. Here is one development: In a chapter of his revised *Lehrbuch* on "chemical energetics," for example, Ostwald began with a "general chemical reaction equation" for a system of two reacting substances,

$$E = E' + q, \tag{9}$$

where E is the total energy of the two-substance system before the reaction, E' is its total energy after the reaction, and q is the energy entering or (usually) leaving the system during the reaction. Proceeding, apparently, from the Factorization Principle, $E = ci$, and the assumption that the chemical capacities obey a quantitative conservation law, he used (9) to obtain the equations

$$E/c = E'/c' + q/c' \tag{10}$$

or

$$i = i' + q/c', \tag{11}$$

where the second term on the right side of both equations, which Ostwald called the "reaction heat," depends not only on the change in chemical energy but on the changes in volume energy and heat energy as well. Then, after noting that $c = c'$ must be a positive value, so that $i = i'$, $i > i'$, or $i < i'$, depending on whether $q = 0$, $q > 0$, or $q < 0$, he argued

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that equilibrium could exist only in the first case. Or, "In order for chemical equilibrium to exist between given substances and their transformation products, the chemical energy of the substances before the transformation must be equal to their chemical energy after the transformation. If this equality does not obtain, then a transformation must take place (when this is possible) in such a way that the total chemical energy decreases." Finally, he extended these results to reactions involving more than two initial substances and transformation products. For such reactions, he claimed, (11) has the form

$$\sum i = \sum i' + \sum q/c', \tag{12}$$

where each term in the reaction heat sum must now be equal to zero in order for equilibrium to obtain between any given substances and their reaction products (1893a, 504–7).

Here is another development from Ostwald's second "Studien zur Energetik." Begin with equation (6), which says that the "sum of the changes in the appearing and disappearing energies must be equal to zero." These energies are related by "machine equations" with the general form $c_1 = Kc_2$, where c_1 and c_2 are the capacity factors of two coupled energies, and K is a transformation factor. If the capacities remain constant during a given transformation, the equilibrium condition requires that $c_1 di_1 + c_2 di_2 = 0$. Introduce the machine equation and this result reduces to $K di_1 = -di_2$. Ostwald called this equation the "generalized intensity law"—"Equilibrium takes place between two intensities when the intensity of one of them is equal to the opposed reduced intensity of the other"—and he applied the equation to different physical processes. For example, this is his explanation of what happens in the free expansion of an ideal gas. Ostwald accepted the idea that no work is done in the expansion but sought to explain the resulting change in terms of energy changes, specifically a decrease in volume energy that is balanced by an increase in heat energy:

$$\Delta E_H = -\Delta E_{VE}, \quad \text{or} \quad cdT = -pdV \tag{13}$$

(1892, 379–82).

There are many problems with both of these formal developments. I confine myself to two. The formal representation of the free expansion requires that the temperature change, although there was not any evidence of that. Moreover, since entropy is the capacity factor of heat only for

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isothermal changes, the c in the left-hand side of equation (13) cannot be entropy.[3]

Does Ostwald then want to say that the process is not irreversible? He waffles in a series of letters with Planck (Ostwald 1961, 51–59). At the same time, the c cannot plausibly be construed as heat capacity either, since (despite the right-hand side of eq. [13]) both pressure and volume are changing.

Much of the first development is also seriously flawed. Ostwald often stressed that one property of the energetic capacities was that they usually obey a quantitative conservation law. Then, however, he would concede an exception to this general rule, which results whenever "the phenomena of heat conduction and radiation" come into play. But, he would add, in the present discussion "this will not be considered" (e.g., 1893c, 50). Ostwald evidently proceeded in this way in moving from equation (9) to equations (10) and (11). Only by effectively ignoring any increase in entropy could he set $c = c'$ in the derivation of either of them. But those derivations apparently seek to do two things that are incompatible within his own version of energetic theory. They rely essentially on a term called the "reaction heat" in each of equations (10) and (11) and yet seek to restrict transformations involving chemical energy to reversible processes! In response, Ostwald might say that the heat in chemical reactions is not free in the sense of radiant energy, that it is coupled to energies of other forms, but he cannot plausibly argue that chemical reactions are not irreversible, however this is explained. In chemistry, as elsewhere, Ostwald has simply ignored the problem of irreversibility in his development of energetic theory.

5. Conclusion: A Role for Irreversibility. Since I have been rather critical of Ostwald's energetic chemistry, allow me to close by suggesting a place where energetic theory likely revealed to him something worth pursuing. I begin with a question: Are systems that comprise different energies in energetic equilibrium or not? Often in his statements of the conditions for equilibrium, he says they are, but reflection on the fact that compensation relations are seldom (if ever) perfect or permanent seems to have convinced him that they are not. In particular, while systems (or systems and their surroundings) may comprise energies whose chemical potentials compensate one another for a time (even a long time) and so are thus in

3. Nor should it be in his "derivation" of the Clausius-Clapeyron equation. Here Ostwald considered the equilibrium between heat and volume energy in a system undergoing a phase change from the liquid to the vapor state. The condition of equilibrium requires that $sdT = Vdp$. By replacing s with the expression ϱ/T (where ϱ is the latent heat of vaporization), he obtained $(\varrho/T)dT = Vdp$, or $dp/dT = \varrho/VT$, a not very precise result, but one that requires s to be entropy, contrary to Ostwald's energetic theory.

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a "quiet state" (*Ruhezustand*), which Ostwald later called "metastable" (1904), they are not *really* in equilibrium, since the compensation relations will eventually "dissolve" naturally or may be encouraged to through, for example, heating or the addition of a catalyst. And these processes are irreversible. Reflection on this apparently encouraged Ostwald to think that the direction of time could be grounded in irreversible physical processes: friction, heat conduction, electrical resistance, magnetic hysteresis, and chemical reaction velocity, or "briefly in the existence of . . . dissipative or dispersive processes" (1898/1904, 250, 252).

Planck noticed Ostwald's new attention to irreversibility:

> I am happy to see . . . that you are now also directing more of your interest to the irreversible or dissipative processes of nature, and I hope that you will join in the task of deepening still more the tremendously important distinction between reversible and irreversible processes. For years I have not tired of stressing on every occasion that the division of natural processes into mechanical, electrical, chemical, etc. is much less important than the division into reversible and irreversible [ones]. I would also be very happy if a field once again presented itself in which I would be engaged in working in the same direction as you. (Ostwald 1961, 62)

Planck likely sought to appease Ostwald (after all, Planck's attack on "die neuere Energetik" in 1896 for, among other things, ignoring irreversibility was mainly intended for Ostwald), but there is no mention of entropy, the increase of which was Planck's own explanation of irreversibility. There seldom was in Ostwald, either, even after he became interested in irreversible processes as a way of fixing the direction of time.

REFERENCES

Deltete, Robert J. 1995. "Gibbs and the Energeticists." In *No Truth Except in the Details: Essays in Honor of Martin J. Klein*, ed. A. J. Kox and D. Siegel, 135–69. Dordrecht: Kluwer.

———. 1996. "'Studien zur Energetik': Wilhelm Ostwald's Energetic Theory." *Centaurus* 39:156–78.

———. 2000. "Helm's History of Energetics: A Reading Guide." In *The Historical Development of Energetics*, by Georg Helm. Trans. Robert J. Deltete. Dordrecht: Kluwer. Originally published as *Die geschichtlichen Entwicklung der Energetik* (Leipzig: Veit & Comp., 1898).

———. 2003. "Energetics." In *The Oxford Companion to the History of Modern Science*, ed. John L. Heilbron, 256–57. New York: Oxford University Press.

———. 2005. "*Die Lehre von der Energie*: Georg Helm's Energetic Manifesto." *Centaurus* 47:140–62.

———. 2007a. "Wilhelm Ostwald's Energetics 1: Origins and Motivations." *Foundations of Chemistry* 9:3–56.

———. 2007b. "Wilhelm Ostwald's Energetics 2: Energetic Theory and Applications, Part I." *Foundations of Chemistry* 9:265–316.

https://doi.org/10.1086/656824 Published online by Cambridge University Press

———. 2008. "Wilhelm Ostwald's Energetics 3: Energetic Theory and Applications, Part II." *Foundations of Chemistry* 10:187–221.
Kragh, Helge, and Stephen J. Weininger. 1996. "Sooner Silence than Confusion: The Tortuous Entry of Entropy into Chemistry." *Historical Studies in the Physical Sciences* 27: 91–130.
Ostwald, Wilhelm. 1891/1892. "Studien zur Energetik I." *Berichte über die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig* 43:271–88. Repr. in *Zeitschrift für physikalische Chemie* 9:563–78.
———. 1892. "Studien zur Energetik II: Grundlinien in der allgemeinen Energetik." *Berichteüber die Verhandlungen der Sächsischen Akademie der Wissenschaften zu Leipzig* 44:211–37. Repr. in *Zeitschrift für physikalische Chemie* 10:363–86.
———. 1893a. *Lehrbuch der allgemeinen Chemie: Zweite ungearbeite Auflage*. Vol. 2, pt. 1, *Chemische Energie*. Leipzig: W. Engelmann.
———. 1893b. "Über Chemische Energie." *Verhandlungen der Gesellschaft deutscher Naturforscher und Ärzte* II, 1:49–55.
———. 1895/1904. "Chemische Betrachtungen." In *Abhandlungen und Vorträge allgemeinen Inhaltes* (*1887–1903*), 59–70. Leipzig: Veit & Comp.
———. 1898/1904. "Das Problem der Zeit." In *Abhandlungen und Vorträge allgemeinen Inhaltes* (*1887–1903*), 241–57. Leipzig: Veit & Comp.
———. 1902. *Vorlesungen über Naturphilosophie, gehalten im sommer 1901 an der Universität Leipzig*. Leipzig: Veit & Comp.
———. 1904. "Elements and Compounds: Faraday Lecture." *Transactions of the Royal Institute of London*, 504–22.
———. 1961. *Aus dem wissenschaftlichen Briefwechsel Wilhelm Ostwalds*. Vol. 1, *Briefwechsel mit Ludwig Boltzmann, Max Planck, Georg Helm und Josiah Willard Gibbs*, ed. H.-G. Körber. Berlin: Akademie-Verlag.
———. 1969. *Aus dem wissenschaftlichen Briefwechsel Wilhelm Ostwalds*. Vol. 2, *Briefwechsel mit Svante Arrhenius und Jacobus Hendricus van 't Hoff*, ed. H.-G. Körber. Berlin: Akademie-Verlag.
Planck, Max. 1879/1958. *Über den zweiten Hauptsatz der mechanischen Wärmetheorie*. Munich: Ackerman. Repr. in *Physikalische Abhandlungen und Vorträge*, vol. 1. Braunschweig: Vieweg.
———. 1893. "Der Kern des zweiten Hauptsatzes der Wärmetheorie." *Zeitschrift für physikalische und chemische Unterricht* 6:217–21.
———. 1896. "Gegen die neuere Energetik." *Annalen der Physik* 57:72–78.

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