

- *История и философия на химията* •
- *History and Philosophy of Chemistry* •

A FOURTH LAW OF THERMODYNAMICS

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Abstract. Classical thermodynamics, based on conservation of matter and energy and on the increase of entropy accompanying every natural event, reliably predicts equilibrium properties of macroscopic systems, regardless of the complexity of those systems. Thermodynamic theory historically has had little to say about the far-from-equilibrium evolution of systems. This is in part because the classical laws of thermodynamics, limited to requirements about the degree and direction of change, are silent about the means and pathways for achieving change. We propose a simply stated yet powerful Fourth Law of Thermodynamics that significantly extends the domain of thermodynamics by incorporating evolving systems and thereby adding richness to thermodynamic description.

Keywords: classical thermodynamics; far-from-equilibrium systems; fourth law of thermodynamics

Chemistry embraces two contrasting and complementary theoretical frameworks – the microscopic and the macroscopic. Microscopic chemical theory is an attempt to understand chemical systems in terms of their minute constituents, often by applying quantum theory to the ensembles of nuclei and electrons that comprise individual molecules. Mass-action kinetics describes the evolution of chemically reacting systems in terms of molecular mechanisms; kinetics provides descriptions of chemical change in terms of microscopic reaction models. By contrast, macroscopic chemical theory is a parallel attempt to understand chemical systems in terms of such principles as the laws of thermodynamics. Thermodynamic descriptions – sparse, parsimonious and explicitly independent of mechanistic explanations – make general claims about complex systems without requiring detailed analysis of often unavailable or even unknowable microscopic details.

Stuart Kauffman has observed [1] that “[s]ince all free living systems are non-equilibrium systems – indeed, since the biosphere itself is a non-equilibrium system driven by the flux of solar radiation – it would be of the deepest importance, were it possible, to establish general laws predicting the behavior of all non-equilibrium systems. Unfortunately, efforts to find such laws have not yet met with success.” Kauffman notes that the systems whose behavior he wishes to predict are exceedingly complex. Microscopic models of such systems are so complex as to defy analysis. We propose a Fourth Law of Thermodynamics as a general principle applicable to non-equilibrium systems to provide a productive opportunity for chemists, biologists and other scientists to view the behavior of nonequilibrium systems, no matter how complex, within the framework of a more inclusive macroscopic thermodynamics.

The search for general principles to describe chemical change is as old as recorded history. The concept of chemical affinity [2] as an organizing macroscopic principle dates back at least to the pre-Socratic philosopher Empedocles, and was used by Albertus Magnus (thirteenth century), Paracelsus (sixteenth century), and Johann Glauber and Robert Boyle (seventeenth century). The observation that there is an order of reactivity of the metals is at least as old as the thirteenth century. Étienne-François Geoffroy extended and generalized this observation with his “Table des Differents Rappports”, published in 1718, perhaps the first table of chemical affinities. The concept of affinity was pursued in the hope of finding theoretical ways of reliably predicting the consequences of combining various reagents.

Marcelin Berthelot was a vigorous nineteenth century exponent of the idea that chemical phenomena can be correlated, understood and predicted in terms of thermochemical energetics. He sought relationships between chemical affinity and calorimetric data. He argued, in a series of publications beginning in 1865 and in a two-volume treatise [3], that chemical change proceeds in the direction that produces the most heat. This “principle of least work”, seductive as an organizing principle, was criticized by Pierre Duhem and others as inconsistent with some experiments and inconsistent with the Second Law of Thermodynamics. Berthelot’s critics observed that energy alone cannot account for the direction of chemical change; entropy must also be considered. [4]

The First Law and the Second Law are both required to describe chemical change. Josiah Willard Gibbs showed [5] how energy and entropy together could be used to formulate general criteria for equilibrium in chemical systems. The Gibbs framework for macroscopic descriptions of chemical systems *at equilibrium* was incorporated into the mainstream of chemistry in the English-speaking world by Gilbert Newton Lewis and Merle Randall [6] and into the physical chemistry canon via a succession of influential physical chemistry textbooks. [7] Gibbsian equilibrium thermodynamics had become the foundation theory of physical chemistry by the middle of the twentieth century.

The Gibbs criterion for equilibrium is that an appropriate potential function be minimized, subject to certain constraints on the system. For a system constrained by constant temperature and pressure, the potential function to be minimized is now called the Gibbs Function. Gibbs' philosophical and mathematical contributions to macroscopic chemical theory provided a secure basis for equilibrium systems. However, Gibbs provided no similar treatment for reacting systems, or indeed, for any system that is neither at nor near equilibrium.

In 1931, Lars Onsager provided a clue toward constructing a general law when he observed [8] that thermodynamic systems minimize impediments to increasing entropy. Lord Rayleigh in 1873 had introduced [9] the dissipation function, and Onsager generalized this idea to discuss consistencies in the rates of certain processes with an equation of the form

$$dS/dt - I = \text{maximum}$$

where dS/dt is the rate of entropy change and I is the impediment to entropy increase. Onsager was able to quantify I under certain circumstances. He showed in detail that I is consistently minimized in specific systems; in all systems quantified, the rate of entropy production was a maximum. We earlier proposed [10] a generalization of Onsager's observation as a unifying bio-theme. Since then, we have become convinced that our generalization transcends purely biological systems, and applies to all non-equilibrium systems.

We propose that the Fourth Law of Thermodynamics be formulated as: *Systems increase entropy at the maximum rate available to them.*

The Fourth Law requires that identical systems under identical conditions behave identically. This assertion of consistency applies to every evolving system, whether far from equilibrium or near equilibrium. In the limiting case of an isolated system at equilibrium, entropy has been maximized and the maximum rate available to the system is zero.

The Fourth Law leads to the expectation that dissipative structures will emerge in evolving systems. Rather than being surprised, over and over again, when dissipative structures appear, chemists and biologists are advised to search for such spatially organized regions that facilitate entropy production.

The Fourth Law is a statement of a common and powerful research strategy, complementing classical mass-action kinetics, in which scientists search for reasons that particular complex systems evolve more slowly than others, rather than focusing exclusively (following the mass-action imperative) on elucidating chemical reaction mechanisms. Increasingly, classical chemical kinetics is seen as powerless in describing and analyzing the essential features of complex reacting systems; the Fourth Law suggests an alternative phenomenological description. In the case of a system that is stranded in a metastable non-equilibrium state, the Fourth Law points to identifying the impediment to further evolution.

The Fourth Law brings the vast area of reacting systems within the domain of thermodynamics. By stressing the consistency of system behavior, it explicitly incorporates the concept of causality into the formal foundations of thermodynamics. The significance and manifestations of the Fourth Law are dramatic in far-from-equilibrium systems where spontaneous investments in local ordering – in dissipative structures – inevitably increase the rates at which systems increase entropy.

The appearance of dissipative structures in specific systems is highly predictable. Yet, if the predictive tools are limited to the First and Second Laws of Thermodynamics and to traditional thermodynamic criteria for equilibrium, chemists have no macroscopic rationalization for these ordered structures. The cornerstone of our argument for the new law is the observation that dissipative structures always increase the rate at which their systems increase entropy. No dissipative structure has been observed that decreases the rate at which a system increases entropy. In addition to the inviolability of this function of dissipative structures, their morphologies are remarkably consistent. For example, a regular pattern of hexagonal structures called Bénard cells consistently appears in thin layers of silicon oil heated uniformly from below and exposed to ambient air above. Bénard cells function to enhance heat transfer between the lower and upper surfaces of the system. That is, the cells minimize the I in Onsager's equation and maximize entropy production, dS/dt . The complex self-ordering that is always observed in a candle flame is another example. Among the most dramatic dissipative structures are living cells, multicellular organisms, ecosystems and the biosphere. In biological systems, evolution and the diversification of life forms, the unrelenting diversifications of dissipative repertoires, are most impressive demonstrations of maximizing entropy production.

Traditional thermodynamic theory does not provide a framework for parsimonious rationalizations of the seeming enigma of self-organization. The Second Law alone suggests that Bénard cells, candle flames and life forms would not spontaneously appear. Yet these phenomena are predictable and common. In biosystems, the dissipative structures – cells and organisms – have developed elaborate capacities to store and use entropic memory stored in nucleic acids to reproduce the structures. Mutations and recombinations of genetic material allow exposure of new phenotypes to the rigors of entropic selection.

We also observe consistencies in the rates of chemical reactions. A given set of chemical reactants under a given set of conditions produces products and proceeds toward equilibrium. We would be astounded if rates of a particular reaction under carefully engineered and precisely defined conditions were inconsistent with expectations established by a history of empirical evidence. The First and Second Laws together predict the final equilibrium state, but are silent about the consistency of rates by which that state will be achieved.

Empirical evidence where applicable is unswerving with regard to consistencies in the rate of flow of events, and contemporary scientists plan their research and interpret their experiments with empirically-based faith in those consistencies. Yet no first principle within thermodynamics has previously been framed to rationalize these consistencies. The power of the Fourth Law lies in its capacity to predict consistencies in rates of events and consistencies in the seemingly enigmatic behaviors of far-from-equilibrium systems. The Fourth Law affirms a transcendental confidence in consistencies of the rates and the morphologies of natural events. The consistent appearance of dissipative structures in far-from-equilibrium systems and the consistencies in rates of chemical reactions and other thermodynamic events empirically support the Fourth Law.

The Fourth Law provides a broadly applicable new paradigm that is especially important for biological investigations, from molecular to organismic and evolutionary levels. Life forms are, after all, dissipative structures that have the capacity to store and use information about themselves and to maximize entropic production by natural selection of the most entropically expedient forms. If we could observe the beginnings of extraterrestrial life we could predict, given long-term persistence of a generally supportive environment, that cells would probably evolve, that multicellularity would probably evolve, and that communities of organisms (ecosystems) would develop. Since every adaptive feature in a biological system can be described as an increased capacity to create entropy or as being better at making more individuals that are good at making entropy, we could predict features that would be a characteristic of life forms in any far-from-equilibrium system. We also note [11] that the Fourth Law predicts a tendency toward the evolution of intelligent species on planets capable of supporting life, since intelligent species transcend purely metabolic means of increasing entropy. Intelligent species are able to harvest and focus the use of energy in ways unavailable to non-intelligent species. The direct result of this ability is a quantum leap in the production of entropy.

References

1. **Kauffman, S.A.** *At Home in the Universe: The Search for Laws of Self-organization and Complexity*. Oxford University Press, New York, 1995, p. 21.
2. For history of the concept of affinity, see **Duncan, A.M.** *Laws and Order in Eighteenth-Century Chemistry*. Clarendon Press, Oxford, 1996.
3. **Berthelot, M.** *Essai de mecanique chimique fondee sur la thermochimie*. Dunod, Paris, 1879.
4. The nineteenth-century controversy between thermochemistry and thermodynamics is discussed by **Dolby, R.G.A.** *Hist. Sci.* **22**, 375 (1984).
5. **Gibbs, J.W.** *Trans. Conn. Acad. Arts Sci.* **3**, 108-248, 343-524 (1875-78).
6. **Lewis, G.N., M. Randall.** *Thermodynamics and the Free Energy of Chemical Sub-*

stances. McGraw-Hill, New York, 1923.

7. For example, **Guggenheim, E.A.** *Modern Thermodynamics by the Methods of Willard Gibbs*. Methuen, London, 1933; **Steiner, L.E.** *Introduction to Chemical Thermodynamics*. McGraw-Hill, New York, 1941; **Glasstone, S.** *Thermodynamics for Chemists*. Van Nostrand, New York, 1947.

8. **Onsager, L.** *Phys. Rev.* **37**, 405 (1931).

9. **Strutt, J.W.** (Lord Rayleigh). *Proc. Lond. Math. Soc.* **4**, 357 (1871-1873).

10. **Morel, R.E., G. Fleck, J.** *Theor. Biol.* **136**, 171 (1989).

11. **Morel, R.E., G. Fleck.** *Chem. Intelligencer* **1**(4), 27 (1995).

ЧЕТВЪРТИ ЗАКОН НА ТЕРМОДИНАМИКАТА

Резюме. Класическата термодинамика, основана на запазването на веществото и енергията и на нарастването на ентропията, което съпътства всеки природен процес, предвижда равновесните свойства на макроскопските системи независимо от тяхната сложност. Термодинамичната теория, обаче, малко казва за системи, които се намират далеч от равновесието. Това е така, защото класическите закони не обсъждат пътищата, по които системата променя своето състояние. Тук се предлага Четвърти закон на термодинамиката, *системите увеличават ентропията си с най-голямата възможна скорост*, чрез който се увеличава обсегът на термодинамиката, с което термодинамичното описание става по-пълно.

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