

Unearthing a Buried Memory: Duhem's Third Way to Thermodynamics. Part 2[†]

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Abstract. Duhem considered himself as the upholder of a 'third way' to Thermodynamics. His generalized Mechanics/Thermodynamics aimed at encompassing all kinds of transformations, from spatial changes to the change of physical qualities. From 1886 until 1896 he undertook a demanding design for the unification of physics. He translated Thermodynamics into the language of Analytical Mechanics, and conversely founded Mechanics on the principles of Thermodynamics. Step by step he widened the mathematical and conceptual structure of Analytic Mechanics, in order to hold together 'local motion,' thermal phenomena, electromagnetic phenomena, and many kinds of irreversible transformations. At the same time, he tried to recast methods and targets of physics: from the reductionist tradition of Mechanics he let a new interest in the complexity of the natural world emerge. Modern science had had to fight against the old physics of qualities, in order to supplant it: the complexity of the physical world was set aside, and replaced by a simplified geometrical world. Duhem endeavoured to retrieve and take that neglected complexity into the wide boundaries of a generalized Mechanics-Thermodynamics. He aimed at widening the scope of physics: the new physics could not confine itself to 'local motion' but had to describe what Duhem labelled '*motions of modification.*'

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1. *The Final Target: the Unification between Physics and Chemistry*

From 1886 to 1894 Duhem had attempted to transform Thermodynamics into a wide-ranging mathematical theory on the pattern of Analytic Mechanics. In the 'Commentaires aux principes de la Thermodynamique' he had put forward a very abstract thermodynamics which he had labelled Energetics, because it offered the common framework for both mechanics and thermodynamics. He aimed at a great unification of physics, and the structural analogy between Energetics and Analytic Mechanics was the main hallmark of that unification.

Early in the 1890s, Duhem began on another theoretical pathway, which was in reality a different implementation of the same desire for unification. In this instance he faced

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chemistry and its links to physics. Three issues were at stake: the attempt to unify physics and chemistry, the role of Thermodynamics in that unification, and the design of a generalized physics as described in Part 1 of this article, which would describe every kind of material transformation. In the first lines of the book Duhem published in 1893, *Introduction à la mécanique chimique*, he pointed out both experimental and theoretical advancements, in particular the experimental research on dissociations, and the 'theoretical developments of thermodynamics' (Duhem, 1893a, p. v).

In accordance with the meta-theoretical attitude which was one of the hallmarks of his scientific practice, Duhem put forward a historical rather than 'logical' outline of chemistry in the course of the century. He deployed the scientific achievements in their chronological order: 'the content of a physical law' would have been better appreciated if the reader was given the context of these 'efforts' and the 'mistakes' made on the route to its formulation.

In the first stage, corresponding to the first half of the 19th century, exothermic transformations were identified with chemical combinations, and endothermic transformations with chemical decompositions. In the second stage, around the middle of the century, the theoretical link between the pairs exothermic-endothermic and combination-decomposition was broken: exothermic transformations were identified with spontaneously occurring chemical reactions, and the endothermic with 'indirect' reactions. In the third stage, corresponding to the time when Duhem was writing, the role of temperature was given prominence: an 'exothermic compound should undergo an increasing dissociation,' as well as an 'endothermic compound should be more easily formed' when the temperature rises (Duhem, 1893a, pp. vi–vii).

In the opening chapter of the book, Duhem credited Berthollet as the first person to have 'heralded the possibility' of a 'chemical Mechanics' based on the same general 'principles' of Newton's 'celestial Mechanics' and Laplace and Poisson's 'physical Mechanics.' Duhem traced back the conceptual root of that commitment to Newton's famous XXXI *Query* to be found at the end of his *Opticks*. There the grand savant had envisaged short-range forces besides the long-range universal gravitation.¹

Duhem emphasized two main features of Berthollet's theory: first, the explanation of 'changes of state' taking place in matter in terms of molecular attractions. Second, but more important from Duhem's perspective, was the attempt to give a unified explanation for both 'changes of physical states like fusion, vaporisation, ...' and 'chemical phenomena in the strict sense.' Although Duhem did not trust in the specific mechanical models Laplace and Poisson had put forward, he shared, at least in general terms, Berthollet's meta-theoretical expectation that 'the more general the principles stemming from the chemical theory become, more they will look like those of mechanics.'²

If the opening chapter let the first two characters of Duhem's historical reconstruction emerge, namely chemistry and mechanics, the third character, namely the theories of heat, took centre stage in the second chapter. Duhem credited Lavoisier and Laplace with having been the first to set aside the various 'philosophical ideas of scholars on the nature

of caloric,' since 'the physical consequences drawn from them are the same': the distinction between 'free caloric' and 'latent caloric' did not depend on the different representations of caloric. In the first half of the 19th century, it had been assumed that heat was subject to some kind of conservation over time: in particular, in a closed cycle, its value could not change. In 1850, it was Clausius who changed this point of view, and put heat into a different perspective: heat could be transformed into 'the work done by external forces.' A third physical entity, which W. Thomson would subsequently name 'internal energy,' was assumed to have the property 'attributed to heat by the ancient physicists': it had to depend only on the initial and final state of the transformation. This was 'the radical difference between the modern theory of heat and the ancient theory of caloric.'³

In thermo-chemistry it was assumed that, when the sum of internal and external work was positive, the transformation could actually occur: in this case $EQ > 0$. Duhem criticized this theory, upheld by Berthelot, which could not attain a satisfactory generality. The recent alliance between physics and chemistry was put in danger by the existence of simple phenomena which Duhem qualified as 'merely physical.' Ice melts, water vaporizes, and a salt dissolves in a solution, 'even though these phenomena absorb heat.' The first way out consisted in distinguishing '*chemical* affinities from *physical* affinities.' The fact is that thermodynamics required a sort of symmetry between chemistry and physics: from the point of view of Duhem's design of unification, there was 'nothing more arbitrary than this distinction between chemical and physical forces.' He credited Henry Sainte-Claire Deville with having restored the unity between physics and chemistry. He also criticized the 'kinetic' theory and the theory of 'molecular attraction' which had stemmed from hypotheses on the hidden structure of matter. An invisible world, described by specific microscopic mechanical models had to explain those macroscopic effects 'appreciated by our senses.'⁴ Duhem's struggle against mechanical models was very passionate.

Why should we try to replace the bodies and their transformations with mechanical structures, rather than taking them into account as they appear to our senses, or better, as our faculty of abstraction enables us to understand them through sensorial data? Why should we represent temperature like a certain amount of free fluid, or like the living force of a given motion, rather than simply look upon it as the property of a body to appear more or less warm, or to rise and lower the level of mercury in a thermometer? Why should we try to imagine the changes of state in terms of spatial displacements, or juxtaposition of molecules, or changes of path, rather than qualifying them by means of the corresponding perturbations in the perceptible and measurable features of a body, for instance increases or decreases of density, and absorption or release of heat, etc?

Why should we demand that the assumptions, which every theory must be based on, be statements provided by statics or dynamics, rather than take the laws based on experience and derived from induction as principles, ...? (Duhem, 1893a, p. 88)

He would turn upside down the 'method' or the 'ideal' of mechanical models. He suggested giving up the two pillars of that method, the first being theoretical, and the second meta-theoretical: he rejected 'simple mechanical hypotheses,' and the belief that

they were 'real *explanations*.' His method did not aim at '*explaining* the phenomena but *classifying* them.' The ninth chapter represents in some way the turning point of the book: the second Principle of Thermodynamics takes centre stage. If external forces could be derived by a potential Ω , the uncompensated work could be written as the difference between the initial and the final values of a 'total thermodynamic potential' $\Phi = F + \Omega$. In this way, the formal analogy between analytic mechanics and thermodynamics, as well as between analytic mechanics and chemistry could be fulfilled.⁵

The last chapter dealt with a different query, emerging from the experiments performed at high temperatures. Thermodynamics forbids some transformations and nobody has ever observed these kinds of forbidden transformations. On the contrary, when some transformations are foreseen by the theory, sometimes they do not happen. In other words, when 'the system should be in equilibrium, it actually stays in equilibrium,' but it can stay in equilibrium 'even when, according to the theory, it should not.' The former was called 'true equilibrium,' while the latter 'false equilibrium.' Cases of this kind were in no way unusual: when a mixture of hydrogen and oxygen, or hydrogen and chlorine reached their 'true' equilibrium, namely water and muriatic acid, they released sufficient heat to trigger an explosion. In Duhem's theoretical framework, an explosion was therefore a passage 'from a state of false equilibrium to a state of true equilibrium,' wherein 'a remarkable amount of heat' was released. The theory was 'fruitful': it could account for sudden and disruptive events left unexplained by the old theories.⁶

At the end of his inquiry into the history of Mechanics, Thermodynamics and Chemistry, Duhem drew two conclusions, in which historical and meta-theoretical remarks were mutually interconnected. On the one hand, he remarked that scientific theories, both the old-fashioned and the more recent ones, are always fruitful, although definitely provisional. On the other hand, scientific practice could not survive without theoretical frameworks, no matter how provisional, incomplete or even flawed they were. This fact explained why scientists had sometimes tried to save a flawed theory at any cost, given that a better theory was not at hand yet.

The history of physics shows us that a theory would be over-confident when priding itself on being conclusive. We see that theories emerge and progress only to collapse. Nevertheless a theory, when it has been built up in search of the truth, can never completely disappear. Among its rubble we can find some fragments which could be employed in the building up of a better and more enduring theory. [...]

It is unusual that the conflict with experiments lead science to get rid of a mistaken theory: the upholders of the theory always try to find some subterfuge to turn around the facts that prove their mistakes while pretending to interpret them. Frequently, very illogical behaviours are involved in these procedures: the self-esteem of every inventor, the persistent attachment to the received view, and the excessive deference to authority. Nevertheless, we must also take into account the human mind, which needs to arrange the phenomena in some way around some ideas. After having built up a theoretical system, the mind leans towards its preservation, in spite of the refutations imposed by facts, until a more complete theory emerges and offers a more satisfactory framework to experimental data.⁷

These kinds of meta-theoretical issues were really at stake in the contemporary debate on thermo-chemistry, and physical chemistry in general. In 1894 Berthelot explicitly challenged the role of entropy; in 1895 Wilhelm Ostwald challenged the reliability of mechanical models of matter.

In a paper published in the *Comptes Rendus de l'Académie des Sciences*, Berthelot set the distinction between 'heat of purely chemical nature' and 'heat of different nature' ('quantités de chaleur étrangères'). Among the different kinds of 'external heat,' he listed 'external mechanical work,' and 'purely physical changes of state.' These kinds of heat had to be subtracted from 'the rough heat,' in order to compute 'the chemical heat in its strict sense.' It was purely chemical heat that allowed scientists to class chemical phenomena, when the system was 'on the threshold of dissociation.' He therefore defended his 'experimental principle of maximum work,' in which the word 'work' had the same meaning as 'energy' or 'heat.' The introduction of entropy led only to 'a new utterance' for the old 'principle': rather than deducting 'latent heat of fusion, evaporation, and dissociation' from 'total heat,' we can deduct 'heat not transformable into mechanical work,' whose main component was just 'latent heats.' In brief, what he had labelled '*chemical heat*' was 'essentially equivalent to heat transformable into work.'⁸

Nevertheless, the mathematical equivalence did not convince Berthelot of the conceptual equivalence: he found that the law expressed in terms of entropy had a 'more limited' scope, and its previsions were 'more obscure.' Some chemical systems did not have 'computable entropy': entropy was a physical quantity suitable for 'people dealing with computation in the context of mathematical physics.' In the last passages of the paper, Berthelot acknowledged that entropy played 'an essential role,' and led to 'predictions which elude the original principle of maximum work.' Nevertheless, he found that the old principle should not have been abandoned, and the 'existence and importance' of 'previous laws' should not have been 'neglected.' In some ways, he left the field of specific theoretical explanations, and entered the field of meta-theoretical or epistemological remarks. He claimed that 'the discoveries of experimental sciences form a continuous chain,' and 'the positive facts and relations achieved in Thermo-chemistry today should not be overthrown' (Berthelot, 1894, pp. 1382–1383, 1385, and 1392).

Whereas Duhem believed that the feeble link between mathematical physics and thermo-chemistry could be transformed into a fruitful alliance, this was firmly denied by Berthelot.

In a paper sent to the *Revue générale des Sciences pures et appliquées*, Ostwald, then professor of Physical Chemistry at Leipzig University, sharply criticized scientists who believed in 'the Mechanics of atoms' as an intellectual 'key' for the comprehension of the physical world. To this mechanical world-view, which Ostwald qualified as 'physical materialism,' he opposed 'a new theory' he labelled 'energetics.' Although he claimed that he would have confined himself to 'positive science,' namely 'exact sciences,' in a subsequent passage he did not manage to restrain himself from stating that the rejection

of a mechanical world-view was an attack on 'the general materialistic view.' In general, however, the paper appears as an unmistakable but balanced act of faith in his science of energy (Ostwald, 1895, pp. 953–955).

In the second half of the paper, Ostwald raised some crucial questions. As stressed by Poincaré in his 1893 paper, the most serious hindrance Mechanics had faced was represented by the irreversibility of real phenomena. Mechanics could not explain the temporal direction of natural processes, because 'the processes of rational Mechanics can follow but also go back up the course of time.' He thought that mechanical models could be easily skipped in favour of some kind of direct approach to experience, which would have allowed us 'to see directly' the world, without 'any picture, any symbol.' It seems a very naïve point of view indeed: no physical theory can avoid some kind of 'symbols' or representations. In reality, Ostwald intended something definitely less dramatic: scientists had to confine themselves to quantitative relationships among 'entities which could be handled and measured.' The most important of these entities was 'the most general invariant, the energy,' or, better, any difference of energy (Ostwald, 1895, pp. 955–957).

This phenomenological attitude stood beside an evolutionary conception of science: 'the advantages of the energetic theory over the mechanic theory' notwithstanding, energetics had not to be looked upon as the final stage of science. In an unspecified future, Ostwald expected a wider-scope theory, wherein energetics would have appeared as 'a specific instance of more general relations.' He was 'loath to fix' any a-priori 'boundary to the progress of science' (Ostwald, 1895, pp. 957–958).

When we compare Ostwald's with Duhem's energetics, we find a remarkable difference: the unifying power of very general mathematical structures in the latter, and the unifying power of a specific physical entity in the former.

In 1894 Duhem sent a long paper under the title *Sur les déformations permanentes et l'hystérésis* to a Belgian scientific journal. The following year he sent two other papers under the same title, with the sub-titles *Les modifications permanentes du soufre*, and *Théorie générale des modifications permanentes*. In 1896, *L'Académie Royale de Belgique* published all three papers in the same volume.

The first paper begins with a short historical account of 'infrequent' attempts to 'make the different kinds of permanent deformations match with the principles of thermodynamics.' According to Duhem, the difficulties in coping with permanent deformations stemmed from 'the restrictive hypothesis' which preceded 'the demonstration of Carnot's theorem' or the second Principle of thermodynamics. The hypothesis assumed the existence of '*reversible transformations*' or transformations which could be looked upon as '*a continuous series of states of equilibrium*.' The restriction to reversible transformations led obviously to the exclusion of phenomena like magnetic hysteresis. In this kind of phenomena, '*a continuous series of states of equilibrium is not a reversible transformation*,' and the second Principle of thermodynamics could not be called into play. The only available theoretical pillar was 'the principle of equivalence between heat and work,' namely the first Principle of Thermodynamics (Duhem, 1894a, pp. 3 and 7).

The fundamental entity of the new thermodynamics of permanent, irreversible transformations was a kind of closed cycle, a cycle of hysteresis, consisting of 'a descendant curve and an ascending curve meeting at two points.' After a series of long mathematical steps, Duhem showed the existence of two kinds of permanent deformations, corresponding to two different cycles: he found that the first was stable but the second was not (Duhem, 1894a, pp. 11, 13, 33–34 and 37–38).

A slightly different approach was required in the case of permanent magnetic deformations, namely the phenomena known as 'magnetic hysteresis.' By contrast with the mechanical case, there were two kinds of magnetism: a 'magnetism' acting on the element and the 'surrounding magnets,' and the 'magnetic intensity' or 'the state of magnetisation' of the given element. He was aware of the tentative and provisional nature of his theory. The theory lacked in generality: it could not account, for instance, for 'the influence of mechanical actions or elastic deformations on magnetisation.' A more general theory, 'depending on more than one normal variable,' was required: among the expected 'great difficulties,' Duhem mentioned the impossibility of relying on simple 'geometrical representations' (Duhem, 1894a, pp. 51–53, 59, and 61).

The second paper, which Duhem devoted to permanent deformations, deals with a specific chemical-physical phenomenon: 'the permanent modifications which sulphur experiences under the influence of heat.' Duhem was dealing here with phenomena placed outside the explanatory scope of ordinary mechanics, thermodynamics and chemistry. He tried to compare his graphs to experimental data, but it was only in the third paper that he put forward a general theory of permanent transformations. He stressed the necessity of 'a more general point of view,' which he wanted to develop in three different directions: systems described 'by any number of normal parameters,' simultaneous variations of temperature and external actions, and the theoretical integration with the theory outlined in the *Commentaire aux principes de la thermodynamique*.⁹

Duhem was aware that the conceptual link between his generalized 1891–1894 Mechanics/Thermodynamics and his 1895 irreversible Mechanics/Thermodynamics was a very delicate issue. He remarked that they were 'in general, incompatible,' for they were based on the incompatible hypotheses of reversibility and irreversibility. The logical incompatibility could only be removed by a sort of logical somersault in which reversibility is regarded as a specific instance of irreversibility. As he wrote in the short 'Conclusion' at the end of his third paper on permanent deformations, he had shown a possibility: he had outlined a mathematical theory submitted to various specific conditions. Although provisional, the theory sketched in these papers 'cast some light' on a very demanding subject matter (Duhem, 1895b, pp. 10 and 54–55).

He went on publishing another four papers on the same subject, under the same title *Sur les déformations permanentes et l'hystérésis*, till 1901. At the same time, he tried to insert the theory of permanent deformations into his *Energetics* or generalized Mechanics: the long essay he published in 1896 represented a further effort of

generalisation. The essay, *Théorie thermodynamique de la viscosité, du frottement et des faux équilibres chimiques*, represented in some way the final stage of Duhem's theoretical, meta-theoretical and historical journey through the complex network of connections involving Analytic Mechanics, Thermodynamics and Chemistry.

The *Introduction* was a theoretical and historical summary focussed on the concept of 'false equilibrium' he had introduced 3 years before in his *Introduction à la mécanique chimique*. There was a wide range of temperatures wherein the equilibrium was maintained by a sort of *laziness* of the system: only over and under that region the system became sensitive to temperature. Duhem summarized the situation facing chemists around the middle of the century in the following way:

When the propositions of classic thermodynamics predict the equilibrium of a system under given conditions, the equilibrium actually takes place; on the contrary, the system could actually remain in equilibrium even though it should experience some transformations according to classic thermodynamics.

This general rule can also be expressed in the following way:

Whenever classic thermodynamics predicts the impossibility of a given transformation for a given body, the transformation cannot take place; on the contrary, when classic thermodynamics predicts necessarily the passage from a state to another, frequently the expected transformation does not take place. (Duhem, 1896a, p. 5)

The second part of the *Introduction* is devoted to the structural analogy between chemical 'false' equilibrium and mechanical 'friction.' Duhem took into account a very simple configuration: a body sliding on an inclined plane. According to 'theorems of classic mechanics,' the body cannot be in equilibrium 'under the action of gravity.' In reality, for every real plane, 'there will be equilibrium when the inclination of the plane is under a certain limiting value.' The existence of this limiting value comes out easily from the ordinary procedure of solution of the problem in terms of the forces applied to the body. Equilibrium is maintained when the force of friction is greater than the horizontal component of gravity: $fmg \cos \alpha \geq mg \sin \alpha$, or $tg \alpha \leq f$ (Duhem, 1896a, pp. 8–9).

Duhem made two remarks: the condition of equilibrium is expressed by an inequality rather than an equality, and 'the study of friction and the study of false equilibriums show a very close analogy.' More specifically, the two subject matters, although belonging to different fields of science, physics and chemistry, exhibited a formal analogy.¹⁰

At that point, an important issue emerged from the core of mechanics: was friction a fundamental phenomenon or simply 'a *fictitious* term,' roughly describing those 'various and complex actions which explain friction' itself? In other words, could 'friction' be only a label stuck on a set of 'actions whose explicit and detailed analysis is impossible?' He thought that not all phenomena structurally similar to friction could be reduced to a mere 'appearance,' and could be completely described by 'classic mechanics.' He was

aware that he was dealing with ‘hypotheses,’ or meta-theoretical options, which could not be ‘disputed’: both of them were legitimate meta-theoretical options. He chose to widen the structure of the equations of Analytic Mechanics, in order to express mathematically those mechanical, thermodynamic and chemical phenomena too complex to be given a suitable description in the framework of classic science (Duhem, 1896a, pp. 9–11 and 14–16).

The most general equations of motion contained five terms: generalized forces or ‘actions’ $\mathcal{A}, \mathcal{B}, \dots, \mathcal{L}$, the derivatives $\Phi_a, \Phi_b, \dots, \Phi_l$ of the thermodynamic potential, ‘inertial’ terms J_a, J_b, \dots, J_l , ‘viscous’ terms $\varphi_\alpha, \varphi_\beta, \dots, \varphi_\lambda$, and terms of the kind $g_a \cdot a' / |a'|$, which generalized the mechanical friction discussed in the *Introduction*.

The last functions were negative, and depended on the Lagrangian parameters a, b, \dots, l , their time-derivatives, and the generalized actions. By contrast with the ‘viscous’ forces, they did not vanish when the velocities vanished: on the contrary, they tended to some limiting functions $\gamma_\alpha, \gamma_\beta, \dots, \gamma_\lambda$, which depended only on a, b, \dots, l and $\mathcal{A}, \mathcal{B}, \dots, \mathcal{L}$ (Duhem, 1896a, pp. 70–75).

In the third chapter of the second part of his essay, Duhem faced for the first time a specific chemical problem: a chemical ‘compound together with the elements coming from its decomposition.’ The Lagrangian parameter α was a measure of the degree of combination of the chemical system. He first assumed that the chemical process was exothermic and took place at constant volume. The same kind of considerations were appropriate for endothermic processes taking place at constant volume, as well as for both exothermic and endothermic processes taking place at constant pressure. In Duhem’s graphs, *A* is the region of ‘false equilibrium’; the region *B* ‘is the seat of a dissociation,’ and the region *C* is ‘the seat of a combination.’ (see Figures 1 and 2) Duhem pointed out that the exact shape of the region *A* could not be determined by his theory, but had to be derived from experiments. For every given temperature, different initial states of the system led to different final states of equilibrium. The previous history of the physical system influenced the result of the transformation.¹¹

According to the mechanical analogy suggested in the first pages of the essay, a chemical compound in the presence of its components is in equilibrium until chemical forces become so strong as to trigger off a chemical reaction of combination or decomposition. Duhem focused his attention in particular on the concept of ‘velocity’: in the ‘region of combination,’ $\alpha' > 0$, and in the ‘region of decomposition’ $\alpha' < 0$. In both regions, the chemical ‘reactions’ had to obey a specific equation of *motion*, which contained only three terms, because Lagrangian ordinary terms vanished (Duhem, 1896a, pp. 127–128).

From this equation, Duhem tried to derive ‘the velocity of transformation of the system,’ or in other words, the velocity of the chemical reaction. The derivation seemed too complex, and he ventured to put forward some simplifications involving the two *dissipative* functions $\varphi(P, \alpha, T, \alpha')$ and $g(P, \alpha, T, \alpha')$. The simplified equation allowed

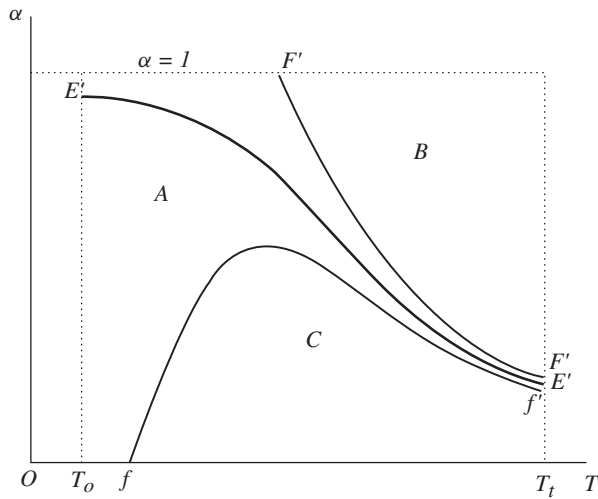


Fig. 1. Duhem's phenomenological graph for exothermic processes: the degree of combination decreases with temperature. (Duhem, 1896a, p. 106).

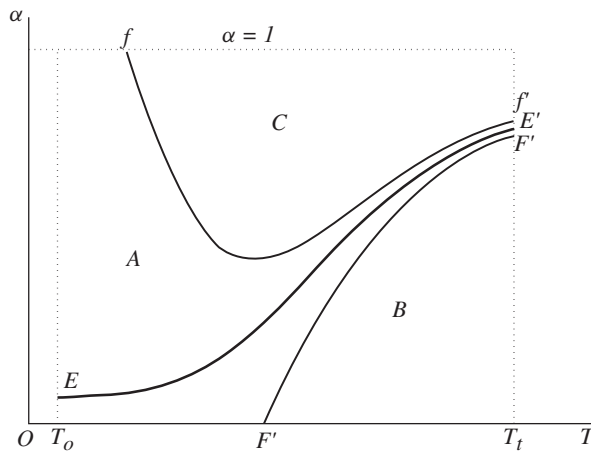


Fig. 2. Duhem's phenomenological graph for endothermic processes: the degree of combination increases with temperature. (Duhem, 1896a, p. 107).

Duhem to compute the 'velocity' of reaction in chemical processes, because α' appeared only in a linear way in the factorisation of the 'viscous' term.¹²

When the generalized viscosity vanished, velocity became infinite: this limiting case did not correspond to modern mechanics but to Aristotle's theory of motion. In order to better explain the theoretical break, Duhem compared a pendulum undergoing free oscillations with a damped pendulum. Starting from the free oscillations, we can imagine

a gradually increasing viscosity acting on the pendulum, until it becomes critically damped, and it approaches asymptotically the position of equilibrium without any oscillation: an infinite velocity is excluded. On the contrary, in Duhem's framework, the starting point was represented by a system strongly damped: the velocity of the process increases with decreasing viscosity, until it becomes infinite when viscosity vanishes. We are facing two theoretical frameworks which cannot be reduced to each other (Duhem, 1896a, pp. 130–131).

The *structural* analogy between Mechanics and Thermo-Chemistry required that an increased *smoothness* in the first field corresponded to the rise of temperature in the second field. In other words, increasing temperatures *smoothed* dissipative effects. Nevertheless there were 'essential differences' between 'the theory of motion of systems as taught by Dynamics' and his 'theory on the modification of a system.' The difference dealt just with the role of 'velocity.'¹³

Duhem had looked upon his generalized physics as a generalisation of classic dynamics, involving systems undergoing dissipation, but now he realized that he had arrived at a sharp mathematical and conceptual gap between mechanics and chemistry. He realized that, starting from a *structural* analogy, he had reached a *structural* difference between classic dynamics and the application of his generalized physics to chemical reactions. The role of 'velocity' in Duhem's theory of dissipative systems was consistent with another *structural* analogy: Aristotle's theory of motion as a theory of material transformations. In the context of Aristotle's *physics*, it is not strange that, in the absence of some kind of resistance, velocity becomes infinite.

The summary Duhem outlined in his 'Conclusion' was, in some ways, a plan for further researches. The second Principle of Thermodynamics stemmed from the negative work performed by dissipative actions and permanent deformations. The specific feature 'the term of *viscosity*, the term of *friction*, and the term of *hysteresis*' had in common was the behaviour with regard to time, in particular time-symmetry. Under the transformation $t \rightarrow -t$, the first time-derivatives $d\alpha/dt, \dots, d\lambda/dt$ were transformed into $-d\alpha/dt, \dots, -d\lambda/dt$, whereas the second time-derivatives $d^2\alpha/dt^2, \dots, d^2\lambda/dt^2$ remained unchanged. Purely mechanical equations contain only quadratic terms in the first time-derivatives, and therefore they are invariant under the time-symmetry transformation $t \rightarrow -t$.

This invariance, or reversibility, does not occur in physical systems affected by 'viscosity,' 'friction' or 'permanent transformations.' The mathematical terms corresponding to 'these three classes of actions' change their sign when generalized 'velocities' change their sign under time-symmetry. These physical systems are affected by time-irreversibility: this feature 'deeply differentiates' them from purely mechanical systems. Duhem found that this deep difference represented an 'insuperable hindrance' to reducing 'complete thermodynamics . . . to classic dynamics' (Duhem, 1896a, p. 202).

He was 'forced to acknowledge' that 'the fundamental equations of dynamics' are 'more complex than Lagrange's equations.' He looked upon his 'doctrine' as a

theoretical contribution in the wake of a conceptual stream recently established by Rankine. From that stream, which he labelled *Energetics*, two main issues emerged: the intrinsic existence of dissipative effects, and the necessity for a more general science of transformations (Duhem, 1896a, p. 205).

In Duhem's theory, Clausius' inequality did not follow from 'logical' or 'experimental' reasons. It was the consequence of a specific hypothesis: the work done by 'viscosity' or 'friction' had been assumed to be negative. In this sense, Clausius' inequality, namely the second Principle of Thermodynamics, was not a physical necessity, but the consequence of an 'arbitrary' hypothesis. Duhem's theory would not have been overthrown by the opposite choice of 'positive friction.' The fact that the hypothesis of negative work was in accordance with experience could not mean that subsequent experiences could not lead to a 'contradiction.' He pointed out the analogy between a hypothetical positive work and the creative power of life.

When we inquire into the properties of system in which the work done by viscosity and friction would not be basically negative, and uncompensated transformations would not be basically positive, it is impossible not to be struck by the analogy between those properties and those of living tissues, both animal and vegetable. It is impossible not to notice how easily they account for the majority of organic syntheses, which cannot be explained by ordinary chemical mechanics, and cannot be performed outside the living body, *under the thermal conditions which allow the living body to operate.* (Duhem, 1896a, p. 206)

The life Sciences suggested the possibility of a 'new thermodynamics' or '*physiologic thermodynamics*,' which would satisfy the Principle of conservation of energy but not '*the principle of the impossibility of perpetual motion.*' In the course of almost three centuries, most scientists had tried to reduce the phenomena of life to mechanical actions. Duhem was showing another, complementary perspective: the study of phenomena occurring in living matter could enable scientists to better understand physical and chemical phenomena of high complexity.¹⁴

Duhem hinted at a mere possibility far from being fulfilled: at that time, the creative power of life was far beyond the horizon of physics. Only after many decades, would some physicists and chemists try to recollect these scattered remarks.

2. Concluding Remarks

Theoretical physics, history of physics and meta-theoretical remarks were mutually interconnected in Duhem's actual praxis. In his search for a new generalized Mechanics, Duhem analysed the different stages in the history of Mechanics: they had been fruitful and meaningful, even though, at the end of the 19th century, science called for a new stage, namely an abstract generalization, which could account for the complexity of the physical world. Since the time of Galilei, modern science had had to fight against the old physics of qualities, in order to supplant it: the complexity of the physical world was set aside, and replaced by a simplified geometrical world. Duhem endeavoured to retrieve

and take that neglected complexity into the wide boundaries of a generalized Mechanics-Thermodynamics. He aimed at widening the scope of physics: the new physics could not confine itself to 'local motion' but had to describe what Duhem labelled 'motions of modification.' If Boltzmann had tried to proceed from 'local motion' to attain the explanation of more complex transformations, Duhem was trying to proceed from the mathematical laws of general transformations to reach 'local motion' as a simplified specific case. In his generalized Analytic Mechanics, both inertial and dissipative terms were at stake. When inertial terms were dropped, a rough model of explosive chemical reactions emerged; when dissipative terms were dropped, classic mechanics re-appeared.¹⁵

Duhem continued to publish papers and books on theoretical physics till his death in 1916: now we can ask ourselves what heritage Duhem left to 20th-century science.¹⁶ As far as I know, something survived, although in an unexpected way. The majority of Duhem's specific theoretical models, and his specific mathematical approach did not survive, but some issues survived, and found new implementations. Among them, I list:

1. Thermodynamics can be re-shaped into a generalisation of analytic mechanics;
2. Physics can describe the complexity of the real world.

The design of a generalized and fully mathematized Thermodynamics was pursued by Clifford A. Truesdell in the 1960s. In the second edition (1984) of his book *Rational Thermodynamics*, he reminded the reader that he had 'returned to the sources' of Thermodynamics. He regretted that 'DUHEM's work had fallen into the general oblivion of classical mechanics in the interbellum,' although he acknowledged that 'most of the work since 1960 follows the example of DUHEM.' Truesdell recommended that 'DUHEM's researches be studied until justice be done them,' and qualified Duhem's preface to *Treatise on Energetics or General Thermodynamics* as a 'program of modern rational thermodynamics.'¹⁷

Truesdell remarked that, before Duhem, Thermodynamics was swaying between technology and cosmology: the operation of technical devices, on the one hand, and 'the speculations about the universe,' on the other. He found that, although 'its claims are often grandiose, its applications are usually trivial.' The mathematics of thermodynamics appeared to Truesdell obscure and misleading: he aimed to state and teach Thermodynamics 'just as classical mechanics is stated precisely and learned.' Truesdell's aim was not different from Duhem's: in his words, he was looking for 'a thermodynamic theory formally similar to the classical one but vastly more general in scope.' His generalized Thermodynamics should 'extend the concepts of mechanics so as to allow for diffusion and chemical reactions as well.'¹⁸

Duhem's anti-reductionist design attracted the attention of a small section of the French scientific community. In 1917, 1 year after Duhem's death, E. Jouguet, *Ingénieur en chef des Mines*, and *Répétiteur à l'École Polytechnique*, published a paper in the *Revue générale des Sciences pures et appliquées*, in which he gave a short account, and

attempted a comprehensive appraisal of Duhem's contribution to theoretical physics. Jouguet had followed the tradition of French engineers who, in the second half of the 19th century, had steered French physics out of the arid lands of mere experimentalism. Having collaborated with Duhem at Bordeaux, he could appreciate both Duhem's physics and Duhem's meta-theoretical commitments. He was aware that 'Duhem had a very peculiar place in French science': he had not taken part in the building up of 'recent theories,' 'his method contradicted some habits,' and his theories could be understood at the price of 'efforts which some people were not able to make.'¹⁹

Jouguet considered Duhem the founding father of the 'thermodynamics of irreversible processes': before the appearance of his mathematical theories on 'viscosity, friction, and hysteresis,' these phenomena had only been taken seriously into account 'in exceptional circumstances.' But Duhem had realized that 'chemical Mechanics' required new 'differential equations of motion,' namely differential equations of the first order, corresponding to 'variables without inertia.' Those equations, just like the equations of ordinary mechanics, were 'specific instances of the equations of Energetics.' In this sense, Energetics encompassed different kinds of Mechanics, corresponding mathematically to different kinds of differential equations.²⁰

Jouguet's most interesting appraisal deals with the much-debated concept of 'Mechanism.' He qualified Duhem as a 'mechanist,' but then he specified that 'a mechanist should not be identified with mechanical attitudes.' The statement sounds puzzling unless we distinguish between the two traditions which had emerged in the history of Mechanics: specific mechanical models, on the one hand, abstract mechanics, on the other.²¹

In 1927, the physicist O. Manville, 'chargé de conférence' at the Science faculty of Bordeaux university, published an extensive book on Pierre Duhem's physics. Two 'Mémoires' concluded the book: in the first, the mathematician Hadamard commented on the mathematician Duhem; in the second, the historian A. Darbon commented on the historian Duhem. Manville's analysis is quite detailed, and for many decades his book remained the sole study on Duhem's theoretical physics. He pointed out that Duhem's choice of mathematising 'qualities' stemmed from the rejection of any distinction between quantities and qualities, namely any distinction between primary and secondary features of a body or process. In its turn, this rejection stemmed from the distrust in any pretension of explaining the natural world. No hidden structures could lead us to understand 'the real features of bodies' to be found underneath their 'tangible aspect' (Manville, 1927, pp. 18–19).

After some years, in 1941, outside the French context, the American experimental physicist Percy William Bridgman published a book on the foundations of Thermodynamics. Although his approach to Thermodynamics was not so different from Duhem's, he never mentioned him, and it is debatable whether he had previously encountered Duhem's work. The fact is that in the 1940s Duhem's scientific legacy had already become a sort of buried memory. The scientific community, which had become a homogeneous international community, was focussing its intellectual and material resources

on sub-nuclear physics. Both the interest in the foundation of Thermodynamics, and the foundation of physics in general had progressively faded away. The new theoretical physics was quite different from the wide-scope theoretical physics of the late 19th century.²²

In the end, we find an interesting re-interpretation of Duhem's attempt to tame complexity in Prigogine's theoretical researches. In 1947, in the essay *Etude Thermodynamique des Phénomènes irréversibles*, he pointed out 'the deficiencies of classic thermodynamics.' First of all, classic thermodynamics is 'confined to states of equilibrium and reversible transformations,' and cannot account for chemical reactions, in which the system is not in chemical equilibrium. Secondly, the two principles of classic Thermodynamics are confined to closed systems, namely systems allowed to exchange energy but not matter with the external world. Other difficulties arose from the applications to electro-chemistry or to systems crossed by a temperature gradient. According to Prigogine, a more general Thermodynamics was required, in order to account for irreversible phenomena, states far from equilibrium and open systems. Prigogine acknowledged explicitly the role played by Duhem in the setting up of a new Thermodynamics, even though Duhem's researches 'had not had any valuable effect' on the scientific community, even in French speaking countries.²³

Even Miller's approach to thermodynamics of irreversible processes is not so different from Duhem's Energetics, apart from some naïve remarks on the alleged simple derivation of 'axioms' from experiments. He reminded the reader that '[T]he only processes which can be treated in detail' by classic thermodynamics 'are the physically unrealizable reversible ones.' As Prigogine had done some years before, Miller also stressed the difference between 'the entropy produced *inside the system*' ΔS_i , and 'the entropy *added to the system* by heat transport across its boundaries': the former stemmed from 'the more familiar uncompensated heat of Clausius.'²⁴

Half a century after Duhem's death, the complexity of the physical world began to attract some physicists and chemists. The buried memory of his theoretical physics re-emerged and found new implementations. But that re-emergence was, in some ways, a fresh start.²⁵

NOTES

1. Duhem, 1893a, pp. 2 and 8. Duhem made reference, in particular, to Berthollet's, 1803 *Essai de statique chimique*.
2. Duhem, 1893a, pp. 9 and 11. Duhem quoted from Berthollet, 1803, p. 2.
3. Duhem, 1893a, pp. 12–17. Duhem specified that the term 'living force' dealt only with 'the living force of *sensible* motions,' namely macroscopic motions. In no way could he make reference to 'the living force of the hypothetical motions by which many physicists explain heat' (*Ibidem*, p. 16, footnote 1).
4. Duhem, 1893a, pp. 35, 52, 56, 58, 68–69, 74–75, 81 and 87. Sainte-Claire Deville had emphasized the strong analogy between 'the mechanism of chemical reactions and the mechanism of physical changes of state.' It is worth mentioning that, in 1880, in a brief *Note* sent to *Comptes Rendus de*

- l'Académie des Sciences*, Sainte-Claire Deville had claimed that he could accept 'neither atoms, nor molecules, nor forces': he could not rely on entities he could 'neither see nor imagine.' See Sainte-Claire Deville, 1880, p. 342.
5. Duhem, 1892a, pp. 89, 93, 96, 100, and 112–113. As already stressed, that *structural* analogy was quite different from the contemporary attempts to transfer specific *mechanical models* from mechanics to thermodynamics and chemistry.
 6. Duhem, 1893a, pp. 157–159 and 173–174. In the previous pages Duhem had described some processes giving rise to 'false' equilibrium. See *Ibidem*, p. 155: 'The decomposition of water absorbs heat. When we increase the temperature of a mixture of oxygen and hydrogen, and we let it grow gradually, we do not observe any chemical reaction until, at a temperature of about 500°C, by a violent explosion, part of the mixture will suddenly transform into steam.'
 7. Duhem, 1893a, p. 176. In 1902 Duhem published a historical and critical account of the concept of mixture in the long-lasting tradition of philosophy, as well as in the recent tradition of chemistry. The book widened and deepened the researches which Duhem had already published in 1892. The book has recently been translated into English and commented by Paul Needham. See Duhem, 1892b; Duhem, 1902; Duhem, 2002 and Needham, 2002.
 8. Berthelot, 1894, pp. 1378–1379 and 1382. A recent historical and conceptual reconstruction of Duhem's opposition to Berthelot's 'principle of maximum work,' which involved the distinction between endothermic and exothermic reactions, and the distinction between physical and 'purely chemical' transformations, can be found in Brenner and Deltete, 2004, pp. 204–207. On the criticism about Berthelot's law of maximum work outside France, see Needham, 2002, p. xxiii.
 9. Duhem, 1895a, pp. 4–5, 8–9 and 54, and Duhem, 1895b, p. 4. Liquid sulphur had a very peculiar behaviour: the temperature of solidification depended on the *thermal path* experienced by the liquid phase, namely the series of temperatures it had subsequently assumed. (See, for instance, *Ibidem*, p. 38).
 10. See Duhem, 1896a, p. 9: 'The conditions of equilibrium of a system with friction are not expressed by equalities . . . but inequalities. As a consequence, when the acting forces are given, the equilibrium is not defined: we can see an infinity of states of equilibrium, which form a continuous set.'
 11. See Duhem, 1896a, pp. 106–107: 'When it is held at a constant temperature, the system does not tend towards a single limiting state: it depends on the initial state, which could be a state of mixture or combination. Only at high temperatures the two limiting states approach to each other.'
 12. Duhem, 1896a, pp. 128–129 and 131. There is a plus/minus misprint in Duhem's equation.
 13. This fact led Duhem to state: 'The concept of inertia cannot be extended to such transformations.' See Duhem, 1896a, p. 130 Duhem's previous hypothesis concerning the thermo-chemical behaviour of a system with regard temperature can be found at page 104. The values of the function which expressed the viscous term had to be small at high temperatures, and great at low temperatures. (See *Ibidem*, p. 131).
 14. He hinted at the possibility that 'another interpretation of organic synthesis' could reverse 'the expectations of thermodynamics.' See Duhem, 1896a, p. 207.
 15. In the time span we are interested in, Duhem published some papers specifically devoted to the history and philosophy of science in the Belgian journal *Revue des questions scientifiques*. See Duhem, 1892a, 1893b,c,d, 1894b and 1896b. Duhem's design was also explained in a subsequent book: see Duhem, 1903, in Duhem 1992, pp. 199 and 218–219.
 16. Duhem did not manage to encompass all physical and chemical phenomena in his Energetics: electromagnetic phenomena, radioactivity, and radiant heat remained unrepresented. As Deltete and Brenner reminded us, the new interpretations of those phenomena, which emerged at the turn of the 20th century, involved 'microscopic discreteness and discontinuity of the kind forbidden by his energetics.' See Brenner and Deltete, 2004, p. 223.
 17. Truesdell, 1984, pp. 2, 7, 24–25, 38, 40–41 and 45. Truesdell made reference to the massive two-volume treatise Duhem published in 1911, *Traité d'énergétique ou de thermodynamique générale*,

- which was a sort of *summa* of Duhem's generalized thermodynamics. It is worth mentioning that, in 1964, Louis de Broglie had stressed a fundamental formal analogy between Analytic Mechanics and Thermodynamics. From the relativistic point of view, Hamiltonian 'action' is the 'fundamental invariant of Mechanics,' and entropy is 'the fundamental invariant of Thermodynamics.' De Broglie remarked that the relativistic invariance is consistent with Boltzmann interpretation of entropy as 'an integer number of complexions.' See De Broglie, 1964, pp. 25 and 49.
18. Truesdell, 1984, pp. 59, 61–62, and 106. He regretted that the reader had to face odd inequalities like $T \cdot dS \geq \delta Q$: 'He is told that dS is a differential, but not of what variables S is a function; that δQ is a small quantity not generally a differential; he is expected to believe not only that a differential can be bigger than another, but even that a differential can be bigger than something which is not a differential.' (*Ibidem*, p. 61).
 19. Jouguet, 1917, p. 40. In 1908–1909, Jouguet had published a two-volume history of Mechanics, *Lectures de Mécanique*, wherein he claimed that the history of science allowed scientists to 'better understand the nature of principles and laws of Mechanics.' In the *Préface*, he acknowledged the role played by Duhem in the comprehension of the ancient sources of modern mechanics. Moreover, when he briefly discussed peripatetic physics, he stressed the deep theoretical connections among that ancient physics, dissipative processes, and 'the foundations of Thermodynamics.' See Jouguet, 1908, pp. VII–VIII and 4.
 20. Jouguet, 1917, pp. 43–45.
 21. Jouguet, 1917, pp. 48–50. He looked upon Energetics as a wider mechanics, extended to 'physical and chemical transformations;' it could rely on equations which were an extension of Lagrange's equations. (See *Ibidem*, p. 50).
 22. Bridgman mentioned 'de Groot, Prigogine, and especially Onsager.' See Bridgman, 1961, p. v. According to Bridgman himself, the 1941 edition of his book was re-published in 1961 'with no essential change.'
 23. Prigogine, 1947, pp. 3–5 and 11. It is worth quoting the Prigogine passage on Duhem: 'Those researches had a scarce effect: we can say that the actual development of the thermodynamics of irreversible phenomena began with De Donder's fundamental researches on irreversible chemical phenomena.' (*Ibidem*, p. 3).
 24. The second volume of Duhem, 1911 is only mentioned in a footnote in connection with the computation of entropy production in specific cases: viscosity and heat conduction. In another footnote, Duhem is mentioned because he had mentioned Stokes and some symmetries in linear relations between forces and fluxes. Duhem does not appear in the list of 'important monographs' which, in Miller's words, '[t]his survey is primarily based on.' See Miller, 1956, p. 433, fn. 1, p. 434, and p. 436, footnote 11 included.
 25. On the subsequent debate on the new trend in physics after the second World War, and on the re-emergence of the interest in the complexity of the physical world, see Cocconi, 1970, pp. 83 and 87, Anderson, 1972, pp. 393 and 395, and Schweber, 1997, pp. 659–671.

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