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Dossier Pierre Duhem

Was Duhem Justified in not Distinguishing Between Physical and Chemical Atomism?

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Abstract:
Chemists in the late nineteenth century were apt to distinguish the theory of chemical structure they advocated as chemical, as opposed to physical, atomism. The failure on Duhem's part to consider any such distinction in his critique of atomism might be taken to be a lacuna in his argument. Far from being a weakness in his stance, however, I argue that he had good systematic reasons for not taking such a distinction seriously.

Keywords:
Pierre Duhem; atomism; caloric; chemistry; thermodynamics

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In this short note I want to take up an aspect of Duhem's critique of atomism relating to a nineteenth-century distinction between physical and chemical atomism. Chemists such as Williamson and Kekulé who developed molecular theories of the underlying nature of chemical substances in the wake of Dalton's atomic explanation of the laws of constant and multiple proportions thought of their theories of matter as concerned with chemical atomism. This they distinguished from what they called physical atomism, one of the major applications of which was the kinetic theory of gases developed in the same period, possibly because they could see no systematic connection between the two. At all events, chemical atomism was specifically concerned with the problems chemists were interested in—the variety of chemical substances and their interactions. Physicists concerned with analysing matter were not interested in distinctions of substance. Duhem took no account of this distinction in his critique. Is this an omission that weakens his argument? I think Duhem had good systematic reasons for not acknowledging a nineteenth-century distinction between physical and chemical atomism that are part and parcel of his overall argument.

Duhem developed his detailed critique of atomism in chemistry at the turn of the twentieth century. In retrospect this seems to have been a misdirected effort. Whether it was undermined by the current state of chemistry at the time is, I think, doubtful. But my interest in the matter is to understand what his arguments were and whether it was reasonable for a man in Duhem's position to propound them. Having written extensively on this subject earlier (Needham 1996, 2004a, 2004b, 2008), I don't intend to rehearse all the

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details here but simply to emphasise a point of fact and pursue one aspect of his view. The point he recognised is that the laws of chemical combination (constant, multiple and reciprocal proportions) are just that—concerned with proportions. As such they don't entail that matter is discrete; though consistent with atomism (or discrete matter at one or more levels), they are also consistent with a continuous view of matter. Duhem's response was that the reasonable position to adopt was one of neutrality between these two interpretations until decisive reasons favoured the one or eliminated the other. Most of the effort in Duhem (1892) and (1902) went into elaborating a neutral interpretation of the use of chemical formulas embodying the basic laws, which he established as perfectly possible even though some might think it easier to adopt an atomic interpretation.

Even if decisive reasons on which to base a choice were not available, it was quite legitimate to examine what was currently on offer and give voice to problems arising. Here it is apposite to raise questions about the very coherence of the notion of an atom. Doubts on this score have been a feature of the atomic debate since ancient times. They were a live issue in the latter part of the nineteenth century and constituted one line of thought in the general scepticism regarding atomism that was rife in the nineteenth century. A well-known example is the paradox of atomic collision. Either direction is changed instantaneously, requiring what is impossible, namely an infinitely large force, or the "atoms" are elastic in virtue of a structure of subatomic parts and hence not atoms after all. Another example is the discrepancy between the specific heat ratios of diatomic gases as observed on the basis of thermodynamic reasoning and as calculated on the basis of the kinetic theory.

But aren't these worries about the physical nature of atoms, which chemists could circumvent by focusing on chemical atoms? This strategy might be interpreted to the effect that chemists were thereby avoiding any claim to adopt an atomic theory of chemical substances. The term "chemical atomism" should in that case be understood as being used in what analytic philosophers like Nelson Goodman called a syncategorematic sense. It is not a certain kind of atomic theory, just as a broken glass is not a certain kind of glass—not something which is both a glass and broken. Although the expression is built from two distinct words, they don't each retain their separate senses in the combined expression. If this is so, and what is meant is simply a theory founded on the laws of proportion, then it is not substantially different from Duhem's account, which is not an atomic theory. I find it very difficult to see how a view or theory can be regarded as an atomic view or theory unless it says something about atoms—ascribes to them properties from which the macroscopic properties of chemical substances can be derived.

This brings us to the related line of questioning concerning how the atomic hypothesis could provide any explanation of chemical combination or whatever it is they are postulated to explain. Dalton was clear about this. He ventured to explain his law of partial pressures by endowing his atoms with a coating of caloric, so distributed about the atoms of a particular kind that they repulsed other atoms of the same kind but not atoms of different kinds. This raises a number of questions, of course: What distributions of caloric could function in this way? Would the repulsive power of caloric allow atoms of the same and different kinds to combine chemically to form polyatomic molecules of elements and compounds, as distinct from a mechanical mixture? What is it that explains the combining power if the caloric explains the repelling power? Above all, there is the question of whether trying to explain repulsion or combination by postulating a substance endowed with just these proclivities isn't directly circular or leads to an infinite regress, as Lavoisier realised when speaking of the tendency of air to expand and increase in pressure with temperature by virtue of the elastic property of caloric:

> It is by no means difficult to perceive that this elasticity depends upon that of caloric, which seems to be the most eminently elastic body in nature. Nothing is more readily conceived, than that one body should become elastic by entering into combination with another body possessed of that quality. We must allow that this is only an explanation of elasticity, by an assumption of elasticity, and that we thus only remove the difficulty one step farther, and that the nature of elasticity, and the reason for caloric being elastic, remains still unexplained. (Lavoisier 1789, 22)

Duhem thought that ascribing atoms combining powers in the form of atomicities (valencies) amounted to simply reading properties of elements in compounds apparent at the macroscopic level into atoms, providing, to paraphrase Lavoisier, an explanation of the combining power of elements by an assumption of the combining power of elements. The atomic theory of the hydrogen molecule proposed by Heitler and London is not at all like this, but provides a substantial theory of the quantum nature of hydrogen atoms from which the stability of the hydrogen molecule is derived. What was on offer at the time Duhem was writing which went beyond empty ascriptions to atoms of the properties that were to be explained seems to have been restricted to ideas about the shape of microentities or the vortex theories. These may not have incited a great deal of interest on the part of chemists (although Jones (1902, 38-9) is an example of a chemist who found some interest in vortex theories) and Duhem's dismissing them without difficulty may have been equally uninteresting to chemists. But it served to make the point that there was nothing on offer beyond tautology that looked like a promising start to an atomic theory of chemical combination.

Whatever the explanatory merit of a substantial atomic theory, how could it be anything but a physical theory of atoms? To say otherwise is surely to court the occult, bringing to mind the pre-enlightenment division of the universe into sub- and superlunary regions with modes of explanation peculiar to each. Certainly Duhem thought it was anathema to modern science to bifurcate phenomena into separate realms with laws appropriate to each. This was the philosophical basis of his opposition to Berthelot's defence of the principle of maximum work, which presupposed that a distinction could be made between physical and chemical processes and the principle restricted to the latter. Let us recall Duhem's case. According to Thomsen's law of maximum work, chemical reactions proceed spontaneously only if they are exothermic. Although the majority of reactions conform to this principle, evidence of exceptions bringing into question the universal validity of the law was mounting. Berthelot proposed to interpret the apparent counter instances as constituted of two processes, a chemical change alone subject to the law of maximum work, and a physical change not restricted by the law. Duhem (1886, ii-iii) maintained that the demarcation between chemical and physical phenomena was illegitimate, criticising the distinction on which Berthelot's defence of the law was based as ad hoc.

> Sulphuric acid, for example, combines with ice and this combination produces cold. In order to bring this exception within the rule, the reaction must be divided into two phases: one part being the fusion of ice, a *physical* phenomenon which absorbs heat, and the other part, the combination of liquid water with sulphuric acid, a *chemical* phenomenon which releases heat. But it is by a purely mental conception, and not as a representation of reality, that it is possible to thus decompose a phenomenon into several others. Moreover, accepting that chemical phenomena obey the law of maximum work while physical changes of state would be free is to suppose that there is between the mechanism of these two orders of phenomena a line of demarcation which the work of Henri Sainte-Claire-Deville has removed. (Duhem 1886, ii-iii)

Berthelot's interpretation supposes that a chemical reaction produces a reduction in internal energy of the reacting material, and thus that a stable state of chemical equilibrium corresponds to the lowest possible value of energy of the system, just as does the stable state of a mechanical system. The failure of Berthelot's rule shows that energy alone cannot serve as the basis of a general criterion of chemical equilibrium. If the analogy with mechanical systems is to be upheld, a generalisation of mechanics is required and something other than energy must be found to play the role analogous to that which the potential plays in mechanics. Duhem goes on to show how work in thermodynamics by Massieu, Horstmann, Helmholtz and Gibbs had led to a better appreciation of the conditions governing chemical equilibrium. All cases could be accommodated in terms of the general notions of thermodynamic potentials, which take account not only of the energy change, as Berthelot in effect did, but also of the entropy change.

Duhem continued to argue in this spirit for a unified view of science according to which all phenomena are subject to the same general principles rather than constituting different worlds, notably when rejecting the reduction of thermodynamics to mechanics in favour of a vision in which the old mechanics is incorporated into a broader theory (Duhem 1892; 1892; 1894). Unification, not by reduction to preconceived ideas but by expansion and integration into a general theory without internal contradictions is the way to achieve the goal of what he called a natural classification.

To summarise, then, advocacy of a specifically chemical atomism might be seen as a device for avoiding commitment to a discrete view of matter at the microlevel. But the rejection of any substantive distinction between chemical and physical realms was a matter of principle for Duhem. The absence of any recognition of a distinction between chemical and physical atomism that chemists of the time might have entertained is one of the strengths of his general argument.

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