"Chemistry beyond the 'positivism vs realism' debate"

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It is often assumed that chemistry was a typical positivistic science as long as chemists used atomic and molecular models as mere fictions and denied any concern with their real existence. Even when they use notions such as molecular orbitals chemists do not reify them and often claim that they are mere models or instrumental artefacts.

However a glimpse on the history of chemistry in the *longue durée* suggests that such denials of the ontological status of chemical entities do not testify for any specific allegiance of chemists to positivism. Rather it suggests that the dilemma positivism vs realism is inappropriate for characterizing the ontology of chemistry. This alternative shaped at the turn of the twentieth century in the context of controversies about atomic physics does not take into account the major concern of chemists, i.e. making up things. Only by considering what matters for chemists, their matters of concern rather than their matter theories, can we expect to get an insight on their ontological assumptions.

The argumentation based on historical data is twofold. It is wellknown that generating new substances out of initial ingredients which is the *raison d'être* of chemistry raised a vexing puzzle which has been alternatively solved with the Aristotelian notion of mixt and the Lavoisieran notion of compound. I will argue that an essential tension remains intrinsic in chemistry between the two conceptual frameworks.

The second section tries to make sense of the long tradition in chemistry of ontological non-commitment. I will argue that what is usually considered as a denial of the existence of the basic units of matter would be better characterized as a focus on more important actors on the chemical stage.

The chemical puzzle

Paul Needham who gave detailed analyses of Aristotle's conception of mixts convincingly argued that Aristotle raised the fundamental issue of chemistry. The issue raised by Aristotle in *De generatione and corruptione* I, concerned the mode of presence of the constituents in a mixt. The problem emerged from a critical review of atomism. If atomist doctrines were right, then a mixt would be just a collection of atoms placed side by side, like grains of wheat and grains of barley. "To the eye of the Lynceus nothing would be combined". [1] Constituents would be physically present in the compound although not visible at first glance. They can be recovered without changing the properties of the compound. However Aristotle insisted that if the ingredients are preserved then the mixt is only apparent. By contrast a true process of mixing involves the interaction of qualitatively differentiated ingredients in such a manner that they do not persist unchanged in the resulting compound. A true mixt is not just constituents sticking together. Something new is created, with properties not possessed by the original ingredients. The emergence of a new stuff implies that the ingredients no longer coexist with the mixt. Consequently a true mixt can be characterized by an **either…or** condition. Either you get a compound, and you lose the properties of the initial ingredients; or you recover the original ingredients and you lose the properties of the mixt. By contrast, the atomic conception of chemical combination does not require such a disjunction.

[1] Aristotle, *De generatione et corruptione* I.10, 328^{a}13f)

However Needham's clear recognition of the importance of the Aristolian puzzle for chemistry does not allow to claim that Aristotle had shaped a "theory of chemical reaction and chemical substances", [2] for chemistry did not exist as an identifiable branch of knowledge in his time.
Avoiding such anachronisms is important for grasping the presence of what I dub an "essential tension" between two competing views of chemical combinations that both shaped the identity of chemistry.

Between mixts and compounds, between Stahl and Lavoisier
At the turn of the eighteenth century, Georg-Ernst Stahl echoed Aristotle distinction between true and apparent mixts in zn attempt to delineate the territory of chemistry from that of physics. He acknowledged that mechanical physics could account for 'aggregates', whereas only chemistry could deal with 'mixts'.[3] Aggregation was a juxtaposition of units, and could be understood in mechanical terms such as mass and movement. Mixtion was the union of principles involving individual affinities. The decomposition of an aggregate would not affect its properties whereas mixts could only be analyzed by changing their properties. Stahl thus centered chemistry on the notion of mixt, against tentative annexations by mechanism. So successful was this conceptual strategy, that Stahl has been celebrated as the founder of chemistry throughout the eighteenth century.
However one century later, chemists no longer used the word 'mixt', as the notion of composition prevailed. In particular, Lavoisier's famous definition of elements as undecompound substances was integral part of a reorganization of chemistry along the backbone of another distinction, between simple and compound. Lavoisier, who came to be celebrated as the founder of "modern chemistry", redefined chemistry as the science aiming at decomposing the natural bodies and "examining separately the various substances entering in their combination". [4] To be sure the compositional perspective was nothing new, but it became the dominant paradigm with the reform of chemical language.[5] In the new language names of compounds were coined by simple juxtaposition of their ingredients names, and were considered as "mirror images" of the actual composition of material bodies.[6] Lavoisier, who admired and extensively quoted Etienne Bonnot de Condillac's *Logic,* adopted his views of languages as analytical methods as well as his notion of analysis as a two-way process, from simple to compound and from compound to simple. According to Condillac, analysis is a mental process to visualize successively the elements of a picture given simultaneously in sensation. Condillac used the metaphor of the vision of a castle. Immediately I see a castle, then by analysis the mind will distinguish and name each element of the landscape, which preexisted in the global view. [7] Condillac's logic, inspired by algebra, in turn inspired Lavoisier's use of equations to describe chemical reactions. A compound is described as the addition of two constituent elements. It is entirely characterized by the nature and proportion of its constituents. The use of the sign "equals" in the equation clearly indicates that chemists no longer care for the either/or condition. The puzzling issue raised by Aristotle about the mode of presence of ingredients in the compound has been ignored, simply discarded rather than being solved.
The compositional paradigm proved very successful when reinforced by John Dalton's atomic hypothesis. By the middle of nineteenth century, the definition of a compound by the nature and proportion of its constituents has been challenged by a structural paradigm, taking into account the arrangement of atoms in molecules. However condensed formulas and structural formulas equally eliminate the either/or condition. The actual presence of constituent elements suffices to account for the properties of the compound.
Pierre Duhem's return to Aristotle's notion in the title of *Le mixte et la combinaison chimique* (1902) was clearly intended to undermine the compositional paradigm. The familiar example of sugared water

[2] Needham 1996, 2006.
[3] I keep using the ancient term "mixt" (derived from the Greek *mixis*, rather than the standard term "mixture" in order to avoid confusions with the modern notion of mixture, which is clearly distinguished from "combination".
[4] Lavoisier (1789) second section "chapt sur le tableau des substances cimples"
[5] The compositional interpretation of the chemical revoltuion has been emphasized by Robert Siegfried and Betty J. Dobbs (1968)
[6] Guyton de Morveau et al. (1787) p. 14.
[7] Condillac (1780). II, VII, p. 413.

in the introductory chapter summarized Aristotle's theory in a few words, and restored the legitimacy of the either/or condition.

> "What in general, then, is a mixt? Some bodies, the one different from the other, are brought into contact. Gradually they disappear, they cease to exist, and in their place a new body is formed, distinguished by its properties from each of the elements, which produced it by their disappearance. In this mixt, the elements no longer have any actual existence. They exist there only potentially, because on destruction the mixt can regenerate them." [8]

Duhem mainly reproached atomistic explanations for assuming that the properties of compounds could be deduced from those of constituent elements or atoms. His criticism also encompassed Lavoisier's notion of element as simple substance, since elements are not conserved as such in chemical reactions.

Emile Meyerson indirectly addressed the same issue although, unlike Duhem, he claimed that chemists could not dispense with the existence of atoms. He nevertheless pointed out the either/or issue involved in chemical equations. When chemists write the equation Na + Cl = Na Cl, they obviously presuppose the conservation of matter.[9] However taken literally, a chemical equation is a non-sense. In assuming that the addition of a soft metal like sodium and a greenish gas like chlorine equates a colorless salt, chemists seem to be oblivious of the very conditions of their laboratory practice. Although they continuously play on the potentialities of various individual substances and take advantage of their differences, they admit that the compound "equals" the sum of initial ingredients.

Thus chemistry seems to be moved by two antagonist forces. On the one hand, chemists aim at reducing the qualititative diversity of substances to identity. They would like to deduce their empirical data from an ultimate hidden cause in order to "satisfy their rational tendency to identification", in Meyerson's terminology. [10] Chemical equations balancing inputs and outputs of chemical reactions are the best expression of this effort towards identification. They presuppose the permanence through chemical changes, or the conservation of elements in chemical reactions. However the diversity of substances and their idiosyncratic behaviors are the *raison d'être* of chemical practices. There would be no chemical reactions without a diversity of substances with individual properties and without a diversity of processes of reaction. So chemists have no choice but to face "irrationals" (in Meyerson's terminology). They sense that it is useless to get to the bottom, and hopeless to try reducing them.

"Surprising fact" is the phrase that Linus Pauling used to express a similar view in his elementary textbook *College Chemistry*:

"That the substance salt is composed of a metal (sodium) and a corrosive gas (chlorine) with properties quite different from its own properties is one of the many surprising facts about the nature ofsubstances that chemists have discovered". [11] Although he was a staunch advocate and propagandist of electronic theories of valence, Pauling still emphasized the Aristotelian puzzle and defined chemistry as the study of individual "substances". "Chemists study substances, in order to learn as much as they can about their properties (their characteristic qualities) and about the reactions that change them into other substances".[12]

The tension between the two conflicting views of chemical combinations is not necessarily to be understood as a fight between the rational and the irrational, or as a contrast between a rational tendency and a more pragmatic tendency. After all, atomic theories do not hold the monopoly of rationality.[13] Moreover, atomic notions, and molecular models are man-made "artifacts", tools forged for theoretical and practical purposes.[14] Nevertheless the tension is essential. None of the two

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[8] Duhem, 1902, p. 5

[9] Meyerson (1931) §54-55, p. 84-85

[10] Meyerson, Emile (1931) §112 p. 191-93

[11] Pauling (1950) p. 4

[12] Pauling (1950) ibid.

[13] Meyerson convincingly argues that Stahl's doctrine of qualitative principles was more rational than Lavoisier's theory because Stahl assumed the conservation not only of the quantity of matter but also of qualities such as combustibility. See Meyerson, 1921 appendix II "The resistance to Lavoisier's theory".

[14] Meyerson himself presented atoms as artefacts. See

perspectives is sufficient to account for chemical combinations. But the two descriptions do not work harmoniously together. Chemical combinations thus offer a new case of complementarity in Niels Bohr's sense, i.e. two necessary and nevertheless exclusive descriptions of a phenomenon. [15]

Ontological denial ontological preferences?

Because chemists are not really concerned with understanding the fine structure of matter, they have often dismissed all hypotheses about the real existence of atom. For instance, August von Kekulé who conjectured the hexagonal structure of benzene, which was the basis of most artificial organic compounds manufactured by the end of the nineteenth century, denied the existence of atoms. More precisely, he rejected the ontological issue out of chemistry, as belonging to metaphysics. Thus chemists made an extensive use of atoms and molecular models while denying their existence or claiming that atoms were fictions. This apparently inconsistent attitude survived (at least in France) long after demonstrations of molecular reality and the establishment of atomic physics. For instance, the French chemist Georges Urbain wrote in 1921: « It is not absurd to suppose that the atomic model is identical to the absolute reality. However we positively know nothing about it. This model is art work".[16] Such claims have been sometimes viewed as providing the evidence that under the pernicious influence of Auguste Comte, French chemists were sticking to strictly positivistic positions, and consequently lagging behind modern chemistry. [17] However this apparently inconsistent attitude was not confined to the small circle of the French chemists. The ontological status of bonds and orbitals has been discussed among the founders of quantum chemistry. Some of them denied their physical reality in an effort to demarcate the chemical approach of concepts borrowed from physicists, such as resonance for instance.[18] Chemistry thus appears as a science bound to ontological non-commitment by contrast with the attitude of modern physicists.
If we resist the temptation of identifying the philosophy of physics as the "right model" for all sciences, how are we to describe the strange attitude of unbeliever chemists? For Meyerson, the chemists who denied the existence of atoms simply lacked authenticity.[19] He assumed that all chemists professed a naive realism, a belief in the existence of things such as barium sulphide, for instance. Meyerson is right: chemistry is certainly not ontology-free. However he misunderstood its ontology. The assumptions underlying chemical practices do not concern things such as barium sulphide. More precisely, this sort of "thingism" (*chosisme*) is not typical of chemists. Two major matters of concern more adequately characterize their ontology: i) a concern for relations, and ii) a concern for action.
i) Relations
To be sure chemists deal with individual substances, and pay attention to their molecular structures. However these things are only of interest to them in so far as they enter in relations with other units. Nineteenth-century structural formulas were not meant as images of reality. They were not however pure conventions. Rather they displayed capacities of bonding, the so-called atomicity or valence. Similarly the series of compounds were essentially viewed as potential combinations or syntheses. Ernst Cassirer emphasized the functional determination of the concept of atoms in *Substance and Function*. He convincingly argued that it is only apparently that an atom is considered as the "absolute substrate" of properties. In fact, the concept of atom is just a mediator for mapping out a network of interdependent relations between objects. [20]
Bachelard also emphasized that chemists are concerned with relations rather with their substrate. Since relations imply at least two terms, chemistry necessarily presupposes various kinds of beings. Plural and relational are the two features that Bachelard selected to define the rationalism of modern chemistry that he dubbed "non lavoisian". For him, Mendeleyev system epitomized the shift from realism to rationalism, because "law prevailed over matter of fact".[21]

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[15] Bohr (1958)
[16] Urbain (1921) p. 11
[17] Charpentier-Morizé (1997), see Bensaude-Vincent (1999)
[18] Simoes, Gavrolu (2001)°
[19] E Meyerson, Conférence du 23 avril 1911 sur « Evolution de la pensée allemande dans le domaine de la philosophie des sciences » p. 22. (archives A 408/11)
[20] Cassirer (1910) chapter "Conceptualization in natural science"
[21] Bachelard, (1940), p. 57.

If atoms for chemists are above all units capable of being related to other units, their physical reality is not a matter of concern. Urbain could still consider atoms as fictions in the 1920s, although he had supported atomism against equivalentists. The fictional status was his way of emphasizing the specificity of the discipline of chemistry. In his view, atomic theories were just like tools in the hands of craftsmen so that two rival theories – such as energetism and atomism - could work together. [22] The focus on relations allows chemists to chose the unit of matter that best suits their views. For instance, in Pauling's valence bond theory, atoms are the combining units, and their interaction results in the formation of molecules. By contrast, in Mulliken's molecular orbital approach, atom is no longer the relevant concept for understanding chemical bonds. Molecules are taken as the basic building blocks, formed by feeding electrons into molecular orbitals. [23]

When quantum chemistry prompted cooperation between physics and chemistry, chemists continued to debate about the ontological status of relations themselves. For instance a debate occurred between G.W. Wheland and Pauling about double bonds and resonance. [24] Wheland assumed the reality of molecules and double bonds, while he considered resonance a "man made concept", which described "the mental process of the person who makes the statement". Pauling fundamentally disagreed. For him, both double bonds and resonance were man-made concepts. The theory of resonance involved "the same amounts of idealization and arbitrariness" as the valence-bond theory". "The theory of resonance in chemistry is an essentially qualitative theory which, like the classical structure theory, depends for its successful application largely upon a chemical feeling that is developed through practice".[25] Thus time and again chemists claim originality through their rejection of the physical meaning of the concepts they are using. They champion artificiality or "facticity" not only in their experimental practice but in their intellectual practice, as well. Thus chemistry remains an "art" as much as a science. This art made of skills, rules of thumb, and know-how acquired through personal experience, they simply call it "chemical feeling".

ii) Agencies

The chemists' beings are implicitly described in terms of structures, properties and functions. Molecular structures are above all conditions of properties, which themselves are viewed as dispositions for desired or undesired performances. While chemists do not care for matter, they are looking for materials, i.e. substances useful for something. For instance, in the eighteenth-century, Hermann Boerhaave and Guillaume-François Rouelle redefined the four elements in terms of agencies. They were both the constituent units of compounds, responsible for the conservation and transport of individual properties through chemical changes, and instruments of chemical reactions. Rouelle introduced his four-element theory under the heading "Instruments", comprising "natural instruments" - fire, air, water and earth -, and two artificial instruments - menstrues and vessels. The ancient radical distinction between nature and human artifacts was thus blurred in favor of an instrumental view of matter as an active process of operations. Material principles were always at work, circulating from mixts to mixts, whether in laboratory vessels or in the depth of earth and the heights of heavens. Later on, although the compositional paradigm prevailed after the reform of chemical language, and the structural paradigm with the emergence of organic chemistry, chemical names and formulas have been mainly used as "paper tools" for predicting operations and substitutions.[26] They display the possible uses of the compounds through their structure. This action-oriented language inspired Bachelard's description of structural formulas as "rational substitutes", providing a clear account of the possibilities for experimenting.[27] Therefore nineteenth-century chemists could deny any ontological commitment with atoms and molecules, while using them just as plumbers use screws, nails, and joints. They refused to bestow the atomic theory with the power for

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[22] Urbain (1921) p. 21-24 Later on in the 1930s, Urbain never adopted the electronic theories of chemical bond because he had forged an alternative theory of the chemical bond, based on Werner's theory of complex that better suited his own practice of chemistry.

[23] Simões, Gavrolu (2001)

[24] Simões, Gavrolu (2001)

[25] Pauling, L. "The nature of the theory of resonance", Perspectives in Organic Chemistry, 6-7, quoted in Simões, Gavrolu (2001) p. 66.

[26] Klein ed, 2001.

[27] Bachelard, 1940, p. 60

representing the world, as they were concerned with powers for intervening. Atoms and molecules are just potential actors in chemical drama.
Ian Hacking's comments on the way physicists use electrons typically suit the way chemists view the constituents of matter.[28] Electrons are less explanatory notions, as they are instruments for acting or creating phenomena. Hacking's distinction between "realism about theories" and "realism about entities" could thus apply to chemistry. To be sure, chemists are realists. They believe in the reality of entities, which allow them to operate on the outside world or to be affected by it. "Operational realism" would thus be the right phrase to characterize the chemists' philosophy. The material world is a theater for operations; the entities underlying observable macroscopic phenomena are above all agencies.
In this respect, the three categories structures, properties, and functions are not fully adequate for the philosophy of chemistry. Aristotle provides better resources, in addition to his notion of potential, which remains appropriate to characterize the modality of constituent elements in combinations. The dual nature of chemistry – science and technology – requires the whole panoply of subtler distinctions his treatise on *Categories, 8*.[29] Properties belong to the category of quality, but there are many kinds of qualities. States (for instance, hard or soft) differ from dispositions. The former are stable and durable "possessed"qualities, whereas the latter are only ephemeral and easily altered. Both possessions and dispositions being acquired in specific circumstances differ from natural capacities embedded in the subject. They all differ from "affections" (bitterness, sweetness), which simply refer to sensory properties.
If Aristotle again comes into the picture, it not just for philosophical debates about the ontology of chemistry. His subtle distinctions between qualities could prove useful in the current hot debates about REACH, (EnRegistrement, Evaluation and Authorization of Chemicals), the system of control of chemicals in the European Community. When it comes to environmental and societal issues, definitions of chemical substances in terms of their molecular structure are not adequate. Rather it is what they do on human tissues or could do that is meaningful. For setting the standards of toxicity and correlative responsibility of industrial companies, distinctions between natural stable capacities, and dispositions really matter. Chemical substances have to be clearly redefined by their intrinsic properties as well as by the dispositions they acquire in acquired in specific circumstances, or the affections they cause on human tissues or senses.
The chemists' art of synthesis takes advantage of the whole spectrum of qualities in order to put molecules at work, to make them do what humans cannot do with their fingers. In a 2003 conference, Susan Linquist, a biologist from MIT Whitehead Institute, said: "About 10,000 years ago, [humans] began to domesticate plant and animals. Now it's time to domesticate molecules."[30] But domesticating molecules is what chemists have been doing for centuries. At the cost of repeated experimental trials, they managed to tame an incredible number of molecules, to get sufficient control over their reactions to be able to use them as agents for performing specific tasks. However domesticated beings never work like man-made tools or machines. They operate according to their own nature, even when they are chemical "creatures". Through a number of more or less spectacular hazards and deplorable accidents, chemists have learned that they are still at the mercy of unexpected circumstances and that reagents do not always behave in a predictable way.
In addition, chemists usually work with huge populations of molecules in their flasks or vats. Unlike nanoscientists who are trying to domesticate isolated molecules, they have no control on individual molecules, although they may know a good deal about the species of molecules, especially when they are their own creations. In fact, the shift in length scale determines radically different relations between men and materials. The slogan of the nano-initiative, "shaping the world atom by atom" expresses the ideal of control and full command that inspires nanotechnology. Individual molecules are supposed to be reliable entities, responding to precise signals. So deep is the contrast between this culture of precision and the more crude style of chemists, that to Eric K Drexler, the champion of nanotechnology, chemical synthesis is an improbable adventure, that he compares to putting together automotive parts in a large box, shaking it with the expectation of finding an assembled car when the

[28] Hacking, 1983
[29] I am grateful to Pierre-Michel Vauthelin for drawing my attention back to this treatise.
[30] Susan Linquist quoted by Zhang, S. (2003) p. 1177.

shaking is finished.[31] Such miraculous achievements are nevertheless daily practices in chemical factories. But the car they manufacture is a new whole thing, the parts of which are no longer visible or tangible. In their art of making molecules work for them, chemists are not like Plato's *demiurgos*, who builds up a world by imposing his own rules and rationality on a passive matter. Rather they are like the ship-pilot at sea, who conducts or guides forces and processes supplied by nature, thus revealing the powers inherent in it.

To conclude,the purpose of this voyage in the past of chemistry was to identify the kind of problems and projects, which helped generations of chemists overtime to define this trajectory, while unabetedly reconfiguring the identity of chemistry.
Centuries of chemical practices oriented toward cognition and action have generated a set of specific obligations, which can be characterized both as epistemological and ethical rules. Caution, utility, efficiency have been as highly valued as the quest for truth in the sense of *adaequatio rei et intellectu*. Chemical sciences are not aimed at unveiling the underlying reality beneath the surface. Rather they are dealing with a jungle of molecules and striving to take advantage of their dispositions.

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[31] Drexler (1995) p. 2

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