

## What is a Chemical Species?

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The idea of establishing a taxonomy among substances is as old or even older than the idea of a unified chemical science, formulated by Andreas Libavius at the end of the 16<sup>th</sup> century. Crucial point of every chemical taxonomical system is the definition of the *chemical species*, or, in Wilhelm Ostwald's terms, the *chemical individual*. A chemical species should not be conceived as something that cannot be subjected to chemical analysis or as an individual physical body of a given chemical composition, but rather as a substance that fulfils some strictly defined criteria. The relation between a substance and a chemical individual resp. a chemical species is analogous to the relation between a population of plants or animals and a biological species. Biological species are populations, but not every population is a biological species. Between biological species a certain kind of relationship exist that renders establishing a biological taxonomy possible, based on their degrees of kinship. In contrast to a biological taxonomy, however, a chemical taxonomy is not limited to revealing the kinship between the chemical species, but it is also a genealogical one. In other words, it reveals the *way* of obtaining a given chemical species from other chemical species by means of chemical reactions.

It was to Lavoisier's credit to have shown that the proposed system of genealogical taxonomy of substances has some "natural" ending points, the so-called *elements*. Lavoisier's elements can be regarded as chemical species that are parental to every other chemical species and to every other imaginable substance. Defined as the natural end of every chemical decomposition they can be obtained by decomposing a given substance up to the point where the method of decomposition (usually pyrolysis, in our days naturally also other lytic methods like electrolysis etc.) fails to produce a new substance. However, in order to determine the *chemical properties* of the elements, i.e. their capabilities to combine with other elements and substances to produce new substances, one should have a method of discrimination between such substances that are formed solely due to the chemical properties of the elements and substances that are just "mixtures" and could be produced and destroyed without chemical means.

The proper definition of chemical species occupied a great part of the chemical theoretical discourses in the 19<sup>th</sup> century and was at the centre of the dispute between Louis Berthollet and Josef Proust over the constancy of the composition of chemical species. At the end of this century it was generally accepted that only substances that displayed a constant elemental composition should be regarded as chemical species. The validity of this norm, however, was not founded, neither empirically nor logically. One attempt to explain why only substances with constant composition should be regarded as chemical species was Avogadro's atomic resp. molecular theory. It postulated that each element consisted in principle of an infinite number of indivisible material units, the atoms, that displayed the same properties (mass, ability to combine with other units etc.) and that each chemical individual consisted of identical material units – the molecules – that came into existence by the combination of the atoms of the elements of its elemental composition. Assuming that each atom of a given element displayed the same capability of combination with other atoms, the so-called *valence*, according to well-defined natural laws, it became evident that chemical individuals owed their constant chemical composition to the valence of the atoms in their molecules. The introduction of the theoretical concepts of atom and molecule into the chemical theory although very successful in explaining a multitude of chemical phenomena and of great prognostic

power, was regarded at the beginning of the 19<sup>th</sup> century by many chemists just as a convenient tool and not as an adequate and “true” description of the phenomena.<sup>1</sup> It was not until the end of the century that chemists began to ascribe to chemical atoms and molecules the status of real microscopic existence, like bacteria and grains of dust – only several orders of magnitude smaller. However, this “realistic” point of view gained rapidly influence among the chemists, being also enhanced by similar ideas in physics, so that at the dawn of the 20<sup>th</sup> century the microscopic existence of atoms and molecules was the predominant metaphysical dogma in the European scientific community.<sup>2</sup>

Nevertheless, a minority of dissidents still existed who tried to propose a way of explaining the validity of the “law” of constant proportions of chemical individuals without a recourse to such “hypothetical” entities like atoms and molecules. To this minority belonged Wilhelm Ostwald who in his 1904 Faraday Lecture<sup>3</sup> confronted the chemical scientific community with a concept of a system of relations between chemical substances, chemical species and elements that rested on the idea that chemical transformations were governed solely by the energy introduced in a reaction system making no account to the concept of atom or molecule.

The starting point of Ostwald’s reasoning is the thermodynamics of phase transitions. He defines as a *physical phase* a volume of matter that is homogeneous with respect to certain specific properties like density or specific entropy. All volumes of matter that share a given value of these specific properties are members of the same phase. During a phase transition in a one-phase system like a volume of liquid, a new phase comes into existence that displays its own characteristic properties. If now the value of these properties during the phase transition remains constant in both phases involved, then the phases are called *hylotropic substances* (or phases), otherwise they are called *solutions*<sup>4</sup>. However, chemical species are not identical with hylotropic substances; they constitute a subclass of them. Ostwald defines as a chemical species a hylotropic substance that retains its hylotropy independently from the pressure at which the phase transition takes place.<sup>5</sup>

He states that, since every chemical species is composed of other chemical species, a chemical species in order to fulfil the criterion of pressure independent hylotropy has to have a fixed composition. In other words chemical species are composed according to the “law” of constant proportions. Ostwald continues in deriving also the law of the multiple proportions and the concept of compound weight that corresponds to the atomic weight in the atomistic idiom.

The step from chemical species to chemical elements is done by assuming that every composed chemical species can be transformed into a solution, i.e. can lose its hylotropy under sufficient extreme temperature and pressure conditions. This process of subsequent decompositions comes to a halt when the obtained chemical species retain their

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<sup>1</sup> Cf. W.H. Brock and D.M Knight, The Atomic Debates, in: W.H. Brock (Ed.), *The Atomic Debates*, Leicester 1967.

<sup>2</sup> Cf. A.J. Roche, *Chemical Atomism in the Nineteenth Century*, Columbus 1984.

<sup>3</sup> W. Ostwald, Elemente und Verbindungen, *Ann Naturphilos.*3 (1904), 355-377.

<sup>4</sup> Ostwald 1904: 361 ff.

<sup>5</sup> Ostwald 1904: 367.

hylotropy at every possible external condition. In other words: «[E]lements are substances that under all known conditions can form solely hylotropic phases». <sup>6</sup> In this manner it is possible to obtain elements from every substance, hylotropic or not.

On the background of the idea that each substance constitutes a homogeneous phase, and that homogeneous phases can be subdivided into solutions, hylotropic phases, chemical species and elements that differ from each other in the specific values of their thermodynamic properties, Ostwald outlines a system of genealogical taxonomy that has the form of a n-dimensional co-ordinate system where the free energy of each substance is plotted against the other thermodynamic values. Each element in this plot takes a position of a relative free energy minimum surrounded by the higher lying minima of the chemical species that this element forms. In the three dimensional representation that Ostwald uses in his explication, where the free energy is plotted against two arbitrarily chosen specific thermodynamic properties, «the plot area has the form of the roof of a dripstone cave; every tip of a stalactite corresponds to a chemical element». <sup>7</sup> Chemical species are in this picture like smaller stalactites, solutions merely “hubs” on the roof.

Is it then possible to overcome the energy barrier between two elements? According to Ostwald yes, even if this hasn't been achieved by the technical means of his time. He can, however, integrate the phenomenon of radioactive decay in his system:

«In the area of our cave, where the elements with the highest compound weights are situated, the stalactites become increasingly shorter and form, finally, no more any cones, but edges on the sloping roof. While on a proper stalactite a drop of water can flow only up to the tip, where it has to stop – a picture for the stability of the element in question –, on such a place (on an edge, NP) it will experience only a momentarily delay, and then it will continue to flow. Such elements have thus only a limited existence in time». <sup>8</sup>

The system of a genealogical taxonomy of substances as delineated by Ostwald in his Faraday Lecture is coherent and consistent, in spite of the fact that it was presented only as a rough sketch. Its most striking – and for his contemporaries shocking – consequence is that at no point is an account to a corpuscular theory of matter made. Ostwald's theory contains only “macroscopic” concepts, like energy, mass, and the specific properties of chemical species and elements.

At this point two questions arise, a philosophical and a historical one. The philosophical question concerns the relationship between the atomistic approach and Ostwald's ideas as delineated in the 1904 Faraday Lecture. Is Ostwald's thermodynamical taxonomy of substances a mere paraphrase of the classical atomistic taxonomy presented in Mendeleef's periodic table, or a completely different approach that if pursued further could have opened up new ways in comprehending chemical phenomena and integrating them in a uniform theory as the concurrent atomistic one? The historical question is about the roots of Ostwald's ideas. Were Ostwald's efforts an isolated event, or was there something like a school or research programme with more than one contributor?

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<sup>6</sup> Ostwald, *ibid.*

<sup>7</sup> Ostwald 1904: 372.

<sup>8</sup> Ostwald 1904: 373-374, expanded fonts in the original.

With regards to the second question, Ostwald admits openly in his lecture that he employs some basic ideas of another chemist who remained in the background of the atomic debates for the most of his scientific life and was almost ignored by his colleagues. They state that the definition of the concepts of substance and element is in a certain way an arbitrary one, and that the concept of phase is a more general one than the concept of the chemical species, or chemical individual. Ostwald about the source of these ideas:

«I would like to stop at this point for a while in order to report some historical facts. The question if one could find an explanation for the stoichiometric laws also outside the realm of the atomic hypothesis has been so far raised only to be answered negatively. As far as my knowledge reaches only one man has worked on it hoping to find a positive result. I do not think that many of you know his name: He's called Franz Wald and he is a chemist at the iron plants of Kladno in Bohemia. I owe Wald two fundamental ideas [...] I do not know if Wald would acknowledge my reflections as being in his sense; I feel the urgent need, however, to express my deep respect and my thank to this lone researcher who pursues for many years incessantly his targets»<sup>9</sup>

Franz, or as he preferred to be called, Frantisek Wald was born on January 9, 1861 at Brandýsek in Bohemia from parents of German origin. After high school he studied chemistry at the German College of Technology in Prague. He left this institution 1882 without passing the final examination because this was not required for his intended career as industrial chemist. He joined the "Prague-Iron-Plants" as laboratory chemist at the Kladno plant of the company and advanced in 1886 to the position of the chief chemist. Since that time Wald was occupied also with theoretical research that was documented in a series of publications mainly in the *Zeitschrift für Physikalische Chemie* and in the Czech journal *Chemické Listy*. In 1908 Wald took an appointment as chair of theoretical and physical chemistry and metallurgy at the Czech Technical University in Prague where he remained until his retirement in 1928. He died on October 19, 1930 in the Moravian Vitkovice, where he lived after his retirement with his youngest son.

His theoretical chemical work was pervaded with the idea that chemical transformations could be treated as phase transitions obeying Gibb's law of phase transitions:

$$v = n + k - r$$

where  $v$  is the "degree of freedom" of the system,  $n$  the number of independent constituents,  $k$  the number of the variables and  $r$  the number of the phases.

He regards the law of constant proportions as a norm stating that only those phases should be considered as chemical species in a genealogical taxonomy that display constant composition over a broad range of physical conditions:

«In which sense does a phase system that is composed of chemical compounds differ from a phase system in general? This kind of question gives a glimpse to my conception of the object: I can accept "chemical" phase systems only as a special case of the phase systems. When the chemist commences his operations with natural raw materials, then the phase systems thus formed obey the known thermodynamic laws. However, the chemist is not content with those substances; he looks for "chemically pure",

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<sup>9</sup> Ostwald 1904: 368.

“stable”, “well characterised” substances. He finally finds them; he isolates them and brings them into new interactions. Obviously, the general phase laws are still valid for these substances. Besides them, new relations arise that have been caused by the selection of the materials under investigation. This insight brought me to the conclusion that the whole of chemistry is nothing else than the product of the art of its adepts. Nevertheless, one should not neglect that the study of phase systems made up by unknown components is an insoluble task because of its sheer magnitude. One could regard the chemists’ selection among the substances as an arbitrary one, however, one cannot deny that it is also a very useful one. One cannot expect that it will be replaced by anything better in the near future [...]. Admittedly, it is not new that chemical compounds retain a constant composition even under variable conditions. It is also known that other phase systems show a different behaviour in this matter. The important point is, however, that I do not regard the behaviour of the chemicals as being governed by a law of nature: There are phase systems, in which some phases display a variable and some, a constant composition. The second case is as possible as the first, it is perhaps more rare because less probable. Nevertheless, the phases with variable composition are neglected by the chemist, and those ones with a constant composition make up the special object of his studies». <sup>10</sup>

The main target of the chemist during a chemical reaction is to create conditions that enable the emergence of new phases with constant composition. In order to achieve this goal one does not need to employ “equivalent amounts” in atomic theoretical sense of the reactants, but only to calculate which amounts of them form under the given conditions a phase that displays the desired composition and properties. These amounts can be obtained by solving a system of homogeneous equations, which for a system of  $n$  components and  $j$  phases have the following general form:

$$\begin{aligned}x_1 a_1 + x_2 a_2 + \dots + x_j a_j &= 0 \\x_1 b_1 + x_2 b_2 + \dots + x_j b_j &= 0 \\&\dots\dots\dots \\x_1 n_1 + x_2 n_2 + \dots + x_j n_j &= 0\end{aligned}$$

The factors  $x_1 \dots x_j$  determine the direction of the change. From these equations Wald obtains the stoichiometric coefficients in the atomistic idiom.

Unfortunately Wald’s ideas were met with scepticism or even vigorous disapproval by his fellow chemists, with few exceptions like Ostwald who as mentioned tried to apply them in his system of genealogical taxonomy of substances. There is a difference, however, between Wald and Ostwald in the point that the latter still follows the idea that there are “parental” substances, namely the elements, while Wald regards all substances as being of “equal rights”, as phases. The atomistic and Ostwald’s system are “hierarchically” ordered ones, from substances of lower to such of higher complexity, Wald’s system on the other hand has a “topological” character: The substances/phases are points on a “phase surface” connected by paths that are determined by the solution of his equations.

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<sup>10</sup> F. Wald, Die Genesis der stöchiometrischen Grundgesetze, in: *Zeitschrift für physikalische Chemie* (1895) 18: 337-375.

We come thus to the first question, namely the relationship between Wald-Ostwald's system and the classical atomistic system of chemical taxonomy. From an atomistic point of view that is founded on a metaphysical conviction concerning the "reality" of atoms and molecules, Wald and Ostwald's approaches have to appear at least as incommensurable in a Kuhnian sense. The atomistic idiom is hardly compatible with the terminological suggestions Ostwald's presented in the 1904 Faraday Lecture and completely incompatible with Wald's "phase calculus". This incompatibility should not, however, distract our attention from the fact that the atomistic approach is also a calculus, in which the symbols of the elements, the stoichiometric coefficients (and also the structure formulas) are in principle nothing else than terms of an equation system that enables the "construction" of certain figures – substance formulas – that correspond to chemical individuals, in Wald's terms to phases with constant composition and properties, including also stereochemical and kinetic properties. The success of the atomistic calculus does also not exclude the possibility that Wald's system, either in its original form or in the form given to it by Ostwald, would not be as successful or even better. Unfortunately for the antiatomistic approach today's chemistry has already gone a lot of way on the atomistic path in order to resume the debates of the beginning of the 20<sup>th</sup> century.