František Wald's Empiricism

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Abstract: In this paper I present an ordered selection of citations from František Wald's publications and correspondence to give some idea of how he fitted in his times, how his views were received by contemporaries, and to illustrate his epistemological views. I highlight the originality of Wald's aim to develop a theory of chemistry on the basis of the concept of 'phase', instead of the concepts of compound and element. In chemistry (including the material sciences) there has been a vast increase in substances that are phases (and not pure compounds), which makes Wald's work still relevant.

Keywords: *František Wald, Wilhelm Ostwald, phase concept, pure substance, non-stoichiometric, physical chemistry*.

1. Introduction

In this paper I present a selection of citations from František Wald's writings to give some idea of how he fitted in his times and to illustrate his epistemological views, in particular with respect to the theory and practice of chemistry.[1] My primary aim is not to describe and explain his concrete contributions to theoretical and physical chemistry.[2] I will focus on his epistemological views, his relations to important scientists of his time and the reception of his ideas. In the final section I consider the question whether we should ascribe a lasting importance to Wald's views. My answer to the last question will be positive with respect to his claim that 'phase' should be the basic concept of chemistry, not compound or element.

As my title indicates I consider Wald to belong to the empiricist tradition. I will not use more specific time-bound labels such as 'phenomenalism' and 'positivism'. One might think that all (empirical) scientists are empiricists, but this is not the case; in fact it is rather rare to find a 'true' empiricist. What is empiricism? Bas van Fraassen (2002, pp. 37-53) has argued that empiricism cannot be a dogma in the sense of a fixed belief. Instead he proposes that empiricism is a stance (which may involve beliefs, but is not itself a belief). Important features of the empiricist stance are: admiration of science, calling

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us back to experience, dissatisfaction with and disvaluing of explanations that postulate the reality of certain entities or aspects of the world not already evident in experience, rejection of explanation demands, an idea of rationality that does not bar disagreement. This characterization fits Wald rather well (see also section 6 below); hence my title.

As Görs (1999, p. 187) remarks, Wald is one of the few chemists who reflected on his science and this reflection led him to argue against atomistic views of chemical substances. Wald used strong words when he expressed his concern about the "damage [that] has been wreaked by the blind faith in atoms in the minds of chemists … [which] destroys every trace of neutral scientific thought; … the future historian will see from the writings of our age full well how deeply seriously – and how terribly naively – the existence of atoms was taken as truth."[3] But he does not deny the practical usefulness of the atomic hypothesis (Wald 1908a, p. 310), although there is a flipside to this utility (1909b, p. 175): "it is true that this hypothesis allows even the simplest of souls to understand certain basic experiences of chemistry, yet for its services it expresses gratitude not dissimilar to a cruel master to his slaves." As we know, Wald was wrong about the future historian. He missed the significance of Wilhelm Ostwald's 'conversion' to atomism in 1908.[4]

Although, in a letter to Ernst Mach (1896.07.19), Wald outlined his view of the (dis)unity of the sciences and their relation to philosophy,[5] he emphasized on several occasions, in particular when he was attacking the atomists, that his concern was with chemistry only (1909b, p. 150): "I have limited myself to the standpoint of chemistry and only chemistry; I wished to know whether the reasons that the atomists derive from chemistry are irrefutable."

However, Wald's project should not be seen as simply opposing atomism. He emphasised that his project was completely independent from the (success of) atomic physics (1916, p. 182):[6] "If today's physicists count atoms like nuts, it is of absolute indifference to my theme." The issue is more serious (1909b, p. 150): "over time I have become convinced that the divergence lies far deeper […] the one-sided nature of the entirety of current scientific work in chemistry."[7] His aim was to develop a more general kind of chemistry (see next section). Limiting himself to chemistry does not make his task less important (*ibid*., p. 151): "Chemistry contributes to the contemporary scientific view of the world, hence to all of our current philosophy of nature, through many of its basic observations that are no longer examined elsewhere and for which only chemistry remains responsible."

Although Wald's writings are often abstract in the extreme, he did not see himself as merely offering a different 'model' for the same data or phenomenological laws. His *Chemistry of Phases*, the title of Wald 1918, would also make a difference for practical work in the laboratory (1909b, p. 151):

> I am convinced of the existence of certain realms of chemistry that hitherto could not be successfully tended experimentally, since the image provided by the common atomistic beliefs does not fit them, being too simple for these complex phenomena.

2. Chemistry of phases: no need for elements

Wald's aim was to develop a chemistry of phases, in which phases, not elements and/or compounds were the founding matter (culminating in his 1909a, 1918, 1929, and by the time of his death still not finished).[8] He looked for general (phenomenological) laws that constrain the (chemical) transformation of phases (1908a, p. 310), "*without asking for the elementary constituents of natural substances*" (1902, p. 194; emphasis in original). He saw himself standing in the tradition of Jeremias Benjamin Richter and Claude Louis Berthollet, advocating a major paradigm shift: "were chemistry to remain a science of phases in the more general sense of Berthollet […] the whole of chemistry would have taken on a totally different shape than it has today" (1895, pp. 357f) and he said his reflections " were already in part applied by *Richter*" (1909b, p. 170). This self-appraisal was confirmed by Ostwald (1907b) in his article 'Ein Österreichischer J.B. Richter'.

For Wald there is no principled difference between elements, compounds, and mixtures. Chemists focus on pure substances with fixed composition and forget about substances with variable composition.[9] "The theory of chemistry has until now treated only pure substances, other substances being valued only as material for the preparation of elements and compounds" (1916, p. 183). This is a big limitation. Stuff which turns out to have a constant composition is a special case, brought about, not by inherent properties of this stuff, but by the relations of its phase(s) to other phases (1902, p. 187). This has consequences for, *inter alia*, the interpretation of stoichiometric laws and the issue of isomers. Wald considered the atomic theory internally inconsistent because it seems to be saying that isomers are both completely equal and different (1903, p. 130). Of his own theory he said (1916, p. 198): "it can never lead to the same values for the variables for different materials, such that it contains no isomery."[10]

We do not *need* elements.[11] Chemical formulae do not represent real molecules built of real atoms; they are arbitrary, although useful:[12]

> I view it as a highly important matter that every chemist knows that the common formulae are entirely conventional and that they could be replaced by others to no small advantage. […] New basic substances can be chosen in many different ways; […] in place of elements we could use other founding

> substances; and indeed the other chemists of earlier eras likewise did not involve in their work the idea of elements, since they still did not know them, let alone have the ability to prepare them.

Wald did not deny the importance of pure substances for chemical practice (1929, p. 41),[13] but one should be well aware that chemistry restricts itself to an arbitrary *selection* of (systems of) phases and "it has determined a series of peculiar laws which apply to them" (1896, p. 25). To account for these laws, the atomic hypothesis was invoked. However "these laws are simply consequences of the conditions under which they are distinguished from phases in general. The stoichiometric laws hold, not for all phases whatever, but only for very definitely characterized ones" (*ibid.*). Wald looked for general laws in which the stoichiometric laws are contained as special cases.

He held that the phase rule could define a phase of constant composition such that the law of definite proportions would follow without atomic assumptions.[14] In a letter of recommendation from Pierre Duhem,[15] after having mentioned Wald's contribution to thermodynamics, Duhem summarized Wald's articles in the *Zeitschrift für physikalische Chemie* in the late 1890s succinctly as follows: Taking the phase rule of Williard Gibbs as the foundational postulate of all of chemistry and deriving from it the various stoichiometric laws.[16]

We need a more general theory that covers all homogeneous phases (1909a, p. 215). If phases of variable composition were not governed by "purely chemical laws", chemical analysis would not be possible (1906, p. 272). "Following in the footsteps of Gibbs, I have come to the conviction that the phase rule itself can be considered as a special case of a more general law." (1904, p. 283). Then he presented a derivation of the phase rule without using any thermodynamic relations (*ibid*., p. 291).[17]

Ostwald took up Wald's proposals and added them to his own voluminous publications, always making sure to point out that it was Wald's original work that he was implementing. Typically, in the preface to the fifth edition of his *Die wissenschaftlichen Grundlagen der ANALYTISCHEN CHEMIE, elementar dargestellt* (1910) he writes:[18]

> The deepening of the conception of the foundations of scientific chemistry, proposed by F. Wald [*die durch F. Wald angeregte Vertiefung*], the elementary consequences of which I tried to develop in my *Prinzipien der Chemie* (Akad. Verlagsgesellschaft, Leipzig 1907), also has not remained without influence on the systematics of analytic chemistry.

Note that Ostwald wrote this preface in 1910, two years after he accepted experimental proof for the existence of atoms. This proves that Ostwald valued the work of Wald not merely for his anti-atomism. The "deepening" refers to the fact "that in a certain sense the stoichiometric laws are consequences of the methods of preparing and characterizing pure substances" (Ostwald 1910, Preface).

3. Wald and his times (Gibbs, Mach, Ostwald, Duhem)

Until 1907, when he became Professor at the Czech (Bohemian) Technical University in Prague, Wald was a chemist at the steel works of Kladno, living in a small town without access to libraries. Nonetheless one gets the impression that he saw himself as one of those on whom the future of science and chemistry in particular depended. For example, on many occasions Wald spoke very favorably about the work of "a genius like Gibbs," (1929, p. 45) and baptized his 'own' phase or activity space "Gibbsean space" (*Gibbsscher Raum*, 1909a, p. 257) in honor of Gibbs; but he also suggested that Gibbs "avoided all problems, which are *specifically* chemical" and pointed out that Gibbs' definition of "phase" is rather sloppy.[19] For these and other reasons, Wald set as his next task (shortly before his death) a "revision of the ingenious investigations of Gibbs", "abandoning the chemical notion of a *phase component*" (1929, pp. 46, 47).[20]

Mach acknowledged in his publications both Wald's proposals to derive an 'entropy law' and to derive the stoichiometric laws without making atomistic assumptions.[21] Although Wald did not consider himself a member of the energetics group,[22] Ostwald supported Wald for many decades, providing him with publication space for his esoteric articles, arranged an introduction for Wald to present his work at the 1900 World Philosophy Conference,[23] and was highly instrumental in Wald being offered a professorship.[24] Ostwald's acknowledgement of Wald's ideas for his own work was already mentioned.

In the light of Wald's complaints that nobody took notice of his work (apart from Ostwald),[25] I would like to highlight that Wald's only publication in English appeared in the very first issue of the *Journal of Physical Chemistry* in October 1896, translated by the co-editor Joseph Trevor.[26] As this journal was established partly in order to compete with Ostwald's *Zeitschrift für physikalische Chemie*, it is not insignificant that Wald was asked for a contribution to the first issue. Further, it is apparent from a note of the translator that there were similarities between Trevor's own work and that of Wald.[27]

Probably nobody would deny that Wald was an independent mind. He did not hesitate to insist on his views, which he usually thought to be absolutely on the right track (admitting that details still needed to be worked out). For example, at some point Ostwald wrote to Wald (1892.10.14), returning Wald's manuscript (which contained criticisms of Ostwald's work in thermodynamics). Wald was not impressed by Ostwald's further explications of his views and asked Duhem for his opinion, but without mentioning Ostwald's rejection. Duhem replied (1892.10.22), saying:[28] "Your idea is exceptionally ingenious and, according to my knowledge, nobody has yet remarked this." Wald replied immediately (1892.10.25), apologizing for his "stratagem" (*unschuldige List*) not to tell Duhem about Ostwald's refusal to publish the paper. Duhem offered to mediate to have Wald's paper published in French, in the *Journal de Physique* (1892.11.12). Wald then sent a copy of Duhem's last letter to Ostwald with the necessary explanations. Ostwald replied that he did not agree with Duhem (1892.11.22), but appreciated Wald's openness ("die Aufrichtigkeit Ihrer Mitteilung"). Because he valued Wald as an independent thinker he now said that he was willing to publish Wald's paper.[29] As it happened Wald's paper was never published in either German or French. First Wald informed Ostwald that the paper was now in Duhem's hands (1892.11.24). Then it transpired that the *Journal de Physique* was not going to publish it after all. As an aside, I quote the passage Wald (1907a, p. 128) cited from Duhem's letter (1893.01.16) as an illustration of the omnipresent power of Marcellin Berthelot in French chemistry at the time:[30]

> My dear Sir, it has certainly not escaped your attention that M. Berthelot is omnipotent in French science, and that it is not allowed, even most vaguely to deny his Principe du Travail Maximum. Moreover, the editors of the Journal de Physique have told me that they will not publish your work: I am truly at a loss as to where to turn; scientific journals independent of M. Berthelot can be found nowhere in France. You will have an impression of our state of affairs if I inform you that no publisher in Paris has had the courage to take up the publication of my own monograph […] and that I was forced to have it printed in Ghent.

We can conclude that Wald's work was recognized by leading physical chemists (Ostwald, Duhem, Trevor).

4. Wald and his times (Tammann, Kurnakov)

Although from a philosophical point of view Wald's relations with Ostwald, Mach, and Duhem are no doubt the most interesting, the extent to which Wald influenced and is influenced by other physical chemists of his time has perhaps received insufficient attention as yet.[31] Gustav Tammann had shown that sometimes what would seem to be a pure substance has a composition that depends on the conditions in which the stuff had been synthesized. His work on the unique polymorphism of the solid phase of water was generally known. Duhem knew about his work and Tammann's experimental work is still mentioned today in the context of the Gibbs-Duhem theorem. In a letter to Duhem (1902.06.04), Wald thanked Duhem for sending him a copy of Duhem's study of Tammann's theory. Tammann's work clearly fitted Wald's paradigm.

In 1899 Wald wrote a brief comment on an article of Tammann (1898) in the *Zeitschrift für physikalische Chemie*. It characterizes Wald's liking of (if not addiction to) polemics that he did not see in Tammann somebody who could perhaps support his theories or, at least, Wald should have been happy because Tammann reviewed and reported new experimental work, which showed that the laws of constant and multiple proportions are not universally valid; their range of application is limited (*eingeschränkt*). Wald quoted Tammann saying: "One can imagine absolutely clear crystals with a continually changing water content." Although Wald welcomed that such issues were addressed in the *Zeitschrift*, he spent most of his commentary wondering why "in the next issue of this journal some faithful guardian of the status quo [did not] raise his energetic protest" (1899, p. 14); a writing style that would not have given him many supporters. Wald even seemed to have misread Tammann, who said that, because of such and such empirical observations, restrictions (*Einschränkungen*) have to be added to the laws of constant and multiple proportions. Wald read this as Tammann being forced (*genötigt*) to introduce restrictions, which seems to suggest that Tammann would have preferred not to be forced to give up the alleged universality of the stoichiometric laws.

It may also be speculated that Wald had some influence on physical chemists in Russia, later U.S.S.R., such as Nikolai Semenovich Kurnakov. In his important article "Compound and chemical individual" Kurnakov (1914, pp. 114-15) said he took the notion of phase as fundamental because this concept "includes also the large class of homogeneous bodies of variable composition or the solutions", adding that science is indebted to Wald for this insight, referring to Wald (1897c, 1899, 1900).[32] There are phase systems, some of which have variable composition, some do not. The latter are especially studied by chemists, the former neglected, as Wald had put it (1895, p. 343).[33]

Kříž (1931, p. 15) correctly drew attention to the fact that in Wald's times polydimensional geometrical figures were already used in mineralogy in the study of crystalline mixtures. Both Tammann and Kurnakov made important contributions to the discussion of phase diagrams for inorganic substances. Although Wald explicitly said he received the idea that the application of polydimensional geometry could be useful in chemistry from Mach,[34] more historical investigation is needed to trace the development of polydimensional geometry in phase theory. In retrospect it only seems natural to go this way, not particularly original. Perhaps Mach's use of polydimensional geometry was more original, because Mach's remark should be situated in the context of his sophisticated ponderings about the nature of space;[35] which was not Wald's interest when he embarked on his chemistry of phases built on polydimensional geometry. Wald often remarked that theoretical chemists were afraid of mathematics,[36] but this may not be true for the 'new' physical chemistry of his days.[37]

We may conclude that Wald's ideas fitted the interest in non-stoichiometric compounds very well. His work was recognized as original, but interest in non-stoichiometric compounds remained marginal, in particular in mainstream chemistry.

5. Epistemology (in Wald's times)

Wald only made epistemological remarks in passing. Perhaps his epistemology is something like this: The "facts" are "old experiences known to all chemists" (1929, p. 37). These experiences allow abstractions (empirical generalizations or phenomenological laws?).[38] Theory is the "logical construction [...] following from them" (*ibid*., p. 32).[39] Perhaps Wald's most explicit epistemological statement is that his aim is to remove hypothetical images from chemistry and, following Mach, only give a phenomenological presentation of chemical experience (Wald 1918, p. 223).[40] We should focus on "the relation between observed facts" and "avoid the interposition of hypothetical auxiliary constructions" (Wald 1897a, p. 253), a view he would often repeat with varying emphasis.[41] For example (1909b, p. 163): "The endless intellectual manipulation with hypotheses has brought it about that chemists have grown utterly unused to the differentiation of what is experimentally confirmed fact and what is the hypothetical expression of these facts."

On the whole, Wald expressed empiricist views on epistemological and metaphysical issues. Like Hume Wald was strongly aware that induction provides no proof (1909b, p. 151): "The suspicion emerged within me that many of the reasons listed in diverse fields of science for atomism resemble the legal proof of circumstantial evidence: not one of these reasons is sufficient in itself and all of them together provide at most a kind of probability." And he used the word 'metaphysical' with a negative connotation: "this doctrine of the pre-existence of 'elements' in 'compounds' is utterly useless, an absolutely scientifically unfounded, metaphysical hypothesis" (1909b, p. 160).

In addition to Wald's familiarity with the work of Ostwald and Mach, it is clear that in the 1890s Wald was also well aware of Duhem's writings. He rarely gave concrete references in his writings, but would mention the work of others by name.[42] In Wald 1897c, p. 646, we come across the phrase "in the sense of Mr. Duhem". In the same paper, when discussing Gibbs' phase rule and raising the question of irreversibility, he said we need "a more general theory, like that of Duhem" (*ibid.*, p. 649). Later on he wrote: "to act in the spirit of Mach and Duhem" (Wald 1909a, p. 263). Although Wald remarked he was following in Mach's footsteps and it seems well-documented that in the 1890s he was studying Mach's works,[43] his views on epistemological issues are at least as similar to those of Duhem as to those of Mach.

For example, Wald's views can be compared with Duhem's according to which a theory, preferably mathematized and axiomatized, provides abstract relations between appearances, useful for making predictions, but not a picture of reality.[44] Pictorial, allegedly explanatory elements of theories are superfluous. Like Duhem, Wald is in favor of mathematical formulation (1916, p. 181) and constrains what is real to "the existence of certain equations" (letter to Mach, 1900.07.02). Like Duhem and Mach, Wald is dismissive of any talk of images. An image is not "an expression of a metaphysical reality, [… it] will always remain merely an aid to thought, serving so that from our earlier experiences we can predict the results at which we arrive in our chemical investigations" (1916, p. 201). This is quite similar to Duhem's view of models as presented by Hesse (1963, pp. 7-56) in her imaginary dialogue between modern disciples of Duhem and Campbell.

We may conclude that Wald's views are similar to the empiricist, antimetaphysical views of Mach and Duhem.[45]

6. Labels (epistemology today)

Although one has to be careful with anachronisms, sometimes it can be justified in concrete cases to label the work or stance of a scientist or philosopher using labels from another era. For example, it makes some sense in the Western tradition to refer to one empiricist tradition all the way from Hume to van Fraassen (as van Fraassen himself does). Wald clearly fits into this tradition. It also makes some sense to refer to an 'essentialist' tradition all the way from Aristotle to Kripke and Putnam. Wald definitely does not fit into the latter tradition. He strongly opposed what might be called 'psychological essentialism', the human inclination shared by children and scientists alike to believe that there are underlying essences that make things what they are. In an interesting remark in a letter to Mach (1897.03.18), Wald foresaw what would happen if reports on polywater would appear.

> If, under whatever circumstances, condensation of supersaturated water vapor would persistently not occur, surely there would be a chemist at hand who would explain this by the 'isomerism' of water vapor and liquid water and undergird the different 'constitution' by means of 'structural formulae'.

Something like this happened in 1971 to explain the peculiar properties of polywater or water II (which turned out to be a silicic acid sol).[46]

Commentators have referred to Wald as a positivist, pragmatic atomist, instrumentalist, phenomenalist, operationalist, constructive empiricist, or more neutrally as a philosophizing chemist.[47] The operationalist side of Wald can perhaps best be associated, not with Percy Williams Bridgeman's operationalism (with respect to physical magnitudes and concepts), but with the technological side of making 'preparations', along the lines later suggested by Gaston Bachelard (1940) and Joachim Schummer (1996, 2008) as being characteristic of chemistry. Characteristic for Wald's 'operationalism', early and late, is the strong emphasis on the active contribution of the chemist:[48]

> *Chemistry undoubtedly is a science of preparation*s, and the method of preparation takes at least as much part in its laws as nature itself. […] Man and Nature are standing opposite one another as completely equal causes. […] In the chemical laboratory the chemist is as much the master as nature: neither of them rules alone and rules absolutely, […] Both factors are in coordination. […] Man *shares* with nature the control of chemical phenomena.

Because for Wald preparations are the joint product of nature and chemists, we may even see a similarity to Latour-type social constructivism. Instead of presenting elements and compounds as 'building blocks' of natural substances, unprejudiced consideration will show them to be "artefacts (*Kunstprodukte*), as results of a series of difficult chemical operations, that is to say as preparations, somewhat like a skeleton or mummy".[49]

Also there are similarities between Wald's views and the so called culturalist view (also called protochemistry), which stresses the everyday lifeworld as the basis of chemistry.[50] In particular Nikos Psarros' (1994) arguments, in support of the view that stoichiometric laws are norms, not empirical laws or generalizations, can be seen as a sophisticated follow-up of Wald's views. Wald claimed that the chemists themselves *prepared* the laws of simple and multiple proportions into their phase systems (Wald 1895, p. 338).[51] The normativity of stoichiometric laws is apparent from their role in distinguishing between mixtures and pure substances (1897a, p. 256): "What would a chemist do when (which is not rare) it turns out that a substance that was assumed to be a chemical substance, later appears to have variable composition depending on circumstances?"

Like van Fraassen and other 'anti-realists', Wald opposed anything resembling an inference from the most plausible hypothesis to what therefore would be true and right. On several occasions he stressed that what is useful is not therefore true and correct: "utility and truthfulness are evidently ideas of differing stamps" (1909b, p. 150). And he took a sceptical attitude with respect to any form of what today might be called metaphysical or essentialistic realism, a world out there made up of natural kinds each having its defining essence (1909b, p. 153). For Wald 'natural kinds' (*i.e.* chemical substances) are a joint product of the chemist and the world. Wald also seemed to be committed to what we now call the Quine-Duhem thesis of underdetermination, for example, when he discussed the 'economic' status of chemical formulae, using as an example Kekulé's formula for benzene (1909b, p. 164): "Let us simply bear in mind that it is possible to have thousands of differing and equally correct 'formulae' for benzene, in which neither carbon nor hydrogen is present, but rather different basic substances."

But Wald was not committed to van Fraassen's agnosticism. Although he sometimes used 'as if' terminology,[52] he did not oppose the atomic theory as a matter of principle, as already indicated in the introduction. Although he strongly objected to an optimistic appeal to an inference to the best explanation, he was prepared to be convinced by the realist, provided there is *good* evidence: "Though I do not believe in atoms, I would believe if I could find enough reasons for them."[53] But it remains unclear what kind of evidence Wald would have accepted. Perhaps he sensed that Duhem's anti-atomism was more fundamental than Ostwald's.[54]

We may safely conclude that Wald's epistemology was of an empiricist stance (in the sense of van Fraassen mentioned in the introduction). Perhaps the best modifier of empiricism we could add is 'constructive', which is also the label of van Fraassen's stance: 'constructive empiricism'.

7. Concluding remarks: Wald's lasting influence

Wald's empiricism and constructionism has been elaborated in the last two sections. As to the reception of his more concrete ideas, one may note that philosophy-minded scientists and major physical chemists (Mach, Ostwald, Trevor, Duhem) noticed the originality of Wald's esoteric writings, at least for Wald's work prior to 1907. However, what Wald might have considered his life work (1909a, 1918, 1929) remained unnoticed, because it was only published in Czech.[55] His early work on entropy was acknowledged by Mach and Duhem, but not important enough to be remembered in the history of science. His final work on the polydimensional representation of chemical space did not receive any reception. As yet nobody has drawn on Wald's polydimensional proposals, developing it further. The most detailed and sympathetic studies on his life work had to conclude (correctly I think) that he (only) offered "intriguing and substantial pointers" (Ruthenberg 2012; *cf.* Ruthenberg 2011). Wald did not succeed in showing the relevance of his abstract considerations for concrete systems. He never gave a sufficiently worked out example to show what difference his theory would make for the practice of chemistry. He certainly did not make it easy for his readers, including those who were sympathetic to his work such as Ostwald's assistants (1896.01.24) and Wald's colleagues, such as Dr. Baborovský (Wald 1909a, p. 249). On many occasions Ostwald encouraged Wald to be less polemical and "come down to his readers" by illustrating his insights by means of concrete chemical examples (1892.10.14, 1902.02.27, 1907.10.05). There is no sign that Wald ever tried (or was capable) to do so (*cf.* note 25).

Nevertheless, I suggest three items can be distinguished among Wald's ideas that received a favorable reception in his times. First his contributions in the fight against atomism, in which battle he was on the side of Mach, Ostwald, and Duhem. Bulloff (1953), describing the "noble enterprise" of the anti-atomists Ostwald and Wald, wrote that when cathode rays, radioactivity, and Brownian movement appeared on the scene, "Ostwald half-recanted and Wald retreated into silence". It is not strictly true that Wald retreated into silence, but it is true that as of 1909 Wald published his original work only in the Czech language. Furthermore, the developments in physics were irrelevant for him. He was an anti-atomist with respect to chemistry, not with respect to physics. Hence, developments in physics did not matter for him. But such subtleties went unnoticed. Somewhat provocatively one might say that when Wald did not follow Ostwald's 'conversion' in 1908 and did not continue publishing in German journals, he was forgotten. Perhaps Psarros (2000, p. 155) is right to say that "for a short time there existed an alternative for the (chemical) atomic theory". But if it did, then Wald was 'merely' a supporter of Ostwald and Duhem (although Wald himself would not have put it that way). That is to say Wald's anti-atomism did not have a lasting importance. However, if Wald would have accepted atomism as an instrumental tool and would "come down to his readers," he might have had more influence with his ideas concerning phases, pure substances, and the derivation of stoichiometric laws.

Perhaps more original than the anti-atomism he shared with others were Wald's attempts to give a macroscopic definition of pure substance. This work was not only acknowledged by Ostwald, but also by physical chemists who were not on the anti-atomistic side. In a footnote in the authoritative text book of van der Waals and Kohnstamm, the latter wrote that the first attempts to give a strictly macroscopic definition of pure substance are due to Wald, referring to three of Wald's contributions in the *Annalen der Naturphilosophie* (1902, 1904, 1906) and commenting: "Although the proposed solutions appear to me unacceptable on many grounds, posing the problem seems to me commendable" (van der Waals & Kohnstamm 1927, p. 229).[56] Actually three macroscopic definitions of 'pure substance' were given in van der Waals *Lehrbuch*.[57] But Wald was the first to address this issue in a systematic way. In recent years, the status of a macroscopic definition of pure substance has been an issue of continuing debate in the philosophy of chemistry.

Connected with the previous point is Wald's emphasis on chemistry being in the business of producing various "stuff" (*Stoffe*), the operational or constructivist side of Wald's epistemology, discussed in the previous section. Ostwald (1910, Preface) was already cited acknowledging Wald's insight that the stoichiometric laws are consequences of the methods of preparing pure substances. More philosophically, Bachelard (1940, p. 45) said, without referring to Wald: "true chemical substances are the products of technique rather than bodies found in reality".[58] Schummer (1996) speaks of the "undeservedly forgotten originality" of Wald and gives several examples illustrating Wald's innovative but forgotten contributions to physical chemistry.[59]

I suggest the most original of Wald's ideas is his claim to develop a chemistry of phases, in which phases, not elements and/or compounds would be the founding matter. Wald expressed this goal clearly in his discussion of Svante Arrhenius's views: "I consider each possible phase system subject of chemical study. He moves all variable phases to physics. He wants to consider solid solutions as rare exceptions, while I do not. He wants to stay on the traditional road. I am motivated to discover new things" (1907b, p. 3). From early on Wald had set as his goal that his theory should say something about all possible substances, not only about the known ones (1897a, p. 264) and it should also cover phases which do *not* have a constant composition (1908a, p. 324), the "unchemical [*sic*] mixtures" (1897a, p. 264; 1896, p. 27). Constant composition has to be ascribed to special circumstances (1895, p. 340).

His priority concerning this issue has been generally acknowledged (provided it was noted). For example, as noted in Section 5, Kurnakov (1914, pp. 114-15) said science is indebted to Wald for the insight of taking the notion of phase as fundamental. But the interest in non-stoichiometric compounds (Berthollides) was marginal in chemistry, to say the least. With rare exceptions (Timmermans 1928), research on non-stoichiometric substances only continued in the margin of the material sciences.[60] In this context it may be noted that Wald worked for many years as the chief analyst at a steel factory. In the history of making hard steel, austenite, lederburite, and cementite were identified as different mixtures with rather different characteristic properties, long before 'theory' told us that lederburite is an eutectic mixture of the phases austenite (a saturated solid solution of the component C in the component Fe) and pure cementite (Fe_3C), a compound (Findlay, 1951, pp. 200-205).[61]

Wald's commitment to develop a theory of chemical substances for the general case of non-stoichiometric substances is certainly not without justification and is still relevant. Wald was right in stressing that stoichiometric substances are a special case, as the current increasing importance of so called composites and the move from a pure-substance-discourse to a phase-discourse illustrates.[62] Many old and new composites do not claim to be 'pure substances'. Stimulated by the proliferation of more and more polymorphisms of well-known substances, as well as the proliferation of new substances existing in one phase only, there is an increasing tendency to divide the material world into phases. Today one hears of stable non-stoichiometric phases in the system $Sr_{1-x}Bi_{2+2x/3}Ta_2O_9$ (x=0-0.5), of an amorphous phase interlaying crystalline lamellae in nylon 6, or of amorphous $Ni_{64}Zr_{36-x}M_x$ membranes.[63] Such applications were undreamt of in Wald's times, but have created evidence for Wald's claim that 'pure compound' and 'element' are very much theoretical notions. In practice 'mixed' or 'impure' phases (Aristotle's mixts) may be the preferred stuff.[64] According to Wald "all substances, pure or not, have equal rights" (Ruthenberg 2012, p. 130), to which I would add that in practice *all* substances are impure (*cf.* Bachelard) and sometimes the impurities make the relevant properties.

Notes

1 Of his epistemological works Wald said they are only necessary preliminaries for his aim to present an alternative paradigm for chemistry (1901.06.28 to Ostwald). I will refer to the letters to and from Wald by date only if they can be found in Pinkava 1987. Part of Wald's correspondence with Mach was already cited at length in Thiele 1973. References in brackets without author mentioned are always to Wald's publications.

2 See on this issue Ruthenberg (2008, 2011, 2012), who divides Wald's work in three periods. 1889-1893: work in thermodynamics, in particular entropy; 1893-1907: algebraic reconstruction of stoichiometry; 1907-1930: polydimensional representation of chemical variety on the basis of the concept of 'phase'.

3 Wald 1909b, pp. 175, 165. For the last sentence Wald refers to Mach 1900, p. 363.

4 See preface dated November 1908 of Ostwald's *Grundriss der allgemeinen Chemie*, 4. Auflage (1909).

5 In a long letter to Mach (1896-07-19), Wald wrote that knowledge is a polydimensional structure (*Gebilde*). Different sciences look at the matter from different sides; hence they are independent and cannot come into conflict. But he never developed these (perhaps rather simplistic) intuitions further. In Wald's polydimensional view of science one may discern a hint of anomalous monism (see for the sense of this expression in connection with chemistry van Brakel 2010).

6 Probably Wald arrived at his anti-atomism through reading Mach's work. Ruthenberg (2009, p. 24) has suggested that Wald's 'conversion' to anti-atomism dates from 1893 (cf. letter to Duhem 1893.02.13). The first explicit statements occur in his articles of 1895.

7 The one-sidedness of course refers to the universal agreement all around, which Gibbs (writing to Wald 1896.01.06) expressed as follows: "The doctrine of atomic

constitution of matter is supported by so many and various phenomena, that I confess that I find myself among them to whom it hardly seems a matter of serious discussion."

8 For a general discussion of the definitions of 'phase' given by Gibbs, Wald, and others see van Brakel (2012b, §9). Phases are identified by Wald according to their behavior when brought into intimate contact. All substances which mix continuously and homogeneously are counted as one phase. Kříž 1931 is a very well structured account of Wald's theory of phases and chemical stoichiometry, perhaps better than any of Wald's own publications. Notwithstanding Wald's approval of the text (briefly before his death), it may not be 'correct' in every respect, drawing perhaps too much on Ostwald's 'application' of Wald's phase-paradigm.

9 I assume this corresponds to whatever is today treated under the heading of 'non-stoichiometric compounds'; in this discourse 'variable composition' refers specifically to the situation in which a compound exists over a narrow strip of composition in the phase diagram in which range it is the sole stable phase (van Brakel 2012b, § 12). Compare, in a recent textbook: "all inorganic compounds are non-stoichiometric" (Kosuge 1993, p. 1), an observation that Wald might have liked.

10 Happily he noted, referring to Ostwald's efforts, that catalysis, neglected for a long time, "naturally accords well with my views" (1929, p. 42).

11 As Ruthenberg (2011) highlighted, one of Wald's arguments for the subordinate status of elements was that a laboratory could do without them.

12 Citations from (1909b, p. 159; 1916, p. 191).

13 At various times Wald gave different definitions of 'pure substance' or 'chemical individual'. In his work around 1900 he based his definitions on the phase rule, similar to later formulations by Ostwald (1907a) and Timmermans (1928). "*Phases are chemically identical* [*Stofflich identisch*] *when they coexist and correspond to the phase rule for one constituent. All other bodies are chemically different*" (Wald 1897c, pp. 647f., emphasis original). Substances (*Stoffe*) are identical (*materiell identisch*) if and only if they are mutually interconvertible (without the assistance of other stuff). At this time he considered it necessary to introduce the phase rule already in the "most elementary chemical education" (*ibid*., p. 647). Perhaps as a result of his doubts about the notion of "phase rule component" (1929, p. 47), Wald later tried to develop his chemistry of phases without presupposing the phase rule (Wald 1918, Ruthenberg 2011). But in 1918 (p. 129) he still seems to stand behind the definition of 'pure substance' via de notion of 'phase' referring to Wald 1896, 1897c, and 1899. Wald 1896, p. 27, gives a precise definition of chemical individual such that "a substance may be declared a chemical individual before any idea has been formed regarding either its components or the relative proportions in which these components appear".

14 "In chemistry, it is commonly said that the laws of chemical composition from elements, discovered partially by *Richter* and fully by *Dalton*, cannot be explained differently than through atomism, yet I have found that this is an error" (1909, p. 152). Duhem (1906, pp. 214-16) used the law of multiple proportions to illustrate his view that such laws cannot be subjected to experimental test by themselves (cf. Poincaré); experiment "bears as a whole on the entire group [of propositions] constituting a theory without any possibility of designating which proposition in this group should be rejected" (*ibid*., p. 216).

[15] The letter was written some time during 1900 to Prof. Thomas Masaryk (later the first president of Czechoslovakia) in connection with Wald's (eventually unsuccessful) candidacy for a professorship (Pinkava 1987, p. 102).

[16] Compare: "The present studies have been performed with the determined purpose to exchange the atomic hypothesis, in particular in the chemical realm, for considerations which on the one hand rest on the two main laws of thermodynamics, but on the other hand take account of the peculiarities of chemical methods of investigation" (Wald 1895, p. 337).

[17] See also Wald 1909a, pp. 246-252.

[18] See also Ostwald's Faraday lecture (Ostwald 1904, p. 517f); and further Ostwald 1908, pp. 57-58; 1910, p. 322; 1927, pp. 371-372, and probably other places as well.

[19] Wald 1918, pp. 128, 146.

[20] Although he said "it" is "already evident from" Wald 1918; and in Wald 1921, he said, Wald 1918 presents his novel theory of chemistry, which unfortunately due to the war could as yet only be published in Czech; in Wald 1929 he was still planning "further investigation", whereas in Wald 1909a, p. 214, he expected his study to be finished in one, at most two years. It seems that Wald got his professorship too late to be helpful. The strains of life had exhausted him and perhaps he was not capable of much more original work. Already in the period 1905-1906 he seemed to be aware of this himself. In his 'building blocks' article (1906) he wrote that he is still far away from reaching his purpose (of deriving the basic laws of chemistry without invoking hypotheses) and expressed the hope that "younger more mathematically orientated researchers" will "better further [this goal] than I can" (p. 272). Cf. his letters to Ostwald (1906.03.07) and Mach (1906.05.04), in which Wald speaks of ill humor (*Misstimmung*) which is hardly bearable. In 1909 Ostwald asked him to contribute a chapter to a handbook (1909.01.07), but nothing came of it. The first world war may have contributed further to Wald's isolation.

[21] For selections from the Wald-Mach correspondence and Mach's acknowledgment of original contributions of Wald, see Thiele 1987.

[22] Energetics might be defined as the attempt to unify all natural sciences by means of the concept of energy (in its various forms). Like Duhem and Mach, as well as the 'official' energeticists Ostwald and Helm, Wald's aim was also to offer an alternative for the mechanistic world view. Helm thought highly of Wald's *Energie und ihre Entwertung* (1889). See Deltete (2005, pp. 153-154).

[23] This contribution (Wald 1900) drew the attention of Hendrik Willem Bakhuis Roozeboom (1901.07.27).

[24] According to Ostwald (1927, p. 372), Wald obtained this position because, coincidentally, an envoy from the Austrian empire was present at Ostwald's Faraday lecture in London in 1904. Later, when Ostwald was in Vienna, he was asked about this unknown person Wald and he replied they should give him a professorship. That Wald was a passionate Czech nationalist should not be seen as an obstacle. And Wald soon got his professorship ("er erhielt bald eine Berufung an die tschechische technische Hochschule in Prag"). See also the penultimate paragraph in Ostwald 1907b. Cf. Wald's acknowledgement (1918, p. 224).

[25] With few exceptions Wald seems to have had difficulty of making himself understood as, among other things, his extensive exchange with the chemist Kuhn in the *Chemiker Zeitung* illustrates. After each had made three contributions, Wald lamented in the very last paragraph of his last contribution that he cannot make

himself easily understood, which is "understandable because I was not a teacher" (1908b, p. 1279). See also the exchange between de Vries (1908) and Wald (1908a).

26 The other editor was Wilder Dwight Bancroft, author of the first book on the phase rule (Bancroft 1897), which contains two references to Wald's publications. There is also an article of Duhem in the first volume of *The Journal of Physical Chemistry* (February 1897) as well as two articles in the second volume.

27 Trevor notes that Wald's proposal to distinguish 'system component' from 'component' is similar to his own proposal to use the word 'constituent' for what Wald calls 'system component'; cf. Wald's use of '*Ausgangskörper*' (1904, p. 292) and 'phase component' (1929, p. 47). The background of these considerations is the issue of the number of independent components (in the sense of the phase rule), which has caused confusions until today (Rao 1987, van Brakel 2012b, note 41). Wald was one of the first who was fully aware of the fact that the fundamental concept 'component' (*Bestandteil*) is undetermined and "wavering" (*schwankend, unbestimmt*) (1897b, p. 649); cf. Wald to Duhem (1902.06.04). Rao (1987, p. 327) mentions Wald 1896 together with Bancroft 1897 as the first "notable attempts" to ascertain the number of components in the sense of the phase rule.

28 "Votre idée est extrêmement ingénieuse et, à ma connaissance, personne ne l'avait encore remarquée."

29 Perhaps this exchange between Wald and Ostwald can be seen as proof that, notwithstanding different nationalistic commitments and at times serious scientific disagreements, they considered each other as working for the same (scientific) cause.

30 Duhem had little sympathy for Berthelot. In a review of one of Berthelot's last books he wrote (1897, p. 233): "His evil genius drove him to cling to the condemned doctrine, and to defend it against attacks from the new ideas. To this sterile and thankless task he directed all his ingenuity, all his time, and all his labor, as well as all the time and labor of his numerous and active collaborators he had the rare good fortune to meet. Today it is all too obvious not to acknowledge that thermodynamics has created without him and in spite of him, the chemical statics to which he had dreamed of associating his name."

31 The connection between Wald/Ostwald and Tammann/Kurnakov was already mentioned in passing by others (Bulloff 1953; Primas 1975, p. 162).

32 Kurnakov also referred to Ostwald (1904, 1907a). But note the sequence of years; Wald was first (1897c, 1899, 1900). Also Timmermans (1928, p. 17) acknowledged Wald's priority, as did Ostwald himself (see note 18).

33 In the introduction of Pinkava 1987 it is mentioned that Wald already cited Kurnakov before the first world war. The last letter included in Pinkava 1987, p. 143, is a letter of Kurnakov addressed to Wald's son (sent briefly after Wald's death). In this letter Kurnakov praises Wald ("dieses tiefsinnigen Denkers und Forschers über die Grundlagen der chemischen Wissenschaft"), mentions that he has read his articles in *Annalen der Naturphilosophie* and in the *Zeitschrift für physikalische Chemie* and asks to be sent copies of Wald's most recent work in Czech. Other Russian scientists, in particular in Leningrad, knew about Wald's work as well (Gorbov to Wald 1906.10.17). Pinkava 1987 was published just before the revolutions of 1989 and the introduction ends with the obligatory reference to Lenin. However, the author is correct to note that there was perhaps more interest in Wald's work in the U.S.S.R. then in Western Europe, given that influential Rus-

sian historians of science such as Kedrov and Kuznetsov wrote rather extensively on the issue of non-stoichiometric compounds, a history running from Berthollet to Kurnakov to today – Daltonian compounds and stoichiometric laws are limit-cases, not the general rule (cf. van Brakel 2012b, § 12).

34 Wald to Mach (1906.05.04); Wald 1909a, p. 220; for discussion see Ruthenberg 2011.

35 Mach wished to eliminate the hypothesis of 'spatial atoms', because it is an error to assume atoms were already embedded in three-dimensional space, rather than letting space arise from their physical interactions. Also note that by "chemistry" Mach "simply meant a fully general science that considers general transformations of energy without regard to what physical department they belong" (Banks 2002).

36 When de Vries (1908) criticized Wald's more complicated derivations of the stoichiometric laws for not producing anything that could not be produced with simpler means, part of Wald's response was that de Vries "like other chemists is not a friend of mathematics" (1908a, p. 313). As a contrast to Wald's complaints that chemists were afraid of mathematics it may be noted that Trevor was already giving a course in "mathematical chemistry" in 1895/96 (Duhem 1899, p. 269).

37 Cf. Duhem's (1899) state of the art of physical chemistry and in subsequent years for example the work of Bakhuis Roozeboom. In what is probably the first book length publication on *The Phase Rule* (Bancroft 1897), the author takes for granted that the reader can read ternary phase diagrams, in particular for mixed hydrates, referring to articles in the *Zeitschrift für physikalische Chemie* for the original work. In the next 20-30 years numerous projections and graphical operations were proposed to present phase diagrams for quaternary and quinary systems. Wald must have been aware of this, but he did not take the trouble to explain to his readers in what way his polydimensional approach might be interestingly different from what was going on around him.

38 "It has never occurred to me to make any a priori deduction not founded on experience: I wanted merely to reduce matters to several of those general, easily understandable experiences" (1909b, p. 171).

39 Cf. Wald 1918, p. 225, where he seems to make an anti-positivistic remark: a leading idea or theoretical concept is necessary to build a fruitful system on the 'facts' everybody knows.

40 In Wald 1906, p. 271, he said, without mentioning Mach or anybody else, that he wants to work in the spirit of phenomenological (*phänomenologisch*) research. The word '*phänomenologisch*' does not refer to any *particular* philosophy, although probably it is an implicit reference to Mach. In Wald's somewhat uneducated philosophical terminology there may be influences of Kant, Mach, Husserl, Duhem, and probably other German writers of his time. Note by the way that around 1900 there were many similarities between the views of Edmund Husserl and Mach (Sommer 1985), who would send their publications to one another. Cf. the letter of Husserl to Mach (1901.06.18 in Thiele 1965).

41 Wald 1897a, p. 254; 1897b, p. 634; 1899, p. 14; 1906, p. 271.

42 Wald knew about Duhem's work in thermodynamics (Duhem 1886); but perhaps not about Duhem 1902 and almost certainly not Duhem 1906. But Duhem's epistemological views of science are apparent from most of his writings. In a letter to Duhem, written in German, Wald excused himself that his French is not very good (1892.10.22), which is less of a handicap when reading a thermodynamic text than when reading more philosophical texts. (Duhem replied in French of course.)

[43] In Wald 1909c, p. 135, he refers retrospectively to studying "the writings of *Mach*".

[44] For Duhem (1906, p. 19) a theory is "a system of mathematical propositions, deduced from a small number of principles, which aim to represent as simply, as completely, and as exactly as possible a set of experimental laws." It would be interesting to know whether Wald would have agreed with Duhem's view of "natural classifications", using "modern chemical symbolism" as his main example (1906, p. 28-9). The success of the theory of chemical symbolism in anticipating observations brings about an "act of faith" that it cannot be purely artificial, but must be a *natural* classification, but this is not a claim of a theory *explaining* empirical laws. "Without claiming to explain the reality hiding under the phenomena whose laws we group, we feel that the groupings established by our theory correspond to real affinities among the things themselves" (*ibid*., p. 26).

[45] Although there seems to have been some influence of Kant (Wald 1918, p. 199; Ruthenberg 2011).

[46] Molecular structures proposed for 'anomalous water' or 'water II' included tetrahedral $(H_2O)_4$ clusters, two-dimensional sheets in square arrays, rhombic dodecahedra, $(H_2O)_6$ ring structures, linear chains linked by hydrogen bridges, and others (van Brakel 1993).

[47] See for example Psarros 2000, Ruthenberg 2008, Schummer 1996, Görs 1999, Ruthenberg & Psarros 1994.

[48] Citations from Wald 1895, p. 340; 1904, p. 285; 1916, p. 200; 1929, pp. 32, 45.

[49] Wald 1902a, p. 16; cf. 1899, p. 15; 1897c, p. 648.

[50] On the first page of his *Chemie Fasi*, Wald (1918, p. 127) said that he used the word 'substance' (*Stoff*) in the everyday sense, and elsewhere (1897c, p. 636) he said the same about 'components' (*Bestandteile*); but perhaps his motivation was primarily to avoid associations with the atomistic notions of compound and element and not necessarily a commitment to the necessity of building chemistry on everyday notions (cf. 1929, p. 47).

[51] Wald used the word '*hineinpräpariert*', a play on '*hineininterpretiert*'.

[52] For example, "as if elements consist of atoms" (1918, p. 174).

[53] Wald 1909b, p. 169; cf. 1908a, p. 310. He even said: "within chemistry it [the atomic theory] has a place but only after a radical change" (1909b, p. 175).

[54] For discussion of Duhem's 'Aristotelianism', see Needham 2012.

[55] Cf. note 20 for details concerning Wald's low mood in the years that were left to him. The last text Wald wrote (in Czech) was published in English translation in 1931, shortly after his death (Wald 1929).

[56] This view should be ascribed to Kohnstamm, not to van der Waals. This assessment benefitted from discussions with Klaus Ruthenberg concerning the physical chemistry of van der Waals and Kohnstamm.

[57] Van der Waals & Kohnstamm (1927, §§ 103-104) distinguish four different kinds of definitions of *Stoffe*: (1) pure substance in the sense of phase theory; (2) thermostatic individual (for which *all* thermodynamic properties are the same); (3) molecular individual; and (4) independent component in the sense of the phase rule. Except for (3), strictly macroscopic definitions can be given.

[58] Cf. van Brakel 2012a, § 6.

[59] Citation from Schummer 1996, p. 185, n. 11; see also Schummer 1996, p. 175, n. 4; p. 236, n. 2; p. 255, n. 16.

[60] Recent developments such as nanochemistry have moved material science further into the atomistic paradigm.

[61] An alloy can be a conglomerate, solution, intermetallic or chemical compound, or a complex conglomerate of some (or many) of these. In designing multicomponent high-entropy alloys (such as $AlCoCrFeNiTi_x$), one may prefer the formation of simple solid solution phases, *i.e.* mixtures, instead of (stoichiometric) intermetallic compound phases, *i.e.* (allegedly) pure substances.

[62] See van Brakel (2012b, §§ 3, 11, 12, 21), from which the examples that follow are taken.

[63] A modern cutting tool may consist of a multilayered ceramics structure on a tungsten carbide substrate, containing various non-stoichiometric phases.

[64] Bensaude-Vincent (1998, p. 18) has argued that composite materials, which replace natural material resources by synthetic ones, invite a return to Aristotle's four causes and his notion of mixt, which she contrasts with Lavoisier's notion of compound.

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