
The “Stiffness” of Ions – Ostwald as Anti-Atomistic Ionist

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Introduction¹

Most of the important scientists of the 19th Century working in electrochemistry and related fields held certain views regarding the interrelations between stuff and electricity. Michael Faraday for instance (1791-1867), the inventor of the notion “ion”, in his *Experimental Researches in Electricity*, expressed scepticism when referring to atomism. Contrasting to that, in 1881 Hermann von Helmholtz (1821-1894) speculated about the particular character of electricity, *Elektrizitäts-atome*, and held the latter to be the ultimate driving force in chemistry. Svante Arrhenius (1859-1927) who introduced his theory of electrolytic dissociation in 1887 considered the pertinent mechanisms to be atomistic. Arrhenius, his friend Wilhelm Ostwald (1853-1932), and Jacobus Henricus van’t Hoff (1852-1911) formed a group called “The Ionists” which developed and brought forward the ionic theory through its research and thinking.²

Wilhelm Ostwald is renowned for his *energetical* and *anti-atomistic* attitudes. Yet he was honoured with the Nobel Prize in 1909 for his pioneer work on catalysis. In addition, he was – together with van’t Hoff and Arrhenius – the inventor and multiplier of modern chemical ionic theory. Both catalysis and ionic theory are strongly connected with a corpuscular, if not atomistic picture, at least in modern chemistry. Figure 1 shows a graphic representation of this point of view: In it the most fundamental entities are considered to be the elementary particles of the sub-microscopic world (white boxes). The entities of the manifest world (grey boxes) usually are thought of as being reducible, at least in principle, to these elementary particles, and the properties of the former to be reducible, at least in principle, to the properties of the latter. Ostwald’s own concept had just the opposite direction: Starting with things and bodies, and then considering Gibbsean phases, he ended up with elements which he considered to be particular energy

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forms. Whereas the co-ionists considered themselves to be atomists,³ his (later) philosophy of chemistry offered no place for “hypothetic” sub-microscopic particles,⁴ at least these were not needed conceptually. Hence, as to the on-going philosophical discussions about the interpretation of the term “stuff”,⁵ and because this point has been almost neglected in otherwise very useful historical studies,⁶ it is intriguing which position the anti-atomist but “ionist” Ostwald took, that is which position the box *ions* would have in schemes like that in Figure 1.

Stuff in Ostwald’s Philosophy of Chemistry

The main source for this investigation is the most fundamental non-atomistic if not anti-atomistic treatise within 20th century chemistry, namely the “*Prinzipien der Chemie*”, published 1907.⁷ Surprisingly, this programmatic “introduction to all chemistry textbooks” has only rarely been referred to in accounts of the history and philosophy of chemistry.⁸

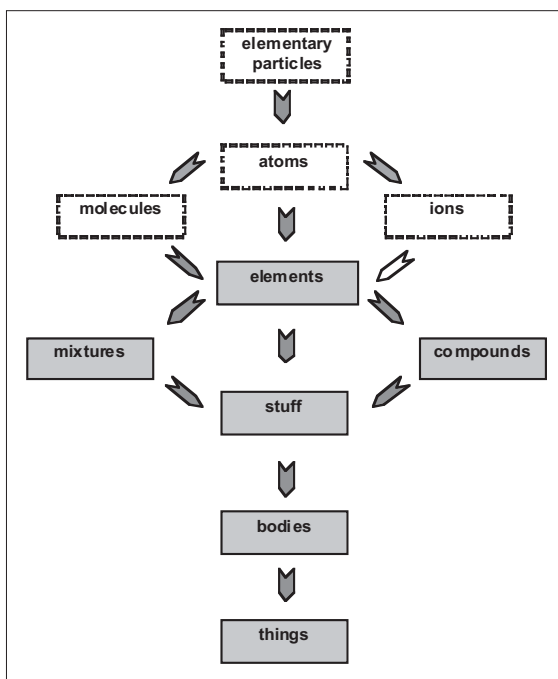


Figure 1. Scheme of the prevailing modern interpretation of the interrelations of central chemical concepts and entities. For explanations see text.

Ostwald considered chemistry as part of a natural philosophy which should be free of what he judged to be metaphysical assumptions and tried to present the fundamentals of chemistry from a phenomenological point of view. To him, there was no need of “hypothetic” atomistic language. Consequently, he made no use of atomistic vocabulary throughout the *Prinzipien*, and he strove for a theoretical closure of chemistry, as in his opinion mathematics, geometry, and mechanics had achieved already.

Repeatedly observed coexistence of certain properties was called a natural law by Ostwald. Some of these properties are arbitrary, others specific.

“The distinction is so important that it is the basis for the separation of two of the sciences: *Chemistry* has to do with specific properties, while the arbitrary properties are the province of *Physics*.”⁹

Ostwald formulated a *stuff law*, a precursor of which is the following statement:

“Substances are said to be *alike* chemically when they have similar specific properties.”¹⁰

From this stuff law an operational recipe (which can be turned into a requirement for investigations on purity) for the identification of substances can be inferred which still is applied in the characterisation of substances by, for instance, measuring the melting point or an infrared spectrum.

Ostwald recognised problems that occur when the laws he develops in the *Prinzipien* are applied to salt solutions:

“There is, however, a large and important group of substances in which regular contradictions to those laws appear, and these are not pure substances but a definite set of solutions. Especially among the aqueous solutions of salts we will find it necessary to extend our general ideas.”¹¹

The extension of general ideas and their epistemological status is the subject of the following main section of the present contribution.

The last Chapter of the *Prinzipien*

Chapter XI, which is the very last chapter of the *Prinzipien*, comprises the following parts: Salt solutions and ions; Faraday’s law; The concept of ions considered chemically; Univalent and polyvalent ions; The molar weight of salts; The application of the phase law; Electrolytic dissociation.

Ostwald gave two separate definitions of chemical salts which are put here into Table 1, together with a modern one, for comparison. During the entire “introduction to all text-books of chemistry” Ostwald meticulously avoided atomistic and molecularistic vocabulary and he indeed made no exception when the text eventually came to electrochemistry. “Conductance of electricity” consists of nothing that refers to corpuscles, and his interpretation of the electrolytic dissociation is likewise held in the language of a substance-related chemistry.

Both of Ostwald’s attempts to define a chemical salt, however, lack generality. The “experimental” one, for instance, neglected that many substances which otherwise should be called salts are not soluble in water, thus cannot exhibit their

second class conductor property (Tab. 1/1). The “chemical” definition did not take into account more complex stuff such as double salts and complex ions, which comprise of more than one elemental constituent (Tab. 1/2). Moreover, in a slightly altered version this statement holds for melted salts, too. Obviously, for both definitions the application of electrical energy is necessary. Hence, using these definitions means to step away from the specific chemical realm comprising typical chemical energy. Nevertheless, Ostwald’s attempts are considerably nearer to laboratory experience than the typical modern version (Tab. 1/3).

Type	Definition
(1) experimental	A salt is a substance whose solutions act as conductors of electricity of the second class. ¹²
(2) chemical	A salt is a substance which has the properties of a pure substance in the undissolved condition, while it exhibits the properties of two different substances while it is in solution. ¹³
(3) modern	A salt consists of particles that have different charge and that build up a crystalline solid at standard temperature.

Table 1. Definitions of chemical salts (1 and 2 from Ostwald, 1909, 3 by the author)

As to his phenomenalist claims, Ostwald stepped on very thin ice in the following passage in which he referred to the mechanism of conductance in salt solutions:

“A reasonable description of the facts may be based upon the assumption that the passage of the electric current is accompanied by the simultaneous motion of certain constituents of the solution. These are the *ions*, and the action takes place in such a way that negative electricity moves with one of the constituents of the salt, while positive electricity moves with the other.”¹⁴

At first glance there seems to be no exit from this statement other than a particularistic interpretation. However, taken literally, “constituents” do not denote small charged particles in a modern, sub-microscopic sense. Rather, these two constituents are the “cation” and the “anion” (both in the singular). Unfortunately, Ostwald was not stressing the discussion of that problem at this part of his book.

The miraculous observation that different elements could be formed at the electrodes during electrolysis was met by Ostwald with the following explanation:

"These ions are of equal chemical composition but of different energetic value with the respective elements, thus they are "electrolytic" isomers."¹⁵

The original salt has no impact on the chemical behaviour of the cation or anion (taken for granted its solubility, of course). Although this original interpretation has not become canonized within chemistry, the phenomenalistic substance definition holds at least at that level of investigation. If complex ions are taken into account the situation becomes problematic, however. The sulphate-ion (SO_4^{2-}), for instance, is discharged during electrolysis yielding oxygen and other species, but certainly not a simple corresponding isomeric substance like " SO_4 " or the like. Another questionable point is the operational requirement of the preparability of chemical elements. Already the electrolytic transformation of the sodium-cation to its isomer metallic sodium from aqueous solutions does not work, because (in modern terms) the reduced sodium-ions instantaneously react with water to yield sodium hydroxide.

As to Faraday's law,¹⁶ Ostwald claimed that this can be applied without atomic hypothesis.¹⁷ The equivalent amount M/z , and with this, the Faraday constant were subjects of convention, as far as he was concerned. Ions, at least in small concentration do behave independently of each other, and the two already mentioned definitions can be homogenized:

"Substances which conduct electrolytically contain constituents which react independently and *vice versa*."¹⁸

There are no electrolytes that consist only of one constituent which, like Faraday's law, can be simply deduced from the requirement of electroneutrality.¹⁹ According to Ostwald, this was another aspect that requires a similar interpretation. These are the results of the determination of the molar weights of salts by measuring the osmotic pressure of dilute solutions of these salts.²⁰ As to these measurements, salts by the formula $\text{K}^{\text{I}}\text{A}^{\text{I}}$ yield the half of the expected molar weight, those by the formula $\text{K}^{\text{II}}\text{A}^{\text{I}}_2$ only one third. Ostwald's explanation was as follows:

"These facts may be explained with the aid of the assumption which we made in considering the electrical and chemical properties of salt solutions. This was that ions exist as independent substances in salt solutions."²¹

Again, the modern reader has to be careful not to interpret expressions like "salts consist of ions" in a modernistic sense, that is ions as sub-microscopic charged particles. In contrast, Ostwald considered "ions" to be substantial and stuff-like, and he used "cation" and "anion" in the singular throughout. Thus he found it natural to apply the Gibbsean phase rule²² to salt solutions. According to the latter,

the degrees of freedom for (only) a solution of a simple salt would come up to $F = 4$. That result is in contrast to observation, because the real number of freedom degrees is $F = 3$ (which becomes smaller if the number of phases is increased). Similar to the other aspects, Ostwald explained this smaller number of freedom degrees with the restrictive role of electroneutrality. The amounts of both ion sorts cannot be chosen independently:

“The various ions are to be considered as independent constituents, and one is to be subtracted from the sum of freedoms and phases resulting from the corresponding enumeration.”²³

In the last part of the chapter analyzed here –*Electrolytic Dissociation*– Ostwald described the transformation of salts into ions as chemical reactions. These reactions were reversible and thus equilibrated:

“When a salt breaks up into its ions, a corresponding increase in osmotic pressure accompanies the increase in the molar concentration of the solution, and if the osmotic pressure is forcibly changed by dilution or concentration, reactions will be set up which resist the change.”²⁴

Dilution fosters dissociation, concentration diminishes it. In the cases of high concentrations the dissociation grade should be taken into account. The derivation of the latter –which he himself introduced in 1888– Ostwald gave in the present passage. Thus he considered the applicability of the law of mass action as unproblematic.

Conclusion – The Stuffiness of Ions

Wilhelm Ostwald conceded that a considerable large field of chemical appearances –he meant the solution of ions– are not easy to describe in terms of (his) phenomenological chemistry. Nevertheless, he made an attempt to present such description. Within the latter a picture of the isomeric nature of elements was applied to dissociated ions in aqueous solutions. Although the concept of isomery may have its merits referring to simple salts like sodium chloride (the chloride-ion is considered to be the isomer of chlorine, the sodium-ion is considered to be the isomer of sodium metal), the situation becomes more complicated when complex ions (“molecular ions” in modern terminology) like NO_3^- or NH_4^+ are taken into consideration. These ions would have needed an extension of the concept such that corresponding uncharged stuff compounds were given. Moreover, even for simple cases it should be possible to prepare the kind of isomers Ostwald was

claiming. This preparation, however, is not possible. Stuff samples of pure chloride-ions, for instance, cannot be produced chemically. It follows from this that we are similarly not able to measure usual stuff properties of the electrolytic isomers. Accordingly, in customary stuff characterizations the electroneutrality was introduced quite early.

Wilhelm Ostwald could only maintain his phenomenological and operational point of view with additional, merely metaphysical assumptions. Hence, his attempt to toss the concept *ion* away from the theoretical or submicroscopic area (see the white arrow in Fig. 1) to the manifest world was questionable and, moreover, jeopardized his phenomenological project.

Notes

¹ Revised version of the paper “To be both ionist and anti-atomist: a contradiction?” presented at the International Conference on the History of Chemistry at Leuven. The author thanks his chairman Carsten Reinhardt and all colleagues for their valuable contributions to the discussion, in particular Pierre Laszlo and Anders Lundgren. The core of this work was developed during a stay as visiting scholar at the Institute of Philosophy of the Catholic University of Leuven (HIW) in summer 2007. The author is greatly indebted to Prof. Dr. Jaap van Brakel of the HIW, who made this visit possible.

² John W. Servos, *Physical Chemistry from Ostwald to Pauling* (New Jersey: Princeton University Press, 1990), 39-45.

³ Arrhenius, for example, left no doubt about this from the very beginning of his writings: Svante Arrhenius, “Über die Dissociation der im Wasser gelösten Stoffe”, *Zeitschrift für physikalische Chemie* 1 (1887): 631-648. See, for the relation between Arrhenius and Ostwald: Elisabeth Crawford, *Arrhenius. From Ionic Theory to the Greenhouse Effect* (Canton: Science History Publications, 1996).

⁴ A pertinent early counter-example from the pre-energetic phase of his scientific work is: Wilhelm Ostwald and Walther Nernst, “Über freie Ionen”, *Zeitschrift für physikalische Chemie* 3 (1889): 121-130.

⁵ Klaus Ruthenberg and Jaap van Brakel (Eds.), *Stuff – The Nature of Chemical Substances* (Würzburg: Königshausen&Neumann, 2008, in press).

⁶ Robert S. Root-Bernstein, *The Ionists*, Ph.D. Thesis Princeton University, 1980; Alan Rocke, *Chemical Atomism in the Nineteenth Century* (Columbus: Ohio State University Press, 1984); Britta Görs, *Chemischer Atomismus* (Berlin: ERS Verlag, 1999).

⁷ The book (Wilhelm Ostwald, *Prinzipien der Chemie*, Leipzig: Akademische Verlagsgesellschaft, 1907) is referred to here as *Prinzipien*, although the English translation (Wilhelm Ostwald, *The fundamental principles of chemistry*, New York: Longmans, Green, and Co., 1909) is used as reference.

⁸ Even more recent publications do not consider this central work, e.g., Britta Görs, Nikos Psarros, Paul Ziche (Eds.), *Wilhelm Ostwald at the Crossroads between Chemistry, Philosophy and Media Culture* (Leipzig: Leipziger Universitätsverlag, 2005).

- ⁹ Ostwald, *Principles*, 4, emphases original.
- ¹⁰ Ostwald, *Principles*, 4, emphasis original.
- ¹¹ Ostwald, *Principles*, 331, emphasis original.
- ¹² Ostwald, *Principles*, 331.
- ¹³ Ostwald, *Principles*, 331.
- ¹⁴ Ostwald, *Principles*, 332, emphasis original.
- ¹⁵ Ostwald, *Principles*, 333.
- ¹⁶ In modern nomenclature: $m = M/z L/F$ (m = obtained mass; z = exchanged charge; L = amount of electricity; F = Faraday's constant = 96485 C/mol).
- ¹⁷ Ostwald, *Principles*, 333-334.
- ¹⁸ Ostwald, *Principles*, 336, emphasis original.
- ¹⁹ Ostwald, *Principles*, 334.
- ²⁰ Ostwald, *Principles*, 337-338.
- ²¹ Ostwald, *Principles*, 337.
- ²² For the present cases the phase rule is $F = C - P + 2$ (the number of constituents, water, anion, and cation, is $C = 3$).