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The Voltaic Origins of Helmholtz's Physics of Ions

Early in his career, Hermann Helmholtz imagined a simple atomistic picture of galvanic and voltaic phenomena that covered all known effects and laws. As we can now judge, this picture contained some essential features of modern electrochemical theory. Yet it remained isolated and unworked for a quarter of a century. Only in the 1880s did it become a basic component of the rising physics of ions.

This outline suggests a number of questions: how did Helmholtz reach his picture of voltaism? Why was it not anticipated or adopted by other experts in this domain? How did Helmholtz revive it? Was it compatible with the methodology applied by Helmholtz to the rest of physics? How did it spread to other domains and cultures of physics in the 1880s and 1890s?

The following is an attempt to answer these questions. While the recent flourishing of Helmholtzian studies helps in this task, much work remains to be done on the history of electrochemistry. Hence the present discussion can only be provisional, and will have to be completed by future research.[1]

1. Voltaism in *Über die Erhaltung der Kraft* (1847)

In 1847 Helmholtz published his famous memoir on the "conservation of force", which defined energy conservation and applied it to the widest possible range of phenomena. It is important to recall that Helmholtz founded his conservation law on the reduction of physical phenomena to central forces acting between pairs of mass points. In this case, the total "force" (energy) is, in Rankine's later terms, the sum of the kinetic energies of the mass points and the potential energies of the central forces. Of this reduction Helmholtz provided two proofs, a transcendental one and

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[1] Wilhelm Ostwald's extensive history, useful though it is, was written from the personal point of view of an actor in this field, with the idea of promoting certain conceptions and dismissing others. More recent histories, for instance those given by Erwin Hiebert and Diana Barkan only deal with a later period, except for the forthcoming work by Nahum Kipnis (which I have not seen). There are, however, satisfactory accounts of the thermochemical aspects of Helmholtz's contributions by Helge Kragh and by Fabio Bevilacqua. See OSTWALD (1980), HIEBERT (1978), BARKAN (1990), KRAGH (1993), BEVILACQUA (1993), and DARRIGOL (2000), ch. 7.

an inductive one (the qualifications are mine). The transcendental proof appealed to the full comprehensibility of nature, the inductive one to the empirical impossibility of perpetual motion (of the first kind).[2]

Two programs may be distinguished in Helmholtz's early applications of the conservation of force. In the weaker program, he tried to identify the quantities that played the role of the energy in various physical phenomena and to show their equivalence in conversion processes. In the stronger program, he tried to reduce phenomena to central forces acting on pairs of mass points. Laplacian physics already provided this reduction for gravitational, electrostatic, and magnetostatic phenomena. Helmholtz extended it to electrochemistry.

The main facts to be explained were the contact tension of two different metals (now called "Volta effect"), electric tension and current in voltaic cells, electrode polarization, chemical transformations in the cells, and Faraday's law of electrochemical equivalents. Helmholtz made the following three assumptions:

i) The molecules of electrolytes are made of parts (atoms or groups of atoms) carrying an integral multiple (positive or negative) of a universal quantum of charge. From the 1880s, these parts were called ions (Faraday originally defined ions as the macroscopic products of electrolytic decomposition).

ii) In conformity with Ampère's double-fluid picture of electricity, the integral charge of ions corresponds to the binding of universal fluid particles, positive or negative, which Helmholtz later called "electric atoms".

iii) The binding energy of the electric atoms to a given ion has a specific value depending on the chemical nature of the ion.[3]

Assumption (i) immediately explains Faraday's law, since the number of ions neutralized and liberated by a given quantity of electricity is then inversely proportional to their common charge. Assumption (ii) explains Volta's contact force. Consider for example the contact surface between zinc and copper. According to Helmholtz, a positive atom of electricity has binding energy a_{Zn} when it is on the zinc side and a_{Cu} when it is on the copper side. Therefore, the equilibrium of electricity requires a potential difference V between the two metals such that the work eV performed by an electric atom when crossing the junction balances the difference a_{Zn}-a_{Cu} of the binding energies.

Now consider a simple voltaic cell made of a copper plate and a zinc plate immersed in a solution of copper sulfate. Let the circuit be closed by the junction of two wires made of the same metal as the electrode they come from. According to Helmholtz, the junction of the two metals implies a potential difference. Consequently, the zinc electrode attracts the negative sulfate ions and the copper electrode attracts the

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[2] HELMHOLTZ (1847). See BEVILACQUA (1993), HEIMANN (1974).
[3] ID. (1847), pp. 48-9, 56-7. See KRAGH (1993).

positive copper ions. This transitory polarization process allows two simultaneous chemical reactions: the copper ions lose their electric atoms at the copper electrode to increase its mass, and the zinc atoms at the surface of the zinc electrode bind themselves to electric atoms and enter the solution. In 1847 Helmholtz did not detail the microscopic forces that permitted these processes. But he could show their energetic possibility. The quantity a_{Zn}-a_{Cu}, as given by the Volta effect or by the difference of the chemical heats for the formation of zinc and copper oxides, is positive. Therefore, the chemical processes and the corresponding current can persist in the voltaic circuit, the excess energy being lost into Joule heat.[4]

As Helmholtz emphasized, with his new picture he could conciliate two conflicting theories of galvanism. According to Volta and his followers, the cause of galvanic effects was the contact between two metals (or two different conductors in general). According to Humphry Davy, Michael Faraday and many other chemists, the cause was the chemical transformations occurring at the electrodes. For Helmholtz, the contact tension and the chemical reactions were manifestations of the same microscopic forces between electricity and matter. They both played a role in a galvanic cell: the contact tension caused the transitory redistribution of charges that started the chemical transformations at the electrodes, and the chemical transformations in turn provided the energy necessary for a permanent current.[5]

2. Helmholtz's Singularity

Helmholtz's scheme seems so simple and powerful that one may naturally wonder why contemporary physicists did not use it. Let us first consider the case of Michael Faraday, who is usually regarded as the initiator of modern electrochemistry.

Faraday was aware of the simple atomistic explanation of his law of electrochemical equivalents in terms of quantized charge. "If we adopt the atomic theory or phraseology", he wrote, "then the atoms of bodies which are equivalent to each other in their ordinary chemical action, have equal quantities of electricity naturally associated with them". He preferred, however, to avoid this speculation: "I must confess I am jealous of the term atom, for though it is very easy to talk of atoms, it is very difficult to form a clear idea of their nature, especially when compound bodies are under consideration".[6]

His own interpretation of the law of electrochemical equivalents was based on a redefinition of the electrolytic current as an alternation of decomposition and recomposition along the electrolytic substance. By analogy, he assumed that every

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[4] HELMHOLTZ (1847), pp. 56-7.

[5] On the contact versus chemical theory, see OSTWALD (1980), ch. 17, pp. 909-13. WIEDEMANN (1882-5), II, pp. 970-1002 and Kipnis's paper, in this volume.

[6] FARADAY (1839), series 7, § 869.

electric current meant the propagation of dielectric polarization. Hence Faraday's new concepts of charge and current were intimately related to his early avoidance of an atomistic interpretation of electrolysis. Moreover, he would never have accepted Helmholtz's assumptions (ii) and (iii), for they admitted electric fluids and Newtonian mechanical reduction, both of which he rejected.[7]

Other physicists were hardly more inclined to reason in Helmholtz's manner. The complexity of electrode phenomena made electrochemistry a very confused field "with the repulsive character attached to any borderland of science", as Lodge put it in 1885.[8] Experts on galvanism remained split between the contact theory and the chemical theory of the pile. They could not even agree on Faraday's law, for it seemed to be violated in many cases of electrode polarization, and it contradicted the received theory of salts.[9] In such circumstances, no consensus could be built on a given microphysical theory of galvanism.

There were more specific reason for the neglect of Helmholtz's picture. In Germany, a growing number of physicists favored a phenomenological approach that avoided microphysical assumptions. Helmholtz himself renounced his early ideal of a reduction to central forces and focused on macroscopic laws controlled by the energy principle or by Hamilton's principle. In Britain, the Laplacian reduction to central forces was judged unpractical and electric fluids unphilosophical. Moreover, James Clerk Maxwell and his disciples did not admit the existence of Volta's contact tension, because the intense electric field it implied at a metal-metal junction contradicted the Maxwellian definition of a conductor.[10]

There were, however, a few exceptions to the general disregard of Helmholtz's picture. Wilhelm Weber and his disciples, being very fond of microphysical speculations, used the concepts of ions and electric particles. In the 1860s, William Thomson provided direct evidence for the contact force by observing the deviation of a highly electrified needle placed under the contact line of half-rings of copper and zinc. Electrometric measurements convinced him that the contact potential difference sufficed to explain the electromotive force of the Daniell cell. From then on, his view on galvanic phenomena were similar to, or at least compatible with that of his friend Helmholtz.[11]

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[7] See, e.g., WILLIAMS (1965).

[8] LODGE (1885), p. 723.

[9] For example, according to DANIELL (1839), Faraday's law implied the decomposition of Na_2SO_4 into $2Na + SO_4$ instead of $NaOH + H_2SO_4$. See OSTWALD (1980), pp. 596-609.

[10] MAXWELL (1873), § 249. Maxwell admitted a smaller contact tension, given by the ratio of the Peltier heat and the current across a junction (in contradiction with Thomson's theory of thermoelectricity). For a perceptive history of the resulting controversy, see HONG (1994). On British theoretical styles, see SMITH and WISE (1989), esp. pp. 155-68; on German theoretical physics, see JUNGNICKEL and MCCORMMACH (1986).

[11] THOMSON (1862). See HONG (1994), pp. 238-43.

3. A More Detailed Picture

In 1856, Wilhelm Hittorf proved that Ohm's law applied to electrolytes under any electromotive force. In particular, the smallest electromotive force was sufficient to start the current. This contradicted the received idea that the decomposition of the electrolytic substance required a minimal electromotive force. In 1857, Rudolf Clausius solved the paradox by means of his kinetic theory of heat. He admitted that molecular collisions, in the absence of any external electromotive force, implied a partial dissociation of the electrolytic molecules into pairs of ions. Then the main effect of the impressed electromotive force was to force the predissociated ions to migrate. In this view, the electrolytic current corresponded to the double flux of ions.[12]

Maxwell, who was the British champion of the kinetic theory, reproduced Clausius's argument in his *Treatise on electricity and magnetism* of 1873. He even remarked, as Helmholtz had done earlier, that Faraday's law required all ionic charges to be an integral multiple of a constant value. "For convenience of description" he called this value "one molecule of electricity". Yet he judged the phrase "gross" and "out of harmony with the rest of [his] treatise". He hoped that the true, future theory of the electrolytic current would banish molecular charges.[13]

Helmholtz had no such inhibition. In the 1870s, he adopted Clausius's idea or predissociation and refined his earlier atomistic picture of galvanism. The main energy-consuming chemical process in an electrolyte, he asserted, was the formation or neutralization of ions at the electrodes, not ionic dissociation within the electrolyte. Accordingly, the positive ions in a voltaic cell tend to accumulate near the negative electrode, thus forming an "electric double layer" of molecular thickness. More generally, Helmholtz conceived electric double layers at each interface between two different conductors. According to the laws of electrostatics, these double layers implied an intense electric field within, and a jump of potential across them.[14]

The electric double layers became a central concept of Helmholtz's electrochemistry. They provided a more detailed understanding of the Volta effect. They accounted for the very high capacitance of polarizable cells noted by Cromwell Varley and Maxwell and soon exploited in chemical condensers. Their intense electric field explained the ionization process next to an electrode. They accounted for various triboelectric phenomena, from the old frictional electricity to Georg Quincke's and Helmholtz's experiments on the flow of electrolytes along electrified metals.[15]

This success of the double layers increased the appeal of Helmholtz's atomistic

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[12] HITTORF (1856), CLAUSIUS (1857). See WHITTAKER (1951), pp. 335-6.

[13] MAXWELL (1873), § 260.

[14] HELMHOLTZ (1880) and (1881).

[15] HELMHOLTZ (1880), and ref. to QUINCKE *ibid.*

picture. Not fearing to disturb Faraday's memory, he made it the core of his Faraday lecture of 1881:

> If we accept the hypothesis that the elementary substances are composed of atoms, we cannot avoid concluding that electricity too, positive as well as negative, is divided into definite elementary portions, which behave like atoms of electricity. As long as it moves about in the electrolytic liquid, each ion remains united with its electric equivalent or equivalents. At the surface of the electrodes, decomposition takes place if there is sufficient electromotive force, and then the ions give off their electric charge and become electrically neutral. [16]

4. A non-Helmholtzian Helmholtz?

Helmholtz scholars have noted the empirical and phenomenological character of most of his researches. For instance, his works on electrodynamics in the 1870s were based on a general framework that included the predictions of available theories without sharing their microphysical or illustrative equipment. As Buchwald and Jurkowitz have emphasized, Helmholtz disliked controversial assumptions such as Weber's on electric particles and their forces. He wanted physical theory to remain as close as possible to laboratory manipulations. His ideal of a unique reduction of all physics to central force only was a youthful dream, which disappeared from his mature epistemology. Against this background, Helmholtz's resumption of a detailed atomistic picture of galvanism seems odd.[17]

Helmholtz himself perceived a methodological difficulty, to the point of delaying the publication of his improved picture for almost ten years. In 1880, he explained:

> I have taught [my hypothesis about galvanic forces] in my physics lectures since 1871; but so far I had no reason to discuss it in my scientific publications, for I believe that following an essential requirement of the scientific method one should not specialize theoretical assumptions further than is required by the subject matter.

In his Faraday lecture, Helmholtz accompanied the presentation of his picture with cautious comments:

> I see very well that this assumption of two ponderable fluids [...] is a rather complicated and artificial machinery and that the mathematical language of Clerk Maxwell's theory expresses the laws of the phenomena very simply and very truly with a much smaller number of hypothetical implications. But I confess I would be at a loss to explain without the use of mathematical formulas, what he considers a quantity of electricity and why such a quantity is constant, like a substance.

Of course, Helmholtz knew he was speaking to a British audience (mostly chemists)

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[16] HELMHOLTZ (1881), p. 69.

[17] See, e.g., BUCHWALD (1993) and (1994), and recent talks by Edward Jurkowitz.

for whom electric fluids epitomized philosophical naiveness. But his caution extended to a much more popular hypothesis:[18]

> That the equivalent relation of chemical elements depends on the pre-existence of atoms may be hypothetical; but we have not yet any other theory sufficiently developed which can explain all the facts of chemistry as simply and as consistently as the atomic theory developed in modern chemistry.

These remarks of Helmholtz not only document his general discomfort with microphysical assumptions, they also indicate how he legitimated such assumptions in some cases. In his view, the ultimate criterion for accepting a hypothesis was the simplicity and consistency of the theory it permitted. Lack of observability and doubts on its physical reality were not sufficient reasons to exclude it. So to say, Helmholtz's pragmatism was stronger than his empiricism. The best theory was the most practical, not necessarily the most empirical one.

In conformity with this defense of a microphysical picture of galvanism, in late writings Helmholtz emphasized the necessity of a "certain power of invention" by which the physicist could imagine hypotheses and suspend their experimental verification. His stand on this issue had certainly evolved. In his earliest epistemological writings, there was no room for hypotheses: physical theories were based on transcendental truths combined with inductive inferences. In his mature epistemology (concluding his work on physiological optics), Helmholtz became more of an empiricist. He based both theory and experimentation on inductive reasoning. The only hypothesis was that of the existence of stable regularities (*Gesetzmässigkeit*), so that one may trust inductive inferences. Lastly, in his latest epistemological writings Helmholtz highlighted the inventiveness of theorists, in conformity with the contemporary rise of microphysics.[19]

5. The Spread of Helmholtz's Picture

In the 1880s and 1890s, Helmholtz's ions became relevant to several physical phenomena other than galvanism. The Faraday lecture of 1881 then acquired the status of a manifesto for a new ionic physics. The first stage of this evolution was the introduction of gaseous ions by a few German physicists close to Helmholtz. In 1882, Walther Giese assumed gaseous ions to explain the electric conductivity of flames. The inseparable Julius Elster and Hans Geitel did the same for heated filaments (thermoionic effect). And Helmholtz's son Robert discussed the condensation of vapor around ions.[20]

In Britain, German electrolytic concepts faced criticism from Maxwellian

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[18] HELMHOLTZ (1880), p. 910; (1881) pp. 60, 69.

[19] See DARRIGOL (1994a).

[20] GIESE (1882); ELSTER and GEITEL (1883) and (1889); VON HELMHOLTZ (1887).

physicists, especially Oliver Lodge who reported on this subject for the British Association in 1885. Yet a few British physicists sensed the power of Helmholtz's arguments. William Thomson was one of them. Another was Joseph Larmor, who in 1885 used Helmholtz's double layers for an estimate of Avogadro's number. Most important, a German born British physicist who had known both Helmholtz and Maxwell, Arthur Schuster, brought Helmholtz's notions to bear on electric discharge in rarefied gases.[21]

Around 1880, the latter topic was beginning to attract major physicists, in part because of the conflict between British and German views of the discharge. Gaseous conduction was originally thought to be essentially different from electrolytic conduction: whereas the former was highly heterogeneous, the latter was homogenous and obeyed Ohm's law. The Germans tended to interpret the discharge in terms of polarization waves, and the British in terms of molecular torrents. In 1884, Schuster realized that Helmholtz's picture of electrolysis, when transposed to gaseous conduction, easily explained a large number of its properties.[22]

The main obstacles to the electrolytic analogy thus disappeared. For example, the discharge threshold corresponded to the need of an initial spark yielding the ions necessary to the formation of a Helmholtzian double layer near the cathode. The spatial heterogeneity of the discharge was a consequence of the macroscopic size of the double layer for very dilute matter. Several mysterious properties of the discharge were explained, for example the high conductivity observed by Hittorf for a gas submitted to a first discharge. New properties could be predicted and verified, such as the existence of characteristic spectra for the ions formed near the cathode.

Yet Schuster was not the first physicist to conceive an analogy between electrolysis and gas discharge. J.J. Thomson did so in 1883 in the context of his vortex theory of chemical combination, which ignored German ions. Whereas Schuster understood electrolysis in Helmholtz's terms, Thomson understood it in Maxwell's or Faraday's terms, with molecular decomposition in chain. For him the molecular fragments were not electrified. The electric current was the alternation of decompositions and recompositions, not the circulation of ions. Nonetheless, toward the end of the 1880s Thomson recognized that his vortex theory failed to explain facts as basic as the rigorous validity of Ohm's law for electrolytes, or the induced conductivity of gases submitted to an electric discharge. He then adopted Schuster and Helmholtz's ions, with a convenient reinterpretation suggested by Schuster.[23]

Schuster knew well how distasteful the notions of electric fluids, electric atoms, space charge, and other idiosyncrasies of his ionic theory of conduction could be to a Maxwellian physicist. As a conciliating gesture, he briefly suggested that an ion

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[21] LODGE (1885); LARMOR (1885).

[22] SCHUSTER (1884). See FEFFER (1989); DARRIGOL (2000), ch. 7.

[23] THOMSON (1883) (1888) and (1891). See DARRIGOL (2000), ch. 7.

could be understood as the abutting of discrete tubes of force on a group of atoms. This conception saved the Maxwellian dogma of the primacy of field processes. At the same time, it permitted a translation of Helmholtz's most important arguments, in which the specific binding energies of electric atoms became the specific abutting energies of the tubes of force.[24]

J.J. Thomson quickly adopted this conception and made it the basis of a complete reformulation of Maxwell's theory. For instance, he now understood electric conduction as the dissolution of the discrete tubes during their sideways penetration into the conductor. Thus hybridizing of Maxwell's and Helmholtz's notions, he developed a suggestive theoretical framework for the new microphysics that he was promoting as the director of the Cavendish Laboratory. His studies of X-ray ionization and his discovery of the "corpuscle" (an ancestor of the electron) were part of this evolution.[25]

Other successful hybrids of Maxwell's fields and Helmholtz's ions appeared in the same period. These were motivated by the need to take into account the molecular structure of matter in the electromagnetic theory of light. To be true, Lorentz's theory of dispersion of 1878 had nothing to do with electrolytic concepts. It simply relied on the picture of dielectric polarization as the shift of elastically bound charged particles. Only later, in the 1890s, did Lorentz identify these particles with electrolytic ions and lastly with electrons. Other ionic and electronic theories all relied on Helmholtz's ions. Larmor's "theory of electrons" did so in a way that is too complex and indirect to be detailed here. Helmholtz's dispersion theory of 1893 was a militantly ionic theory.[26]

Helmholtz directly identified the scatterers of light with elastically bound ions. He even use this opportunity to indicate a conciliation of Maxwell's equations with the exchange of charge between different ions:

> The only requirement of the electrochemical theory that is not contained in Maxwell's equations is that these centers of electric force [in the ions] can migrate, with much expense of work, from ion to ion during chemical transformations, as if they were attached to a substantial carrier that would be attracted with different force by the valence sites of various kinds of ions.

Besides this foreshadowing of the electron, Helmholtz's paper contained the twin equations relating dielectric polarization and electromagnetic field, and a dispersion formula similar to Lorentz's. Interestingly, Helmholtz restricted atomistic considerations to the justification of the macroscopic Lagrangian for the system,

[24] SCHUSTER (1890), pp. 558-9.

[25] THOMSON (1891). See BUCHWALD (1985); FALCONER (1987) and (1989); LELONG (1995).

[26] LORENTZ (1878) and (1895); LARMOR (1895). On Lorentz, see HIROSIGE (1969); MCCORMMACH (1974). On Larmor, see BUCHWALD (1985); HUNT (1991); WARWICK (1991). For a comparison, see DARRIGOL (1994).

whereas Lorentz detailed the interactions between field and ions. Again, Helmholtz's step into microphysics was a cautious and limited one.[27]

Whereas Lorentz's old dispersion theory had remained largely unnoticed, Helmholtz's inspired much derived work. For instance, Richard Reiff generalized it to include motion of the transparent body, and thus obtained the Fresnel dragging coefficient (one year after Lorentz). Most important, Emil Wiechert reified Helmholtz's atoms of electricity to make them the universal mediators of the interaction between matter and ether. He thus reached a theory similar to Lorentz's electrodynamics, with an original emphasis on the empirical foundations of microphysical assumptions. In particular, he tracked Helmholtz's atoms of electricity in gas discharge, and found them in cathode rays in late 1896, a few weeks before J.J. Thomson propounded his "corpuscle."[28]

6. Conclusions

The microscopic picture of voltaism which Helmholtz sketched in 1847 seemed naive to the British and simplistic to the Germans. It was based on Laplacian reduction to electric fluids and central forces, which only a certain kind of German physics would support. In face of the extreme complexity of voltaic phenomena, it fared no better than the numerous competing pictures. Yet, Helmholtz remained convinced that he had captured the essentials of this subject. Some twenty years later, he returned to his picture and perfected it. By that time, he had become skeptical about electric fluids and weary of atomistic arguments. Yet he believed that his picture of voltaism contained a basic structure that was independent of the true nature of electricity.

In agreement with this view, Arthur Schuster and J.J. Thomson transferred Helmholtz's electrolytic reasoning to gas discharge. Thomson offered a modified version of Maxwell's theory that permitted this transfer without giving up the Maxwellian concepts of charge and current. In different contexts, toward the end of the century several physicists proposed other hybrids of Maxwellian and continental concepts that integrated Helmholtz's ions and atoms of electricity. In sum, the ion or electron theories and the new microphysics of the fin-de-siècle owed much to Helmholtz's early reflections on voltaism, despite dramatic changes in the physicists' world-views.

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[27] HELMHOLTZ (1893), pp. 506-7. See HEILBRON (1964), pp. 21-5; BUCHWALD (1985), pp. 233-4; CARAZZA and ROBOTTI (1996), pp. 589-90.

[28] REIFF (1893); WIECHERT (1894) (1896) (1897) and (1898), see DARRIGOL (2000) chps. 7-8.

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