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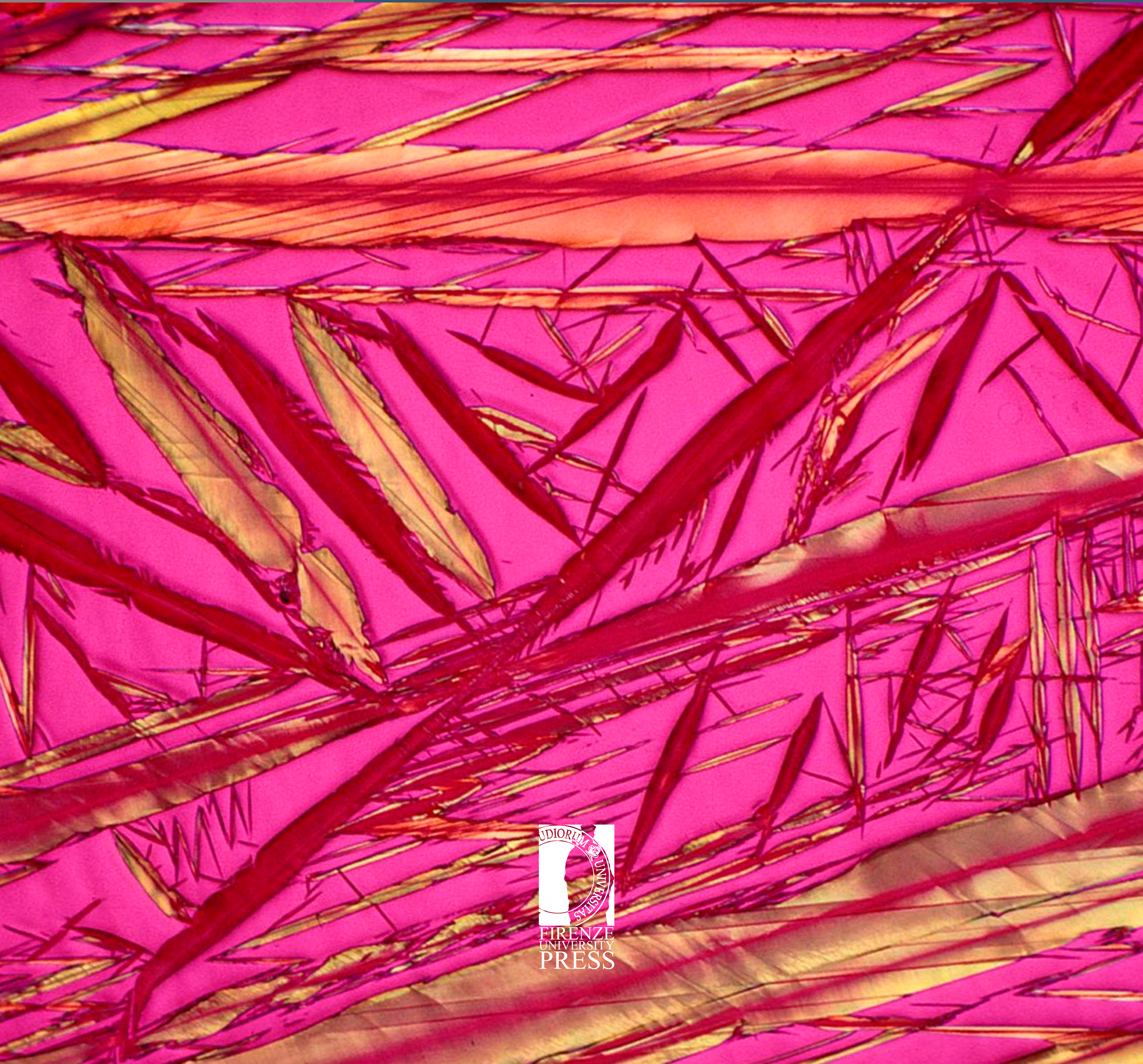

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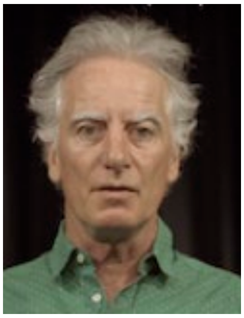

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Editorial

Peer Review – Critical Feedback or Necessary Evil?

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Anyone who has participated in scientific publishing, either as author or editor, has dealt with the process of peer review. Of course, individual opinions on peer review vary, with viewpoints ranging from it being an important part of ensuring the quality and reliability of scientific publications, to thoughts that the process as a whole is completely broken. Unfortunately, it also seems that authors often look at peer review as being a painful exercise forced upon them by journals, while those serving as reviewers too often see it as something expected of them, but not important enough to spend considerable effort performing. Before discussing various points of the peer review process, however, it is worth considering where this process began.

Current historical studies generally suggest that the modern process of formalized peer review developed in the 19th century and grew slowly and haphazardly, encountering skepticism and criticism along the way. One such recent study by Melinda Baldwin[1] suggests that the practice of soliciting written reviews by specialists found its origins in 1831, when William Whewell (1794-1866) proposed that two Fellows of the Royal Society should write their views on submissions to the journal *Philosophical Transactions*, after which the written reports would be published in the new journal *Proceedings of the Royal Society of London*.[2] While the plan to publish the reviews was abandoned, the practice of sending submitted papers out for refereeing endured and by the mid-19th century, coordinating refereeing was one of the chief responsibilities of the Secretaries of the Royal Society. In Germany and France, however, refereeing remained relatively uncommon throughout the 19th and early 20th centuries. Although it had been originally intended for the referees' identities to be known to both the author and the journal's readers, the Royal Society quickly decided that referees would give more candid advice if they remained anonymous. Thus, the modern practice of referee anonymity has been part of peer review since very early in its history, with the most common form referred to as *single blind peer review* (i.e, only the reviewer's identities are anonymous).

Prior to this modern form of peer review, other practices had sought to fulfill some of the same goals. One common practice by some scientific societies was that papers were required to first be orally presented at the meeting of the corresponding society, at which it could be vetted through discussion among the meeting participants. This practice, however, resulted in a number of famously long delays in the publication of critical works. Some societies had other internal practices for evaluating the work of their members before it was circulated,[3] but those systems have not been viewed to be ones that led to the modern form of systematic external refereeing. In Germany, some of the most prominent journals were controlled by powerful editors who preferred to make decisions without relying on the opinions of others, although they would sometimes add their own personal critical comments as editorials after select papers, thus providing review in some form.

Of course, many have voiced dissatisfaction with modern peer review, citing problems with bias,[3,4] problems of objectivity and the ability to gauge reliability or importance, and the opinion that traditional refereeing is antiquated. Such views have led to the conclusion by some that the system has broken down and has become

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[1] M. Baldwin. *Isis* **2018**, *109*, 538.

[2] A. Csiszar. *Nature*, **2016**, *532*, 306.

[3] C. J. Lee, C. R. Sugimoto, G. Zhang, B. Cronin. *J. Am. Soc. Inf. Sci. Technol.* **2013**, *64*, 2.

[4] C. J. Lee. *Philosophy of Science*, **2015**, *82*, 1272.

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an obstacle to scientific progress.[2] As a response, some publishers have attempted to introduce new forms and variants of peer review, including double blind review,[3] open review, and post-publication peer review.[5] Double blind review, in particular, aims to remove the author's identity and thus protect the author against forms of social bias.[3] However, even without knowledge of the author names, all too often it is easy to discern the identity of more established authors in your field and thus bias favoring established authors and hindering newer authors still remains.

Personally, as an author, I am always disappointed with negative reviews. Still, I try to view the overall review exercise as a positive process. I have always realized that my published work is a permanent record and the last thing I would ever want is to include a stupid mistake that will never go away. As such, I always pray that reviewers catch any such possible errors. Even when reviewers fail to understand the point of the work submitted, or I view the reviewer's comments to be in error, this usually leads to a stronger publication. As I always strive to make my publications clear and approachable to the lay reader, such misunderstandings on the part of reviewers result in additional efforts on my part to focus the message or further improve the clarity of my arguments. In that respect, I will always view peer review as a critical part of the publication process, despite its potential flaws.

As a reviewer, I think that my experience as the recipient of peer review influences the way that I provide criticism, as does my decades as an educator. In that respect, I have come to regard peer review as much more than just pointing out errors in the experimental methods or in the interpretation of results. That is, I have come to approach each review as a teachable moment and present my comments in nearly the same way as when I am revising the writing of my graduate students. The goal too is really the same, helping the authors to improve their paper and make it the best it can be. This, of course, includes ensuring that the methodology and analysis is sound, but also includes things like ensuring that prior work on the topic has been properly credited and acknowledged, correcting misconceptions that have crept into the literature, and ensuring that the paper is written in a clear fashion, such that it can be understood by others less familiar with the subject. Along the way, I will suggest alternate wording to improve clarity or remove errors in terminology, and I always try to back up more significant criticisms with specific references for the authors to consult. Furthermore, I try to approach every review the same, whether the manuscript is from one of the top researchers in my field or from those that have little to no prior experience with the topic.

To write a good review, however, takes both effort and time. In addition, it necessitates a sound understanding of the fundamental concepts dealt with in the paper under review. Unfortunately, as an editor, I find that many reviewers are either unwilling to contribute the time and effort required to provide a quality review, or simply lack the ability to do so. Because of this, journals that want to ensure high quality peer review really need to actively cultivate a pool of reviewers that are committed to taking peer review seriously, rather than just a task to be completed as quickly and effortlessly as possible. Of course, this too requires time and effort, and it means keeping track of both reviewers and the quality of their reviews, both good and bad, and then finding ways to encourage the better reviewers to keep accepting future reviews for their journals. In this respect, a number of journals and publishers have done a much better job at recognizing top reviewers for their efforts in recent years.[6]

Lastly, it is important to remember that the value of peer review goes beyond the scientific community and impacts everyone, both the expert and the public at large. We are at a point where public trust in science is diminishing[7,8] and traditions that instill confidence in science are critical. As the process of peer review developed, the referee was gradually reimagined as a sort of universal gatekeeper, with peer review emerging as a mighty public symbol that scientists had a structured process for regulating themselves and for producing consensus in science.[2] Thus, while it may have its flaws, peer review is still the best way to ensure that scientific literature is sound, correct, and presented without bias. If we want the public to feel that they can depend on scientific studies and presented results, then we need to do everything we can to make sure that the scientific literature is as absolutely strong as it can be.

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[5] E. Stoye. *Chemistry World* **2015**, January 12th, https://www.chemistryworld.com/news/post-publication-peer-review-comes-of-age/8138.article (accessed Sept. 19, 2019).

[6] A. Meadows. Recognition for Review: Who's Doing What? https://orcid.org/blog/2016/09/20/recognition-review-who%E2%80%99s-doing-what (accessed Sept. 22, 2019).

[7] G. Tsipursky. (Dis)trust in Science. *Sci. Am.* **2018**, https://blogs.scientificamerican.com/observations/dis-trust-in-science/ (accessed Sept. 22, 2019).

[8] G. C. Kabat. *EMBO Rep.* **2017**, *18*(7), 1052 (doi: 10.15252/embr.201744294).

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Research Article

Particular Symmetries: Group Theory of the Periodic System

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Abstract. To this day, a hundred and fifty years after Mendeleev's discovery, the overal structure of the periodic system remains unaccounted for in quantum-mechanical terms. Given this dire situation, a handful of scientists in the 1970s embarked on a quest for the symmetries that lie hidden in the periodic table. Their goal was to explain the table's structure in group-theoretical terms. We argue that this symmetry program required an important paradigm shift in the understanding of the nature of chemical elements. The idea, in essence, consisted of treating the chemical elements, not as particles, but as states of a superparticle. We show that the inspiration for this came from elementary particle physics, and in particular from Heisenberg's suggestion to treat the proton and neutron as different states of the nucleon.We provide a careful study of Heisenberg's last paper on the nature of elementary particles, and explain why the Democritean picture of matter no longer applied in modern physics and a Platonic symmetry-based picture was called for instead. We show how Heisenberg's Platonic philosophy came to dominate the field of elementary particle physics, and how it found its culmination point in Gell-Mann's classification of the hadrons in the eightfold way. We argue that it was the success of Heisenberg's approach in elementary particle physics that sparked the group-theoretical approach to the periodic table. We explain how it was applied to the set of chemical elements via a critical examination of the work of the Russian mathematician Abram Ilyich Fet the Turkish-American physicist Asim Orhan Barut, before giving some final reflections.

Keywords. Periodic system, group theory, symmetry, elementary particle approach, period doubling, Madelung rule.

At the heart of chemistry lies the Periodic System of Chemical Elements. Since Mendeleev's discovery in 1869 — 150 years ago — the Periodic System has figured as the undisputed cornerstone of modern chemistry. No lecture theatre or scientific laboratory is complete without a copy of the periodic table adorning its walls. From time to time, a new chemical element is added to the taxonomic chart. But its overall structure has remained the same ever since it was developed in the 1860s. "Such has been the scientific and cultural impact of Dmitri Mendeleev's periodic table of the elements that many people assume it is essentially complete", writes Eric Scerri in a recent *Nature* special on the Periodic System.[1]

In reality, however, Mendeleev's iconic chart has remained something of a mystery till the present day. When examining the overall structure of the standard periodic table, two defining features stand out: (1) the organisation of the elements in *s*-, *p*-, *d*- and *f*-blocks which reflects the particular filling order of the orbitals for many-electron systems, and (2) the so-called period doubling — the fact that all periods occur in pairs of equal length, except for the first period. Despite the quantum revolution in the 1920s, both of these characteristic features remain in need of explanation. Quantum chemistry can predict the states of every individual element, but it has great difficulties in treating the Periodic System as a whole.

As a result, chemists commonly use the so-called Madelung rule to rationalize the orbital filling order and to predict the onset of the *s*-, *p*-, *d*- and *f*-blocks in the periodic table. As a welcome extra, the period doubling emerges as a natural consequence of the Madelung rule. But the Madelung rule has never been derived from first principles and remains a purely empirical (or *lexicographic*) rule — a useful mnemonic without quantum mechanical underpinning.

In 1969, a century after Mendeleev's discovery, the Swedish physicist Per-Olov Löwdin (1916–2000) noted how remarkable it was that "the simple [Madelung] rule has not yet been derived from first principles".[2] The quest for an *ab initio* derivation of the Madelung rule came to be known as the *Löwdin challenge*. Allen and Knight called it the "oldest and largest standing problem in quantum chemistry".[3] Many claims to a successful derivation have been published, but all have been dismissed.

As a result, the Madelung rule has witnessed several critical attempts to bury it once and for all.[4] But each time, it has found proponents who have called it back from the grave, and for good reason. The Madelung rule, after all, successfully describes the overall architecture of the Periodic System. It is this aspect of the Madelung rule, in particular, that endows it with explanatory power. It is this aspect also that drew the attention of a handful of group theoreticians in the 1970s, whose work will be the focus of this essay.

As so often happens in the history of science, the insight to study the Periodic System from a group-theoretical perspective cropped up almost simultaneously at several places in Europe and North-America around 1970. The pioneers included the Turkish-American physicist Asim Orhan Barut (1926–1994) in Boulder (Colorado), Octavio Novaro (1939–2018) in Mexico City (Mexico), Valentin N. Ostrovsky (1945–2006) in Saint-Petersburg (USSR), and Abram Ilyich Fet (1924–2007) in Novosibirsk (USSR), each with their respective co-workers.[5]

In their quest for the symmetries that lie hidden in the Periodic System, each of these teams worked independently. Their hope was that symmetry might provide a key to the System's secrets. Since no quantum mechanical derivation of the Madelung rule was known, an important target of their research became the group-theoretical derivation of the Madelung rule. If successful, this project also held the promise of explaining the period doubling in a group-theoretical, rather than quantum mechanical, way.

In this essay, we explore some of the attempts to explain the Periodic System in group-theoretical terms.[6] Our focus will be on the contributions by Abram Ilyich Fet and Asim Orhan Barut. We will not discuss the work of Octavio Novaro and Valentin Ostrovsky. The reason for this is quite simple. Although each team had the same goal in mind — *viz.* the derivation of the Madelung rule and the period doubling — their approaches differed significantly. Novaro and Ostrovsky took a traditional *atomic physics approach*, whereas Fet and Barut adopted an *elementary particle approach*. Let us briefly explain both approaches.

Historically, when simple quantum systems were studied, such as the hydrogen atom or the harmonic oscillator, the Hamiltonians of those systems were exactly known, and their symmetries under various transformations could be directly studied.[7] Since most of these systems belong to the domain of atomic physics, this was called the *atomic physics approach*.[8] Both Ostrovsky

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[1] Scerri (2019).

[2] Löwdin (1969, 332).

[3] Allen & Knight (2002, 83).

[4] For some recent criticisms, see Wang & Schwarz (2009), Schwarz & Wang (2010), Schwarz & Rich (2010) and Schwarz (2010). However, as described in Thyssen & Ceulemans (2017), one really should consider the orbital correlation diagram between two lexicographic orderings: the hydrogenic order and the Madelung order. Both are limiting cases, with the actual systems lying in between. Be that as it may, there is no doubt that the actual ground state configurations of the elements are much closer to the Madelung rule than to the hydrogenic rule.

[5] Some key publications are Barut (1972a), Barut (1972b), Novaro & Wolf (1971), Novaro & Berrondo (1972), Novaro (1973), Novaro (1989), Novaro (2006), Ostrovsky (2004), Ostrovsky (2006), Byakov et al. (1976), Fet (2010), and Fet (2016). For more recent additions to this literature, see Kibler (1989) and Thyssen & Ceulemans (2017).

[6] A detailed account of the symmetry groups involved and the current status of the group-theoretical approach is presented in the recent book by Thyssen & Ceulemans (2017).

[7] The Hamiltonian of a system corresponds to the sum of the kinetic and potential energies for all the particles in the system, and thereby provides a detailed description of that system.

[8] The distinction between the atomic physics approach and the elemen-

(together with Demkov) and Novaro (together with Berrondo) followed this approach when they attempted to construct a Hamiltonian for the Periodic System.[9]

Coming up with such a Hamiltonian, however, proved extremely difficult. This was due, in part, to the fact that no *ab initio* derivation of the Madelung rule existed. Both Fet and Barut therefore felt the need for another approach. They found their inspiration in the recent developments in elementary particle physics, and in particular in the work of the German physicist Werner Karl Heisenberg (1901–1976) and American physicist Murray Gell-Mann (1929–2019). Their approach was therefore called the *elementary particle approach*.

The aim of our essay is threefold. First and foremost, to show that the elementary particle approach required an important paradigm shift in the understanding of the nature of chemical elements. As we will demonstrate, the idea, in essence, consisted of treating the chemical elements, not as particles (as in the atomic physics approach), but as states of a superparticle. Second, our essay retraces the origin of this paradigm shift via the developments in elementary particle physics in the 1960s and the work of Heisenberg, all the way back to Plato (428–348 BC). It was Heisenberg's deep respect for Plato, after all, that led him to propose treating the proton and neutron, not as elementary particles, but as different states of the nucleon. Third, our essay aims to highlight the inevitable tension that the symmetry program created between the formal mathematical treatment and the under-lying physical reality. This becomes particularly clear when comparing the work of Fet and Barut.

OUTLINE

Our essay is structured as follows. In section 1, we briefly introduce the two main characters of our paper: Abram Ilyich Fet and Asim Orhan Barut. In section 2, we provide a careful study of Heisenberg's last paper on the nature of elementary particles. What might feel like a long detour, will turn out crucial to understand the approaches by Fet and Barut. We explain why according to Heisenberg the traditional Democritean picture of matter no longer applied to modern physics, and why a Platonic symmetry-based picture of matter was called for instead. According to this picture, the elementary particles are only material realizations of certain 'particular' symmetries. Indeed, according to Heisenberg, it was not the particles, but their 'particular' symmetries that were truly fundamental.

In section 3, we explain what Heisenberg precisely meant by this philosophical claim via a brief study of isospin. We also show how Heisenberg's Platonic philosophy came to dominate the field of elementary particle physics, and how it found its culmination point in Gell-Mann's classification of the hadrons in the *eightfold way*. In section 4, we return to the Periodic System. We demonstrate that it was the success of Heisenberg's approach in elementary particle physics that sparked the group-theoretical approach to the Periodic System.

In section 5, we show that the history of this approach was marked by the continuous tension between the attraction to beautiful mathematical structures, and the need to keep contact with physical reality. We illustrate this via a critical examination of the work of Fet, in comparison to the work of Barut.

1. BIOGRAPHICAL PRELUDE

Abram Ilyich Fet

Abram Ilyich Fet was a Russian mathematician and philosopher. According to his wife, Ludmila P. Petrova-Fet, and his colleague Rem G. Khlebopros, Fet "belonged to a particular 'species of human' that is becoming extinct today".[10] While he mainly worked in mathematics and physics, he also explored biology, chemistry, economics, history, sociology, psychology, literature, music and the arts. As a dissident of the Soviet regime, he got dismissed twice from research institutes. In the years of unemployment, he nevertheless continued to do science on his own, living from casual translations.

His interest in the periodic table came through his collaboration in the early 1970s with the acclaimed Soviet physicist Yuri Borisovich Rumer (1901–1985). Rumer was convinced of the importance of symmetry groups for the natural sciences in general. He studied the symmetries of the genetic code with the help of B. G. Konopel'chenko, and the symmetries of elementary particles with Fet. The latter work culminated in the publication of a monograph on *The Theory of Unitary Symmetry Groups*.[11]

Having studied the symmetries of biology and physics, Rumer and Fet decided to embark on a "non-traditional" project, as Rumer later phrased it in a letter to the academician M. A. Leontovich (1903–1981) in 1973. They would study the symmetries of the Periodic Sys-

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tary particle approach was first made by Ostrovsky (2006).

[9] A typical example is the attempt by Ostrovsky and Demkov to develop a Hamiltonian based on Maxwell's fish eye potential. See Demkov & Ostrovsky (1972) and also Ceulemans & Thyssen (2018).

[10] Gladky et al. (2015, 283).

[11] See Rumer & Fet (1970).

tem of chemical elements. Inspired by Gell-Mann's work in elementary particle physics, they decided to apply the same elementary particle approach to the periodic table.

Their first paper appeared in 1971 in the journal *Teoreticheskaya i Matematicheskaya Fizika*.[12] Numerous papers and conference proceedings followed in the ensuing decade as Fet continued to develop their initial ideas. In 1984, Fet wrote a monograph, entitled *Symmetry of the Chemical Elements*, which presented a summary of his work on the Periodic System. However, his book was only published by the *Novosibirsk Academy* in 2010, more than a quarter of a century later, and three years after Fet's passing.

In the foreword to Fet's book, Khlebopros explains that Fet's work was edited in 1984 by the Siberian publishing department *Nauka*. Everything was ready for publishing. Even the cover had been approved by the *Arts Council*. But all of a sudden the book was withdrawn from publication, and the type matter was decomposed. The reason for this became clear a little later: on 8 October 1986, Fet was dismissed from work "due to noncompliance with the position held based on the performance evaluation." Fet, in other words, lacked publications; he did not live to see his reputation vindicated.[13]

According to the author's widow, though, Fet was fired for reasons which were entirely political and had no relation to science.[14] Khlebopros suggested that it had to do with Fet's personality: "A talented mathematician and physicist, a very well-educated and intelligent person with a sense of dignity and independence, he was, of course, envied and hated by ungifted science bureaucrats".[15] Recently, an English translation of Fet's monograph was published by *De Gruyter*.[16]

Asim Orhan Barut

Born in Malatya (Turkey) in 1926, Asim Orhan Barut studied at the Eidgenössische Technische Hochschule (ETH) in Zurich (Switzerland), where he obtained his under-graduate diploma in 1949 and his PhD in 1952.[17] After postdoctoral work in theoretical physics at the University of Chicago from 1953 to 1954, Barut served as an assistant professor at Reed College from 1954 to 1955 and at Syracuse University from 1956 to 1961. In 1962, Barut became a faculty member at the University of Colorado (Boulder), where he served for 32 years until his untimely death in 1994 at the age of 68.

Like Fet, Barut had broad interests which ranged from physics to politics, philosophy and religion.[18] But his true love was mathematical physics, and in particular group theory. Barut published more than 500 scientific papers, and authored 6 books.[19] He was also a devoted teacher and sought-after speaker — "his teaching style was blackboard and chalk" — and he travelled the globe to teach and speak at numerous summer schools and workshops.[20]

In 1971, Barut was the visiting Erskine Fellow at the University of Canterbury in Christchurch (New Zealand), where he also attended the Rutherford centennial symposium on the structure of matter. His stay in New Zealand gave rise to two important publications in connection with our topic — the symmetry of the Periodic System. The first one was a small booklet which contained the notes of his lectures as Erskine Fellow on "Dynamical Groups and Generalized Symmetries in Quantum Theory". The second one was his contribution to the proceedings of the Rutherford centennial symposium on the "Group Structure of the Periodic System".[21]

There are important similarities but also crucial differences in the works of Fet and Barut. As we already mentioned in the introduction, both Fet and Barut were greatly inspired by Heisenberg's and Gell-Mann's achievements in elementary particle physics, and both wondered to what extent the elementary particle approach could be applied to the Periodic System. The key to this approach, as we will argue, was a radical revision of the nature of the chemical elements. Fet and Barut were forced to treat the element, not as composite particles, but as states of a superparticle. In order to fully grasp the need for this paradigm shift, we will have to consider the works of Heisenberg and Gell-Mann. This will be done in sections 2 and 3. We will turn to the contributions of Fet and Barut in sections 4 and 5. It is also here that the differences between both will begin to shine through. Fet occupied a position at the mathematical end of the spectrum, whereas Barut's position was more balanced between mathematics and physics.

2. HEISENBERG'S PLATONIC PHILOSOPHY

Heisenberg's last paper was published posthumously.[22] It was devoted to the nature of elementary parti-

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[12] Rumer & Fet (1971).

[13] See Fet (2010).

[14] Private communication with Ludmila P. Petrova, January 4, 2011.

[15] See Fet (2010).

[16] Fet (2016).

[17] Scully (1998).

[18] Dowling (1998).

[19] On top of that, he also co-edited another 25 books.

[20] Scully (1998).

[21] See Barut (1972a) and Barut (1972b).

[22] Heisenberg passed away on 1 February 1976; his paper appeared in

cles. The question "What is an elementary particle?" had haunted Heisenberg for most of his scientific career. According to Heisenberg, "certain erroneous developments in particle theory […] are caused by a misconception by some physicists that it is possible to avoid philosophical arguments altogether." "Starting with poor philosophy", Heisenberg continued, "they pose the wrong questions." As we intend to show in this section, Heisenberg had come to the conviction that the traditional Democritean picture of matter no longer applied, and that it had to be replaced by a Platonic one.[23] The idea that "in the beginning was the particle", in other words, had to be replaced by "in the beginning was symmetry".[24]

In the beginning was the particle

For over 2500 years, scientists and philosophers have pondered what would happen if one continued to divide matter into ever smaller constituents. Would this process go on *ad infinitum* or would one reach a point where no further division was possible? Is matter continuous or discrete?

Different (reductionist) answers were offered by different pre-Socratic philosophers. The material monists (Thales, Anaximander and Anaximenes) thought that matter was composed of a single material substance. The material pluralist Empedocles, on the other hand, claimed that all matter was composed of four *roots*: fire, air, earth and water.[25] It was Plato who first referred to these roots as στοιχειον (*stoicheion* or *elements*) in his major cosmological dialogue *Timaeus*, and who associated the four classical elements with the Platonic solids.

However, according to Heisenberg, the best-known answer to the above questions was given by the pre-Socratic philosopher Democritus.[26] Democritus (like his teacher Leucippus) was a materialist who postulated that all matter was ultimately composed of *atoms* — small, (physically) indivisible, immutable and indestructible units of matter. Indeed, the Greek word ατομον (*atomon*) literally means "indivisible" or "uncuttable". The philosophical atoms of Democritus were too small for us to see, and came in a variety of shapes and sizes. They were infinite in number and in constant motion, colliding with each other in an otherwise empty vacuum (or *void*).[27]

Plato's pluralistic doctrine was very different from Democritus' atomistic doctrine, and despite Plato's influence at the time, it was Democritus who emerged victoriously in the long run. In Heisenberg's opinion, "the strongest influence on the physics and chemistry of the last century undoubtedly came from the atomism of Democritos".[28] Bertrand Russell, in his *History of Western Philosophy*, concurred that the atomistic doctrine of Leucippus and Democritus "was remarkably like that of modern science".[29] Indeed, in the 18th-century, John Dalton (1766–1844) proposed that each chemical element is composed of a unique type of atom with characteristic atomic weight.[30] Like the philosophical atoms of Democritus, Dalton's chemical atoms could not be created, nor divided into smaller constituents or destroyed during chemical processes.[31]

The growing particle zoo

For nearly one century, the chemical atoms were thought to be the smallest possible units of matter. However, with the discovery of the electron by Sir Joseph John Thomson (1856–1940) in 1897, it became apparent that Dalton's atoms were not elementary after all. After the discoveries of the proton in 1917 and the neutron in 1932, the Rutherford–Bohr model of the atom was proposed with a central atomic nucleus of positively charged protons (p^+) and neutral neutrons (n^0), surrounded by a cloud of negatively charged electrons (e^-).

Despite their revolutionary character, these discoveries did not put into question the atomism of Democritus. On the contrary, "the electron, the proton and pos-

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the March edition of the journal *Physics Today*. See Heisenberg (1976a). It was based on a translation of his opening lecture to the *German Physical Society*'s spring meeting, given on 5 March 1975. The original version of his talk was published in the February 1976 issue of *Naturwissenschaften*. See Heisenberg (1976b).

[23] The materialistic interpretation of Democritus' atomic theory is due to Aristotle. Democritus himself thought of the atoms as immaterial entities, in full agreement with Plato's ideas. In that sense, Heisenberg's conviction to replace particles with symmetry principles was not in reaction to a Democritean picture of matter, but rather to the Aristotelian view of atomic theory. However, since our aim is historical (rather than philosophical) accuracy, we will keep with Heisenberg's terminology when representing his ideas on the nature of elementary particles.

[24] Heisenberg (1976a), quotations on p. 32.

[25] Aristotle later added a fifth element to this list of earthly and corruptible elements. The aether or quintessence (*quinta essentia*) was a heavenly substance and formed the constituent of all the stars and planets in the Universe.

[26] Heisenberg (1976a).

[27] The atomistic doctrine of Democritus was further refined by Epicurus and popularised by the Roman poet Lucretius in the first-century BC in his poem *De Rerum Natura* (*The Nature of Things*). See Lucretius (2007).

[28] Heisenberg (1976a, 37).

[29] Russell (1946, 84).

[30] Dalton (1808).

[31] Chalmers (2009).

sibly the neutron could, it seemed, be considered as the genuine atoms, the indivisible building blocks, of matter", dixit Heisenberg.[32] The idea thus originated that all matter is ultimately composed of three fundamental particles: protons, neutrons and electrons. Since they seemed immutable, and their number was therefore fixed, physicists called them *elementary particles*. The elementary particles of modern physics became the modern analogue of the philosophical atoms of Democritus.

This sparse ontology came to an abrupt end in 1947 with the discovery of *pions* by Cecil Powell (1903–1969) in cosmic ray experiments. The pions (π^+, π^0 and π^-), moreover, were observed to disintegrate into yet another class of particles, *muons* (μ^+, μ^0 and μ^-). For example:

$$\pi^+ \rightarrow \mu^+ + \nu$$

The situation only worsened with the construction of particle accelerators. By accelerating particles to tremendous velocities, and forcing them into head-on-collisions, a plethora of new particles were discovered in the 1950s. Among these were the *kaons* (K^+, K^-, K^0 and $\bar{K}^0$), the *lambda* particle (Λ^0), the *sigma* particles (Σ^+, Σ^0 and Σ^-, as well as Σ^{*+}, Σ^{*0} and Σ^{*-}), the *xi* particles (Ξ^0, Ξ^-, Ξ^{*0} and Ξ^{*-}) and the *delta particles* (Δ^{++}, Δ^+, Δ^0 and Δ^-).

In the early 1940s, the Universe was a simple place, composed of only three fundamental particles. By the early 1960s, the Universe had turned unfathomably complicated, with over 30 "fundamental" particles. The parsimonious ontology of the 1940s, in other words, had given way to a baroque ontology in the 1960s, in seeming contradiction with Occam's well-known razor. As we shall see, an entirely new way of looking at the elementary particles was needed before order could be restored in the growing particle zoo.

The loss of elementarity

For Heisenberg, the discovery of the particle zoo was ample evidence that the materialistic picture no longer applied in modern physics. "In the physics of elementary particles of our time," wrote Heisenberg, "good physics has sometimes been unconsciously spoiled by poor philosophy" — referring to the atomistic doctrine of Democritus.[33]

The problem according to Heisenberg was not that physicists were now forced to take these 30 odd particles as elementary. On the contrary, the problem was that their elementary nature was called into question by recent experimental findings.

For example, when an electron (e^-) and a positron (e^+) collide at low energy, they annihilate, producing two gamma-ray photons (γ):

$$e^- + e^+ \rightarrow \gamma + \gamma$$

The reverse reaction, electron-positron creation, also occurs. Here, a high energy photon is converted into an electron-positron pair:

$$\gamma \rightarrow e^- + e^+$$

Clearly then, electrons and positrons are not immutable. They can be created and annihilated. "They are not "elementary" in the original meaning of the word", wrote Heisenberg.[34]

Another example of the breakdown of the materialistic picture is provided by radioactive β^- decay, such as the decay of carbon-14 into nitrogen-14. In order to change the parent nuclide ${}^{14}_{6}\mathrm{C}$ into the daughter nuclide ${}^{14}_{7}\mathrm{N}$ (a process known as *nuclear transmutation*), a neutron must be converted into a proton. Due to the conservation of electric charge and lepton number, this must be accompanied by the emission of an electron and an electron antineutrino ($\bar{\nu}_e$):

$${}^{14}_{6}\mathrm{C} \rightarrow {}^{14}_{7}\mathrm{N} + \mathrm{e}^- + \bar{\nu}_e$$

Generalising, β^- decay always involves the transmutation of a neutron into a proton:

$$n^0 \rightarrow p^+ + e^- + \bar{\nu}_e$$

The reverse process is observed in β^+ decay (or positron emission), with a proton turning into a neutron:

$$p^+ \rightarrow n^0 + e^+ + \nu_e$$

Clearly then, protons and neutrons are not immutable. They can be transmuted into one another. No particle is more elementary than the other one.

What these, and other empirical findings, showed according to Heisenberg, was that the question "What do these particles consist of?" had become meaningless. After all, from the point of view of β^- decay, one might (naively) consider the neutron to be a compound particle, consisting of a proton, an electron and an electron antineutrino. But from the point of view of β^+ decay, it is

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[32] Heisenberg (1976a, 37).

[33] Heisenberg (1976a, 37).

[34] Heisenberg (1976a, 32).

not the neutron, but the proton that is compound, consisting of a neutron, a positron and an electron neutrino. “Experimentally, the concept of “dividing” had lost its meaning”, blurted Heisenberg. In Heisenberg’s opinion, this fading of the distinction between elementary particles and compound particles was probably “the most important experimental result of the last fifty years”.[35]

Plato and that sort of thing

Since the materialistic picture of matter no longer applied in modern physics, a paradigm shift was called for. According to Heisenberg, “If we wish to compare the results of present-day particle physics with any of the old philosophies, the philosophy of Plato appears to be the most adequate”.[36]

Heisenberg had a deep love and appreciation for Plato. According to David Peat, “his scientific attitudes reflect a debt to philosophy and in particular his respect for Plato.” Heisenberg concurred that “My mind was formed by studying philosophy, Plato and that sort of thing”.[37]

Heisenberg’s father, August Heisenberg (1869–1930), was a scholar of ancient Greek philology and modern Greek literature; he became a professor of philology at the University of Munich in 1910 when Heisenberg was nine years old. In 1911, the young Heisenberg entered the *Maximilians-Gymnasium*. At that time, it was still common practice to place more emphasis upon classical Greek and Latin than on the sciences and mathematics. All of this contributed to Heisenberg’s classical-humanistic education.

In his teenage years, as a result of the political turmoil in Munich after the First World War,[38] the young Heisenberg became part of the Cavalry Rifle Command No. 11. Their headquarters were located in the *Theological Training College*, opposite the University. Heisenberg often retired to the roof of the college with a Greek school edition of Plato’s Dialogues. “There, lying in the wide gutter, and warmed by the rays of the early morning sun,” Heisenberg later recalled, “I could pursue my studies in peace.” It was there, in the spring of 1919, that Heisenberg first read Plato’s cosmological treatise, the *Timaeus*.[39]

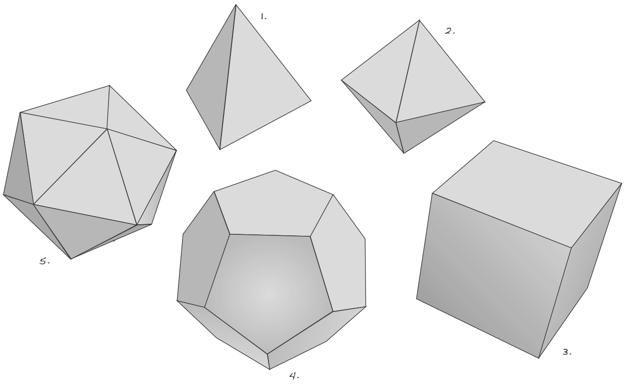

Figure 1. The Platonic solids: 1. tetrahedron; 2. octahedron; 3. cube (or hexahedron); 4. dodecahedron; and 5. icosahedron.

Platonic solids in the Timaeus

Plato believed the Universe had been created out of chaos by a Demiurge using the four elements — fire, air, earth, and water — as basic building blocks.[40] Plato associated each of these elements with one of the five Platonic solids. The element fire was thus identified with the pointy tetrahedron; air with the smooth octahedron; earth with the bulky and weighty cube; and water with the fluid and nearly spherical icosahedron (Figure 1).[41]

Empedocles, who first introduced the four elements, believed the elements could be mixed in various proportions but were themselves immutable and indestructible. What makes Plato’s “theory of everything” so exciting is that the elements are no longer elementary. Each regular polyhedron, after all, is constructed from regular polygons. The tetrahedron, octahedron and icosahedron are built from (respectively 4, 8 and 20) equilateral triangles; the cube (or hexahedron) is built from 6 squares. The elements can therefore be broken down into triangles and squares and recombined to create new elements.[42]

For example, two particles of fire can be broken down into 8 equilateral triangles and recombined to form one particle of air:

$$\underset{4}{\text{fire}} + \underset{4}{\text{fire}} \rightarrow \underset{8}{\text{air}}$$

Likewise, a particle of water, consisting of 20 triangles, can transmute into five particles of fire, or two particles of air and one of fire:

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[35] Heisenberg (1976a), quotations on p. 33.

[36] Heisenberg (1976a, 38).

[37] See Peat (1996, 3) and Heisenberg (1996, 6).

[38] Specifically, the rise and fall of the Bavarian Soviet Republic in Munich during the German Revolution of 1918–1919.

[39] Heisenberg (1971, 8).

[40] See Plato (1976).

[41] The fifth Platonic solid, the dodecahedron, was used for the Universe as a whole. Aristotle later conjectured that it represented the aether which made up the celestial heavens.

[42] Plato (1976, 1259).

$$\underset{20}{\text{water}} \rightarrow \underset{(5\times4)}{5\times\text{fire}}$$

Notice though that since earth is made up from squares, it cannot be transmuted into any of the other elements. These elemental transmutations resemble the ones described above for elementary particles.

In the beginning was symmetry

To Heisenberg, "the whole thing seemed to be wild speculation []. It saddened me to find a philosopher of Plato's critical acumen succumbing to such fancies." Yet one aspect of Plato's account captured his imagination. "I was enthralled by the idea that the smallest particles of matter must reduce to some mathematical form," wrote Heisenberg. In his opinion, "the elementary particles in Plato's *Timaeus* are finally not substance but mathematical forms".[43]

What is more, these mathematical forms — triangles and squares, and the Platonic solids they make up — are highly symmetrical. What is fundamental, in other words, are not the material particles themselves, but the mathematical symmetries underlying them. This Platonic way of thinking moreover seemed applicable to modern physics. According to Heisenberg, "our elementary particles are comparable to the regular bodies of Plato's *Timaeus*".[44] As Heisenberg explained:

> *So far we had always believed in the doctrine of Democritus, which can be summarised by: "In the beginning was the particle." We had assumed that visible matter was composed of smaller units, and that, if only we divided these long enough, we should arrive at the smallest units, which Democritus had called "atoms" and which modern physicists called "elementary particles." But perhaps this entire approach has been mistaken. Perhaps there was no such thing as an indivisible particle. [] In the beginning was symmetry!*[45]

According to Heisenberg, it was not the elementary particles, but the symmetries that lie beyond them, that are truly fundamental. The elementary particles are but material realizations of these underlying symmetries.[46] One eloquent model of such 'particular symmetries' will be presented in the next section.

3. THE SYMMETRY OF ELEMENTARY PARTICLES

In order to make Heisenberg's position more concrete, we will briefly look at the example of *isospin*. After all, the concept of isospin was introduced in 1932 by Heisenberg himself, soon after the discovery of the neutron by Sir James Chadwick (1891–1974) that same year.

Protons and neutrons are sometimes called *nucleonic particles* because they are the components of atomic nuclei. Despite their difference in electric charge, the proton and neutron are nearly identical in all other respects. Both are fermions, and both have almost the same mass.[47] Heisenberg was baffled by this consanguinity, and intent on uncovering the reason for it.

When two or more particles have the same mass (or energy), they are said to be *degenerate*. Degeneracies are a tell-tale sign that there is a symmetry lurking in the background. Symmetry is all about the interplay between change and permanence; it is about the quest for permanence in a world of constant flux. More precisely, an object is said to be *symmetric* when there is a transformation (*change*) that leaves certain aspects of the object fixed (*permanence*). Rotating a ball around its centre, for example, leaves its overall appearance unchanged. Hence, the ball is said to be spherically symmetric.

The same applies to the nucleonic particles. If someone were to exchange a proton for a neutron — as we saw happens during β decay — it would be practically impossible to tell, given their similarity in mass. Indeed, the strong interaction force cannot, as a matter of fact, distinguish protons from neutrons.[48]

In view of all this, Heisenberg suggested treating the proton and neutron, not as two distinct elementary *particles*, but as two possible *states* of one and the same particle, which he called the *nucleon*. Heisenberg did not have to look far to find an equivalent quantum system that also appears in two possible states. Since the so-called Stern–Gerlach experiment, it was known that the electron has a *spin*, which can adopt two states, commonly denoted as spin up $|\uparrow\rangle$ and spin down $|\downarrow\rangle$.[49] In the same way, Heisenberg proposed the nucleon has an *isospin*, which can adopt two states, denoted as $|p^+\rangle$ and $|n^0\rangle$.

Both spin and isospin are characterised by the same symmetry group: the Special Unitary group of degree 2, or SU(2) group. The SU(2) group is an example of a

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[43] Heisenberg (1971), quotations on p. 8.

[44] Heisenberg (1971, 241).

[45] Heisenberg (1971, 133).

[46] See also Peat (1987).

[47] To be specific, $m_{p+} = 938.272046$ MeV/C^2, and $m_{n0} = 939.565378$ MeV/C^2. Fermions are particles that obey Fermi–Dirac statistics, as opposed to bosons which obey Bose–Einstein statistics.

[48] It is only the (weaker) electromagnetic force that makes the distinction on the basis of their difference in charge.

[49] Gerlach & Stern (1922).

Lie group, named after the Norwegian mathematician Sophus Lie (1842–1899).[50] Let us only note here that the fundamental representation of SU(2) is a *doublet*. The spin up and spin down states of the electron form an SU(2) spin doublet; the proton and neutron form an SU(2) isospin doublet.

It is here that Heisenberg crossed the conceptual line between *particles* and *states*. On the one side are two nucleonic particles that are clearly related to each other as they have nearly the same mass. On the other side are the two degenerate states of a spin system that is described by the SU(2) group. The connection consists in associating the two nucleons (*particles*) with the two components (*states*) of the SU(2) doublet.

This was perhaps the first time that such a connection was made. It predates the discovery by Gell-Mann (and others) of the SU(3) symmetry of hadronic matter — to be discussed in the next section — by more than three decades. Above all, it offers support to Heisenberg's conviction that symmetries are more fundamental than particles.

With the help of Heisenberg's isospin, all elementary particles can be assigned into isospin *multiplets*. The pions π^+, π^0 and π^-, for instance, are assigned to an isospin triplet, as are the sigma particles Σ^+, Σ^0 and Σ^-. The delta particles Δ^{++}, Δ^+, Δ^0 and Δ^- form an isospin quartet; the xi particles Ξ^- and Ξ^0 constitute an isospin doublet, and the lambda particle Λ^0 an isospin singlet.

From the SU(2) symmetry point of view, particles within a multiplet are identical. Just as the spherical symmetry of a ball allows one to rotate one orientation into another, the SU(2) symmetry allows one to transform the particles of an isospin multiplet into one another.

The eightfold way

The American physicist Murray Gell-Mann (1929–2019) took Heisenberg's idea a step further in the 1950s and 1960s. For reasons which are beyond the scope of this article, Gell-Mann introduced a new quantum number, which went by the name of *strangeness*, and was denoted *S*. The proton and neutron, for example, were assigned strangeness $S = 0$; the sigma and lambda particles $S = -1$, and the xi particles $S = -2$.

Gell-Mann subsequently ordered the particles on the basis of their isospin component T_3 and strangeness *S*. This process is illustrated in Figure 2 for the baryons n^0, p^+, Σ^-, Σ^0, Σ^+, Λ^0, Ξ^- and Ξ^0.[51] The result is an *octet* of particles, with six particles at the corners of a regular hexagon, and two more particles at the centre. Inspired by the *Eightfold Path* of Buddhism, Gell-Mann named his classification scheme the *eightfold way*.[52]

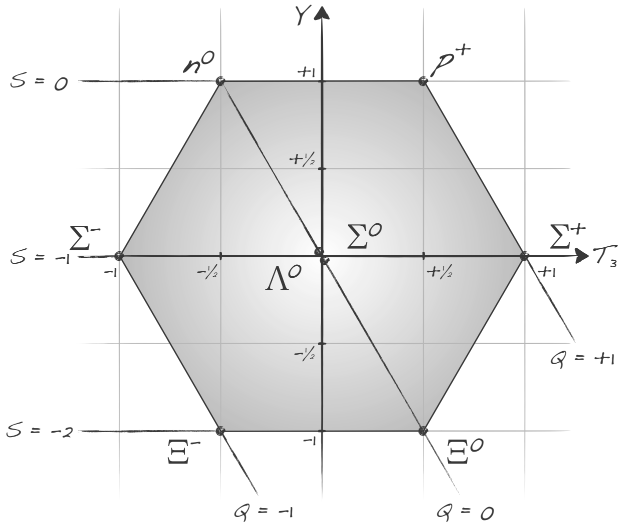

Figure 2. The baryon octet.

Particles along the same horizontal line in Figure 2 form the familiar isospin multiplets. On the upper line, we have the proton-neutron doublet; on the lower line the xi doublet, and on the middle line the sigma triplet superposed with the lambda singlet.

Gell-Mann realised that the eightfold way pointed at a hidden symmetry. Just as the isospin multiplets are representations of the SU(2) group, the baryon octet is a representation of the larger SU(3) group. Indeed, from the SU(3) symmetry point of view, the baryons are no longer treated as distinct particles. Instead, they are taken to be the states of a *superparticle*. This implies that the members of the baryon octet can be transformed into one another. As a result, the strong force cannot distinguish them. The interchange of one baryon for another goes unnoticed in strong interactions.

Broken symmetry

From the SU(2) point of view, the proton and neutron are identical; they appear as two faces of the same nucleonic coin. Hence, in order to tell them apart, the SU(2) symmetry has to be broken. This is done by imposing the quantisation of the charge operator, which

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[50] A full account of the SU(2) group (and the others to follow) is given in Thyssen & Ceulemans (2017).

[51] The name "baryon" refers to the Greek word βαρύς for "heavy".

[52] See Gell-Mann & Ne'eman (2000).

breaks the SU(2) symmetry to the U(1) symmetry. It is only at that point that the proton and neutron regain their identities, and that one can meaningfully distinguish them.

The same principle applies to Gell-Mann's eightfold way. From the SU(3) point of view, all baryons are identical. Hence, in order to tell them apart, the SU(3) symmetry has to be broken. As a first step, the SU(3) symmetry can be broken to the SU(2) symmetry. The SU(3) octet is then split into the familiar SU(2) submultiplets: the nucleon doublet, sigma triplet, lambda singlet and xi doublet (indicated by the horizontal lines in Figure 2). From that point onwards, particles from different isospin multiplets can no longer be transmuted into one another; they are no longer identical. This series of symmetry breakings is typically represented by a chain of subgroups:

$$SU(3) \supset SU(2) \supset U(1)$$

The importance of symmetry breaking cannot be overstated. As the world unfolds, and the phenomena take place, the initial ideal symmetries break down, and only remnants remain, as with Plato's ideals. According to most physicists today, it is the breaking of symmetry that makes the world an interesting and variegated place to live in. As the French physicist Pierre Curie appropriately said: "*C'est la dissymétrie qui crée le phénomène*".[53]

With the eightfold way, the zoo of particles was finally classified, and order was restored to the world of elementary particles. Most importantly, when Gell-Mann drew up his classification schemes, some seats remained unoccupied, hinting at the existence of as yet undiscovered particles. Like Mendeleev a century earlier, Gell-Mann predicted the existence of the eta meson (η^0) and the omega baryon (Ω^-), which were discovered soon afterwards. Such was the predictive force of symmetry. "I was playing around with the particles. [Mendeleev] was playing around with the elements," said Gell-Mann in 1997.[54] "It was natural to make a comparison between them, although I think Mendeleev's work was much more important." Gell-Mann was ultimately awarded the Nobel Prize in 1969, a century after Mendeleev's development of the periodic table.

The key to these revolutionary developments in elementary particle physics was the move from materialism to idealism. As Heisenberg explained, symmetries are ontologically prior to particles. Symmetries represent the fundamental level of reality, whereas particles only constitute a secondary level of reality. The elementary particles, after all, only emerge from these symmetries by a series of symmetry breaking steps, and therefore have a derivative status.

4. THE SYMMETRY OF CHEMICAL ELEMENTS

It did not take long before the same group-theoretical approach was applied to the zoo of chemical elements. The situation with the Periodic System in the 1970s, after all, resembled the one in elementary particle physics in the 1950s. As we explained in sections 2 and 3, when the zoo of elementary particles was discovered, their internal dynamics were still shrouded in mist.[55] The exact Hamiltonian for these hadronic systems was not known, and another approach was called for. Instead of inferring the symmetry group of the system from the behaviour of the Hamiltonian under various operations, the symmetry group was simply postulated on the basis of the known empirical data and phenomenology of particle reactions. That is, instead of adopting an atomic physics approach, Heisenberg and Fet opted for a phenomenological elementary particle approach.

The goal of Fet and Barut was to apply the same phenomenological approach to the Periodic System. After all, despite the developments in quantum mechanics and computational chemistry, the internal dynamics of many-electron systems was also still shrouded in mist. Both Fet and Barut therefore took the structure of the Periodic System as empirical input and looked for a particular symmetry group that could explain this data.[56] Not surprisingly, the key to their approach was once again the move from Democritus to Plato, which required a radical revision of the nature of chemical elements, as we now intend to explain.

The nature of chemical elements

Heisenberg did not treat the proton and neutron as distinct particles, but as distinct states of one superparticle: the nucleon.[57] In a similar vein, Fet and Barut did not treat the chemical elements as distinct elements, but as distinct states of a superparticle, which was later named the *baruton* in honour of Barut for his contri-

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[53] Curie (1894, 127).

[54] Quoted from an interview between Gell-Mann and the former editor-in-chief of *Science News*, Tom Siegfried on September 16, 1997 in Santa Fe, New Mexico. See also Siegfried (2002).

[55] Quantum chromodynamics was only developed in the 1970s.

[56] To be specific, the empirical data consisted of the various period lengths which were assumed to be the dimensions of the various multiplets of the symmetry group.

[57] Gell-Mann similarly treated the baryons, not as distinct particles, but as distinct states of some baryonic matter.

butions to the symmetries of the Periodic System.[58] The chemical elements, in other words, were no longer treated as concrete, physical particles with an internal substructure. The structural conception of the atom was thus excluded from the consideration of these group theoreticians.

This had at least two crucial advantages. First, by treating the chemical elements as states of a *single* quantum system, the Periodic System was being studied as a whole. Contrast this with the atomic physics approach, where each element was treated as a *separate* quantum system. Second, by stripping the atoms from their physical content, the link with quantum mechanics was entirely lost. What remained, was an abstract 'group-theoretical' atom, a structureless non-composite entity, without internal dynamics. Fet and colleagues, for example, emphasised that their approach was "*not* a theory of electronic shells".[59] As a result, there was no mention of electronic configurations, orbitals or quantum numbers. By ignoring the internal substructure of the elements, Fet and Barut could thus circumvent the traditional quantum mechanical challenges, such as the Löwdin challenge referred to in the introduction.

Yet another advantage of the elementary particle approach can be mentioned. Heisenberg and Gell-Mann did not know of the possible substructure of the elementary particles when they studied their symmetries. Yet, the eightfold way did pave the way towards the discovery of *quarks*, the constituents of all elementary particles.[60] Both Fet and Barut wondered whether a group-theoretical study of the Periodic System might similarly pave the way to a deeper understanding of the substructure of the elements and new insights in the internal (quantum) dynamics of many-electron systems.

Fet was well aware of these advantages, and mentioned them on more than one occasion. Interestingly, he also referred to the work of Barut and Novaro and made an important remark about the difference with his own work: these authors, in his opinion, considered "the symmetry developed as a symmetry of the electron shells only, not distinguishing it from the Bohr model".[61] In contrast, in his own perspective the atom system was considered as a whole.[62] Later on, he repeated this claim by stressing the novelty of his approach in the most explicit terms:

> *We'd like to point out again the most important distinct feature of the theory suggested: while the Bohr model considers one element as a separate quantum system (and the atomic number is included in the theory as a parameter, so the number of quantum systems is the same as the number of elements), our model considers the atoms of all possible elements as the states of a unified quantum system, linkable to each other by symmetry group action.*[63]

Despite these claims, it is difficult to maintain that there is a fundamental difference with the perspective in Barut's work, who explicitly asked in his Rutherford lecture: "Are there (global) quantum numbers which would characterize the elements as different 'states' of a single system? All elements would then constitute a single 'multiplet'." Barut then expressed the atomic numbers, not as parameters, but as functions of these quantum numbers.[64]

The symmetry group of the Periodic System

Having thus introduced the baruton, whose states are the chemical elements, the primary challenge for Fet and Barut was to find the symmetry of the baruton (just like Heisenberg had identified the SU(2) group as the symmetry of the nucleon, and Gell-Mann the SU(3) group as the symmetry of the eightfold way). The principal key turned out to be the hydrogen atom.

The symmetries of the hydrogen atom were well-known. Fock had shown that the hydrogen atom possesses rotational symmetry not only in three dimensions but also in four. This rotational symmetry was described by the Special Orthogonal group in 4 dimensions, also known as the Fock group or SO(4) group. As a result, all the hydrogen orbitals of fixed were grouped in SO(4) multiplets of dimension n^2.[65]

The ultimate goal, however, was to treat the *entire* set of hydrogen orbitals, regardless of their principal quantum number n, as a single symmetric object. This called for a so-called *covering group* which would contain the SO(4) group as a subgroup. The orbitals would then form a single infinite-dimensional multiplet of this covering group.

It was only in the sixties of the previous century that this goal was achieved. One of the first proposals came

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[58] Wulfman (1978).

[59] Byakov et al. (1976, 3).

[60] It is telling that Heisenberg, as a true Platonist, remained extremely skeptical about the possible existence of quarks, as this seemed to herald back the Democritean materialism. For him, the quark hypothesis was perhaps useful as a mathematical tool, but it certainly did not provide a picture of reality. "Even if quarks should be found (and I do not believe that they will be)," said Heisenberg, "they will not be more elementary than other particles, since a quark could be considered as consisting of two quarks and one anti-quark, and so on." Quoted from Peat (1987).

[61] Fet (2010, 154).

[62] See also Kibler (2018).

[63] Fet (2010, 155).

[64] See Barut (1972a), quotation on p. 84.

[65] See Fock (1935).

from Barut in 1964. He found an extension of the Fock group, known as SO(4,1), which was able to pack all the discrete states of hydrogen into one infinite-dimensional multiplet.[66] Within a year, two young doctoral students (classmates and childhood friends) in Moscow, Ilya A. Malkin and Vladimir Ivanovich Man'ko (°1940), took this idea a bit further and extended the group to SO(4,2).[67]

The SO(4,2) group describes the conformal or scaling transformations of spacetime. In a later development Barut and Haugen considered a further extension to scale trans-formations of mass and charge.[68] This yields a theoretical framework that incorporates the Maxwell equations, and ultimately the photon. The SO(4,2) group is thereby enlarged to the inhomogeneous conformal group IO(4,2) with 21 parameters. However the physical significance of these conformal generators remains a recurrent matter of debate.[69]

All of these groups are called *conformal symmetries*. From the SO(4,2) symmetry point of view, any hydrogen orbital can be transformed into any other orbital. But the SO(4,2) group also provided an excellent starting point for the group-theoretical study of the Periodic System. Since the chemical elements could be labelled by the same set of four quantum numbers as were used to describe the hydrogen orbitals, the SO(4,2) group served as an ideal candidate to describe the symmetry of the baruton. Both Fet and Barut recognised the conformal symmetry of hydrogen as the master equation from which to start.

From the SO(4,2) symmetry point of view, all chemical elements are identical. The SO(4,2) group, in other words, can *transmute* any chemical element into any other. It can be compared with the *philosophers' stone*, although the transformations induced by the conformal group are of course not physical but merely mathematical. In order to distinguish the chemical elements, the SO(4,2) symmetry has to be broken. It is only by shattering the SO(4,2) group that the elements regain their identities.

The next challenge therefore was to find a proper symmetry breaking that would explain the ordering of the elements in the Periodic System. It is here that the real differences between the treatments of Fet and Barut became clear as both proposed a different symmetry breaking chain. As we will explain in the next section, Fet's approach occupied a position at the mathematical end of the spectrum, whereas Barut's approach retained the link with physics and chemistry to a larger extent.

5. THE MADELUNG RULE AND PERIOD DOUBLING

We evaluate Fet's proposal, as it was described in his monograph on the *Symmetry of the Chemical Elements*.[70] Several introductory chapters of Fet's book are devoted to the construction of the conformal SO(4,2) group for the hydrogen system. In Chapter 4, Fet devoted an extensive discussion to the concept of isospin. Fet had a special interest in representing this example, since later on the SU(2) group would have to come to his rescue, when he was struggling with the period doubling in the periodic table. Of importance at present are chapter 5 and 6. In chapter 5, Fet exposed his views on the symmetry of the periodic table. In chapter 6, he confronted his views with chemical evidence.

In chapter 5, Fet first explained the conformal symmetry and then also introduced the Madelung rule as an observation of the basic regularity in the periodic table. Both Fet and Barut agreed that the Madelung rule offered the most concise explanation of the periodicity. Following this rule, one could regroup the elements of the periodic table in subsets, with the same n and l, and insert these in an (n,l) matrix. The Madelung rule traces a zigzag path through this matrix, which guided both Barut and Fet. In doing so, they observed a distinctive feature of the periodic table, namely that it seems to consist of two separate twin tables. This is the well-known period doubling. The difference between both is the parity of $n + l$. But here, the treatments of Fet and Barut diverged.

Barut solved the riddle of the period doubling by considering a symmetry breaking from SO(4,2) to SO(3,2). He had studied this group chain earlier with Bohm in a study on hadronic matter and found that the mother representation of SO(4,2) splits into two identical representations of SO(3,2).[71] Note that there are no quantum characteristics that discriminate these two subgroup representations. As far as SO(3,2) is concerned, they have the same symmetry. They are distinguished in odd and even according to the parity of $n + l$, but we do not have a symmetry operator in the model to determine this parity.

Here appears a critical turning point in Fet's work, which characterises the author as a mathematician of one piece, not willing to compromise on a matter of principle. Fet reminded the reader that the l quantum number is not really a quantum number, in the sense that it does not correspond to an eigenvalue of

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[66] Barut et al. (1965).

[67] Malkin & Man'ko (1966).

[68] Barut & Haugen (1972).

[69] Jaekel & Reynaud (1998).

[70] Our present analysis of Fet's book is based on a personal copy, which was given to us by Fet's widow. The manuscript was translated for us by Jewgienij Liszczuk., see Fet (2016).

[71] Barut & Bohm (1970).

an operator of the enveloping algebra. It only serves for the development of the square of the total angular momentum which is given as $l(l + 1)$, and so this value is always even.

In the eyes of Fet, the unavoidable consequence was that the $n + l$ sum of the Madelung rule *had no group sense*. No compromise was possible: "That is why from the view of the elements group description, the $n + l$ number should not be included in the 'lexicographic rule' formulation. Therefore we should replace the Madelung indexing by another one, which would also logically describe the properties of the elements, but which would be free from this disadvantageous feature".[72]

Fet concluded that there are thus two separate periodic tables, each of which follows a hydrogen sequence and must thus be described as SO(4,2), but with n and l redefined. For the odd sequence, instead of the quantum number ν, he defined a pseudo principal quantum number as:

$$\nu = ½ \, (n + l + 1)$$

The odd sequences are then mapped onto the new as follows:

$$1s \rightarrow 1s$$
$$2p\ 3s \rightarrow 2p\ 2s$$
$$3d\ 4p\ 5s \rightarrow 3d\ 3p\ 3s$$
$$4f\ 5d\ 6p\ 7s \rightarrow 4f\ 4d\ 4p\ 4s$$

Hence this sequence has become a perfect SO(4,2) representation again. Likewise, for the even sequence, one has to apply

$$\nu = ½ \, (n + l)$$

which will turn the even sequence in an equivalent system:

$$2s \rightarrow 1s$$
$$3p\ 4s \rightarrow 2p\ 2s$$
$$4d\ 5p\ 6s \rightarrow 3d\ 3p\ 3s$$
$$5f\ 6d\ 7p\ 8s \rightarrow 4f\ 4d\ 4p\ 4s$$

These two tables are like Heisenberg's nucleonic matter, forming the states of a spin-like doublet. The resulting symmetry group is the combination of both symmetries. In mathematical terms, this corresponds to the product of an SO(4,2) like group and an isospin-like group: $SU(2) \otimes SO(4,2)$.

In light of Barut's alternative, Fet's proposal appears artificial. It is true that there is no proper operator for l in the SO(4,2) group, but the symmetry breaking from SO(4,2) to SO(3,2) generates exactly the doubling that is observed. Indeed, in this process only operators which either preserve $n + l$ or change $n + l$ by two units are possible. So this group preserves the parity of the sum and is thus the perfect rationale for the existence of an odd and an even half of the periodic table.

This is a valuable insight which we owe to Barut. Fet was aware of Barut's Rutherford lecture, but he missed the point of the argument.[73] The crucial point of the doubling is not the individual value of l, nor n, but only the parity of their sum. And clearly, this is the property that is conserved in SO(3,2).

Later in the chapter, Fet also took into account the spin quantum number of the electron, which allowed all orbitals to be occupied by two electrons. So this was a further doubling, requiring an extra SU(2) group. However, this group was not an artificial construct but simply the true spinor characteristic. T treatment which then followed, however, was quite remarkable again, since Fet combined the spin quantum number ½ with the angular momentum l, thus dividing the $4l + 2$ elements of every manifold into two submanifolds with respectively $2l$ and $2l + 2$ elements. In physical terms, this means that every manifold (except for $l = 0$) is divided into two spin-orbit levels: a lower one with $j = l - ½$, and an upper one with $j = l + ½$. This is at odds with the quantum mechanical description of the elements, which certainly indicates that for the lighter elements spin-orbit coupling is not ruling the ground state terms.

The chemical data

Chapter 6 displayed chemical data to strengthen Fet's case. He took as an example the ionisation potential of the main group elements from boron to neon. According to Fet's claim, this graph should consist of two different trends: one corresponding to the spin-orbit doublet {B, C}, and another one for the spin-orbit quartet {N, O, F, Ne}. The data were plotted in a way to emphasise the existence of two separate parts, with a dashed border line in between.[74]

Nonetheless, this way of drawing the graph was unable to hide that no distinction of the kind is at stake. Indeed, there is a linear increase from boron to nitrogen; the break does not occur between carbon and nitrogen, but between nitrogen and oxygen. The reason for this is

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[72] Fet (2010, 177).

[73] See Barut (1972a).

[74] See Fet (2010, 194).

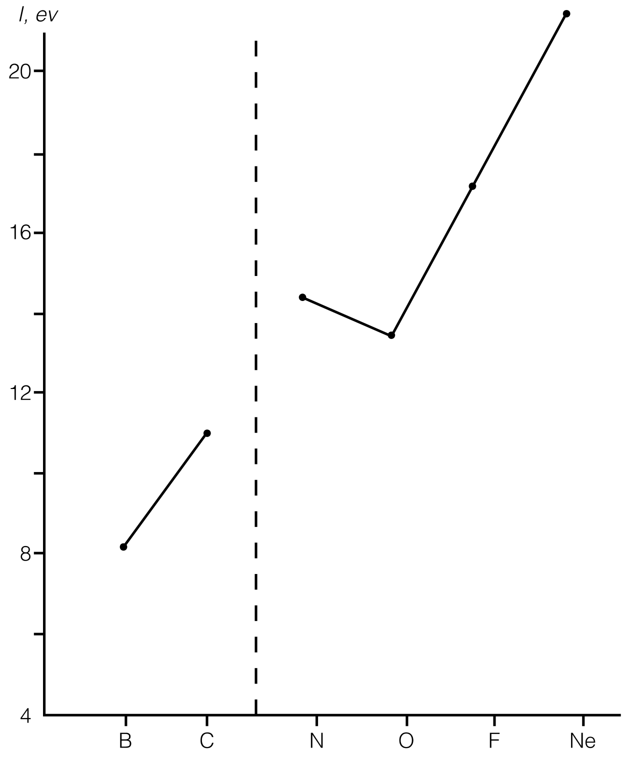

Figure 3. First ionization potentials. [Figure adapted from Fet, 2010, 194]

perfectly clear. It is due to electronic repulsion: in nitrogen, the 2*p* shell is half-occupied, with three electrons nicely distributed in space, at a maximal distance of each other. In oxygen, the nuclear charge increases so all 2*p* valence electrons are expected to feel an increased charge, and it would be more difficult to ionise them. On the other hand, one cannot avoid occupying one of the 2*p* orbitals twice. These two electrons are doomed to occupy the same region in space and to repel each other more strongly. This effect more than offsets the increase in the attraction of the nucleus, and thus the ionisation potential drops.

Similar discrepancies between Fet's claims and the actual data can be found in other properties, such as the dissociation energies of the diatomics.[75] As the number of electrons increases, multiple bonding becomes possible, and the strength of the diatomic bond increases accordingly in an uninterrupted linear correlation from boron to nitrogen. The highest stability is reached for dinitrogen N_2 since it realises a triple bond, based on the sp-hybridization. The bonding in O_2 and F_2 is smaller due to the occupation of antibonding orbitals and finally vanishes for neon.

Perhaps Fet as a mathematician was less susceptible to such chemical explanations. Nevertheless, the graphical representations of his claims were highly misleading.

6. THE LIMITS OF SYMMETRY

When Heisenberg proposed to consider the proton and neutron as the two sides of the same isospin coin, a paradigm shift was set into motion. The materialistic interpretation of the world consisting of particles gave way to a new understanding which views the particles as representations of symmetry groups. Heisenberg depicted this as the confrontation between the atomism of Democritus versus the idealism of Plato. Symmetries, not particles, were taken to be fundamental. They represented the deepest ontological level, whereas the particles only had a derivative status. "In the beginning was symmetry", exclaimed Heisenberg on more than one occasion.[76] The culmination of Heisenberg's symmetry program was attained when Gell-Mann introduced the eightfold way, which provided a classification of all hadronic matter, and which led to the successful prediction of two new elementary particles. To some extent, the ability of a system to make successful predictions echoes Mendeleev's belief in the periodic law that enabled him to make detailed predictions for certain unknown elements (such as gallium, germanium and scandium). It is thus no surprise that the symmetry program was also applied to the periodic system, even though such attempts were relatively scarce.

The success of the symmetry program did not stay confined to the hermetic circles of elementary particle physics, but as this contribution has illuminated, it inspired new perspectives on the periodicity of Mendeleev's table as a hallmark of an as yet unidentified underlying symmetry group. Here as well, the key to the symmetry program was the move from materialism to idealism. The chemical elements were no longer treated as particles, but as states of a superparticle, the baruton, whose symmetry was described by the conformal group SO(4,2). From the perspective of this group, the chemical elements had lost their identities, and merely functioned as different states of a single quantum system. It was only by a controlled breaking of the SO(4,2) symmetry that the elements regained their chemical and physical identities.

As we noted, several groups started the group-theoretical study of the Periodic System almost simultaneously in the early seventies of the previous century. In this account we devoted particular attention to the

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[75] Fet (2010, 199).

[76] Heisenberg (1976a), quotations on p. 32.

contributions by Fet and Barut, both of whom adopted the elementary particle approach of Heisenberg and Gell-Mann. In comparing the work of Fet and Barut, we also illustrated the tension between a formal mathematical treatment and an underlying physical. Fet approached the problem from a rigorous mathematical point of view. The result was a formal scheme that accommodates the chemical elements, but on the other hand did not advance our knowledge of the structure of the periodic table, nor reflected the actual chemical and physical properties of the elements. In that sense, Barut approached the problem from a much more physical and chemical point of view.

As Heisenberg already warned in his last paper, for a theory to be not only successful but also useful, it should not restrict itself to a description of phenomena but also offer an understanding. There is the danger to get lost in the mathematical details of a theory by focusing too much on its structural aspects, and to 'loose touch' this way with physical reality. It is not always easy to find the right balance between mathematics and physics. While the formal system, set up by Fet, perhaps fell short of achieving this balance, other contributions opened a much more promising perspective. Here we mention especially the legacy of Asim Barut who explained the group-theoretical origin of the period doubling from a much more physical and chemical point of view. The original line of thinking in the work of the late Ostrovsky is also worth mentioning, although Ostrovsky adopted an atomic physics approach.[77] Recently, the introduction of non-linear Lie algebras has provided a synthesis of the key elements of both (atomic physics and elementary particle) approaches. This has expanded the study of the Periodic System into a different realm, where its intriguing structure might finally reveal its secrets.[78]

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[77] See Barut (1972a) and Ostrovsky (2006).

[78] See Thyssen & Ceulemans (2017).

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Research Article

Consciousness, Information, Electromagnetism and Water

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Abstract. There are very few things that modern science does not yet understand. One of them is consciousness; another is water. Our main idea is then that if consciousness and water remain mysteries for science, it may be because the apparently different problems they pose are in fact deeply entangled. Shedding light on one of them may thus have the effect of clarifying the other. In this article we explore the idea that a mirror relationship may exist between an immaterial pair formed by consciousness and information on the one hand, and a quasi-material pair formed by electromagnetic radiations and water on the other hand. It is formally deduced through group theoretical arguments applied to Maxwell's equations, that the so-called material world is not a 4D space-time continuum (named M^4 hereafter), but rather a 5D-space-time-scale hyper-surface (named C^5 hereafter) embedded in a 6D-continuum of consciousness (named V^6 hereafter), identified as the vacuum state of quantum physics (static background) or the ether of general relativity (dynamic background). The new fifth degree of freedom in C^5 is associated with the ability of living beings to grow from small size to larger size by keeping invariant their identity at all scales. The sixth degree of freedom in V^6 is associated with the possibility for living beings to behave either as virtual non-observable entities, or as non-virtual observable ones. In both cases, life is associated with the ability to manage the information stored in the quantum structure of the V^6- ether, or in the water shells surrounding all living cells in the C^5- hyper-surface. Memory capacities and associated bandwidths can be quantitatively evaluated from the theory and compared to experimental observations, hereby comforting the proposed approach. It follows directly from this model that space, time and mass can be considered as creations of consciousness in the form of persistent fields of bits. This strongly supports Eastern philosophical ways of thinking based on Vacuity, the only non-dual material reality. For Western minds, the model has the great advantage to address what life and consciousness could actually be, thanks to a mathematical framework unifying physics, chemistry and biology.

Keywords. Consciousness, Group theory, Information, Water.

INTRODUCTION

In a previous paper, a thought experiment reached the conclusion that consciousness has anteriority over information, energy and matter.[1] In other words, the fact that consciousness pre-exists neurons should be both a philosophical as well as a scientific evidence. In another paper, it was proposed that at least three levels of consciousness can be identified: a local rational~~e~~ consciousness (RC) rejecting contradiction and associated to digital information processing; a meta-consciousness (MC) admitting the existence of ~~a~~ contradiction and associated to analogic information processing; and a non-local supra-consciousness (SC) not assigning any specific status to contradiction, thus transcending the digital/analogic duality of information.[2] The non-local SC unveiled by such a scientific approach has obvious resonances with philosophical concepts such as Brahman in Hinduism or Tao in Buddhism, and with the idea of "oneness" exemplified by the mythical "Ouroboros" in certain religions, and by the Möbius strip or the Klein bottle in topology.

Establishing conceptual and logical links between consciousness and information has also the advantage to give an obvious and simple explanation to the occurrence of quantum physics in the visible universe. Moreover, the three notions of particle~~s~~, field~~s~~ and information fit nicely with the three kinds of consciousness (digital, analogic and non-dual). Now, a question having a crucial connection with the understanding of consciousness is: what happens after death? Here, it is worth quoting James Clerk Maxwell, the father of electromagnetism, who said on his death bed:

> *I cannot help thinking about the immediate circumstances which have brought a thing to pass, rather than about any 'will' setting them in motion. What is done by what is called myself is, I feel, done by something greater than myself in me* (Campbell & Garnett 1882).[3]

We will explain below how a fundamental key to the role of consciousness is provided by Maxwell's set of 20 equations (today reduced to 4 equations involving vectors) unifying electricity, magnetism and optics.[4] The mechanism of propagation of light in the universe will help us in finding how many physical dimensions are necessary to qualify the existence of living beings and conscious entities. Having identified the dimensions of our universe, it remains to be shown how information can be read, written and transferred between material/visible structures and immaterial/invisible entities. Concerning the material medium able to store and propagate information, 2D-water layers are the most viable candidates. As for the immaterial storage medium of information, we will propose quantum vacuum (ether), the existence of which is supported by leading physical theories: quantum physics and general relativity. In order to be credible, our approach must be able to give estimates of the different bandwidths associated with conscious processes involving either a watery medium or the ether.

MAXWELL'S EQUATIONS

Our starting point is the fact that, in current physics, any law can be considered a consequence of the existence of a symmetry group. For instance, at the time of Isaac Newton, space and time were seen as separate absolute entities. Then, three laws of motion were formulated to fully account for related mechanical observations. Then, it was realized by mathematicians that Newton's laws were the consequence of the existence of a Lie group named Gal(3,1). In such a notation, Gal stands for the beginning of Galileo's name, the first scientist to have formulated the law of inertia. The two numbers in brackets refer to the fact that movements occur in a space having three dimensions associated to one-dimensional time unrelated with space. Such a Lie group is characterized by ten infinitesimal generators: three spatial translations, three spatial rotations, three Galilean boosts (uniform changes in speed) and one translation describing a 3D-universe with one additional time dimension unrelated with the three spatial ones. It was easy to show that Galileo's group Gal(3,1) has three Casimir invariants corresponding to the laws of conservation of mass (spatial translations), energy (temporal translations) and spin (rotations). The trouble was that such a group is not able to describe electromagnetic phenomena. In other words, the famous Maxwell's equations published in 1865 ruling electricity, magnetism and optics were not invariant through the symmetry operations of Gal(3,1). But, in May 1905 the French mathematician Henri Poincaré (1854–1912), communicating with his Dutch colleague H. A. Lorentz (1853–1928), realized that the coordinate transformations leaving invariant Maxwell's equations form another symmetry group, ISO(3,1), an acronym for "Inhomogeneous Special Orthogonal" group.[5]

In fact, Poincaré's ISO(3,1) group has seven infinitesimal generators in common with Gal(3,1): three spatial translations, three spatial rotations and one translation in time. The difference is the existence of three Lorentz's boosts mixing each of the three space-coordinates with the time coordinate. A direct consequence of such a welding of space with time is that Poincaré's group displays only two Casimir invariants corresponding to the conservation of a single entity called mass-energy (translations in space and time) and another one named spin (rotations in space and time). In group-theory language, mass and energy now belong to the same irreducible representation of ISO(3,1), whereas in Gal(3,1) mass and energy were parts of different irreducible representations. Another consequence of such a welding of space with time was that our observable universe should be considered as 4D (4 = 3+1) space-time continuum as suggested by the German physicist Hermann Minkowski (1864–1909). The existence of such a 4D space-time entity supported by the mathematical structure of Maxwell's equations, was a major step to establish the full validity of the special relativity theory introduced by the joint efforts of Henri Poincaré and Albert Einstein (1879–1955).[7] According to relativistic physics, speaking of an event requires to locate it in M^4, i.e. specify where it has occurred in space (x = left/right, y = front/back, z = up/down) and in time (t = past/future).

However, just after the introduction of M^4 Minkowski's space, it was realized that Maxwell's equations were in fact invariant under a larger Lie's group, named the conformal group ISO(4,2).[8] Here, in addition to the ten infinitesimal generators of ISO(3,1), five new generators had to be considered, one corresponding to dilatation in space and time and the four others to conformal symmetries that preserve angles between two arbitrary directions. The main consequence of such an invariance was that the universe had better be considered as a 6D-continuum (6 = 4+2) with four space-like coordinates and two time-like coordinates. This meant that by specifying only four coordinates in M^4 (x, y, z, t), some ambiguity remained. Taking for granted the existence of these two extra dimensions, their physical meaning had to be established.

A clue was given by the fact that a M^4 continuum devoid of matter remains invariant after any change in scale 's' (a new coordinate measuring the 4D-spacetime dilatation). This means that besides (x, y, z, t) coordinates, one should also specify a fifth coordinate (s) setting the scale at which an observation is made. Such a fifth coordinate is crucial for living entities that could exist either as a single cell or as multicellular organisms. At each cell division, the living entity gets bigger in space and older in time, suggesting that such a fifth dimension describing the ability to change in size (small/big) at a given space-time location (x, y, z, t) has something to do with the existence of life. One may also understand why a second time dimension is needed, as it is a well-known fact that the time coordinate of special relativity has nothing to do with the time of biology. Accordingly, within Minkowski's space-time M^4, the time reversal symmetry operation is allowed and is used to explain the matter/antimatter duality. Moreover, Noether's theorem clearly states that as soon as energy is conserved, the origin of time has no absolute meaning owing to the symmetry of translation in time. It is thus impossible to describe the events of birth and death, typical of living beings in M^4, because a date of birth or death has an absolute character and meaning.

However, moving to the conformal space C^5, i.e. considering an hyper-surface in ISO(4,2), where an event is characterized by five coordinates (x, y, z, i·c·t, s), the last coordinate (s) referring to a position in scale (small/big), it is possible to speak of birth or death in an absolute sense. From a mathematical viewpoint, by combining the dilatation symmetry operation with translation and rotation symmetries, it was possible to build a quantum-mechanical proper time operator conjugated to mass.[9] In a conformal space C^5, it is thus meaningful to state that a given mass has appeared here (birthplace) at a precise time (birth date) and disappeared there (death place) at a posterior time (death date).

It is worth noticing that if inert matter undergoes evolution in M^4 while living matter undergoes birth, evolution and death in C^5 through the fifth dimension s (small/big), we are still describing the observable universe at an object-oriented level. As the conformal ISO(4,2) group operates in six dimensions, it is logical to assume that the sixth dimension is a dimension allowing us to decide if a given C^5 hyper-surface is observable or not. The existence of such a larger embedding space V^6 where supra-consciousness operates on a virtual information field is thus not only in line with the invariance of Maxwell's equations under the symmetry operations of the ISO(4,2) Lie group, but also allows observing the C^5 object-oriented conformal hyper-surface using an upper level meta-language giving meaning to events, and where logical contradictions occurring in C^5 are resolved. Another crucial point is that the use of dilatation symmetry operators may also be related to the fact that a conscious being is free to operate changes of measurement units without alteration of the observed system.[10]

In such an enlarged conceptual physical frame, scale invariance would be a fundamental attribute of the V^6 information field. This is in line with the fact that information is basically a series of bits taking value 0 and 1, and that the memory holding such an information can be of any size. Accordingly, bits may be stored on a polycarbonate support using pits (bit 1) and lands (bit 0) at a 450-780 nm scale. However, the same information could also be written on ferromagnetic domains at a 0.1-1 mm scale. Typical MOSFET channel lengths were once a few micrometers in size, whereas modern integrated circuits are incorporating MOSFETs with channel lengths of tens of nanometers. In biology, information may be coded on DNA at a nanometer scale or at a micrometer scale in neurons. One could also imagine encoding information on galaxies, one galaxy corresponding to bit 1 and no galaxy to bit 0. A crucial point is that it is the alternation of 0 and 1 that defines an entity and not the physical size of the memory device necessary for holding strings of bits. Another crucial point is that a string of bits is meaningless unless a starting point is given for reading the chain, together with a fixed step telling how many bits should be loaded in the register memory at each read or write event. For instance, using the same string of bits, different outputs are expected using 8-bit, 16-bit, 32-bit or 64-bit processors. The choice of the starting point and of the step used for reading/writing information from a support should obviously be a prerogative of consciousness. One could then easily understand why a single and unique information field is able to hold a huge number of conscious beings. The identity of a given conscious being would then correspond to a starting point in V^6, while the level of consciousness would correspond to the size of the register. The bigger the number of bits manipulated simultaneously, the higher the complexity and the level of consciousness.

The fact that the information field V^6 is fundamentally scale-invariant is just another way of saying that space, time and matter do not exist by themselves, being just a construction of a supra-consciousness giving different meanings to various pools of information. This was clearly perceived by Henri Poincaré, in a paper written in 1906 and added to French editions of his book "Science and hypotheses":

> *One of the most surprising discoveries that physicists have announced in the last few years is that matter does not exist.* (Poincaré 1906).[11]

GRAVITATION, MASS AND QUANTITY OF MATTER

As explained elsewhere,[2] the M^4 Minkowski's subspace created by the generators of the ISO(3,1) Lie-group has been characterized by a fundamental equation $W = k_B \cdot T = h \cdot f = m \cdot c^2 = e \cdot U = (2h \cdot \boldsymbol{\alpha}/\mathbf{e}) \cdot I$, stating that inert matter may through thermal, vibrational, mechanical, electrical and magnetic interactions, with a set of universal constants k_B = 0,0138 zJ·K^{-1}, h = 663 zJ·fs, c = 299792458 m·s^{-1}, e = 0.16 aC and α = 1/137. We now understand that the information field of consciousness corresponds to the V^6 space created by the generators of the ISO(4,2) Lie-group. In V^6, nothing is forbidden and everything is fundamentally true. The existence of "forbidden" events is here a consequence of the choice of a particular location in V^6 (identity of the observer) allowing to observe a M^4 space as a projection of a C^5 hyper surface along a line joining a space-time point in M^4 to the fixed point in V^6 and crossing the C^5 hyper surface at a point defining the age of a system since its birth as a physical entity.

For instance it is impossible in M^4 to travel at a speed higher than Einstein's constant c (relativity), impossible to perform an action smaller than Planck's constant $h/4\pi = \hbar/2$ (quantum physics), impossible to have an entropy below Boltzmann's constant k_B (thermodynamics) and impossible to bear an electrical charge lesser than Coulomb's constant e (electromagnetism). Such limitations arise as soon as a conscious entity in V^6 have the experience of living on a particular C^5 hypersurface at a given scale corresponding to the biological age and not to the "time" of M^4 that is just a coordinate for ordering 3D-events. But, in contrast with M^4 space-time coordinates, the scale coordinate in C^5 is a hidden one as direct observation tells us that only the vacuum can be stretched or compressed at any scale. As soon as masses are present, this scale invariance is broken, giving the feeling to live in a M^4 reality involving invariance through translations and rotations, and where dilatations of the C^5 reality are no longer present.

This basically means that in contrast with translations and rotations that are global symmetries of M^4, dilatation symmetries of C^5 are only local, the full symmetry being recovered by introducing forces between masses, explaining the occurrence of gravitation. Alternatively, one may also say that changes of space-time scales preserve the velocity of light. Consequently, only photons are able to perceive the full C^5 space-time symmetry, massive objects seeing a broken symmetry manifested by a clear distinction between inert and living systems. However, from the viewpoint of consciousness able to unfold in a much larger space V^6, such a distinction is meaningless and everything should be considered "living" either as particles, molecules, cells, rocks, plants, animals or humans.

This also explains the existence of a sixth coupling constant $G = c^2 \cdot R_U/M_U$, related to Newton's gravitational constant, linking spatial extent of the universe R_U to its mass content M_U,[12] taking the value G = 66.7384 pJ·kg^{-2}·m. It then becomes possible to define a quantum of spatial area $A_P = \hbar \cdot G/c^3$ (where $\hbar = h/2\pi$ is Dirac's constant) and a quantum of time area $t_P^2 = A_P/c^2$. Alternatively, one may also define a quantum of mass M_P, such that $M_P^2 = \hbar \cdot c/G$, allowing distinguishing between observable elementary particles having a mass less than M_P and non-observable elementary particles having a mass higher than M_P. Existence of Newton's constant G also defines a maximum power in nature $P = c^5/4G \approx 9.1 \times 10^{51}$ W reached at the surface of a black hole.

Finally, it follows that one should recognize the existence of two kinds of masses, a conformal non-observable mass m_{00} displaying scale-invariance in conformal C^5 space and linked to the phenomenon of gravitation, and a relativistic rest mass m_0 responsible for the existence of inertia in Minkowski's M^4 space, breaking vacuum's scale-invariance. It also follows that as mass should be considered an attribute of space-time, it cannot be used to measure the amount of matter. However, from observation we know that all matter is made of atoms with a characteristic universal scaling constant $N_A = 6.022\times10^{23}$ mol^{-1}, named Avogadro's constant, relating the mass of atoms and the one of macroscopic bodies. The fact that this constant may be found through the study of unrelated physical phenomena (gas viscosity, Brownian motions, critical opalescence, color of the sky, black-body spectrum, electricity, X-rays or radioactivity) is good evidence that information is propagating in the fifth dimension of our universe.

Accordingly, at a given scale (coordinate s = constant), one retrieves the standard wave function $\psi_s(x,y,z,t)$ of quantum physics insuring coherence between the descriptions of a particle at several different points in space and time. From quantum physics, we know that squaring the amplitude of a matter wave $\psi_s(x,y,z,t)\cdot\psi_s^*(x,y,z,t)$ measures the probability of observing a particle at a particular position (x,y,z) at a given time (t). Going to another higher scale of the same object, one retrieves a bigger mass that should correspond to a bigger number of particles, as matter particles are not scale invariant. But, as we are in the same object, its identity should not change in C^5. This suggests introducing a new scaling wave function $\psi(x,y,z,t,s)$ taking its values not only in space (x,y,z) and in time (t) but also in the scale (s). Now, by squaring the amplitude of such a scaling wave $\psi(x,y,z,t,s)\cdot\psi^*(x,y,z,t,s)$ we should obtain the probability of observing the mass of a system at any scale of observation. Using conveniently scaled quantum operators, it is then possible to write a generalized Schrödinger's equation whose solutions are waves propagating with time in the scale as well as in space.[13] It then follows that the square of the ratio of the amplitudes of the faster couple of such scaling waves (first two harmonics), are related by a constant $N = ¼\exp(4\pi^2/\ln2) \approx 10^{24}$, giving the right order of magnitude of Avogadro's constant. Including other harmonics in the description changes a little bit the value, but not the exponent.

ELEMENTARY PARTICLES

Physicists may also wonder how the standard model for elementary particles, a well-established description of nature, fits in such a scheme. A possible answer is to go back again to Maxwell's equations that have allowed us to discover the existence of a fifth and a sixth dimension. In fact, it was shown about forty years ago that Maxwell's equations were invariant under the symmetry operations of the highly symmetric $ISO(4,2)\otimes U(2)\otimes U(2)$ group characterized by $6\times5/2 + 2^2 + 2^2 = 23$ generators.[14] This symmetry escaped notice for a long time because the eight integral-differential generators of $U(2)\otimes U(2)$ are associated with symmetry operations of a non-geometric nature. They are much harder to visualize than operations of the Lie algebra in the neighborhood of identity.[15]

The nature of these operators suggests again that it should exist a communication between all scales, from the smallest to the largest and vice versa, whence non-locality and non-separability, which are abundantly confirmed by experiments. The fact that $U(2)\otimes U(2)$ has eight generators allows establishing a direct correspondence with the symmetry group SU(3) that has also eight generators (the so-called "gluons") and responsible for the existence of the "strong" interactions between quarks. Focusing our attention to the U(2) sub-group which has only four generators, it is quite satisfying to find that such a group is isomorphous to the product $SU(2)\otimes U(1)$. Now, the SU(2) group with its three generators (W^+, W^- and $Z°$ intermediate bosons) is responsible for the "weak" interaction involving leptons, while the U(1) group with only one generator (the photon γ) is responsible for the electromagnetic interaction.

Obviously, the introduction of these new internal degrees of freedom means additional coupling constants in addition to the seven external coupling constants (k_B, h, c, e, α, G and N_A). The best way to introduce these new constants is to use dimensionless numbers in order to comply with the basic scale invariance of the universe. Taking the mass of the electron $m_e = 9.109\times10^{-31}$ kg as a reference then leads to a new constant $\beta = m_P/m_e = 1638$ for the strong interaction between quarks (where m_P is proton's mass), $\gamma = G_F\cdot m_e^2 = 3\times10^{-12}$ (where $G_F = 1.166\times10^{-5}$ $GeV^{-2} = 3.67\times10^{48}$ kg^{-2} is Fermi's constant) for the weak interaction ruling beta-decay and $\delta = G\cdot m_e^2/(\alpha\hbar\cdot c) = 2.4\times10^{-43}$ for the gravitational interaction between masses.

The above approach suggests that consciousness should be compliant with physicalism stating that information may be physically stored in the V^6 space underpinned by the abstract structure of the ISO(4,2) symmetry group. Information would be the "substance" of such a space that could well be identified with the "ether" concept introduced by Aristotle and used in the XIXth century for explaining light propagation in a medium devoid of matter. It is worth noticing that in order to justify the negative result of the Michelson-Morley experiment, existence of such an ether was denied in

1905 by Albert Einstein in his special relativity theory. However, the same Einstein was finally obliged to accept its existence in an address given on 5 May 1920 at the University of Leiden:

> *Recapitulating, we may say that according to the general theory of relativity space is endowed with physical qualities; in this sense, therefore,* ***there exists an ether****. According to the general theory of relativity space without ether is unthinkable; for in such space there not only would be no propagation of light, but also no possibility of existence for standards of space and time (measuring-rods and clocks), nor therefore any space-time intervals in the physical sense. But this ether may not be thought of as endowed with the quality characteristic of ponderable media, as consisting of parts which may be tracked through time. The idea of motion may not be applied to it".*[16]

These words by Einstein exactly define the V^6-space introduced above: a non-ponderable information field (embedding ponderable C^5 hyper-surfaces) with no parts which may be tracked through time, a concept belonging to the realm of M^4-subspace (reversible mechanical time) or C^5-subspace (irreversible biological time). In other words, V^6 should be viewed as an entity existing beyond space, time and matter and being the ultimate source of any kind of reality as it holds as strings of bits all the past, present and future events of our universe. The ether of general relativity is thus the physical substance of V^6 onto which it is physically possible to write or read bits of information as on any kind of memory. The only difference is that, owing to the lack of motion, it is a non-volatile random access memory (NVRAM) that can be configured in an infinite number of ways. In other words everything is possible within the space V^6, even unphysical things that are routinely visualized during the dreams as chimera, monsters or other absurdities for the conscious "I" undergoing evolution in a C^5-subspace. V^6-ether is also the repository of all mathematical ideas, all scientific theories, all work of art, all music pieces, all deities, i.e. the common source of inspiration for all people involved in art, science or spirituality. As time does not exist in V^6, it is impossible to use bandwidth for measuring a state of consciousness. Instead, one may consider that the V^6 space is covered by a multitude of trails (like footsteps in the snow) made by each conscious being. All these trails are deeply interconnected, forming a unique motif that we may identify as a state of "oneness".

Concerning the mechanism for reading or writing on such an ether, one may refer to quantum loop gravity stating that the ether may exist under two distinguishable states : looped (bit 1) or un-looped (bit 0).[17] From the knowledge of the age of the universe $t_U = 4.3\times10^{17}$ s and the quantum of length $L_P = A_P^{1/2} = (\hbar\cdot G/c^3)^{1/2}$, it comes that the memory capacity of our C^5-universe embedded in a V^6-ether is currently about $M = (c\cdot t_U/L_P)^4 = c^{10}\cdot t_U^4/(\hbar\cdot G)^2 \approx 10^{244}$ bits. Alternatively, the ether of general relativity may be replaced by the vacuum of quantum theory. At the level of the information stored in V^6 this does not matter. However, after projection in a C^5-subspace, where energy matters, the two viewpoints do not agree. This stems from the fact that mass M scales with length L in general relativity ($M/L = G/c^2$) while it scales with the inverse of a length ($M\cdot L = h\cdot c$) in quantum physics. As a Planck's force may be defined as $F_p = m_P\cdot c^2/L_p = c^4/G$, it follows that vacu-

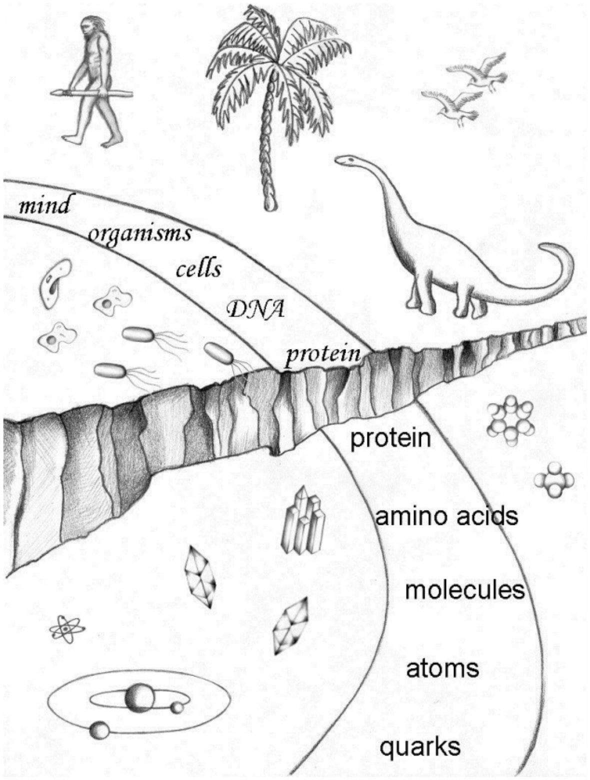

Figure 1. Pictorial representation of the chasm that has opened up in the western scientific description of nature after the advent of molecular biology. The physical sciences are on the southern and biological sciences are on the northern side of the deep divide. In the reductionist landscape of the physical sciences, a road of deterministic logic leads from the most fundamental particles of all, the quarks, through atoms and molecules to complicated chemicals found in living organisms and even in minds, without any gap. This misses the crucial fact that the northern proteins work while the southern ones do not. This strongly suggests that a top-down non-deterministic logic should coexist with the bottom-up logic guiding the road through the northern landscape. Drawing by John Grant Watterson, reproduced with permission. See http://www.thewaterpixel.com/ for a downloadable e-book of the solution proposed by J.D. Watterson for bridging the chasm.

um's energy density may be expressed either as $F_P/L^2 = m_P \cdot c^2/L_p^3 = c^7/\hbar \cdot G^2 \approx 5\times10^{113}$ J·m^{-3} if $L = L_P$ (quantum physics), or as $F_P/R_U^2 = c^4/G \cdot R_U^2 \approx 0.6$ nJ·m^{-3} if $L = R_U$ (general relativity). This huge divergence of more than 120 orders of magnitude is one of the most stunning problems in modern physics.

WHAT IS LIFE?

Our Western scientific mode of thinking is based on a bottom-up approach of reality where big things are thought to arise after aggregation of much smaller components. Atoms are thus made from elementary particles themselves built from quarks and leptons, molecules are aggregates of atoms, cells are aggregates of molecules, tissues are aggregates of cells, bodies are aggregates of tissues, kingdoms are aggregates of bodies while aggregates of kingdoms compose the living world. For the inert world, the dominant view is that solids, liquids and gases are made of atoms or molecules, aggregating into planets belonging to stellar systems, themselves forming galaxies, the clustering of such galaxies defining the observable universe. It thus remains a deep enigma about why molecules should be the bifurcating point between living and non-living things. Figure 1 is a picturing by John Grant Watterson of this strange situation with a chasm separating an inert protein seen as an aggregate of atoms on the one hand, from a living protein being, an entity having a precise function in a cell, on the other hand. Albert Szent-Györgyi who won the Nobel Prize in Physiology or Medicine in 1937 was also quite lucid about such an enigma:

> *One of my difficulties with protein chemistry was that I could not imagine how such a protein molecule can 'live.' Even the most evolved protein structural formula looks 'stupid,' if I may say so.*[18]

In what follows we propose to fill this chasm with water that would then be the material substance making the interface between living beings and the ether. Such a statement directly leads to the conclusion that the conscious 'Me' should somehow be related to water. The fact that a living cell is 99.1 mol% water[19] and that the brain is the more hydrated organ of the body is well in line with such a proposal.

First, in our scheme, the distinction between inert and living things lies in the ability of a given material system to explore the fifth dimension allowing changes in size through a metabolism allowing duplication as well as the sixth dimension by being able to treat information (consciousness). By contrast, an inert thing is limited in its evolution by the M^4-subspace. Such a restriction has the consequence of associating the conscious 'I' to the activity of neurons in the brain. The trouble with such a reductionist view is that it exists other organs in the human body having neurons. For instance it is possible to record electro-gastrograms (EGG) or electro-enterograms (EENG) as well as magneto-gastrograms (MGG) or magneto-enterograms (MENG) for characterizing the electrical activity of the stomach and the gut.[20] It is thus now accepted that it exists an enteric nervous system (ENS) acting as a second brain and able to perform many of its tasks in the absence of central nervous system (CNS) control.[21] Similarly, there is good evidence that the human heart contains a complex intrinsic nervous system comprised of multiple ganglia (clusters of neurons) that network with each other.[22] Neuro-cardiology has thus firmly established that the heart is a sensory organ and an information encoding and processing center, with an extensive intrinsic nervous system that's sufficiently sophisticated to qualify as a little brain.[23] Associating consciousness with electrical activity of neurons then leads to byzantine discussions about the relative roles of brain, gut and heart in the "secretion" of consciousness.

In our hierarchical view, it follows that neurons being made of matter surely holds in M^4 a form of local consciousness (the conscious 'I') embedded in a supra-consciousness that extends in V^6 well beyond the brain, the heart or the gut. Moreover, neurons acting at the level of object-oriented language obeying to classical logic should obviously constitute one channel of expression of consciousness. Accordingly, at least another channel of expression should exist involving the whole body obeying to intuitionistic logic (meta-consciousness). Finally, a third channel may also be identified involving the mind/body combination in the V^6 field and obeying to minimal logic where negation simply does not exist.

WATER, WATER EVERYWHERE

For species living on earth, there is good evidence that water in contact with membranes made of self-assembled lipids could play the role of a hard disk memory.[24] Accordingly, it has experimentally proved that it was possible to convert unobservable virtual photons filling the vacuum into real photons using a mirror undergoing relativistic motion (Dynamical Casimir effect).[25] The existence of such an energy filling the vacuum is granted by quantum field theory through the existence of an operator N whose eigenvalues corresponds to the number of quanta having a pulsation $\omega =$

$\Delta\boldsymbol{\varphi}/\Delta t$, where φ is the unobserved quantum phase angle related to the internal state of each quantum. It is then possible to show that the Hamiltonian of such a quantum system may be written as $H/\hbar\omega = N + ½$, meaning the existence of a zero-point energy $ZPE = ½\hbar\omega$ when the field is in its ground-state (vacuum) characterized by an eigenvalue $N = 0$.[19] Moreover, owing to the non-commutation between the number of quanta operator N and the phase angle operator Θ, $[N,\Theta] = -i$, an uncertainty relationship $\Delta N \cdot \Delta\varphi \geq ½$ exists, responsible for the existence of quantum coherence at all scales and even at a macroscopic scale.[26,27] For an assembly of N similar quanta, the total energy may thus be written $W = N \cdot \hbar\omega$, meaning that an uncertainty ΔN translates into an energy uncertainty $\Delta W = \hbar\omega \cdot \Delta N$. As $\omega = \Delta\varphi/\Delta t$, it finally transpires that the inequality $\Delta N \cdot \Delta\varphi \geq ½$ translates into $\Delta W \cdot \Delta t \geq ½\hbar$. In other words, it is possible in quantum field theory to violate the energy conservation principle for a short duration Δt provided that $\Delta t < \hbar/\Delta W$.

Now the water molecule is a very small entity having a diameter close to 0.3 nanometers with a first excited level rather high in energy at about 1120 zJ and an energy of ionization of 2022 zJ. As low-energy excited levels correspond to O-H anti-bonding states, it seems preferable using non-bonding Rydberg's levels locates on the oxygen atom for performing virtual excitations using vacuum's energy. A good Rydberg-level corresponding to 5d orbitals on oxygen and able to give a coherence gap of the same order of magnitude than the H-bond strength energy is in fact located at an energy W = 1934 zJ above the ground state of the water molecule.[28] This corresponds to a wavelength of self-excitation $\lambda(\mu m) = 198{,}645/\Delta E(zJ)$, i.e. $\lambda \approx 0.1\ \mu m = 100$ nm. As $\hbar = 106$ zJ·fs, the lifetime of such a virtual excitation should be $\Delta t < 106/1937$ fs $\approx 10^{-16}$ seconds. On the other hand, we know that the power radiated by an electron submitted to an acceleration a is given by Larmor's formula: $P = F \cdot v = ⅔\alpha \cdot \hbar \cdot (a/c)^2$, where $\alpha \approx 1/137$ is Sommerfeld's fine structure constant (Larmor 1897).[29] For an electron of mass $m_e \approx 10^{-30}$ kg having a speed $v = a \cdot \tau_e$, we may write that $P = (m_e \cdot a) \cdot v = (m_e \cdot a^2) \cdot \tau_e = ⅔\alpha \cdot \hbar \cdot (a/c)^2$, leading to a characteristic relaxation time $\boldsymbol{\tau}_e = ⅔\alpha \cdot \hbar/(m_e \cdot c^2) \approx 10^{-23}$ seconds as $m_e \cdot c^2 \approx 82$ fJ. This means that the virtual photon extracted from the vacuum and having a lifetime $\Delta t \approx 10^{-16}$ s is available for exciting about $10^{-16}/10^{-23} = 10$ millions of water molecules before its return to the vacuum.

As the excitation is delocalized over $N \approx 10^7$ water molecules, it follows according to quantum field principles that coherent domains sharing the same phase angle could form with a maximum uncertainty on the common phase angle such that $\Delta\varphi \approx 1/2\Delta N$ or $\Delta\varphi < 5 \cdot 10^{-8}$ rad with $\Delta N \approx 10^7$. The size of such coherent domains is given by the wavelength of the photon extracted from the vacuum for excitation of the water molecule, while their stability is insured by the existence of a 2D interface.[30]

Consider now a mammalian cell having a weight of about 1 ng.[31] Assuming a density of 1 $g \cdot cm^{-3}$ into a volume of $10^{-9}\ cm^3$, corresponding to a diameter $D \approx 12\ \mu m$ and an area $A \approx \pi \cdot D^2 \approx 500\ \mu m^2$. A well-known fact is that a lipid bilayer covered by a hydration shell delimits such a cell. With an excitation of water molecules at $\lambda \approx 0.1\ \mu m$, it follows that the amount of coherence domains associated to an eukaryotic cell is about $N_{DC} = 2 \cdot A/\lambda^2 \approx 2 \times 500/0.01 = 100{,}000$. The factor two stems from the fact that there is a water shell facing the extracellular medium and another water shell facing the intracellular one. As the coherence gap responsible for the cohesion of a coherence domain has an energy $\delta W \approx 42$ zJ,[28] it is rather easy for the cell to have regions where coherence is on (bit 1) and other regions where the mechanism responsible for coherence is turned off (bit 0). Physically speaking an energy gap $\delta W = 42$ zJ, corresponds to an associated wavelength $\lambda(\mu m) = 198.645/42 \approx 4.7\ \mu m$, falling in the infra-red region of the electromagnetic spectrum. The energy needed for changing the coherence state in aqueous domains is thus readily available and could be furnished by the sun/earth couple owing to an emission at 0.5 µm by the sun associated to a re-emission at about 10 µm by the earth after processing by the biosphere. Such a picture is also in agreement with the observation on any hydrophilic surface of an exclusion zone (EZ-water) allowing converting IR radiation into an electrical potential in order to perform work.[32]

In other words, the water layers around any cell behave as a soft hard-disk upon which information may be written, deleted or read by consciousness with the help of infrared radiation. As each coherence domain stores 1 bit of information and as 1 byte = 8 bits, the memory capacity of the water shells of a eukaryotic cell may be estimated as $M(cell) = N_{DC}/8 = 10^5/8 \approx 10$ kB. Now, the number of cells in a human body is about $3.72 \cdot 10^{13}$ cells,[31] leading to a static memory capacity of at least $M(membranes) = 3.72 \cdot 10^{17}$ bytes or 372 PB, as one petabyte (PB) = 10^{15} bytes. Another upper estimate of the watery storage capacity of a human body is to consider a reference value of 36 liters of water, an average value between male and female in adult (20-79) US white population (Ellis 2000).[33] An elementary calculation also shows that water forms in a cell a hydration shell around bio-polymers corresponding to at most four monolayers of water.[19] The diameter of a water molecule being about

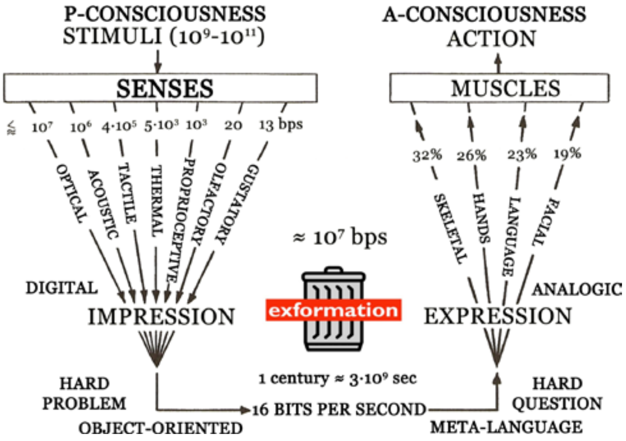

Figure 2. Consciousness, information processing with bandwidths and exformation (non-transmitted information or context).

0.3 nm, this corresponds to a thickness of about 1 nm. A coherence domain having an area of 100×100 = 10^4 nm^2, then occupy a volume $V_{DC} = 10^4$ nm^3 leading to a volume of 8×10^4 nm^3 per byte of information. As 1 L = 10^{24} nm^3, the number of bytes that can be stored in 36 L of intracellular and extracellular water is $36\times10^{24}/8\times10^4$ = 450 EB as 1 exa-byte (EB) = 10^{18} bytes. The recent discovery of a fluid-filled space within and between tissues named "interstitium"[34] is an obvious candidate for being the watery hard-disk of the human body able to hold such a big amount of information.

Besides cell membranes and the interstitium, one may also consider the human gut known to hold about 3.8×10^{13} prokaryotes.[35] We also know that a prokaryotic cell has a diameter ten times smaller than the diameter of a eukaryotic cell, meaning an area 100 times smaller. Consequently, the memory capacity of the hydration shell of a prokaryote could be estimated as M(prokaryote) = $2{\cdot}A\times10^{-2}/8\lambda^2 \approx 5/0.04$ = 125 bytes. The memory capacity of the human gut is then M(microbiote) = $3.8\times125\times10^{13}$ = 4.75 10^{15} bytes = 4.75 PB, i.e. about 1% of the memory capacity of the cell membranes. However, if one considers that there are about 5×10^{30} prokaryotes on earth (Whitman & al. 1998),[36] this corresponds to a total memory capacity of 6.25×10^{32} bytes. By comparison, for 7.7×10^9 human beings in 2019 (http://www.worldometers.info for an instantaneous counting), each carrying 4.50×10^{20} bytes in their bodies, the amount of information is only $4.5\times7.7\times10^{29}$ bytes = 3.5×10^{30} bytes. This means that humanity participates in the memory capacity of the earth through its biosphere at a modest level of about 1%.

However, as far as consciousness is concerned, considering memory capacity alone M is not enough. As recently suggested, a good measure of consciousness should be bandwidth BW(t) = dM(t)/dt, i.e. the rate of variation of information content with time.[37] A reasonable bandwidth for information processing by a human being is about 10 millions of bits per second (or 1 Mb·s^{-1}) coming essentially from the sense of vision (Nørretranders 1991).[38] As a century is about 3 billions of seconds, the information processed in his life by a human being is thus about $3.2\times10^9\times10^6 = 3.2{\cdot}10^{15}$ bytes = 3.2 PB. This corresponds to only 1% of the memory capacity of the body membranes. However, assuming an external stimuli bandwidth of 100 Gb·s^{-1} (higher value in figure 2), corresponding to the memorization of all events (even those ignored by the senses) experienced during a whole human life translates into a memory capacity of $32{\cdot}10^{18}$ bytes = 32 EB, i.e. about 10% of what is available in the body water (450 EB). This means that a human body is able to record and store any kind of raw data without the need to process them with the help of the conscious 'I'. Consequently, consciousness is needed for giving meaning to such raw data memorized in our body and defining what is usually called the "context".[39] As shown in figure 2, during a communication the conscious "I" discards a large part of this context that is not transmitted (exformation).[38]

Knowing that water is the information vector in the body it is now easy to compute a bandwidth for the body, as the average water turnover of a sedentary adult is 3256 mL per day or 37 µL·s^{-1} (Leiper & al. 1996).[40] With $V_{CD} = 10^4$ nm^3 and 1 µL = 10^{18} nm^3, this translates into a bandwidth of BW(t) = $37\times10^{18}/8\times10^4$ = 460 TB·**s**$^{-1}$. By comparison, this is of the same order of magnitude as the global internet traffic estimated for the year 2021 at 106 TB·s^{-1} (Cisco 2017).[41] However, a much larger bandwidth may be obtained by considering water movement inside the body, independently of external losses. Here, we may use the fact that on the one hand blood is distributed to the cells through about 10 billions of capillaries having an internal diameter of D_C = 3.5 µm and accumulating a total cross-section of A_C = 6 m^2 in *Homo Sapiens*.[42] On the other hand, the largest artery of the heart is the aorta with an average diameter D_A = 30 mm[43] (Hager & al. 2002) associated to an average blood flow velocity v_A = 76 cm·s^{-1} (Haugen & al. 2002).[44] Writing the equation of continuity for steady flow of a non-compressible fluid leads to $\frac{1}{4}\pi{\cdot}D_A^2{\cdot}v_A = A_C{\cdot}v_C$ = 537 cm^3·s^{-1} corresponding to a blood velocity in capillaries $v_C \approx 90$ µm·s^{-1} associated to a quite large bandwidth BW(t) = $537\times10^{21}/8\times10^4$ = 6.7 EB·s^{-1} (as 1 cm^3 = 10^{21} nm^3).

It should be obvious that the most probable place where such information fluxes occur are cell membranes. This means that any cell membrane could be the host of local consciousness and that primitive intel-

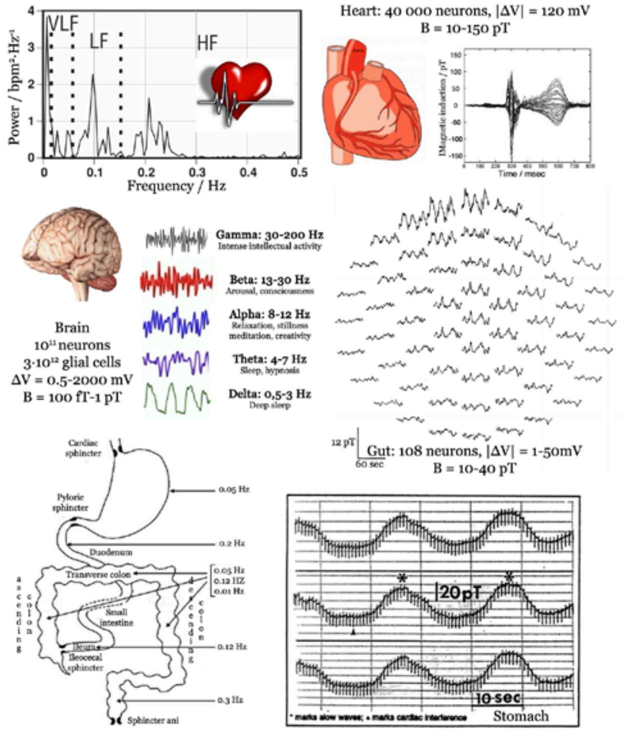

Figure 3. Overview of analogic electromagnetic signals emitted by the heart, the gut and the brain, three organs containing neurons.

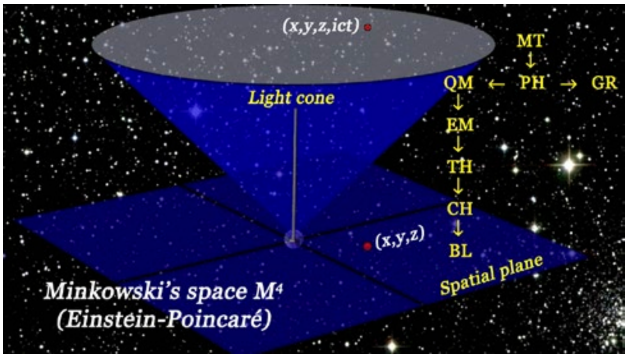

Figure 4. A picturing of the current paradigm concerning the universe according to western science. Reality is manifested in a 4D-continuum called Minkowski's space having inaccessible zones out of a light cone associated to each observer. On the left, a schematic hierarchy for physical sciences according to figure 1 represented here as the progression: mathematics (MT) → physics (PH) → quantum mechanics (QM) → electromagnetism (EM) → thermodynamics (TH) → chemistry (CH) → biology (BL). General relativity (GR) is represented as a separate branch owing to the considerable difficulties met for merging this science with quantum mechanics.

ligence is expected in amoebae for instance, as observed experimentally with the plasmodium of the slime mold *Physarum polycephalum*.[45] It has also been demonstrated that this mold was also able to anticipate periodic events.[46] As the permeability osmotic coefficient of a lipidic bilayer for water is about 100 $\mu m \cdot s^{-1}$,[47] we may predict for an area A(prokaryote) = 5 μm^2 a bandwidth $BW(t) = 5 \times 100 \times 10^9 / 8 \times 10^4 = 6.25 \times 10^6$ $byte \cdot s^{-1}$ = 6.25 $MB \cdot s^{-1}$. The total bandwidth for all the prokaryotes on earth is then estimated as $BW_{tot}(t) = 5 \times 6.25 \times 10^{36} \approx 3.1 \times 10^{37}$ $bytes \cdot s^{-1}$. By comparison, for the whole humanity we get $BW_{tot}(t) = 6.7 \times 10^{18} \times 7.7 \times 10^9 \approx 5.2 \times 10^{28}$ $bytes \cdot s^{-1}$, showing that our contribution to the overall consciousness of the earth is only one part per billion (ppb). In fact, in view of these huge bandwidths, it should be obvious that we are speaking here of consciousness at an object-oriented level, that is largely "unconscious". Consequently, for the blood flowing in our capillaries one may speak of personal unconscious or Freud's "Id",[49] while for the water flowing across prokaryote membranes we are probably facing the collective unconscious.[50]

Concerning consciousness at a meta-level, we are leaving the digital object-oriented mode for landing in an analogical mode associated with muscles movements (figure 2) or with electromagnetic signals emitted by the brain, the gut and the heart (figure 3). Here, it is possible, using Shannon's theory, to retrieve an information content $C(t) = -\Sigma P_N(t) \cdot \ln P_N(t)$ using a time-dependent probability function $P_N(t)$ extracted from the correlations functions of such signals observed in measurements at N points.[37] Then, the conscious "I" bandwidth could be computed as the time derivative of this information content $D(t) = dC(t)/dt$. Unfortunately, such a technique has not yet been applied in practice, but from figure 2, it could be anticipated a very low bandwidth of a few tens of bits.[38] However, focusing heavily on information content or bandwidth miss an essential point that is a direct consequence of our modeling. Accordingly, we know from the invariance of Maxwell's equations under the symmetry operations of the mathematical group $ISO(4,2) \otimes U(2) \otimes U(2)$ that all electromagnetic reality should be embedded in a V^6-ether. Figure 4 pictures such M^4-reality with its associated pyramidal hierarchy for scientific knowledge represented by eight disciplines.[51] Fitting consciousness in such a M^4 restrictive frame is generally perceived as a "hard problem",[52] while fitting free will of living beings may be referred to as the "hard question".[53]

By contrast, in our proposal (figure 5), there should be no hard problem or hard question linked to consciousness. Here, each conscious being occupies a certain volume in V^6 with highly significant bits that never change and other bits that can be reconfigured according to experiences made on a C^5 hyper-surface at a given

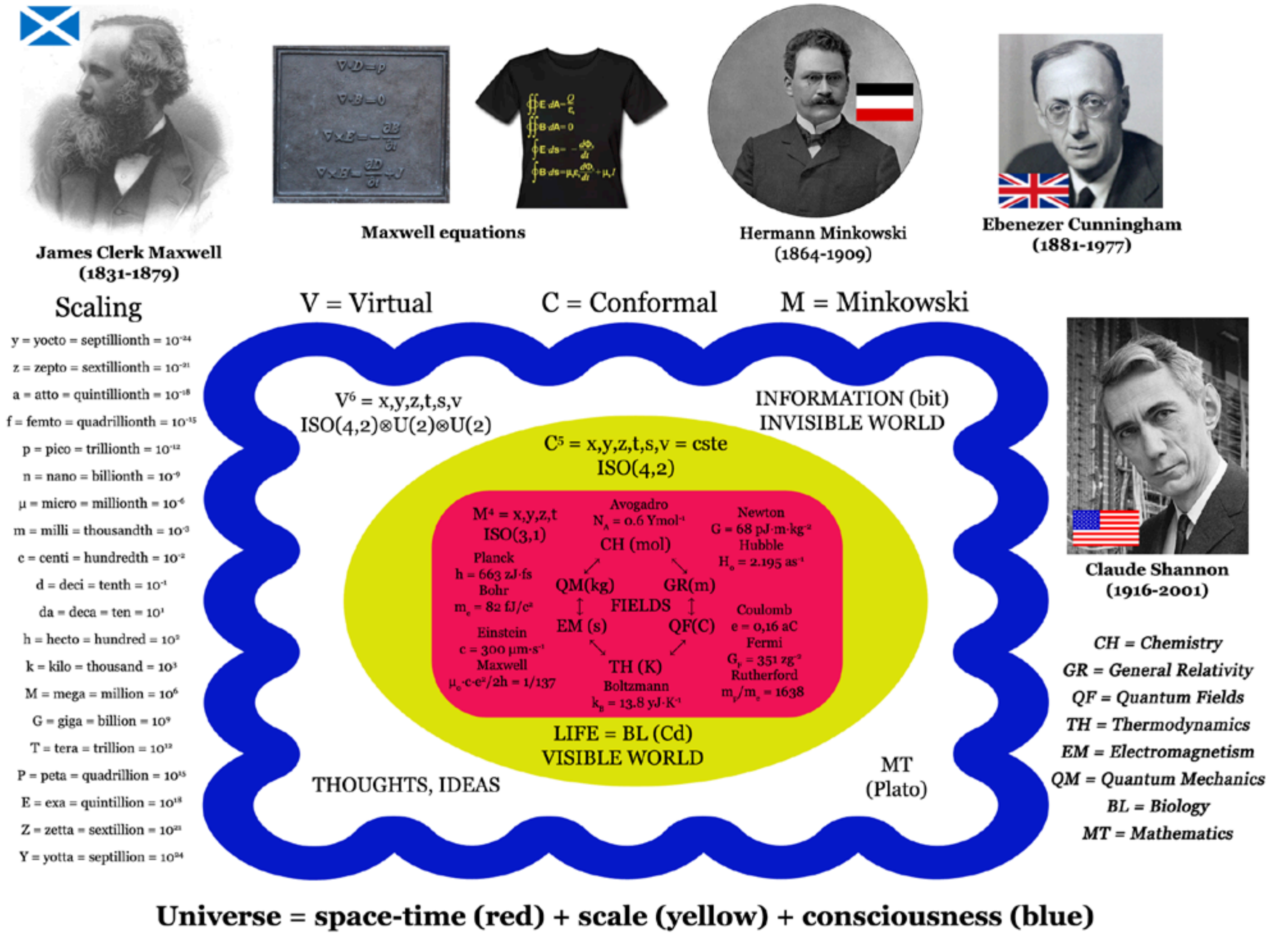

Figure 5. A schematic view for the proposed new paradigm suggested by the invariance of Maxwell's equations through symmetry operations of the SO(4,2)⊗U(2)⊗U(2) group. Same abbreviations as in figure 4.

location (x-,y-,z- coordinates), at a given time (t-coordinate) and at a given scale in space and time (s-coordinate). Using group theory language, reducing the reality to a C^5–space means separating the ISO(4,2) group having infinitesimal generators describing an external world, from the U(2)⊗U(2) group having finite generators and describing the internal world of elementary particles (strong and weak interaction). Consequently, our approach is compliant with physicalism as well as dualism.

As explained above, the s-coordinate in C^5 is crucial for differentiating between living being and non-living things. Accordingly, a rock has an existence in space and time at a given scale, but it is lacking software in V^6 allowing it to grow by itself. In other words, for inert matter, V^6 space and its M^4 subspace appears to be completely disconnected owing to a poor water content. This is in deep contrast with a seed that has also an existence in M^4, but owns in V^6 a little ROM containing down-loadable instructions on how to grow in time, i.e. change in size, using matter and energy (metabolism). At birth, the necessary information stored in the ethereal substance of V^6 is transferred as ROM on DNA and as RAM onto the hydration shells of membranes and bio-polymers. At death, information is transferred to hydration shells of earth's microbiote or of animals after being eaten by them. The same is true for animals, but here the ROM in V^6 can be updated using their metabolism during their life in C^5. This explains why animals, in contrast with plants, have the ability to move in C^5 in order to look for food. Being animals, humans are also able to reconfigure their software in V^6 through their metabolism, but they have the additional capability of doing that after focusing mentally their attention (through meditation for instance) towards a particular pool of bits in V^6 in a state called "mindfulness".

This would mean that humans have the ability to access mentally to the internal world of matter spanned by the U(2)⊗U(2) symmetry, while animals are doomed to use only the ISO(4,2) part of reality. As the generators of the U(2)⊗U(2) group are of integral-differential nature, coupling the macrocosm with microcosm at all scales, more work is needed to understand fully their role in nature.

When exchanging information between the V^6 space and the C^5 hyper-surface, the conscious being has the feeling of being traversed by a pure energy that could be identified with the "Prana" or "Qi" of eastern civilizations and whose flux is oriented by information content perceived as entropy for a western mind. Accordingly, moving in the scale can only be experimented as an energy as presence of matter breaks locally the ISO(4,2) symmetry, reducing it to ISO(3,1) with apparition of a force named gravitation needed to restore the full symmetry on a global scale. Consequently, our modeling of consciousness is intimately linked with gravitation, as proposed in the Orch-R model of consciousness.[54] Such a reduction from ISO(4,2) symmetry in C^5 to ISO(3,1) symmetry in M^4 may be identified with wave-function collapse in quantum physics. As quoted by the cognitive neuroscientist Marcel Kinsbourne: "*What's make any problem hard is that something false but attractive stands in its way*".[53] Here the thing that is false but attractive is obviously the fact that matter exists by itself. As quoted before, the fact that matter does not exist and is an illusion was lucidly perceived by great scientists such as Henri Poincaré, Max Planck, Werner Heisenberg, Erwin Schrödinger and John Wheeler.[2] In our approach, Einstein calls for thinking at a higher level[55] means replacing the group ISO(3,1) by its father ISO(4,2).

Obviously, eastern philosophies have not waited the discovery of group theory or quantum physics to reach the conclusion that matter was an illusion and that consciousness should be the ultimate reality. What is nice is that, as demonstrated here, western science based on powerful mathematical models reaches exactly the same conclusion. Our approach is also fully compliant with the concept of reincarnation typical of Hinduism, the karma being the trails left in V^6 by conscious beings experimenting several forms of life in C^5. It is also compliant with shamanism, V^6 becoming the world of spirits and more generally with all altered states of consciousness where one has a direct access to the invisible V^6-reality without the necessity of experimenting death, the "normal" door to the V^6-ether. Another consequence is that near-death experiences (NDE) or out-of-body experiences (OBE) should be considered real travels in V^6 with the help of consciousness and not as unreal mental images generated by a brain short of oxygen.

Finally, our approach points to at least three different ways of healing. Healing in M^4 using material drugs, healing in C^5 using the ability of water to store or transmit information or by using energy (electromagnetic fields for instance), and also healing in V^6 using information manipulated in a state of pure consciousness for instance.

CONCLUSION

Time is now ripe for science to include the phenomenon of consciousness in a physical description of the universe. According to the proposed modeling, consciousness should be the unique "true" reality of the universe generating through specific strings of bits memorized in the physical ether (ROM) and written of water shells (RAM) material things. Such a proposal is suggested by the structure of the ISO(4,2)⊗U(2)⊗U(2) symmetry group leaving Maxwell's equations through translations, rotations, boosts, scaling and conformal transformations and has the great advantage of being fully compliant with an eastern more philosophical way of thinking. Our proposal also explains why the most prominent component of any living entity should be water. Another important point is that it is a quantitative modeling able computing memory sizes as well as bandwidths for information processing based on the universal constants of physics conjugated with quantitative data accumulated by molecular biology as well as physiology. Consequently, it is a model that is easily falsifiable by making both physical and biological measurements, a prerequisite for being accepted as a scientific model of consciousness. A very satisfactory consequence of the model is that consciousness and life are primitive attributes of the physical universe. This leads to the conclusion that the line of demarcation between physics, chemistry and biology becomes very thin, not to say imaginary. Basically, depending on the hydration state, we have a whole continuous spectrum of material things ranging from inert matter with a very low level of consciousness to living matter able to express consciousness with no limits. This works by going not only from unicellular to multicellular entities, but also from multicellular entities aggregating into species and civilizations. With such a model in hand, it is easy to understand that as soon as dehydration occurs, illnesses first and then death are doomed to occur. This is just because without water bits of information "evaporate" into the ether. However, the most important thing, is that such an information transfer from water to the ether if it alters the body made of matter does not alter consciousness that has always been located from the beginning of space and time in the non-observable V^6-information field and definitively not in the observable M^4-volume or C^5-hyper-surface. We thus sincerely do hope that such a modeling will stimulate a large amount of legitimate scientific research around the phenomenon of consciousness. As with any kind of modeling, the fact of being right or wrong does not matter. This is because if we are right, then we have a possibility of unifying physics, chemistry and biology. On the other hand, if future research in this field would lead to the conclusion that the model is wrong, this would mean that a better modeling have been found whose discovery would have not been possible without first thinking in the wrong way. The best evidence for the necessity for science of being wrong in order to improve itself is provided by Newton's beautiful unification that was in fact based on false ideas that were rectified after the discovery of Maxwell's equations ruling electromagnetic phenomena. Similarly, the marvelous Maxwell's unification was itself based on false ideas that were rectified after the discovery of quantum mechanics. And there is also pretty good evidence that quantum mechanics is probably based also on false ideas… So wrong reasoning seems to be a powerful driving force for improving knowledge of the universe and try elucidating such deep mysteries such as life and consciousness.

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Feature Articles

Leonardo and the Florence Canal. Sheets 126-127 of the Codex Atlanticus

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Abstract. The folios 126 r-v and 127 r-v of the *Codex Atlanticus* represent the most exhaustive account of a project developed by Leonardo over many years: the construction of a waterway between Florence and the sea. This navigable canal was supposed to restore the country from the Arno floods and encourage commercial traffic, bringing wealth to the entire region. Its length of no less than 72 km, the system of automatic locks designed to overcome the total height difference of 34 meters between Florence and Pisa, and the idea of feeding it with a water reserve located in Valdichiana would have made it one of the most imposing and technologically advanced hydraulic works of the time.

Keywords. Hydraulic engineering, river navigation, locks, siphons, cartography.

The "Florence Canal" is one of the most famous 'technological dreams' of Leonardo da Vinci. It was conceived as a navigable canal from Florence to the sea; a waterway that was supposed to restore the country from the Arno floods and encourage commercial traffic, bringing wealth to the entire region[1]. The project was developed on several occasions over many years but it never reached a final stage because, in fact, there was never an official appointment for its drafting. Leonardo worked on it with the hope of sensitizing the Floren-

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[1] According to Giorgio Vasari (*Lives* 1568), Leonardo "was the first who, as a young man, talked about the Arno river to put it in a canal from Pisa to Florence" (G. Vasari, *Vite de' più eccellenti pittori scultori e architettori, 1550 e 1568*, ed. by R. Bettarini and P. Barocchi, Firenze 1966-1987, vol. 4, p. 17). On the Florence canal project, see Mario Baratta, *Leonardo da Vinci negli studi per la navigazione dell'Arno*, "Bollettino della Società Geografica Italiana", fasc. 10-12 (1905), p. 739-761; Girolamo Calvi, *I manoscritti di Leonardo da Vinci: dal punto di vista cronologico, storico e bibliografico*, Zanichelli, Bologna 1925, pp. 225-232; William Barclay Parsons, *Engineers and engineering in the Renaissance*, The MIT Press, Cambridge (Mass.) 1975, pp. 323-334; Carlo Pedretti, in Jean Paul Richter, *The Literary Works of Leonardo da Vinci / Commentary by C. Pedretti*, commentary to fol. 127r-v, Phaidon, Oxford 1977, pp. 174-175; Carlo Zammattio, *Acqua e pietre: loro meccanica*, in Carlo Zammattio, Augusto Marinoni, Anna Maria Brizio, *Leonardo scienziato*, Firenze 1980, pp. 10-67; Sara Taglialagamba, *Il Canale di Firenze. Foglio 126v*, in *Leonardo e Firenze. Fogli scelti dal Codice Atlantico*, catalogue of the exhibition, Firenze, Palazzo Vecchio (March 24th – June 24th 2019), ed. by Cristina Acidini, Giunti, Firenze 2019, pp. 52-53; Alessandro Vezzosi, *Il Canale di Firenze. Scienza, Utopia e Land Art*, in *Leonardo e Firenze,* cit., pp. 55-63.

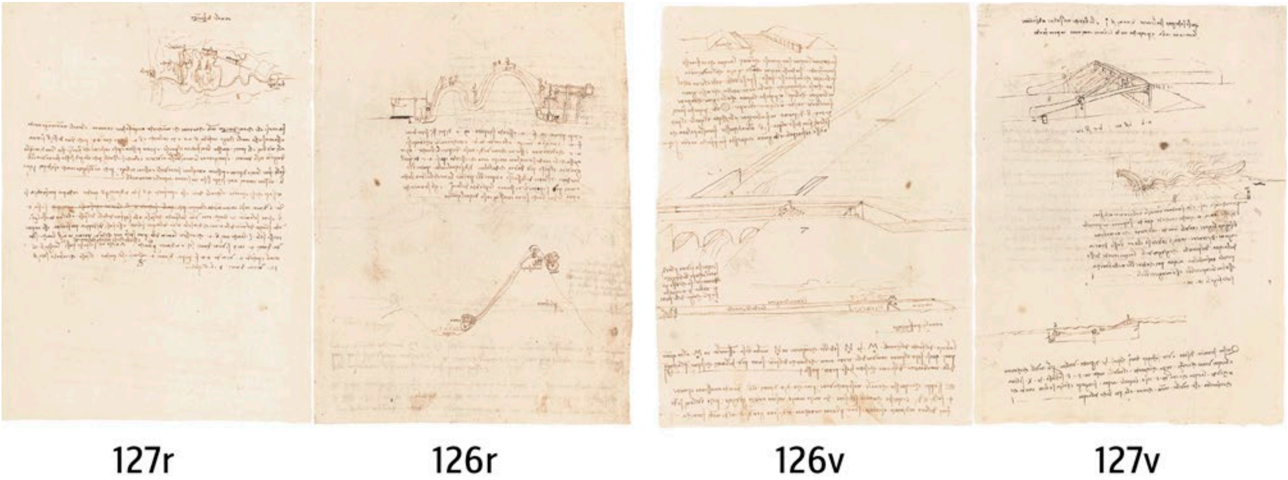

Figure 1. Recomposition of sheets 126r-v and 127r-v of the *Codex Atlanticus*.

tine Republic, especially after the assignment obtained in the summer of 1503 to divert the Arno at the gates of Pisa during the siege of the Florentine troops.

The failure of that enterprise, however, soon quenched the enthusiasm, and put a limit also to the ambitions of its main supporter, Niccolò Machiavelli, the strategist of the Pisan siege. The two men had met at the court of Cesare Borgia, when Leonardo held the office of "architect and military engineer" of the prince, and Machiavelli that of ambassador of the Florentine Republic[2].

When Leonardo was dismissed, Machiavelli called him to supervise the fortress of Verruca at the gates of Pisa, newly conquered by the Florentines, and to present a project for the deviation of the Arno towards Stagno, next to Livorno[3]. It was in the year that elapsed between the presentation of the project and its implementation that Leonardo seems to have devoted himself more assiduously to the ambitious project of the Florence Canal.

The folios 126r-v and 127r-v of the *Codex Atlanticus* represent the most exhaustive account of the project. Even in their extreme textual and graphic synthesis, the sheets contain all the elements necessary to understand the scope of the project which, for technological innovations and impact on the territory, far exceeded the expectations of the possible clients. Most likely, the sheets derive from a bifolio that Leonardo began to write from the last page, as usual for his left-handed writing. The last page (the first for Leonardo) was folio 127r, followed by 127v, then by 126v and then by 126r (fig. 1). The double sheet was presumably part of a series of "notebooks" on water engineering, mentioned by Leonardo on sheet 26r of the Codex Leicester, the treatise that he dedicated to the nature of water and its cosmological implications[4].

Sheet 127r opens with a cartographic sketch of the area affected by the construction of the canal, namely the plain of Florence and the lower Valdarno, up to the mouth of the Arno river (fig. 2). It is a very summary sketch that, however, we are able to read thanks to the much more accurate maps, now kept in the Royal Collection of Windsor Castle and in the Codex Madrid II[5]. The names of the cities of Florence, Prato and Pistoia, of the Serravalle pass, and of the Lake of Sesto (or, of Bientina), mark the route of the canal that, once deviating from the Arno at the gates of Florence, would once again have entered the river next to Vicopisano. Above the drawing, the title "Canale di Firenze" can be read, and below it there is a text that immediately indicates the essential condition for the realization of the work:

> *Facciasi alle chiane d'Arezzo tali cateratte che, mancando acqua la state in Arno, il canale non rimanga arido.*
>
> *Let's construct sluices in the Chiane of Arezzo so that, lacking water in the Arno in summer, the canal would not dry out.* (f. 127r)

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[2] Permission letter issued to Leonardo by Cesare Borgia on August 18 1502, Melzi d'Eril Archives, Belgioso (Pavia): Vaprio d'Adda 1993.

[3] See Emanuela Ferretti, *Fra Leonardo, Machiavelli e Soderini. Ercole I d'Este e Biagio Rossetti nell'impresa "del volgere l'Arno" da Pisa*, "Archivio Storico Italiano", 2019, 2, a. 177, n. 660, pp. 235-272.

[4] The hypothesis is supported by G. Calvi, *op. cit.*, pp. 224, 229. For the Codex Leicester, see *Leonardo da Vinci's Codex Leicester: A New Edition*, ed. by Domenico Laurenza and Martin Kemp, Oxford University Press, Oxford 2019; Paolo Galluzzi, ed., *L'acqua microscopio della natura : il Codice Leicester di Leonardo da Vinci*, catalogue of the exhibition (Florence, Uffizi Gallery, October 30th 2018 – January 20th 2019), Giunti, Firenze 2018.

[5] The topographical drawings of the Lower Valdarno are kept at the Royal Library of Windsor, inv. 12279 and 12685, and in the Codex Madrid II, cc. 22v-23r.

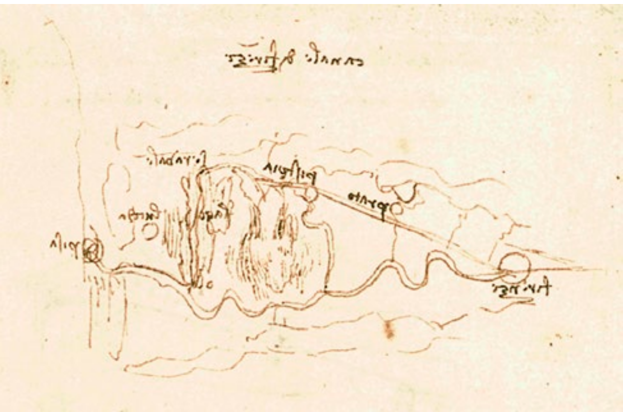

Figure 2. C.A., fol. 127r: detail of the topographic map with the plain of Florence and the lower Valdarno.

Figure 3. *Map of Valdichiana*, Windsor, Royal Library, 12278r

In order to make the canal navigable throughout the year it was necessary to guarantee a water reserve sufficient to ensure navigability even when the Arno had a limited water flow, that is, in the summer months. The water reserve was located in Valdichiana where the large swamp existing at that time could be transformed into a huge reservoir suitable for the purpose. Leonardo does not specify how, but the Valdichiana map drawn up between 1502 and 1503, and the Map of Tuscany, presumably of the same period, allow us to identify some elements of this project[6]. The swamp of the “chiane d’Arezzo” was formed in the Middle Ages perhaps due to a phenomenon of bradyseism that had caused the raising of the ground in the middle of the valley, breaking in two branches the Chiane master canal, once a commercial waterway between the Arno and the Tiber[7]. One of the two branches underwent a reversal of flow, beginning to flow towards the Arno; the other continued to flow towards the Tiber. The lack of maintenance of the water courses, due to the interruption of commercial activities in the period of the barbarian invasions, contributed to provoking the swamping of the valley that already at the time of Dante was known for its unhealthy air[8].

In Leonardo’s drawing, one of the most refined cartographic products of the time, the two branches of the Chiane’s master canal are traced with a darker blue inside the large swampy expanse that crosses the valley from north to south (fig. 3).

The map was drawn up for military purposes in the aftermath of the Arezzo uprising but it is likely that it was also conceived for a reclamation project necessary to restore the region that Cesare Borgia had just annexed to his conquests in central Italy[9]. To betray the possibility of a hydrographic project in the mind of Leonardo is the presence of a dry ditch not indicated in the other maps of the region, and insignificant for military purposes. The ditch is also reported in the general map of Tuscany accompanied by a significant note: “Braccio da Montona closed it, thence it has disappeared” (fig. 4).

This specific note reveals an attention to the issue of waters that goes beyond the mere cartographic recording. The dried-out canal, is called “Trasumeno” (fig. 5). It was an emissary of the Lake Trasimeno that poured the floods of the lake in the Chiane’s master canal, periodically aggravating the swamping of the valley. Braccio da Montone, the lord of Perugia, closed it around 1420 in an attempt perhaps to reclaim the valley. The floods of the lake were then poured into the Tiber through the opening of a new emissary towards the south that in the map of Leonardo, as well as in other contemporary maps, is recognizable by the characteristic graphic interruption due to the tunnel path under the hills in prox-

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[6] The map of the Valdichiana and the general map of Tuscany are both kept at the Royal Library of Windsor, respectively with the inventory numbers 12278 and 12277.

[7] See, Vittorio Fossombroni, *Memorie idraulico-storiche sopra la Val-di-Chiana*, Firenze 1789; A. Bigazzi, *La bonifica della Val di Chiana (secoli XVI-XX): gli aspetti tecnici*, “Atti e Memorie della Accademia Petrarca di Lettere, Arti e Scienze”, nuova serie, LXIX, 2007, pp. 267-298.

[8] Dante recalls the summer miasmas of the Chiane in the 29th *canto* of *Inferno* (vv. 46-48, “Qual dolor fora, se de li spedali / di Valdichiana tra ‘l luglio e ‘l settembre / e di Maremma e di Sardigna i mali”), while a little later Fazio degli Uberti attributes to the unhealthy air of the region the cause of the dropsy or anasarca: *Dittamondo*, book III, chapt. X, vv. 23-24, “Quivi son volti pallidi e confusi / perché l’aire e le Chiane li nemica / sì che li fa idropichi e rinfusi”.

[9] The revolt of Arezzo against the Florentine domination broke out in June 1502 and was strongly supported by Vitellozzo Vitelli, captain of fortune in the service of Cesare Borgia and friend of Leonardo to whom he lent a book of the works of Archimedes. Arezzo came back under Florentine rule already in August thanks to the intervention of the king of France who ordered Cesare Borgia to renounce the city.

Figure 4. Detail of the dried-out canal, called "Trasumeno", from the *Map of Tuscany*, Windsor, Royal Library, 12277.

Figure 5. Detail of the "Trasumeno" from the *Map of Valdichiana*, Windsor, Royal Library, 12278r.

Figure 6. Detail of the southern emissary of the Lake Trasimeno from the *Map of Valdichiana*, Windsor, Royal Library, 12278r.

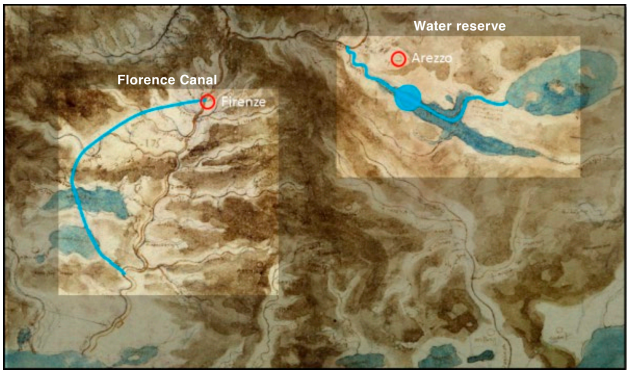

Figure 7. Scheme of Leonardo's hydrographic project (traced on the *Map of Tuscany*, Windsor, Royal Library, 12277).

imity of the lake (fig. 6). At the point where the southern emissary enters the Tiber Leonardo writes "here is the outflow of the lake". This note, together with the actual height difference between the lake and the Tiber, which is here much lower, rules out the hypothesis that Leonardo may have considered to convey Tiber´s water to the Trasimeno in order to create a compensation basin in the Chiane that fed into the Arno in the summer months[10]. It is possible instead that for that purpose he planned to reopen the northern emissary which had been closed by Braccio da Montone, a hypothesis still put forward in the sixteenth century by the savant priest Baldassarre Nardi[11]. If Duke of Valentinois´ intent was to acquire riches from a potentially productive area, by reclaiming the whole swampland, then Leonardo seems to have conceived a more elaborate regional water system that connected the large valleys of Tuscany to one another, in order to ensure the feasibility of the great project for the "Canale di Firenze" (fig. 7).

> *E facciasi esso canale largo in fondo braccia 20 e 30 in bocca, e braccia 2 sempre [ac]qua o 4, perché dua d'esse braccia serva[n] alli mulini e li prati.*

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[10] This hypothesis is put forward by Carlo Zammattio, *Acqua e pietre: loro meccanica*, in C. Zammattio, A. Marinoni, A.M. Brizio, *Leonardo scienziato*, Firenze 1980, p. 23.

[11] The hypothesis to convey water from Lake Trasimeno into the Canale Maestro of the Chiana was resumed at the end of the 16th century by Baldassarre Nardi (*Discourse on the Reclamation of the Chiane*, ms., 17th century, Florence, Biblioteca Riccardiana, Ricc. 2575), who seems to have dreamt of the possibility to make the entire stretch a navigable canal that would have connected "Livorno to Rome through the Arno, the Chiane, the Paglia and the Tiber"; see V. Fossombroni, *op. cit.*, p. 312, note 11.

> *And make the canal wide at the bottom,* braccia *20 and 30 in the mouth, and deep* braccia *2 always or 4, so that two* braccia *will serve the mills and the fields.* (f. 127r)

The canal would have had such a width to allow the comfortable passage of two boats in the opposite direction. Considering that the major boats used at that time had a maximum width of 7.5 *braccia* (about 4.5 meters) - so we read in sheet 1007r of the Codex Atlanticus[12] - Leonardo fixed the width of the canal at 20 *braccia* on the bottom and 30 on the surface, and established a depth of 4 *braccia* that could contain a sufficient amount of water to operate the mills, irrigate the fields and allow navigation. The minimum depth for navigation was set at 2 *braccia*, or just over one meter, sufficient to guarantee the floating of the large flat-bottomed boats of the river waterways. The canal measurements indicate a trapezoidal section that Leonardo draws in other notes of the Codex Atlanticus. In the third page of this bifolio, instead (fol. 126v) the canal has a rectangular section. The banks are formed by thick palisades with a robust plank that holds the ground to form two "3 or 4 *braccia*" docks before the gravel embankment that protects the surrounding lands from possible flooding.

> *Questo [canale] bonificherà il paese; e Prato, Pistoia e Pisa insieme con Firenze fia l'anno di meglio dugento mila ducati, e porgeranno le mani a spesa a esso aiutorio, e i Lucchesi il simile.*
>
> *This [canal] will reclaim the country; and Prato, Pistoia and Pisa, together with Florence, will make the year better than two hundred thousand ducats, and they will help with the expenses, and the Lucchesi the like.* (f. 127r)

In addition to the aforementioned functions, the canal would also have served to absorb the overflows of the Arno avoiding the periodic floods that always represented a danger for the city of Florence and the surrounding countryside. Instructions "for the canalisation of the Arno" along the urban stretch were issued from 1458 to 1477, while, before 1469, Luca Fancelli had elaborated a project for Piero de' Medici for making the river navigable from Mulino di Ognissanti to Signa. The difficulties arisen in that plan, which Fancelli still discussed in a letter to Lorenzo the Magnificent in 1487, were due to the torrential nature of this river[13]. For slowing the flow of the Arno down, it was necessary to block its course by a series of kiddles, which, however, turned out to be a barrier during floods; but it was not possible without kiddles, since in the canalised stretch the stream would have been even more impetuous, therefore it would have brought about the erosion of the riverbed and the consequent breakage of the river banks.

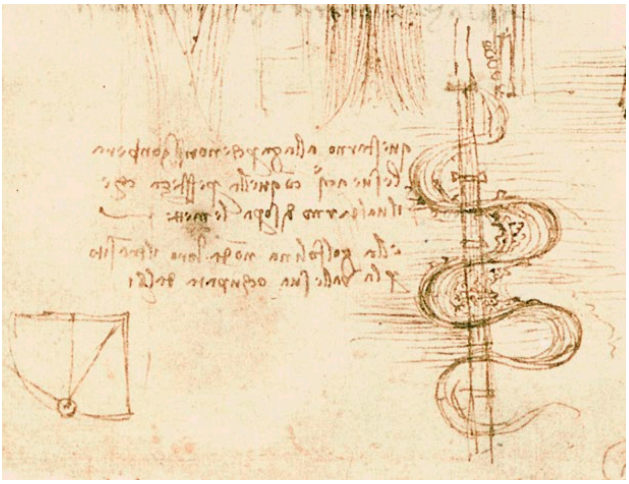

Figure 8. C.A., fol. 785ii r: detail of a study for the Arno canal.

In order to find a solution to this problem Leonardo thought to build a canal alternative to the natural course of the Arno which, by its nature, was not suitable for this plan: "This Arno floods – Leonardo explains – because it does not let its water run off with the same promptness as waters flow into it from the upper Arno Valley. And the Golfolina obstructs the passage of them through its valley filled with trees" (fig. 8)[14]. The alternative way was a navigable canal with a very slight slope, then without kiddles, which would have reached Prato and Pistoia from Mulino di Ognissanti and would have passed through the marshes of Fucecchio for flowing into the Arno near Cascina.

Prato, Pistoia and Pisa are indicated as the main cities that, together with Florence, would have benefited from the construction of the canal and should therefore have contributed financially to its construction. But Leonardo also indicates Lucca that having small commercial landings on Lake of Bientina, could have benefited equally from that important infrastructure, if the canal had been in communication with that lake.

> *Perché il lago di Sesto sia navigabile, falli fare la via di Prato e Pistoia e tagliare Serravalle e uscire nel lago.*

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[12] Codex Atlanticus, fol. 1107r: «Le maggiori barche che si faccino, sono larghe 7 braccia e 1/2 [4,5 m] e lunghe 42 braccia [24 m] e alte di sponde uno braccio e ½ [0,9 m]» (The major boats that are built are 7 *braccia* and 1/2 wide[4.5 m] and 42 *braccia* long [24 m] and one *braccio* and ½ high at the sides[0.9 m]).

[13] Luca Fancelli to Lorenzo de' Medici, Milan, August 12 1487; in Corinna Vasić Vatovec, ed. by, *Luca Fancelli architetto. Epistolario gonzaghesco*, Firenze 1979, pp. 60-62.

[14] Codex Atlanticus, fol. 785ii r.

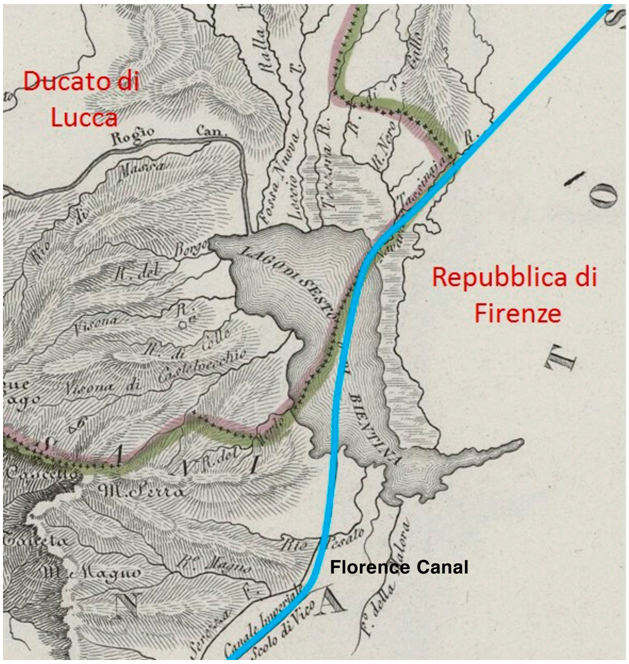

Figure 9. Lake of Sesto, or "of Bientina", *Carta orografica e idrografica del Ducato di Lucca*, in A. Zuccagni Orlandini, *Atlante Geografico degli Stati Italiani*, Firenze 1844, II.

Figure 10. *Map of the Lower Valdarno*, Windsor, Royal Library, 12685.

> *For Lake of Sesto to be navigable, let it [the canal] pass through Prato and Pistoia and cut Serravalle and exit into the lake.* (f. 127r)

Figure 11. *Map of the Lower Valdarno*, Codex Madrid II, cc. 22v-23r.

Figure 12. *Map of the Lower Valdarno*, Windsor, Royal Library, 12279.

The "lake of Sesto" or Lake of Bientina was partly marshy (fig. 9); it dried up during the dry season but only in the outlying areas. A large central area always remained navigable and had an emissary, the ditch of Serezza, which conveyed the excess waters into the Arno near Vicopisano. The lake was half in the Lucca territory and half in the Florentine dominion. Two of the maps drawn by Leonardo to trace its route - Windsor 12685 and Madrid II (figg. 10-11) – show the canal that grazes the southern shore of Lake of Bientina, crossing a slightly hilly area that would have required a work of excavation certainly excessive. Only the Windsor map 12279 (fig. 12) shows a sinuous path that seems to bring the canal slightly further north, where it would have crossed a totally flat area to enter the lake at Altopascio. Keeping the slopes minimal was a necessary condition to avoid the construction of locks whose maintenance would have represented an important burden.

> *perché non bisogni di conche o sostegni, i quali non sono etterni, anzi sempre si sta in esercizio a operarli e mantenerli*

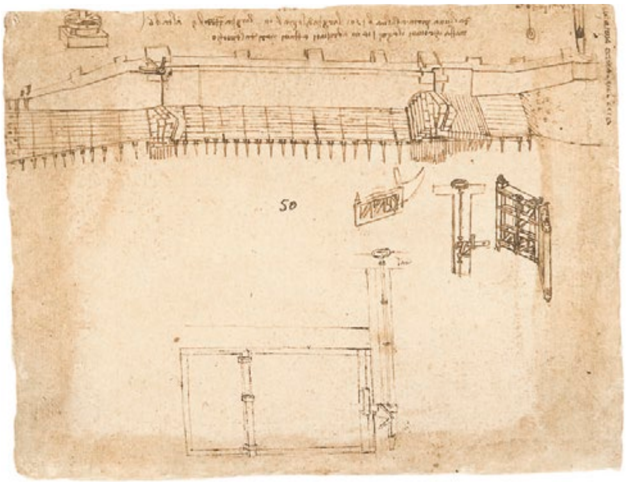

Figure 13. C.A., fol. 935r: Chamber, or navigation basin, with the kind of locks called "porte vinciane".

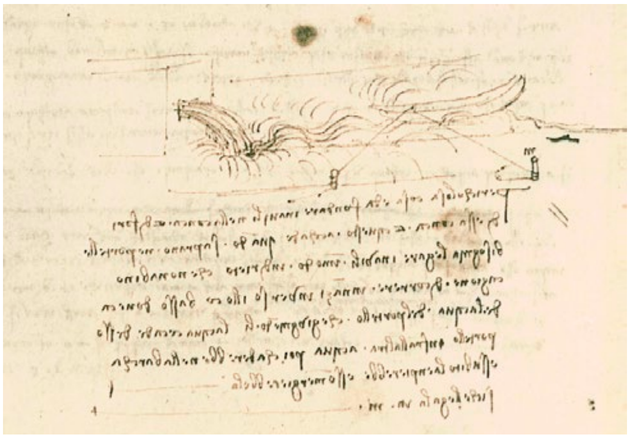

Figure 14. C.A., fol. 127v, detail: filling of the navigation basin through the door of the lock.

> *So that it does not need chambers or locks, which are not eternal, rather it is always necessary to operate and maintain them.* (f. 127r)

The technology of 'chambers', 'bulkheads' or 'locks' was known to Leonardo for having experimented and perhaps perfected it during the Milanese years. The gates system fully illustrated by him in the Codex Atlanticus, for example in sheet 935r, is known today as "Porte Vinciane" or 'Da Vinci Gates' (fig. 13). Two large doors close the canal forming an angle of about 120° in upstream direction so as to resist the thrust of the water better than any transverse plane barrier. The doors remained tight thanks to the push of the water, and they were secured to the ground by a stone step that served as a 'doorstop'. Two gates of this type delimited the chamber where the boat was let in to reach the upper or lower level of the canal. In Lombardy canals, locks of this type allowed to overcome up to four meters in altitude. When a boat entered the chamber and the gates from which it had passed were closed, two small shutters hinged to the doors of the second gates were opened to let water enter the chamber itself, or to let it out in the event of a passage to the lowest level. The operation was risky, especially uphill, since the introduction of water into the chamber caused vortices that could push the boat too close to the inlet with consequent danger of sinking, as Leonardo explains in the verse of sheet 127 (fig. 14):

> *Pericolosa cosa è da fondare i navili nella conca e di fori d'essa conca; e questo accade quando s'aprano le portelle. Bisogna legare i navili in modo indirieto che non abbiano cagione di correre innanzi in verso il loco basso, dove cade l'acqua del portello, che giugnendo lì l'acqua, che cade d'esso portello infra l'altra acqua, poi caderebbe nella barca e subito la empierebbe, e sommergerebbela. Sicché legala in* m.

> *Dangerous thing is the risk of sinking the boats in the chamber and outside, and this happens when the doors open. We have to tie the boats behind, so that they have no way of running forward towards the low place, where the water falls from the doors, because arriving there, the water that falls from the doors into the other water, then it would fall into the boat and immediately would fill it and submerge it. Then tie it in* m. (f. 127v)

The water level between the two doors went up to that of the upper section of the canal and only then could the second door be opened to let the boat pass. This system made it possible to overcome considerable differences in height but required high construction costs and, according to Leonardo's concerns, even more significant maintenance costs. Leonardo does not say it but we should consider that having to periodically absorb the floods of the Arno, the sluices would have represented a problem to the gradual outflow of the waters.

However, even without the flood problem, the Florence canal could not have been built without water supports. Even if his path could have had a constant slope, we would still have an inclination that would generate too much stream for a comfortable navigation. In its total extension of approximately 72 km between Florence and Vicopisano, the canal would have had to overcome a drop of 34 m, developing a slope of about one meter every 2 km. In the Lombardy canals, the average slope is about one meter every 3 km, a limit beyond which it was not advisable to proceed[15]. But the ques-

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[15] On water engineering in the Lombardy area see, Cesare S. Maffioli, *I contributi di Leonardo da Vinci e degli ingegneri milanesi : misura delle*

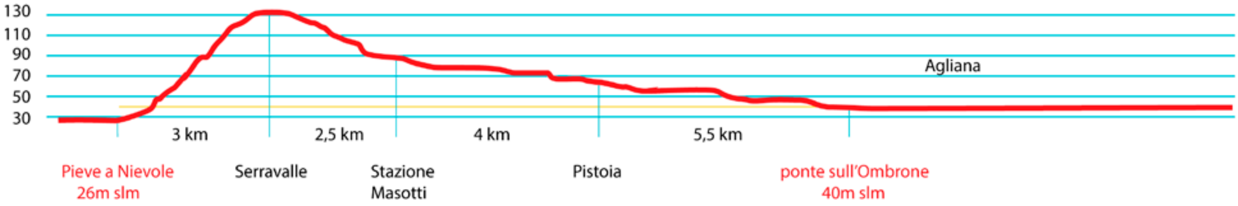

Figure 15. Topographic section between the Ombrone river and the Val di Nievole.

Figure 16. Satellite view of the plain between Florence and Pistoia with the route of the canal and the crossing of the tributaries of the Arno.

tion did not arise even in these terms because at least as far as Pistoia the canal should have had a minimum slope, finding itself having to overcome a difference in height of 14 m in the short stretch that separates Pistoia from the Val di Nievole, beyond the relief of Serravalle (fig. 15). The stretch in question measures about 14 km, impossible to navigate without water supports.

Between Florence and Pistoia the ground has a minimal slope and in that stretch the canal would have had to exceed four tributaries of the Arno, two of which, the Bisenzio and the Ombrone, particularly dangerous during the autumn floods (fig. 16). Leonardo intended to use the water of the tributaries to feed the canal through special aqueducts with controlled access, but the torrents themselves could not enter the canal; they had to be crossed with a bridge of the type illustrated in the third page of the bifolio (126v) (fig. 17). The bridge is on three arches, the central one corresponding to the usual width of the watercourse, the other two necessary to cover the riverbed to absorb the floods: "*if this river usually occupies the width of an arch, let it the bridge having 3 arches, and this is for the causes of floods* ". Above the bridge runs the navigable canal whose depth here is reduced to the bare minimum. And beyond the bridge we can see a navigation basin with corner gates.

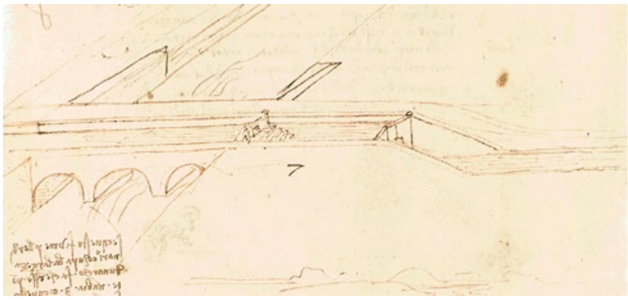

Figure 17. C.A., fol. 126v, detail: perspective view of the canal bridge.

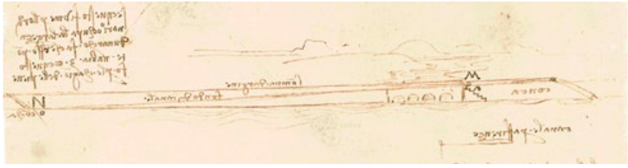

Figure 18. C.A., fol. 126v, detail: cross section of the canal bridge.

In the cross section drawing it is clear that the canal proceeds from a higher level than that of the river that is crossed (fig. 18). In this case the filling of the navigation basin occurred by fall, as in the case of the Ivrea canal that Leonardo mentions on the sheet 563r of the Codex Atlanticus. In the section between Florence and Pistoia, on the other hand, the canal runs at the same altitude as the rivers it must pass. The bridge therefore required a navigation basin that was necessarily higher than both sections of the canal that it connected and its filling took place from below. The only technology that Leonardo could have entrusted with this artifice was that of the siphon, or "cicognola" as it was called at that time; a tube of adequate dimensions which, by exploiting the

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acque e navigazione dell'Adda tra fine XV e XVI secolo, "Archivio storico lombardo", anno 142 (2016), pp. 97-127.

Figure 19. C.A., fol. 126r, detail: double siphon.

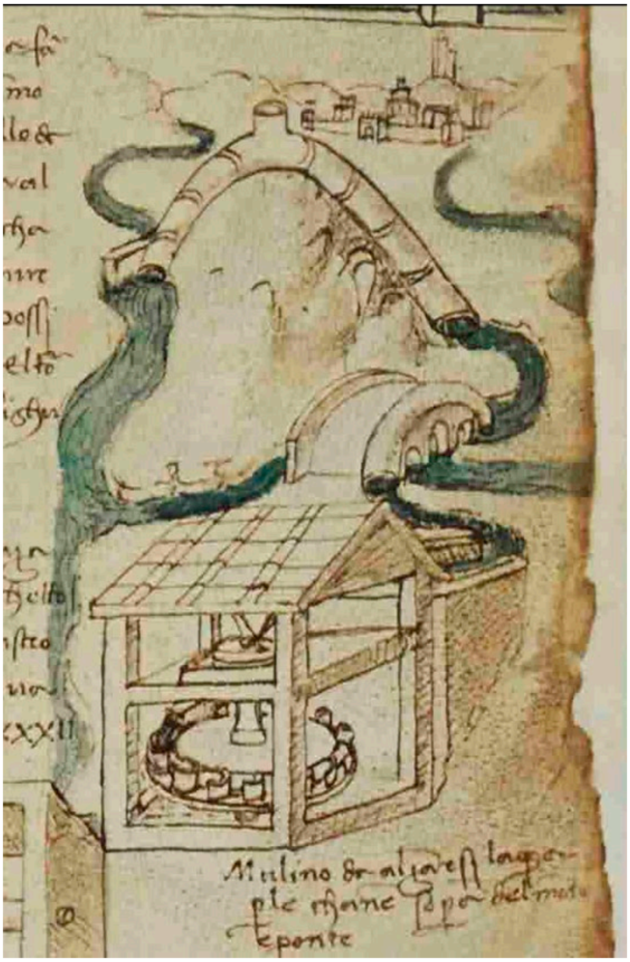

Figure 20. Francesco di Giorgio Martini, *Trattati di architettura, ingegneria e arte militare*, Firenze, Biblioteca Medicea Laurenziana, Cod. Ashb. 361, c. 38r, detail: bridge with siphon to carry the water of a canal from one bank to the other of a river.

phenomenon of communicating vessels, would have put the two canal sections separated from the bridge into communication, ensuring the continuous feeding of the canal itself and, when necessary, filling the navigation basin to allow the boats to pass from side to side. This problem probably refers to the singular siphon drawn in the last page of the bifolio (126r) (fig. 19).

The siphon technology applied to the aqueduct bridges is illustrated by Mariano di Jacopo, known as "il Taccola", and by Francesco di Giorgio Martini (fig. 20)[16]. In their writings the solution contemplated by Leonardo is clearly prefigured, namely a siphon bridge that crosses a river bringing the water of a canal from one bank to the other. Leonardo certainly considered this technological solution, taking into account, however, the possibility of adapting it to the navigability of the canal. The greater length of the exit pipe that characterizes the siphon technology, here seems to be obtained with the help of a double curve with a gooseneck joint whose function was to increase the flow velocity. Once the siphon was filled from the mouths placed at the top of the two curves - keeping both mouths closed at the bottom of the canal - and the filling of the upstream channel was ensured, the mouthpieces could be opened to let the water flow into the section of canal downstream. The continuous flow of the canal would keep the siphon in constant operation. To guarantee the simultaneous opening of the mouthpieces, Leonardo studied a mechanical system with balance and counterweights that is activated by cutting a rope stretched between the two ends of the siphon.

The drawing does not explain how the navigation basin was to be filled, but if this was to be the second function of the siphon - necessary to guarantee the navigability of the canal - we should imagine an opening at the top of one of the two curves; an opening of such dimensions as to allow the introduction of water into the basin without interrupting the flow in the siphon. This solution is indicated by Leonardo in sheet 301r of the Codex Atlanticus, where it is applied to an extremely ambitious case, that of bringing the boats to the top of the hills (fig. 21): "*ogni grosso fiume si conducerà in su l'altissime montagne per la ragion de la cicognola* (every big river will lead up the very high mountains for the reason of the siphon)". The siphon

---

[16] See Mariano di Jacopo, called il Taccola, *De ingeneis*, ed. by Gustina Scaglia, Frank Prager, Ulrich Montag, Dr. Ludwig Reichert Verlag, Wiesbaden 1984, fols. 73v, 83r, 94v, 105r, 115r, 134r; and Francesco di Giorgio Martini, *Trattati di architettura, ingegneria e arte militare*, ed. by Corrado Maltese and Livia Maltese Degrassi, Il Polifilo, Milano 1967, fols. 40r, 42v, 45r.

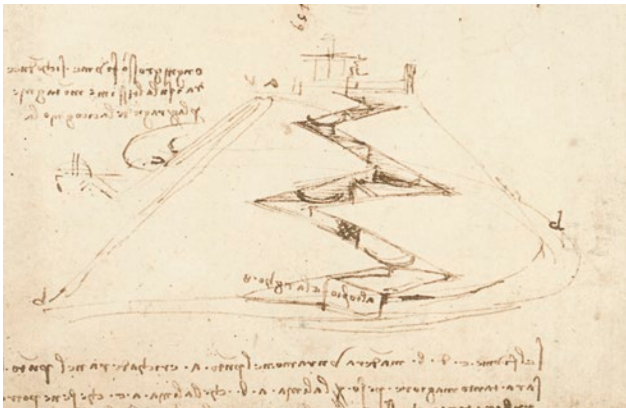

Figure 21. C.A., fol. 301 r, detail: big siphon to feed the highest navigation basin of a system of locks to bring boats up to the mountains.

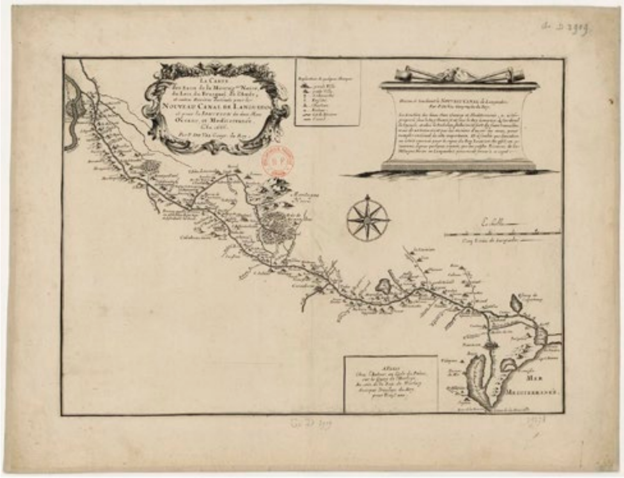

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Figure 22. Map of the *Nouveau Canal de Languedoc*, Paris 1677.

is used to feed the highest of a system of navigation basins which, proceeding in a zig-zag fashion, would have allowed for *"condurre delle navi in sulle montagne* (carrying ships on the mountains)". The idea would have found application in France in the seventeenth century with the construction of the Canal du Midi which connects the Mediterranean See with the Atlantic Ocean, overcoming an intermediate relief of 190 m (fig. 22). In this case, however, the supply of the highest basin occurs through a water reserve located further upstream.

If the canal had not also served as a spillway, and if it had been possible to guarantee a water supply in the Pistoia mountains, this solution would have been applicable also to the Serravalle problem. But the conditions were different.

Figure 23. Codex Madrid I, c. 111r: level used to guide the excavation of a tunnel.

The mountainous relief that separates the plain of Florence-Pistoia from the Val di Nievole is today crossed in a tunnel by a stretch of motorway and by the railway line, and it has been repeatedly suggested by scholars that this could be one of the solutions meditated by Leonardo. To support the hypothesis is usually the 111r sheet of the Codex Madrid I where Leonardo illustrates a new "way to drill a mountain" (fig. 23). The excavation of tunnels for canals and aqueducts is illustrated in the works of Taccola (fig. 24) and a real case well-known to Leonardo was the tunnel of the southern emissary of the Trasimeno. However, unlike the approximately 900 meters covered in tunnel by the Trasimeno emissary, overcoming the relief of Serravalle required a dig of several kilometers. If the excavation had been done horizontally, as Leonardo shows and before him Taccola, the exit of the tunnel towards Pieve a Nievole would have been found 14 meters higher than the valley that it was supposed to reach. In conclusion of his description, Leonardo states that by tilting the level the excavation

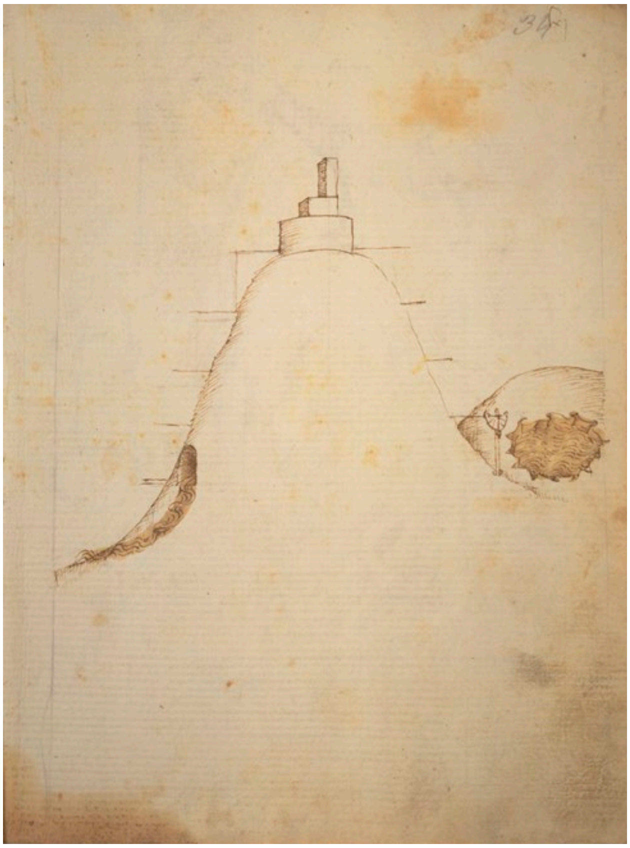

Figure 24. Mariano di Iacopo, called il Taccola, *De ingeneis*, Biblioteca Nazionale Centrale di Firenze, Ms. Palat. 762, c. 34r: method for digging a tunnel for the passage of canals and aqueducts.

could follow an inclined plane, but there is no evidence that this excavation technique was related to the passage of the canal to Serravalle.

In the first page of the bifolio, Leonardo clearly writes "cut Serravalle" and it seems clear that his solution foresaw a passage in trench, or the cutting of an artificial gorge that would have allowed to proceed gradually downwards with a series of "steps" interrupted by weirs of the type illustrated in sheet 90v of the Codex Atlanticus (fig. 25). This drawing shows navigation basins with a system of locks simpler than the one with corner gates. These are sluice gates raised like a drawbridge that certainly required lower construction and maintenance costs. For this part of the Florence canal, and for the following stretch as far as Lake Bientina, Leonardo seems to have thought of even simpler water supports that we see illustrated in the second page of the bifolio (127v). These are counterweight systems designed to support just one *braccio* of water, the minimum allowed for river navigation, which could be operated by the boats themselves (fig. 26).

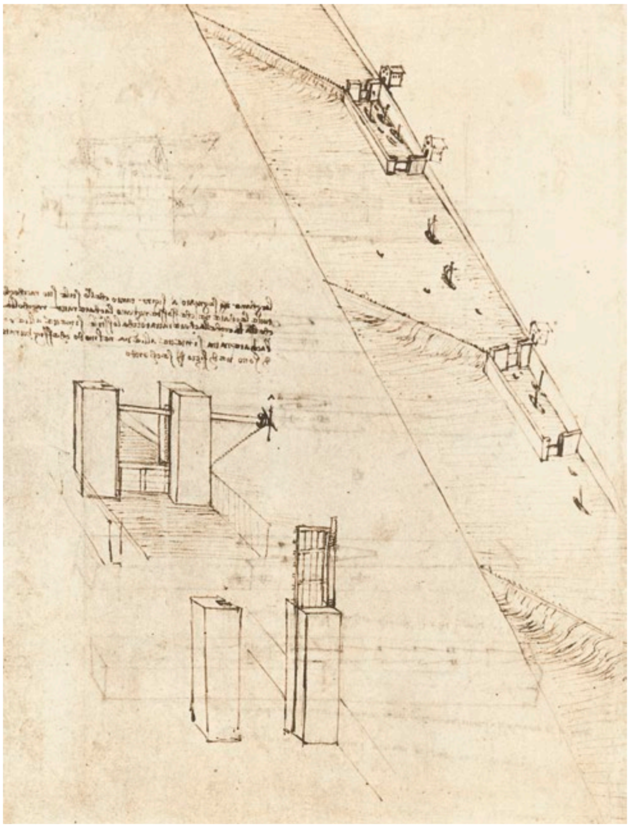

Figure 25. C.A., fol. 90v: canal with kiddles and locks.

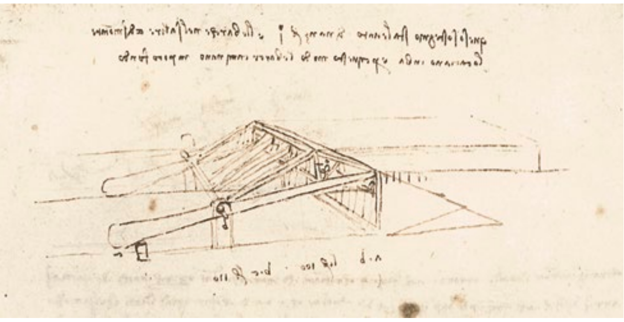

Figure 26. C.A., fol. 127v, detail: counterweight water support.

> *Ques[t]o sostegno sta levato dinanz[i] braccia uno, e le barche nel salire e dismontare lo cacciano in ba[sso], e per questo modo le barche camminano in poco fondo.*
>
> *This support rises on the front one* braccio, *and as the boats go up and down they drive it down, and in this way the boats walk in little depth.* (f. 127v)

Two similar supports had to be located at the two ends of the navigation basin (fig. 27). Arriving from

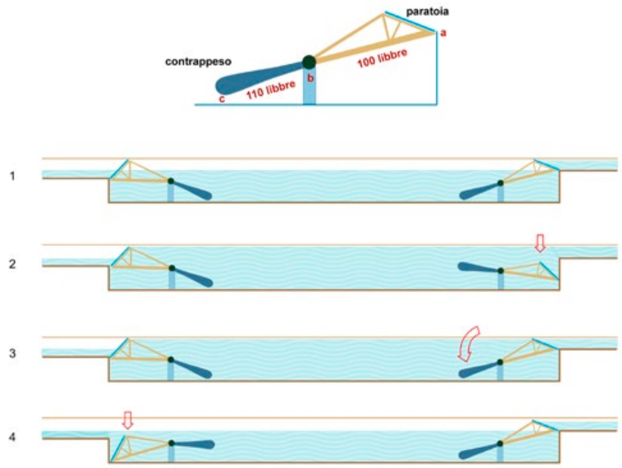

Figure 27. Operation of the counterweight system designed to support one *braccio* of water.

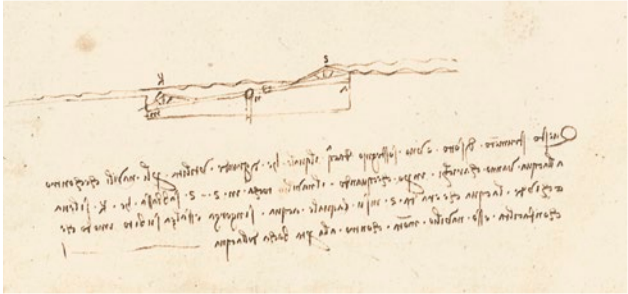

Figure 28. C.A., fol. 127v, detail: rocker water support.

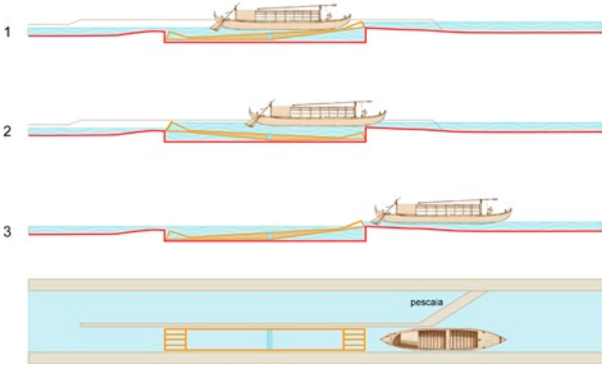

Figure 29. Operation of the rocker arm system designed to support one *braccio* of water.

the top of the canal (right, in the drawing), and tapping lightly on the sloping sluice of the support, the boat would have caused the lowering of the sluice itself which the water, pouring inside the basin, would have helped to push even more down. The opposite gate would have blocked the passage of water allowing the basin to fill up to the upper level of the canal. At that point the boat could enter the basin and proceed until it touched the second support which, by lowering, would allow the basin to empty itself until it reached the lower level of the canal. The emptying took place after the first support, brought back in position by the counterweight, had blocked the access of the water from the upper part of the canal. Alternatively, the two supports could be connected like a rocker arm, as in the drawing at the bottom of the sheet (fig. 28).

> *Questo strumento di sotto è un sostegno d'acqua, il quale è di grande utilità per li navili che contro all'acqua vanno carichi; imperò che, quando il navilio tocca in S, S s'abbassa, e K si leva e chiude l'acqua che era da S in su. La quale acqua s'ingorga, e s'alza subito in modo che con facil[i]tà esso navilio monta contro all'aperta bocca dell'acqua.*
>
> *This instrument below is a water support, which is very useful for loaded ships sailing upstream; so that when the ship touches in S, S is lowered, and K rises and closes the water that was from S upwards. Which water is engorged, and immediately rises so that with ease the boat gets in the open mouth of the water.* (f. 127v)

Here Leonardo imagines a boat that sails upstream (fig. 29). The navigation basin has the same level of the lower part of the channel; the boat enters the basin and knocks against the sluice gate which blocks water access to the upper level. This is lowered causing at the same time the raising of the downstream sluice gate which closes the access to the water in the meantime poured into the basin from the highest part of the canal. The water level in the basin then rises up to that of the upstream channel, and at this point the boat proceeds in its navigation. Here it is not clear if the system should remain in this position until the passage of another boat or if the difference in weight between the two parts of the rocker arm would have gradually brought the basin back to the initial condition. It is clear, however, that in both cases the height difference exceeded by the boats had to be minimal, no more than one *braccio*, and although numerous, these water supports would have been less expensive than the traditional locks. To overcome the 14-meter difference in height between Pistoia and the Val di Nievole, the section of the canal in Serravalle would have required about 23 water supports of this type located at a distance of about 600 meters from each other.

The next stretch, up to Lake of Bientina, would have required as many supports. Then the canal would have continued with a minimal slope until it re-entered the Arno at a point where the river itself, having no more tributaries, would have become navigable up to the mouth.

The final part of the text we are examining contains an estimate of the costs for the excavation of the canal, a decisive and unavoidable aspect that Leonardo methodically tackles in other sheets of the Codex Atlanticus.

> *E sappi che se cavando il canale dove esso è profondo 4 braccia, si dà 4 dinari per braccio quadro, in doppia profondità si dà 6 dinari.*
>
> *And know that if you dig the canal where it is 4* braccia *deep, you give 4* dinari *per square* braccio*, in double depth you give 6* dinari. *(f. 127r)*

Leonardo carries out the calculation of costs in Milanese *dinari* probably because that was the unit value of reference most familiar to him for hydraulic works of such a scale. It was an estimate of the costs which he maintains in this form because the annotations on these sheets are still entirely personal. If the project had been translated into an official document, the costs would certainly have been converted into Florentine currency.

> *Se fai 4 braccia, e' sono solamente 2 banchi, cioè uno dal fondo del fosso alla superfizie de' labri del fosso, e l'altro da essi labri alla sommità del monte della terra che d'in sulla riva dell'argine si leva.*
>
> *If you make 4 arms, they are only 2 banks, that is, one from the bottom of the ditch to the surface of the laps of the ditch, and the other from them to the top of the pile of earth that rises on the shore. (f. 127r)*

Leonardo divides the ground into layers, or "banks," of four arms in height and considers that the ground excavated for the depth of the canal would have been used for the construction of the embankments.

> *E se fussi di doppia profondità esso argine cres[c]e solo uno banco, cioè braccia 4, che cresce la metà della prima spesa; cioè che dove prima in due banchi si dava dinari 4, in 3 si viene dinari 6, a 2 dinari per banco, essendo il fosso in fondo braccia 16.*
> *Ancora se 'l fosso fussi largo braccia 16 e profondo 4, venendo a 4 soldi per opera[io], dinari 4 milanesi il braccio quadro, il fosso che in fondo sarà braccia 32, verrà dinari 8 il braccio quadro. (f. 127r)*
>
> *And if it were of double depth, it would only grow of one bank, that is 4* braccia*, which grows half of the first expenditure; that is, where 4* dinari *were given first for two banks, for 3 banks is 6* dinari*, 2* dinari *per bank, the ditch being at the bottom 16* braccia.
>
> *Still if the ditch was 16* braccia *wide and 4* braccia *deep, costing 4 soldi per worker, 4 Milanese* dinari *per square* braccio*, the ditch that at the bottom will be 32* braccia*, will coast 8* dinari *per square* braccio. *(f. 127r)*

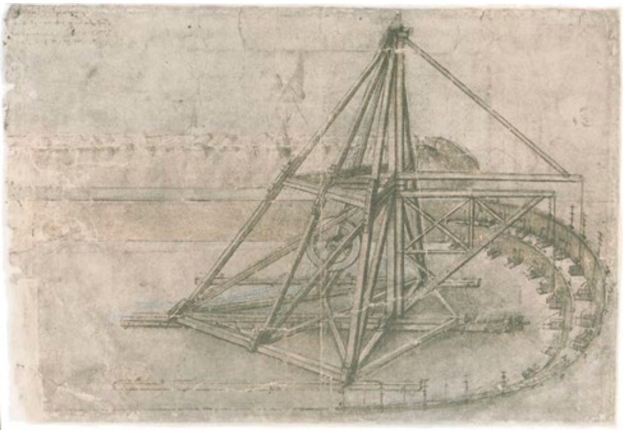

Figure 30. C.A., fol. 4r: Earthmoving machine.

Sheet 126r replicates the cost per worker and suggests the best period for carrying out the work between March and June, when farmers cost less because they are free from work in the fields, the days are longer, and the heat is not excessive.

> *E sappi che questo canale non si po cavare per manco di 4 dinari il braccio [quadro], dando a ciascun operatore 4 soldi il dì, e questo canale si de' fare da mezzo marzo insino a mezzo giugno, perché i villani, sendo fori del loro ordinario esercizio, s'hanno per buono mercato, e dì sono grandi e 'l caldo nolli stanca.*
>
> *And know that this canal cannot be excavated for less than 4* dinari *per square* braccio*, giving each worker 4* soldi *per day, and this canal must be made from mid-March until mid-June, because the villains, being free from their ordinary exercise, they are cheap, and the days are long and the heat does not tire them.*

To reduce labor costs and accelerate excavation times, Leonardo devised specific excavation and earth moving machines (fig. 30). The design commitment that transpires also from the conception of these machines betrays a deep involvement and perhaps the real conviction of being one step away from the official assignment which, however, does not appear to have ever been conferred.

The 126 and 127 sheets of the Codex Atlanticus are usually referred to the Milanese period. Calvi dates them to 1490 while Pedretti proposes a date around

Figure 31. Codex Madrid II, c. 52v-53r: map of the surroundings of Pisa. The place where the deviation of the Arno was carried out is marked as "rotta d'Arno".

1495[17]. Only Heydernreich is pronounced for a later date, referring to the second Florentine period, around 1503[18]. The first two datings are based on critical considerations relating to the style and *ductus* of the writing, and could find support in the cost estimation that Leonardo carries out in Milanese currency. However, as anticipated, Leonardo's estimate could simply refer to a unit value familiar to him, and would not necessarily indicate the place where he made those calculations. To raise doubts about the dating of the Milanese period is the fact that there is no strong motivation to justify the drafting of a project so detailed in economic as well as technological terms. The eventual creative stimulus produced by the frequentation of Luca Fancelli when he was in Milan to deal with the *tiburio* of the cathedral, is not sufficient to explain the level of application found in these sheets. The estimate betrays a feasibility study that implies the presence of a client, or at least the occurrence of circumstances that would have favored a specific interest. There were no such circumstances except after Leonardo's involvement in the Arno deviation project of 1503, a period in which it seems reasonable to trace the resumption of the navigable canal project (fig. 31).

However, the project was not followed. The failure of the deviation of the Arno was presumably the most immediate cause but, perhaps, we should also consider the fact that, in view of the important economic commitment required by the grandeur of the work, lacked the political stability necessary to ensure that such an infrastructure could actually work. Pisa was still out of control and the recent revolt in Arezzo did not play in favor of such an important investment in Valdichiana. For such a project a unitary state was needed that would guarantee political stability and total control over the territory. It is no coincidence that the project was resumed in the middle of the century by Cosimo I de 'Medici, when Tuscany was almost entirely under the rule of the Medici[19]. But even in that case the idea remained only an ambitious desire, a technological dream evidently still too far from the possibility of being realized.

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[17] For Calvi and Pedretti see the bibliographical references at note 1.

[18] Ludwig H. Heydernreich, *Leonardo da Vinci*, New York 1954, pl. 218.

[19] The project is described in a letter of Bartolomeo Concini to Vincenzo Borghini, March 26 1572, in L. Cantini, *Vita di Cosimo de' Medici primo Gran Duca di Toscana*, Firenze 1805, pp. 228, 477-478, 668-669.

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Historical Articles

The Reinvention of the Nitrous Gas Eudiometrical Test in the Context of Dalton's Law on the Multiple Proportions of Combination

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Abstract. Dalton's chemical atomism was inspired by his physical fascination with gases and developed through his chemical investigation. In regard to the latter, Dalton's very first chemical experiments on nitrogen oxides enabled him to identify the first verifiable case of multiple proportions of combination, as well as playing a significant role in the process of establishing the basis for the reinvention of the nitrous gas eudiometer. Nevertheless, the eudiometrical background of Dalton's trials on the oxides of nitrogen is yet to be elucidated. His interest in the nitrous gas test was in principle concerned with the justification of his statement on the multiple combining proportions, rather than with the improvement of the test as a eudiometrical method for verifying the oxygen content in common air. On the whole, after passing through Dalton's hands, the nitrous gas test was returned to eudiometrists as a simpler type of the eudiometrical test than those performed with the latest nitrous gas eudiometers. In 1809, in line with Dalton's suggestions, Gay-Lussac was eventually able to deliver a reshaped version of the nitrous gas eudiometer.

Keywords. Nitrous gas test, Dalton, eudiometry, proportions of combination, Gay-Lussac.

AN OVERVIEW OF THE NITROUS GAS TEST

In a landmark paper, *Observations on Different Kind of Airs*, read in 1772 but published in the following year, Joseph Priestley (1733-1804) proposed a nitrous air (nitrogen monoxide) test to replace the use of mice and birds for checking the goodness (i.e. the respirability) of an air sample.[1] For this test, Priestley was indebted to Stephen Hales' (1677–1761) work *Statical Essays* of 1738.[2] Nevertheless, the chemical phenomenon underpinning the test had already been observed by John Mayow (1640-1679) in 1674, and described by Hales himself in his previous work *Vegetable Staticks* of 1727.[3] The purpose of this development was not only to achieve a greater precision, but also to remove the inconvenience of maintaining a stock of mice in the appropriate conditions.[4] This nitrous air test relied on the contraction in volume that an air sample underwent when mixed with nitrous air.[5]

The relevant reactions taking place in the nitrous air test carried out over water are equilibrium processes that do not occur independently. They are outlined in the following chemical equations:

$2\ NO\ (g) + 2\ O_2\ (g) = 2\ NO_2\ (g)$	Relatively slow and proceeds essentially to completion within minutes.
$2\ NO_2\ (g) = N_2O_4\ (g)$	Rapidly achieve equilibrium.
$NO\ (g) + NO_2\ (g) = 2\ N_2O_3\ (g)$	Rapidly achieve equilibrium.
$N_2O_4\ (g) + H_2O\ (l) = HNO_3\ (aq) + HNO_2\ (aq)$	Fast and irreversible.
$N_2O_3\ (g) + H_2O\ (l) = 2\ HNO_2\ (aq)$	Fast and irreversible.

Additionally, oxygen dissolved in the water can play a role.

The goodness of air was considered to be inversely proportional to the content of phlogiston. Priestley was of the opinion that nitrous air appeared to consist of the nitrous acid vapour combined with an excess of phlogiston. On mixing nitrous and common air, this nitrous acid vapour disengaged from the phlogiston, which united with the acid principle of the common air, while a fixed air that it contained was precipitated out, and the water in which the mixture was made absorbed the acid of the nitrous air. These two latter phenomena caused the contraction in volume of the air mixture.[6]

Indeed, during the last quarter of the eighteenth century, doubts began to be cast on the simple nature of atmospheric air, and the idea that only a part of the common air was breathable started to gain acceptance. Then, in parallel with the hygienist approach to atmospheric air, a more analytical and quantitative methodology to determine the composition of common air was adopted, mainly in regard to the uncertainty about its proportion of respirable or vital air; that is, our oxygen.

Priestley presented the experimental device he conceived for conducting the nitrous air test in the first and second volumes of his work *Experiments and Observations on Different Kinds of Air* (1774-1775, 1776).[7] This experimental device was very simple. It consisted of collecting the common air measures by means of a number of vials of proportional capacities (Figure 1: f, f, f), and a cylindrical tube (g) on which all these measures were engraved in order to indicate where to mix the common and nitrous air.

This experimental device was to become a source of inspiration for investigators such as Marsilio Landriani (1751-1815), Felice Fontana (1730-1805) and, in particular, Jan Ingenhousz (1730-1799). Priestley did not christen his experimental device with any particular name, and it was Landriani who in 1775 coined the term "eudiometer" for his own instrumentalist version of the nitrous air test (Figure 2).[8] Hereafter I will refer to this test as the "nitrous gas test".

From 1778 onwards, the nitrous gas eudiometers had to coexist with different kinds of eudiometers. As experimental devices, all eudiometers were based on the fact that the respirable part of atmospheric air could be extracted from an air sample by the action of a particular substance. These absorbent substances could be solid materials (phosphorus, iron filings with sulphur and potassium sulphide), aqueous solutions (iron sulphate

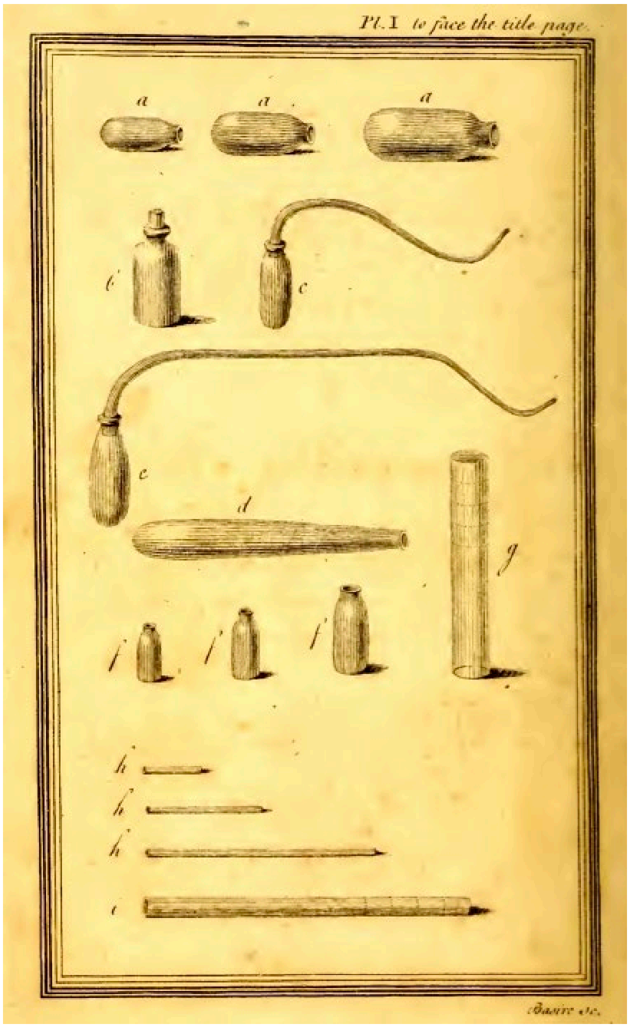

Figure 1. Priestley's glass vials used for eudiometrical measurements. From Joseph Priestley, *Experiments and Observations of Different Kinds of Air* (London, 1776), plate I

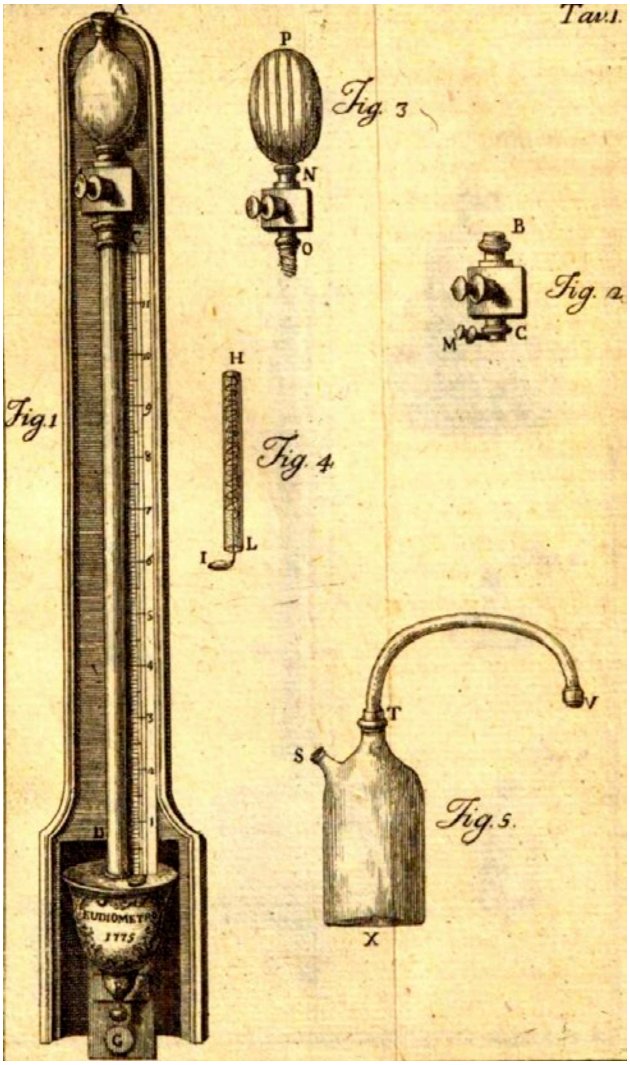

Figure 2. Landriani's eudiometer. From Marsilio Landriani, *Ricerche fisiche intorno alla salubrità dell'aria* (Milano, 1775), plate 1.

impregnated with nitrous gas and alkaline or calcium sulphides) and gaseous substances such as nitrous gas (nitrogen monoxide) and hydrogen, this latter being the basis of Volta's eudiometer (Figure 3).[9] The existence of these competing eudiometers and the difficulties surrounding the procedural standardisation of the nitrous gas eudiometer eclipsed its utility.[10] Nevertheless, the nitrous gas test was far from being dismissed and would mutate into a new version at the beginning of the nineteenth century.

After this overview of the nitrous gas test, it is time to examine John Dalton's involvement in this eudiometrical test.

JOHN DALTON (1766-1844). LAYING THE FOUNDATIONS FOR THE RECONVERSION OF THE NITROUS GAS TEST

The first public description of Dalton's experiments on nitrogen oxides appeared in his paper *Experimental Enquiry into the Proportions of the Several Gases or Elastic Fluids Constituting the Atmosphere*, read on November 12th, 1802, at the Literary and Philosophical Society of Manchester, and which remained unpublished until 1805. Dalton's account of his experiments is commonly regarded as the confirmation of his understanding of multiple proportions in the nitrogen oxides.

Unfortunately, Dalton's notebook, together with many of his papers held in Manchester, were destroyed as the result of an air raid in 1940 during the Second World War. The only surviving references to the notebook are to be found in the work by Roscoe and Harden, *A New View of the Origin of Dalton's Atomic Theory*. In a discussion of Dalton's experimental results on nitrogen oxides, these authors state that the interesting question was not *how* Dalton managed to obtain them, but *when* he obtained them.[11] The chronology of these experiments undoubtedly constitutes a crucial part of the origin and development of Dalton's widely studied chemical atomic theory.[12] Even so, a knowledge of *how* these experimental results were obtained would enable both they and the origin of the atomic theory to be placed in their instrumental and procedural context.

Dalton gave an account of the first clear instance of multiple proportions of combination in the first section of his 1805 paper. This section, entitled *Of the Weight of the Oxygenous and Azotic Atmospheres*, was devoted to assessing different eudiometrical procedures in relation to the composition of common air. Although Dalton had had the opportunity, prior publication, to revise the draft of this paper, which he read in 1802, the eudiometrical context of his early experiments on the oxides of nitrogen nevertheless remained unclear.[13] Notwithstanding, there is no doubt that in the published and debatable version of his 1805 paper, Dalton wished to frame these experiments in a eudiometrical context.

A beginner in chemistry and eudiometry

In order to gain an understanding of Dalton's knowledge in the field of eudiometry, it would first be worthwhile to become acquainted with the extent of his training in chemistry before 1805. During his stay in Kendall (1781-1793), his post as an assistant teacher at a boarding school provided him with access to the vast library of his tutor and friend, the natural philoso-

Figure 3. (Left) A view of the lower part of a copy of the Volta-type eudiometer. (Right) Modern replica of Spallanzani's phosphorus eudiometer exhibited at the Centro Studi Lazzaro Spallanzani. Courtesy of Tempio Voltiano, Musei Civici di Como, Comune di Como and of Centro Studi Lazzaro Spallanzani, Scandiano, photography by the author.

pher John Gough (1757-1825), as well as to the impressive library at the school, where he became familiar with Boyle's and Boerhaave's works. In 1793, he moved to Manchester to teach mathematics and natural philosophy at the New College, but soon found himself obliged to teach chemistry as well. While in Manchester he entered a more challenging scientific world than the one he had known in Kendall, and in 1794 went on to become an elected member of the Manchester Literary and Philosophical Society, of which he became Secretary in 1800 and President in 1817. Dalton's involvement in the activities of this Society and his close friendship with William Henry (1774-1836) considerably extended his scientific knowledge and experience.

It was in Manchester, in early 1796, where Dalton received his first formal education in chemistry thanks to a series of thirty chemical lectures given by Thomas Garnet (1776-1802), who was to become a professor at the Royal Institution in London. After these lectures he felt confident enough in his expertise in chemistry to agree to give some six lectures on chemistry the following summer in Kendall. In 1800, he resigned his teaching position and opened his own Mathematical Academy, where he offered tuition in mathematics, experimental philosophy and chemistry. In March 1803, he informed his brother that in his leisure time he had been very busily engaged in his chemical and philosophical enquiries.[14] It would not be presumptuous to say that prior to 1805 Dalton had had access to the foremost chemistry books and scientific journals, first, in Kendall, in Gough's private library, and then in Manchester in the extensive Chetham's Library as well as in the Society's library, not to mention his own private library.[15]

There exists no published trace of Dalton's involvement in eudiometrical tests before the publication of his 1805 paper on the proportions of the several atmospheric gases. Nevertheless, it seems that Dalton was well acquainted with the current eudiometrical methods after attending the chemical lectures in 1796. Thus, in the sequel to a paper on the constitution of the atmosphere, published in 1837, Dalton affirmed that he had been engaged in the investigation of the proportions of oxygen and nitrogen in mixtures of both gases for more than forty years.[16]

The eudiometrical context of Dalton's law of multiple proportions

Dalton began the first section of this 1805 paper by listing the five eudiometrical tests widely used at that time: nitrous gas, alkaline or calcium sulphides, hydrogen ignition, green sulphate or chloride of iron impregnated with nitrous gas, and phosphorous fast combustion. He then made it clear that he regarded the finding that atmospheric air contained 21% oxygen as an accepted fact, explaining past discrepancies as a misunderstanding of the nature of the different tests and of the circumstances influencing them.

It was nothing unusual for Dalton to focus his attention in the nitrous gas test, given his work on meteorology and mixed gases. While he acknowledged the discredit attaching to the nitrous gas test, he valued it for being not only the most elegant and expeditious of all the existing eudiometrical tests, but also as accurate as any other when properly conducted. It appears that Dalton had not been fully aware that the reliability of the test depended on skilful trained experimenters to conduct it. His intimate friend William Henry had discarded it because the sources of error inherent in the employment of the test had caused him to mistrust the results obtained thereby. Henry's reference to Humboldt's researches on the nitrous gas published in the *Annales de chimie* may have influenced Dalton's experimental design and textual presentation of his enquiries into the combination of nitrous gas with atmospheric oxygen. Humboldt's researches proved useful for demonstrating that the test should be performed over water instead of mercury, as well as the influence on the experimental outcomes of the size of the eudiometrical recipient and the order in which gases were added to it.[17] Dalton began his conclusions by criticising the nitrous gas test in four comments mainly regarding some material and procedural aspects of the test already addressed by Humboldt in his paper:[18]

> *I shall, on this occasion, animadvert upon it [the nitrous gas test]*

In his first comment, Dalton pointed out the need of using nitrous gas that was virtually free of azotic gas (nitrogen), with less than 2-3% at most, and nitrous oxide (dinitrogen monoxide). The remaining comments were devoted to summarising his experiments in the form of two eudiometrical trials.

> *The first trial consisted of adding 100 measures of common air to 36 of nitrous gas (NO in Dalton's terms) in a tube 3 $^1/_{10}$ inches wide and 5 inches long. After waiting for a few minutes, the whole mixture was reduced to 79 or 80 measures, without exhibiting signs of either oxygen or nitrous gas. In the second trial, 100 measures of common air were added to 72 of nitrous gas (twice as many in the first trial) in a wide vessel over water so as to form a thin stratum of air.[19] After an immediate momentary shaking, as before, a residue of 79 or 80 measures of pure azotic gas was found.*
> *Finally, if fewer than 72 measures of nitrous gas had been used, there would have been a residue containing oxygen, but if more, then some residual nitrous gas would have been found.*

At this point, all the foregoing findings led Dalton to state what has been regarded as a key step in the development of his atomistic reasoning; the discovery of multiple combining proportions:[20]

> *The elements of oxygen may combine with a certain portion of nitrous gas, or with twice that portion, but with no intermediate quantity*

In order to account for the diversity of the results obtained with the nitrous gas test, Dalton suggested that nitric acid (NO_2 in Dalton's terms) had been formed in the first trial, and in the second nitrous acid (N_2O_3 in Dalton's terms).[21] However, since both acids could be formed at the same time, one part of the oxygen went to one of nitrous gas, while another part of oxygen went to two others of nitrous gas.[22] Therefore, the quantity of nitrous gas absorbed had to be variable across a range of 36 to 72 parts for 100 parts of common air. Regarding the size of the tube used, he concluded that the wider the tube the quicker the test could be completed, and the more the mixture was exposed to water the greater was the quantity of nitrous acid and the lesser of nitric acid yielded.

Sometime between October and November, 1803, Dalton carried out a series of experiments on the oxides of nitrogen that he reported in the two trials in his paper of 1805. According to Dalton's notebook, nitrous gas and common air should be suddenly mixed in the second trial.[23] In earlier trials, Dalton had calculated the corresponding nitrous gas–oxygen ratio. Actually, this ratio was nothing but the proportion between nitrous gas and oxygen at the point of saturation.

As far as eudiometrical purposes were concerned, Dalton recommended attempting to form either nitric acid (first trial) or nitrous acid (second trial) entirely alone rather than a mixture of both. However, he decided on the first experiment because it appeared to be the most easily and accurately performed. To this end, he recommended the use of a narrow tube, but wide enough to allow nitrous gas to be absorbed by water without the need for any shaking.[24]

> *The test was executed by providing a little more nitrous gas to the oxygen gas than was sufficient to form nitric acid. As soon as the diminution in volume appeared to be complete, the gaseous residue was transferred to another tube. 7/19 of the loss was due to oxygen.[25] This was necessary to prevent the nitric acid, formed and combined with water, from absorbing the remainder of the nitrous gas to form nitrous acid.*

On October 21st, 1803, nearly a year after the reading of the 1802 paper, Dalton read a paper at the Literary and Philosophical Society of Manchester *On the Absorp-*

tion of Gases by Water and Another Liquids, which also remained unpublished until 1805 in the Memoirs of the Society. By that date, therefore, Dalton had already arrived at the conclusion that the rapid mixture of oxygen and nitrous gas over a broad surface of water occasioned a greater diminution in volume than otherwise.[26]

From 1806 onwards, more details emerged about the development of Dalton's nitrous test thanks to the new editions of William Henry's work *An Epitome of Chemistry*. A personal communication to Henry provides the conclusions of Dalton's study regarding the influence of the size of the tube and the manner in which the gases were mixed on determining the proportion of oxygen in an air sample.

> *If pure nitrous gas was admitted to pure oxygen gas in a narrow tube so that the oxygen gas was uppermost, the two gases united very nearly in the proportion 1.7 [First trial]. If, on the other hand, the nitrous was the upper gas, a much smaller quantity of it disappeared [1 oxygen/1.24 nitrous gas]. If nitrous gas was admitted to pure oxygen gas in a wide vessel over water, the whole effect took place immediately and one measure of oxygen united with 3.4 of nitrous gas [Second trial]. To render this rule more intelligible, Dalton gave as an example the case of 100 measures of common air that were delivered to 100 measures of a mixture of nitrous gas with an equal proportion of azotic or hydrogen gas, which after standing for a few minutes in the eudiometer were found to give 144 measures. When this loss of 56 was divided by 2.7, it gave a measure of almost 21 for the oxygen gas present in 100 measures of common air.*[27]

When analysing atmospheric air samples, it was scarcely necessary to dilute the nitrous gas with any other gas prior to its use. The recommendation was to wait for a certain period of time - 10 minutes, for instance - before noting the diminution in volume, without the need to transfer the residue to another vessel. If the gas sample under examination contained much more oxygen than in atmospheric air, then it was appropriate to dilute the nitrous gas with an equal volume of hydrogen, in which case the narrower the tube the more accurate would be the result.

As regards the experimental equipment, two graduated tubes with funnel-shaped extremities (Figure 4: **1** and **2**) were employed, each from 3 to 4 tenths of an inch in diameter and 8 or 9 inches long.[28]

By 1806, Henry had changed his mind about the employment of nitrous gas for determining the purity of air. He came to prefer Dalton's method to all the others because of its facility, quickness and accuracy, at least for gaseous mixtures of a very similar standard to the atmosphere. Notwithstanding this constraint, the method was valued because it could be applied to determining the proportion of oxygen in some gaseous mixtures to which other eudiometrical tests were not applicable, such as mixtures of hydrocarbons and oxygen gases. The application of nitrous gas to eudiometrical purposes would still admit of further accuracy when used by Gay-Lussac.[29]

GAY-LUSSAC'S STUDY ON THE OXIDES OF NITROGEN. RESHAPING THE NITROUS GAS EUDIOMETER

The combinations of nitrous gas with oxygen constituted one of the issues in chemistry about which little agreement existed at the beginning of the nineteenth century. On March 13th, 1809, Gay-Lussac read the *Mémoire sur la vapeur nitreuse et sur le gaz nitreux considére comme moyen eudiométrique* at the Institut de France, where he reported on his research work, the aim of which was not only to establish the theory of the formation of nitrous and nitric acids using nitrous gas and oxygen, but also the transformation of the nitrous gas eudiometer into an instrument of accuracy.

Joseph-Louis Gay-Lussac (1778-1850) had been appointed to the post of demonstrator (*répétiteur*) at the École Polytechnique in September 1804. He had attended the chemistry lectures given at this same institution by Antoine-François Fourcroy (1735-1809) and Louis-

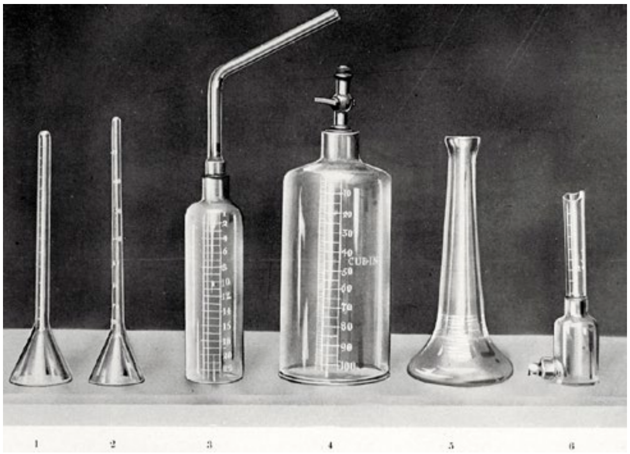

Figure 4. Apparatus that belonged to Dalton.[29] **1**, **2**. Glass funnels with long graduated stems closed at the ends used by Dalton as eudiometrical tubes. **3**. Graduated bell jar with bent tube attached for collecting and measuring gases. **4**. Graduated bell jar with brass cap and stopcock for measuring gases. **5**. Conical glass vessel containing mercury. **6**. A fragment of Hope's eudiometer. From *Memoirs and Proceedings of the Manchester Literary & Philosophical Society*, 1904, Vol. 48 (No. 22), plate 2.

Nicolas Vauquelin (1763-1829) in the first year, by Jean-Antoine Chaptal (1756-1832) in the second year, and by Louis-Bernard Guyton de Morveau (1737-1816) and Claude-Louis Berthollet (1748-1822) in the final year. All were luminaries of French chemistry in the late eighteenth century. Gay-Lussac had the good fortune to be recruited for the Arcueil group by Berthollet, who eventually became the supervisor of his scientific career. His volumetric approach to matter, i.e. his concern with gases, volatile liquids and volumes rather than condensed matter and weights, was largely due to the influence of Berthollet and Pierre-Simon Laplace (1749-1827), the patrons of the Arcueil group.[30]

In his landmark paper of 1808 on the law of combining volumes of gases, Gay-Lussac had ascertained that the nitrous gas (nitrogen monoxide) was composed of equal parts in volume of oxygen and nitrogen.[31] In other words, 100 parts of oxygen and 100 of nitrogen produced 200 parts of nitrous gas without any diminution in volume. He also recalled that nitric acid (dinitrogen pentoxide) was composed of 100 parts of nitrogen and 200 of oxygen. Nitric acid could therefore be regarded as composed of 100 parts of oxygen and 200 of nitrous gas, because the latter contained as much oxygen as nitrogen without any diminution in volume. He also found that 100 parts of nitrogen required 50 parts of oxygen to form nitrous oxide (dinitrogen monoxide).

To obtain the nitric or the nitrous (nitrogen dioxide) acids by combining nitrous gas with oxygen was not simply a matter of first introducing one gas and then the other, but of which gas predominated in the mixture. When oxygen and nitrous gas were mixed in the appropriate ratios, the absorption of the vapour formed thereby was prompt and complete. Thus, by using a narrow tube, nitric acid containing 100 parts of oxygen and 200 of nitrous gas was obtained. However, when both gases were mixed in a slightly larger tube, absorption did not vary significantly, providing that no shaking took place, because water would dissolve the nitrous gas. In this case, the acid obtained was nitrous acid gas. On the other hand, if either of the two gases predominated to excess, the nitrous gas was prevented from coming into contact with the water and dissolving easily. Thus, with an excessive amount of oxygen, nitric acid was produced, while on the other hand an excessive amount of nitrous gas produced nitrous acid.[32]

Despite the discrepancy between Gay-Lussac's results and Dalton's on the composition of the oxides of nitrogen,[33] he did not refrain from stating his conclusions on the influence of the size of the tube in which the gases combined - a key factor in the design of his eudiometrical device. Gay-Lussac's volumetric approach to matter was not the only influence of his mentor Berthollet, whose experience with procedures in large scale chemical productions was probably decisive for his view that chemical phenomena were to a large extent conditioned by their surrounding circumstances. From this perspective, the fact that Gay-Lussac gave so much importance to the size of the reaction tube and its effect on the outcome of the combination of gases may be better understood.

Since the aim of eudiometrical analysis was to remove all the oxygen in an air sample, an excess of nitrous gas was needed in order to obtain a volume reduction four times larger than the volume of oxygen in the sample. Thus, possible errors corresponded to only a quarter of the oxygen, and since it was not possible to err by four degrees, the oxygen content in a gas mixture could be estimated by much less than one-hundredth. The only precautions to be taken were to avoid shaking the mixture and to ensure that nitrous gas was always predominant without too much excess, since the more it was absorbed the less it would be mixed. Even in this case, however, error would never reach a hundredth part of oxygen. In addition to these precautions, two sources of error also had to be taken into account. First of all, if the gases were mixed in a very narrow tube, nitrous acid would scarcely be absorbed by water because of the lack of contact, which would necessitate shaking, in which case nitrous gas would also be absorbed. It was for this reason that by mixing 100 parts of common air with 100 parts of nitrous gas very variable absorptions were obtained. Secondly, the question of whether to introduce the nitrous gas into the tube before or after the air sample was also important, because if it was introduced first, both nitrous and nitric acids might be formed.

To avoid these two shortcomings Gay-Lussac conducted a nitrous gas test that employed an apparatus very similar to that used by Humboldt for assessing carbonic acid in a gas mixture or for analysing common air by means of nitrous gas and chlorine.[34] This test was performed in the following manner (Figure 5):[35]

> *The sample of the air to be analysed was collected in the measure (N), equivalent to 100 parts of the tube (K) graduated in 300 parts. The air sample was then introduced into this tube (K) with the copper funnel (M) coupled to the ferrule (HI) of the tube. The number of parts of the air sample contained in the tube was noted. Afterwards, the air sample was transferred to a wide glass vessel (A) with a flat bottom, containing about 250 parts and closed by a copper component (BFGC). This component consisted of a slightly funnelled part (BC), a funnel (FG) and a sleeve (DE) abraded with emery so that the ferrule (HI) of the tube (K) fitted exactly. The nitrous gas was measured in*

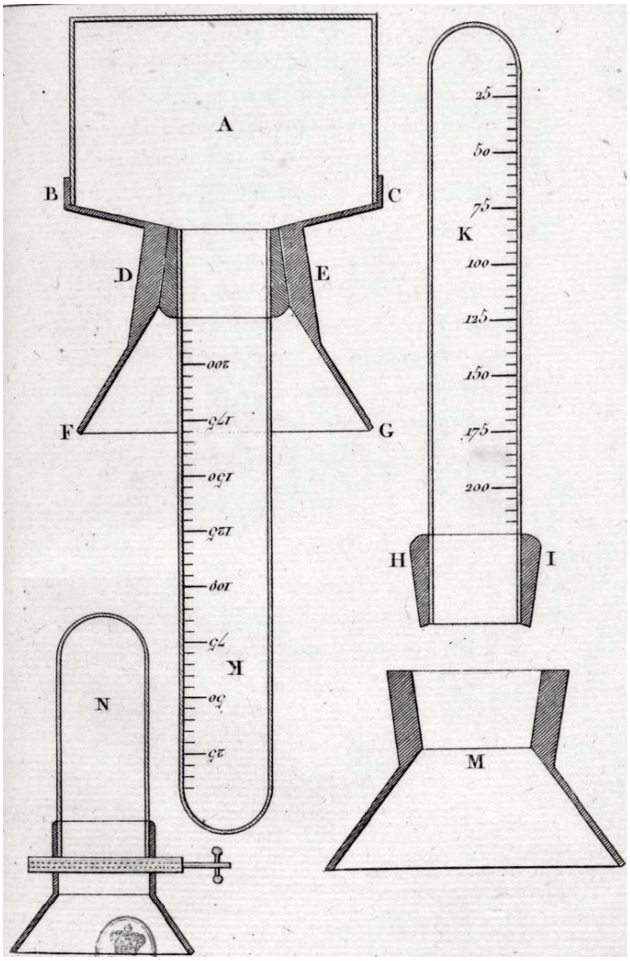

Figure 5. Gay-Lussac's nitrous gas eudiometer. From *Mémoires de physique et de chimie de la Société d'Arcueil,* 1809, Vol. 2, plate 2.

> *the same way and rapidly mixed with the air sample by coupling the tube to the sleeve (DE) without agitating. A red vapour appeared immediately and then disappeared very quickly. After half a minute, or one minute at most, absorption could be regarded as complete. The device was then turned upside down and the residual gas ascended in the tube. After that, the tube (K) was removed from the vessel (A) to restore the pressure equilibrium and the residue was assessed. The total absorption divided by 4 gave the quantity of oxygen.*

Gay-Lussac reported having performed many varied analyses, always finding a perfect agreement among them. In 1818, William Henry still regarded Gay-Lussac's application of nitrous gas to eudiometrical purposes as an accurate procedure, provided certain precautions suggested by his theoretical views of the constitution of nitrogen oxides were taken into account.[36]

FINAL REMARKS

The sources of Dalton's criticisms of the nitrous gas test were very precise: the influence of the size of the eudiometrical vessel and the shaking of the gas mixture in its volume reduction. He opted for the use of a narrow tube that allowed nitrous gas to be absorbed by water without shaking in an attempt to obtain nitric instead of nitrous acid. Nevertheless, he was aware that a greater reduction in volume was obtained if the test was performed over a broad surface of water. His assumptions about these two factors were in principle concerned with the justification of his statement on the multiple combining proportions, rather than with the improvement of the nitrous gas test, and he was in fact obliged to conduct the test in vessels of different sizes and with variable procedures until he obtained the results he was aiming for.

From 1806 onwards, Dalton contributed material as well procedural improvements to the nitrous gas test employed as a eudiometrical method. Thus, in addition to recommending the use of narrow tubes, he emphasised the advantage of adding the nitrous gas once the oxygen gas was already in the tube and not the other way around. Arguably, the nitrous gas test that in the hands of Dalton had evolved from a eudiometrical method to an iconic case of multiple combining proportions was returned to eudiometrists in a simpler and more trustworthy version of the eudiometrical test than those performed with the latest nitrous air eudiometers. In a certain sense, it was as if Priestley's conception of the nitrous air test, characterised by simplicity of materials, apparatus and experimental procedures, had won out in the end.

Dalton's investigations on the nitrous gas test engendered further developments in 1809 at the hands of Gay-Lussac, who had already begun his research work on eudiometry some years earlier. He did not agree with Dalton's experimental results on the proportions of combination of nitrous gas with oxygen, mainly because these proportions did not match his law of combining volumes. However, this discrepancy proved to be no obstacle to Gay-Lussac's acceptance of Dalton's conclusion on the influence of the size of eudiometrical recipients on the experimental outcomes. His own researches on the oxides of nitrogen, together with Dalton's recommendations on the size of the recipients, guided him in the reshaping of the nitrous gas eudiometer that culminated in a more definitive version of this type of instrument.

ACKNOWLEGMENT

The author wishes to acknowledge the Vernon Press for its permission to reproduce a number of excerpts from the author's book (see note 9).

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4. The expression 'mouse-free route' encapsulates the meaning of this replacement. T.H. Levere in *Instruments and Experimentation in the History of Chemistry* (Eds.: L.H. Holmes, T.H. Levere), The MIT Press, Cambridge, MA and London, **2000**, 105, p. 110.
5. Upon contact of NO with atmospheric oxygen, a brownish gas [NO_2] forms immediately and the color dissipates within a few minutes as NO_2 dimerises to N_2O_4 and completely and irreversibly dissolves in water, giving a mixture of HNO_3 and HNO_2. Simultaneously, NO and NO_2 react to form N_2O_3, which also dissolves in water to give additional HNO_2. Consequently, a contraction in volume of the gas mixture is observed. In stoichiometric ideal conditions the global process would be: $6\ NO\ (g) + 2\ O_2\ (g) + 3\ H_2O\ (l) = 5\ HNO_2\ (aq) + HNO_3\ (aq)$. Therefore, the only residual gas with a common air sample in such conditions would be nitrogen. M. C. Usselman, D.G. Leaist, K. D. Watson, *ChemPhysChem*, **2008**, *9*, 106, p. 107.
6. J. Priestley, *Experiments and Observations Relating to various Branches of Natural Philosophy, with a Continuation of the Observations on Air*, J. Johnson, Birmingham, **1779**, p. 69. Chemists believed that phlogiston was an intangible fluid released in combustion that was impossible to handle. Atmospheric air was believed to consist basically of a mixture of phlogisticated or mephitic air (later called nitrogen) and dephlogisticated or vital air (later called oxygen). With regard to animal respiration, the prevailing belief was that expired air conveyed the phlogiston released from the lungs during breathing and evacuated it from the body. Phlogisticated air (i.e. saturated with phlogiston) was consequently unable to absorb more phlogiston and would not be appropriate for breathing; that is, it would be unhealthy or mephitic air. On the other hand, dephlogisticated air was deprived of more than its normal allocation of phlogiston, and therefore was more wholesome. In other words, the healthier an air the less phlogiston it contained.
7. J. Priestley, 1775, *Experiments and Observations of Different Kinds of Air*, J. Johnson, London, **1775**, pp. 20-21, 110-112.
8. This term is derived from two Greek words. The first part of the term (εὔδιος) means "clear or mild weather", but also with the implication of good air, because (διος) - stemming from Zeus - can mean "weather" or "air". The second part of the term (μέτρο) means "measure". M. Landriani, *Ricerche fisiche intorno alla salubrità dell'aria*, s.n., Milano, **1775**, pp. 3, 6.
9. To explore and comprehend how eudiometers work, the materials used in making them and the reagents employed in each eudiometrical test, all with special attention paid to the experimental procedures involved over the course of the test, constitute the main aims of the author's book. P. Grapí, *Inspiring Air. A history of air-related science*, Vernon Press, Wilmington, DE, **2019**. To understand eudiometers, it is essential to stress the interplay between the instruments themselves and their contextual environment and, in this sense, it is equally indispensable to emphasise that eudiometers took on a life of their own in many different contexts; human and animal health, quantification, gas analysis, chemical theory, medical therapeutics, plant and animal physiology, atmospheric composition, chemical compound composition, gas lighting, chemical revolution, experimental demonstration and the chemical industry.
10. Progress in the nitrous air test and eudiometer was mainly reflected in their use in research experiments and in the search to obtain a standard test procedure in order to arrive at a reliable test. The reliability of the test depended on many intrinsic and extrinsic factors, which were not always easy to define and control. However, the factors that proved to have the most significant effect were: the establishment of the test endpoint; the determination of the saturation ratio of nitrous and dephlogisticated air (oxygen); the dosing of the air samples; the time spent on particular operations; the water source used, and the

quality of the nitrous air as a reagent. Standardising the nitrous air test to make it more reliable involved working out an operating protocol that demanded skilful experimenters with the appropriate training. The issue was not that skilful experimenters such as Ingenhousz were able to execute that protocol successfully, but rather that novices in eudiometry would also be capable of performing it.

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19. Dalton gave no details of the size of this wide vessel.
20. A. J. Rocke, **1984**, 45, note 28. See note 12.
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22. The first trial yielded the most oxygenated nitric acid [$O + NO = NO_2$, in Dalton's terms], while the second yielded the least oxygenated nitrous acid [$O + 2\ NO = N_2O_3$, in Dalton's terms]. The latter reaction took place rapidly in the thin gas stratum of the wide vessel, but slow enough in the narrow tube to enable nitric acid to be the sole product (Usselman *et al.*, 107. See note 5).
23. H. E. Roscoe, A. Harden, **1896**, p. 35. See note 11.
24. J. Dalton, **1805a**, pp. 247-251. See note 18.
25. The 136 [100 +36] parts of the mixture gave a residue of 79 parts in the first trial (assuming 21% of oxygen in common air). Therefore, the loss was 57 [136-79] and 7/19 [21/57] of the diminution was oxygen.
26. J. Dalton, *Memoirs of the Literary and Philosophical Society of Manchester*. **1805b**, 2nd series, *1*, 271, pp. 274-275, note. In this way, nitrous acid was formed, whereas when water was not present nitric acid was obtained, which required just half the quantity of nitrous gas. The replications of Dalton's experiments reported in his 1805 paper proved that in the narrow tube conditions (first trial) the greatest diminution in volume occurred at a ratio of 1.7, as Dalton reported. Nevertheless, the contraction in volume reported at a ratio of 3.4 (second trial) was significantly different from the replicated value. All in all, it is necessary to recognize that the influence of dissolved oxygen in water could make the second trial results plausible. The lack of published details on the exact size of the reaction recipients rendered a meaningful replication of the second trial impossible. (Usselman *et al.*, **2008**, pp. 108-109. See note 5)
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33. Gay-Lussac's results on the composition of the oxides of nitrogen did not agree with those published by Dalton in 1805. According to Dalton, 21 parts of oxy-

gen could unite with 36 of nitrous gas or with twice 36, i.e. 72 parts. In other words, 100 parts of oxygen united with 171.4 or 342.8 parts of nitrous gas. In Gay-Lussac's opinion, these results were inaccurate because the first ratio of nitrous gas was too small and the second was too large, in addition to which the two gases did not combine in simple ratios. It should be remembered that Gay-Lussac's law of combining volumes established that gases combined in very simple ratios, and that the volume reduction they underwent on combination also had a simple ratio to their volume, or at least to the volume of one of them. (Gay-Lussac, **1809b**, p. 244. See note 32)

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Historical Articles

Astatine – The Elusive One

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Abstract. Astatine has proven, since its isolation by Corson, Mackenzie and Segre in 1940 to be an element with a fascinating history with respect to its discovery, confirmation and naming. It has also proven to have an interesting set of physical and chemical properties as well as isotopes of significant note. This element also has several applications of note as well as a captivating chemistry and the question whether it is or is not diatomic.

Keywords. Astatine, discovery/naming, properties of the element, applications of the element, chemistry of the element.

INTRODUCTION

Since 1922, a search for Element 85 [eka-iodine as per Dmitri Mendeleev's terminology] was underway involving the efforts of many scientists world-wide (1). Claims to the discovery [and confirmation] of the element were made by many individuals until the isolation of the element by Dale Corson, Kenneth MacKenzie and Emilio Segrè.[1] Significant discussion about the element's name also occurs in this paper. In addition, this paper also notes selected physical and chemical properties of astatine as well as its many known isotopes. An introduction to the applications of astatine follows and the chemistry of the element is then explored with a final examination made of whether or not astatine is diatomic.

DISCOVERY AND NAMING

Early Efforts

Reports of the search for element 85, termed eka-iodine by Mendeleev, go back to the year 1922.[1] In that year, Frederick Loring, working with numerical analysis, was led to believe that the element either did not exist or existed in very minute quantities.[2,3] A few years later, in X-ray experiments looking for element 87, he and his co-worker John Gerald Frederick Druce

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[1] A picture announcing the discovery of astatine is seen in Figure 1. This image is from www.diarystore.com.

Figure 1. An announcement of the discovery of the element astatine.

reported promising results suggesting the presence of both element 87 and element 85.[4] Many other individuals worked trying to isolate and characterize eka-iodine without noteworthy success during the 1920's and 1930's in the UK, Germany, British India, Denmark, France and Switzerland.

As the 1930's drew to a close, Horia Hulubei and Yvette Cauchois reported X-ray wavelengths for three spectral lines of eka-iodine in the emission spectra of radon that were closely related to Henry Moseley's predicted positions.[1,5] This was followed up by Manuel Valadares, who in the middle of World War II in Italy, repeated Hulubei's work with a large sample of Rn and saw new characteristic lines of element 85.[6]

In the time period 1942-1944, Berta Karlik and Traude Bernert noted the detection of α particles and element 85 with a mass of 218. Karlik and Bernert were also involved in the discovery of naturally occuring astatine in 1942.[6-13] Even though these [and other] aforementioned scientists did stellar work, they were publishing their research in journals that were not well known. A good number of them also did not have available journal articles from the United States due to, in large part, World War II.

Element 85 Discovery

In 1939 with construction nearing completion on the Radiation Laboratory at the University of California at Berkeley, Segrè postulated that adding an α particle at 32 MeV to Bi-209 would produce an element with atomic number 85.[14] This work was done by Robert Cornog and Corson who, with the assistance of MacKenzie, saw a number of forms of radiation, including the emission of α, γ, and X-rays and also low energy electrons all having a half-life of about 7.5 hours.[15-19]

This group was also able to perform chemical analyses on the "material" and track its radioactivity. As a result, Corson, MacKenzie and Segrè, in large part, are regarded as the actual discoverers of Element 85. A great deal more is written about the search to find this element in an excellent article written by Brett Thornton and Shawn Burdette.[1]

Confirmation of Discovery

Even with the announcement of the discovery of astatine in 1940, confirmation was still needed. This was done by Joseph Hamilton and Mayo Soley who put a minimum amount of the new element [with a half-life of approximately 7.5 hours prepared according to the method of Corson, MacKenzie and Segrè] into the food of a guinea pig. Given that eka-iodine lay directly beneath iodine in the periodic table, it was logical to assume that this newly found element would have similar properties to those of iodine. After several hours of digestion, the iodine-craving thyroid gland of the guinea pig had filtered and concentrated this new element. Therefore, confirmation of the discovery of this new element was, in part, forever ascribed to the digestive system and thyroid gland of a guinea pig.[20,21]

Naming the element

From the initial tentative claim of the discovery of eka-iodine in 1925 by Loring to the actual discovery of the element in 1940 by Corson, MacKenzie and Segrè, a variety of names were proposed for this new element. In 1931, Fred Allison used a later discredited magneto-optic method to attempt to discover eka-iodine at the Alabama Polytechnic Institute [now known as Auburn University]. Using this method, he tested sea water, hydrohalic acids, apatite and Brazilian monazite sand; a material that was a source of rare earth minerals.[22]

In work reported in 1932, he suggested the name Alabamine (Ab later changing to Am) to honor the state where the work was done.[22] Allison also described, in his paper, chemical tests that unfortunately depended on the magneto-optic method. This method, and Allison's claim to have discovered Alabamine, were shown by Herbert MacPherson to be due to imperfections in Allison's equipment.[23] Though Alabamine was no more, its name and symbol stayed in textbooks and reference works until 1947; in addition the name Alabamine, surprisingly and Allison, as its discoverer, were still listed in the 1991 *Concise Columbia Encylopedia*.[5]

In 1937, an Indian chemist named De read about Allison's efforts and proceeded to study Travancore monazite sand which he believed to contain a significant amount of eka-iodine.[1] After performing a series of chemical tests on the monazite, De noted the presence of a black, sublimable substance that he identified as eka-iodine; he named it Dakin likely in honor of Dacca [now known as Dhaka, the capital of Bangladesh].[24,25]

Hulubei and Cauchois, in 1939, were examining the radioactivity of radon in the hope of seeing eka-iodine. In 1936 they had observed a line that corresponded with where the K_{a1} line for eka-iodine was expected. In 1939, they reported two further X-ray lines that were consistent with predictions from Moseley's law and the presence of eka-iodine and Hulubei announced the discovery of the element. This new data came about from experiments that used higher resolutions than their 1936 work and thus led to enhanced confidence that they had discovered eka-iodine.[14]

In 1944 Hulubei wrote up his work and that of others who had been looking for this new element. This summary included a description of six X-ray lines that were thought to be due to natural radioactive decay. He suggested, as a name, "dor" which was taken from Romanian word for "longing" and given that the world was at war and "longing for peace".

Unfortunately, there were many reasons why Hulubei and Cauchois did not receive due credit for their independent discovery of element 85. Reasons for this omision were: the statement of Karlik and others that Hulubei and Cauchois's sample size was too small and that there were interferences from other elements in the spectra of Hulubei and Cauchois; other work on Element 85 had been refuted even though Hulubei and Cauchois's work had not been refuted; wartime scientific communications were generally poor, Hulubei had mistakenly claimed discovery of element 87 and that their work was rejected by Paneth in 1947 who noted that the work of Hulubei and Cauchois did not have sufficient means to characterize discovery of element 85.[1] In addition, Hulubei's discovery only received experimental confirmation from the work of Valadares in Italy; the one and only country outside of France that did so confirm Hulubei's work.

An additional significant claim of discovery of element 85 came from the work of the Swiss physicist Walter Minder.[26] In 1940 he said he saw an extremely weak β decay of radium. In this work, a couple of ionization chambers were attached to an electrometer. Chemical tests confimed, in Minder's opinion, a new element which he named helvetium with the symbol Hv. In 1942 Minder repeated his work and announced the "discovery" [with his British colleague Alice Leigh-Smith] of anglohelvetium. However, this work was not reproducible and discussion of it faded rapidly into obscurity.

As a result, credit for discovering eka-iodine went to the team of Corson, MacKenzie and Segrè and not to Hulubei and Cauchois. Now with the definitive discovery of element 85, a name had to be chosen. Given that this element is so rare, only having been discovered as naturally occurring by Karlik and Bernert in 1942,[9,13] and elusive as far as its discovery was so concerned, the Greek word *astatos* meaning unstable seemed appropriate.[27]

Element 85 now had a name - Astatine!

In closing this section, it is significant to note the total amount of naturally occurring astatine on planet Earth might be as little as a few hundred milligrams to, at a maximum, perhaps 30 grams.[27] This amount of astatine is soley due to the decay of thorium and uranium present in the Earth's crust.[28] Thus, astatine is the rarest naturally occuring element in the periodic table.[20]

DISCOVERY/CONFIRMATION OF ASTATINE AND SCIENTIST NATIONALITY

With any new scientific discovery, there is of course great joy, satisfaction and a sense of accomplishment. Though these feelings were likely true for Corson, MacKenzie and Segrè, the same was not true for others involved in the search for element 85. This story showed that nationalistic [and even regional as seen with the work of Allison] prejudices strongly influenced who was given credit for the discovery/confirmation of this member of the periodic table.

PROPERTIES

With the discovery, confirmation and naming done for the element astatine, characterization was next. Some of this work is reported in the NUBASE evaluation of nuclear and decay properties as compiled from archived information by Audi et al.[29] Work was reported on mass excess, half-life, probability of alpha decay and electron capture of the element. In addition, reports on astatine in nature came from the efforts of Karlik and Bernert who studied the α-activity from the thorium decay series[9,13] and also found a small number of previously unreported 8.4 MeV α-particles related to a short-lived

At-215 isotope.[11] One other significant work on naturally occurring astatine showed that At-219 was present in U-235 ores in minute amounts.[30,31]

Astatine is quite difficult to work with – if one were to have a visible piece of the element, the element would immediately be vaporized due to heat generated by radioactive decay. It has not yet been determined if this issue in exploring the element can be overcome by appropriate cooling.[32] As a result, most physical properties of astatine are not known with any degree of certainty. It is also interesting that astatine may only be found in uranium 235 ores, nuclear facilities and/or research laboratories. Otherwise, the element is undetectable.

Physical Properties

Some of the physical properties of astatine are seen in Table 1.[33,34] Based on the colors of the halogen group elements it is likely that a hypothetical solid astatine may be very dark in color, perhaps even black.[32] Of all the natural halogens, astatine is the least chemically reactive and may even exhibit metallic properties – perhaps even being a superconductor.[35,36] A good number of these tabulated properties are theoretical.

Table 1. Selected Physical Properties of Astatine.

Atomic number	*85*
Atomic mass	*~210 grams/mole*
State at 20°C	*Solid (predicted)*
Density (estimated)	*6.35 – 6.50g/cm^3*
Boiling point	*230-233°C (estimation)*
Heat of fusion	*~ 6 kJ/mol (estimation)*
Electron configuration	[Xe] $4f^{14}5d^{10}6s^2 6p^5$
Covalent radius	*150 pm*
Van Der Waals radius	*202 pm*
Crystal structure	*fcc (predicted)*

Chemical Properties

Astatine has many possible oxidation states [-1, 1, 3, 5 and 7] with -1 and 1 being most common.[33] Only francium is less stable than astatine out of the first 101 elements in the periodic table. When astatine undergoes radioactive decay, the element decays into Bi, Po, Rn or other isotopes of astatine. Astatine has an electronegativity of 2.2 [on the revised Pauling scale] and a first ionization energy of 899 kJ/mol. The chemistry of astatine, difficult due to its short half-life, is "clouded by the extremely low concentrations at which astatine experiments have been conducted, and the possibility of reactions with impurities, walls and filters, or radioactivity by-products, and other unwanted nano-scale interactions".[35]

Of interest also is the fact that astatine is the least reactive of the halogens. In order to ensure a reaction, dilute solutions of astatine are mixed together with larger amounts of iodine. Iodine, acting as a carrier, ensures that there is sufficient material for such techniques as filtration and precipitation to be properly conducted.[37-39]

ISOTOPES

Currently, astatine has 39 known isotopes with atomic masses ranging from 191 to 229. According to theoretical modeling, another 37 isotopes might exist.[30,40] Out of all these possible isotopes, not one is likely to be stable or even long-lived. The most stable isotope, known to date, is At-210 and it has a half-life of 8.1 hours. This isotope has as its primary decay mode β^+ which gives the α emitter Po-210.

Of all the possible isotopes, only five have half-lives greater than one hour and they are: At-207 (1.80 hr), At-208 (1.63 hr), At-209 (5.41 hr), At-210 (8.1 hr) and At-211 (7.21 hr). The shortest lived isotope found to date is At-213 has a half-life of 125 nanoseconds (29); this isotope undergoes α decay to the extremely long-lived Bi-209 (half-life of 1.9×10^{19} yr).

INTRODUCTION TO APPLICATIONS OF ASTATINE

With the discovery and initial characterization efforts on astatine somewhat complete, significant interest turned to potential applications of the element. Given astatine's similar behavior to iodine in concentrating in the thyroid gland as found by Hamilton and Soley,[21] medical applications of the element and its isotopes became interesting. Later work showed that fairly small amounts of astatine could lead to significant changes of structure in the parathyroid gland and other peritrachial tissues.[41]

Further investigation of this take-up of astatine by bodily tissues was then made in guinea pigs, rats and monkeys; in fact the treatment of hyperthyroidism in human beings by astatine was proposed. This was substantiated by the results of tracer experiments where it was found that human beings accumulated astatine in their thyroid glands. Benefits of this "tendency" were noted to have to be weighed against hazards from exposure to the radiation of astatine.

Actual Applicatons of Astatine

With the half-life of even the longest-lived astatine isotope only about 8 hours, finding any real world applications have been quite difficult, to say the least. At-210 decays quite readily into Po-210 which is notorious; it was used to kill Alexander Litvinenko in November 2006.[42] Fortunately though, At-211 is an isotope that has seen some use in nuclear medicine and may also be helpful in the future.

Much like I-131, At-211 does not emit high-energy β-particles, but instead emits α particles and it is known as one of the few α-emitting radionuclides considered for medical use;[43] most other α-emitters cause severe damage to internal organs. A typical α-particle released by At-211 may travel only 70 mm through bodily tissues; an average β-particle emitted by I-131 can travel more than 25 times farther in bodily tissues.[44] Given this short path length of α-particles in the human body and their high energy (6.0 to 7.5 MeV), such particles are very effective at killing cells bound by carrier-targeting agents.[45]

This short range effectiveness of At-211 can possibly reduce risk of exposure to other bodily tissues and perhaps then be used throughout the human body in treating cancer. This short half-life of At-211 and lesser penetrating ability is a definite advantage in situations where the "tumor burden is low and/or malignant cell populations are located in close proximity to essential normal tissues".[46] Significant morbidity in cell culture models of cancers in humans have been achieved with from one to ten At-211 atoms bound per cell.[47]

There is though a problem with the low stability of astatine to aromatic carbon bonds i*n vivo*.[48] Developing labelling reagents with more stable aromatic astatine-boron bonds has helped in lessening this difficulty and it is possible that further study with other elements may lead to additional scientific advances.

Astatine-based radiopharmaceuticals have seen a variety of obstacles during the 20th and 21st centuries. World War II brought such research to a halt for at least a decade. Experiments noted that a cancer-selective carrier would need to be developed and it was not until the 1970's that monoclonal antibodies became available for this purpose. Given that astatine tends to become detached from its compounds, is toxic and is also retained in the body [preferentially accumulating in the thyroid gland, lungs and spleen].[47,48] At needs to stay attached to its host molecule. Mitigating the effects of astatine induced radiolysis of labelling chemistry and carrier molecules is another area needing additional work.

CHEMISTRY OF THE ELEMENT

The chemistry of astatine is typically done using masses of 10^{-13} to 10^{-8} grams of the element[49] or at extremely low concentrations. Unfortunately, this low-level method allows reactions with impurities, walls, filters and even radioactive byproducts.[35] A good number of astatine's properties have been observed in very dilute solutions typically at concentrations of less than 1×10^{-10} mol/L. Even though "Astatine … [is] miserable to make and hell to work with," as noted by Patricia Wallace Durbin,[50] it does undergo a variety of chemical reactions. The element has the ability to form compounds with metals; combine with hydrogen; interact with boron and carbon; react with oxygen and other chalcogens and also form compounds with chlorine, bromine and iodine.

Though there are only a few compounds of astatine with metals, astatides incorporating sodium, magnesium, palladium, silver, thallium and lead have been formed.[51,52] Given the extraordinarily limited amount of available astatine, estimations, by extrapolation, of the characteristics of AgAt and NaAt have been made based on other metal halides.[53]

Astatine also exhibits chemistry with boron and carbon. A variety of boron cage compounds have been made with At-B bonds stronger than At-C bonds.[51,54] The compounds carbon tetraastatide (CAt_4) and astatobenzene (C_6H_5At) have been prepared.[51] Astatobenzene (C_6H_5At) can also be oxidized to $C_6H_5AtCl_2$ by exposure to Cl_2. This chlorinated compound can then be treated with a basic hypochlorite solution to give $C_6H_5AtO_2$.[55] A perchlorate of astatine has also been prepared, $[At(C_5H_5N)_2][ClO_4]$ where the astatine is bonded to each nitrogen atom in the two rings of pyridine.[56]

Reactions of astatine also occur with oxygen and other chalcogens. With oxygen, there is evidence to support the existence of AtO^-, AtO_2^- and AtO^+ in aqueous solution.[57,58] An AtO_3^- ion can be obtained by the oxidation of astatine with KOCl in a solution of KOH.[59,60] Further chemistry of this AtO_3^- species has seen the formation of $La(AtO_3)_3$ through the oxidation of astatine in a hot $Na_2S_2O_8$ (sodium peroxodisulfate) solution.[44] The AtO_4^- ion also exists; further oxidation of AtO_3^- in a hot, basic solution of XeF_2 so gives this anion.[61] Substituting periodate (in either neutral or basic media) will also yield the AtO_4^- ion – which is only stable in neutral or basic media.[62,63]

Astatine can also form, with sulfur, the S_7At^+ ion and the thiocyanate ion species $At(CSN)_2^-$.[64] In addition, cationic astatine compounds with thiourea, thiourea derivatives and some N-acyl thioureas in aqueous solution have been reported.[64] Astatine also has the ability to form a selenourea coordination compound with selenium and a colloidal tellurium compond.[64]

Reactions of astatine in the vapor state with chlorine, bromine and iodine have produced the diatomic compounds AtCl, AtBr and AtI.[65] AtBr is also formed by interacting astatine with an iodine/iodine monobromide/bromide solution whereas AtI is prepared by reacting astatine with iodine/iodide solution in an aqueous media.[66] Excess of iodide or bromide could lead to the formation of $AtBr_2^-$ and/or AtI_2^- ions or if in a chloride solution, species such as $AtBrCl^-$ or $AtCl_2^-$ can come about via equilibrium reactions with the chlorides.[67] Oxidation of At with $Cr_2O_7^{2-}$ (while in a HNO_3 solution) showed that when adding chloride a compound of either AtCl or AtOCl was produced; similarly, the ions $AtOCl_2^-$ or $AtCl_2^-$ may also be produced.[65] Polyhalides like $PdAtI_2$, $CsAtI_2$, $TlAtI_2$ are directly known or have been presumed to be precipitated in chemical reactions.[68-70] The existence of PbAtI is also likely.[71] The possibility of the $IAtBr^-$ ion, as determined by quantum mechanical calculations, was found by Galland to exist and even predominate in aqueous solutions.[72]

ASTATINE - DIATOMIC OR NOT?

All serious students of chemistry know the seven diatomic elements. Whether astatine is also diatomic is a matter of debate to this date. As an analog of iodine, it may have an orthorhombic crystalline structure composed of diatomic astatine molecules and also be a semiconductor.[73] Unfortunately, the structure of solid astatine is not known though some expect it to be a black solid with a metallic appearance.[34,74]

Takahashi, in work reported in 1986, described interactions of astatine with benzene, toluene and monochlorobenzene. In this study, the chemical bond between At_2 is quoted to cleave in a two-step mechanism that worked for benzene and toluene but not for monochlorobenzene.[75] Additional work by Takahashi reported in 1991 looked deeper at the chemical behavior of astatine.[76] On the other hand, condensed astatine is calculated to behave like a metal at 1 atmosphere of pressure and might possibly be a superconductor but would be monoatomic.[77]

Simply enough, in the gas phase, astatine might be weakly diatomic but when it is solid it is the spin orbit coupling contribution of relativistic effects that weakens the covalent character of a bond in At_2 and thus makes solid astatine monatomic.[77,78] This also extends to the ability of At to be a halogen bond donor.[79]

CONCLUSION

The discovery [and confirmation of the existence] of the element astatine involved the efforts of many scientists and many years of work in Europe, India and the United States. These investigations gave the world the properties of astatine and its chemistry as well as some isolated but medically important applications of the element. The question of whether At_2 exists was explored. All in all, element 85 has shown that even though it has an unstable nature, it is still a fascinating and vital member of the periodic table.

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Historical Articles

Vladimir Nikolayevich Ipatieff (1867-1952) – The Eminent Russian-American Chemist of the First Half of the XX Century

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Abstract. Vladimir Nikolayevich Ipatieff (1867–1952) was one of the most prominent chemists of the first half of the 20th century. He studied catalytic processes in organic chemistry. His discoveries include, among others, the explanation of the structure of isoprene, the method of obtaining butadiene from ethanol, dehydrogenation of alcohols to aldehydes and ketones, dehydration of alcohols to alkenes, including ethanol to ethylene, hydrogenation of benzene to cyclohexane, polymerization of ethylene in the presence of various catalysts. Much of his experimental studies were carried out at high pressure in a rotating autoclave, the so-called "Ipatieff bomb". The purpose of this article was to familiarize readers with important events in the life of V. N. Ipatieff and his research activities, in particular with selected results of his experimental studies. In addition, the statements by American and Russian chemists about V. N. Ipatieff and his research were presented.

Keywords. V. N. Ipatieff, Organic chemistry, Catalysis and catalysts, Russia, United States - XX century.

> *Just as rays of the sun are distributed to all men, rich and poor, good and evil, so also scientific ideas, new discoveries, and inventions serve all humanity.*
> V. N. Ipatieff (1867-1952) [1]

THE IMPORTANT EVENTS IN THE IPATIEFF'S LIFE[1]

Vladimir Nikolayevich Ipatieff (Fig. 1) was called a man of the unusual fate, a brilliant experimenter and an outstanding organizer of industrial production. Sixty-eight years have passed since his death, but in that time little has appeared in the literature about this outstanding man. His contribution to catalytic organic synthesis, as well as to major change in the chemical industry, is enormous. Therefore, his name was forewer written in letters in gold in the history of chemistry.

Vladimir N. Ipatieff was born in Moscow on November 9 [according to the Julian calendar (Old Style); Nov. 21, by the Gregorian calendar (New Style), adopted in Russia on February 1, 1918] 1867, the son of Nikolay Alekseevich Ipatiev (1841-1891)[2], an architect from an old and respectable merchant family, and Anna Dmitrievna Ipatieva (née Gliki) (1847-1880)[3].

At the age of 11, after two years of study at the Fifth Classical Gymnasium, he continued his education at the Third Moscow Military Gymnasium. In 1884 he began studying at the 3rd Alexandrovskaya Military School in Moscow. After two years, he transferred to the Mikhaylovskaya Artillery School in St. Petersburg, which he graduated in 1887. For the next two years, he served in the artillery brigade in Serpukhov, near Moscow.

To continue with his education, Ipatieff successfully passed the entrance exams at the St. Petersburg's Mikhaylovskaya Artillery Academy in August 1889. After three years of study, he graduated from the Academy and became a tutor there. From September 1892, he began to give lectures on inorganic and theoretical chemistry. He also perfected his experimental skills in the organic chemistry in the chemical laboratory at the St. Petersburg Imperial University. Lecturer of the organic chemistry, privat-docent, Alexey Evgrafovich Favorsky (1860-1945) offered him help and advice. In May 1895, after working for three years as tutor, he defended his dissertation in chemistry entitled *Deystviye broma na tretichnyye spirty i bromistogo vodoroda na atsetilenovyye i allennovyye uglevodorody v uksusnom rastvore* (Action of Bromine on Tertiary Alcohols and the Action of Hydrogen Bromide on Acetylenic and Allene Hydrocarbons in an Acetic Solution) and was nominated a full-time lecturer of chemistry at the Academy.

Figure 1. Vladimir Nikolayevich Ipatieff (1867-1952) (Public domain, from reference 20]· The image was made in 1914. V. N. Ipatieff is in the uniform of Lieutenant General [13].

A foreign internship in Germany, which Ipatieff began in 1896, was very important to shape him as a scientist. He worked there in the Chemical Laboratory of the Academy of Sciences in Munich (*Das chemische Laboratorium der Akademie der Wissenschaften zu München*) with Adolf von Baeyer (1835-1917). In December 1896, Baeyer and Ipatieff published a paper, "Ueber die Caronsaüre", in which the authors described their

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[1] Presented facts from Ipatieff's life were collected, basing on the following sources of information from 1905-2017 [2-14,16,17,19]. A brief description of the life and achievements of 38-year-old Ipatieff was found in the Encyclopedic Dictionary, published in 1905 [2]. Very useful turned out to be the book with his scientific biography published in Russian in the early 1990s [3]. Interesting information on his life and scientific activity was also found in scientific literature, both in Russia [4-9] and the USA [10-13]. Many descriptions of Ipatieff's experimental studies were found in his authoritative book published in Russian in 1936 [14]. This book was translated into English in 1937 [15]. A great source of information about the life of Vladimir N. Ipatieff was a two-volume book with his memories from the years 1867-1930, published in Russian in New York in 1945 [16,17]. This book was published in English by Stanford University Press a year later [18]. In the ex-Soviet Union excerpts from this book were published in the journal Khimiya i zhizn' (Chemistry and Life) in 1989 [19].

[2] In 1890, he became seriously ill due to asthma and arteriosclerosis. A year later, he died at the age of 50 [16].

[3] She died of tuberculosis at the age of thirty-three [16].

study on the structure of the caronic acid (3,3-dimethylcyclopropane-1,2-dicarboxylic acid; $C_7H_{10}O_4$) [21]. On March 1, 1897, he completed his an internship abroad. Travelling from Munich to Paris, he stayed 2 days in Strasbourg, where he attended a lecture of the German chemist-organic Wilhelm Rudolph Fittig (1835-1910). In Paris, he for three months worked in the *Laboratoire Central des Poudres et Salpêtre* (Central Laboratory of Gun Powder and Saltpeter) with chemist Paul Vieille (1854-1934), discoverer of the smokeless gunpowder, and physicist Emile Sarrau (1837-1904). On the end of June 1897, on his way from Paris to Russia, he stayed in Germany – first in Frankfurt am Main, where he visited factory manufacturing carbolic acid [phenol], next in Ludwigshafen, where he visited factory producing dyes and soda. Then, he reached Russia via Berlin. After a 3-week rest in Moscow, he went to St. Petersburg.

In 1898, Ipatieff submitted his professor's dissertation to the Academy, entitled *Allenovyye uglevodorody, reaktsiya khloristogo nitrozila i dvuoksi azota na organichaskiye soyedineniya, soderzhashchiye dvoynuyu svaz', i sintez izoprena* (Allene Hydrocarbons, the Reaction of Nitrosyl Chloride and Nitrogen Dioxide on Organic Compounds with Double Bond, and the Synthesis of Isoprene) and paper under the title *Prigotovleniye i vzryvchatyye svoystva trinitrokrezola i trinitronaftalina* (Preparation and Explosive Properties of Trinitro-cresol and Trinitro-naphthalene). At the end of February 1899, after successful public defense of the dissertation, he was unanimously awared the title of Professor of Chemistry and Explosives at the Academy. In 1902, he was appointed Professor Ordinary at the Academy. In the same year, Physico-Mathematical Faculty at the St. Petersburg Imperial University invited Ipatieff as the privat docent to lecture thermochemistry. Since that time, he maintained constant contact with the University up to 1916. From 1906, he was given obligatory lectures of the general chemistry for physicists, mathematicians, and astronomers.

In the thirds decade of March 1908, Ipatieff defended his dissertation for the Doctor of Chemistry degree at the St. Petersburg Imperial University entitled *Kataliticheskiye reaktsii pri vysokikh temperaturakh i davleniyakh* (Catalytic Reactions at High Temperatures and Pressures).

V. N. Ipatieff was elected the supervisor of the chemical laboratory at the St. Petersburg's Mikhaylovskaya Artillery Academy in 1909. His helper was a full-time lecturer, chemist Nikolay Mikhalovich Vittorf (1869-1929).

Ipatieff's military career did not interfere with his scientific life. In 1910, he was promoted to the rank of major general of the *Russkoy Imperatorskoy Armii* (Russian Imperial Army). At the age of forty-seven in 1914, he had obtained the rank of lieutenant general.

During World War I, from February 1915, Ipatieff served as a head of the Commission for Preparation of Explosives, which controlled almost the entire Russian chemical industry until the end of the war, among others, the production of potassium nitrate, dinitronaphthalene, benzene, toluene, sulfuric acid, nitric acid, and picric acid from benzene. In 1916, he was named chairman of the Chemical Committee of the Chief Artillery Administration, which was formed mainly due to the use of poison gas by the Germans on the Eastern Front in May 1915. Thanks to the activities of the Chemical Committee and included in its composition the Commission for the Preparation of Asphyxiating Gases, the production of liquid chlorine, phosgene, chloropicrin and sulfuryl chloride from liquid sulfur dioxide was started.

After the October Revolution in 1917, Ipatieff began to cooperate with the Bolsheviks. He was appointed chairman of both the Chemical Committee and the Technical Department of the Military Economic Council of the People's Commissariat for Military Affairs. In June 1918, he was relieved from these positions. In the years 1921-1926, he served as chairman of the General Chemical Directorate of the Supreme Council of the National Economy. At the beginning of 1927, he was relieved of all posts in state structures. He returned from Moscow to Leningrad [name of the city of St. Petersburg in 1924-1991], where he founded and directed the Institute of High Pressures.

On October 23-26, 1927, Ipatieff took part in the jubilee celebrations organized in Paris on the occasion of the 100th anniversary of the birth of the French chemist Marcellin Berthelot (1827-1907). The ceremony was attended by scientists from 60 countries around the world, including Richard Willstätter (1872-1942), who was honoured by the award of the Nobel Prize for Chemistry in 1915, Heinrich Wieland (1877-1957), Fritz Haber (1868-1934), who was awarded the Nobel Prize for Chemistry in 1918, Wilhelm Schlenk (1879-1943), and Walther Nernst (1864-1941), who was the winner of the 1920 Nobel Prize in Chemistry. There he first met with 73-year-old Paul Sabatier, who received the Nobel Prize in Chemistry in 1912. Their meeting took place in a pleasant and friendly atmosphere.

In 1929, the political situation in the Soviet Union worsened. The campaign against specialists has begun. Many people were arrested in Moscow and Leningrad by the G.P.U. (State Political Administration), among them those, who worked with Ipatieff for years. He, coming back from the International Engineering Congress in Tokyo, was agitated by the execution of five military engineers-technologists. All were his very smart students at the Academy, who since the very beginning of the October Revolution worked on the bringing factories manufacturing military equipment to work. Moreover, physicochemist Yevgenii Ivanovich Shpitalsky (1879-1931) was arrested. Later, in 1945, Ipatieff wrote in his memoirs: "My mood became especially alarming, because Ye. I. was my great friend, knew all the details of my life and during an interrogation, purely incidentally, he could report some facts, that would allow to bring me to interrogation, and subsequently to be arrest" [17].

In early June 1930, Ipatieff was appointed as one of the ten delegates to the International Energy Congress in Belin called *The Second World Power Conference*. He replaced one of the professors of electricity who was arrested. On June 12, 1930, he and his wife Varvara Dmitrievna (1869-1952) crossed the Soviet Union (USSR) border in Negorloe[4]. Their matured children – Anna Vladimirovna and son Vladimir Vladimirovich stayed in USSR[5]. The oldest of their two other sons, Dimitri (1893-1914) was already dead. He was killed near Vilnius during the World War I. Their next son Nicolay after the October Revolution left Russia with participants of the White Movement called *Belogvardeytsi* (White Guardsmen) and has lived in Belgium since 1919[6] [22]. Ipatieff's half-brother chemist Lev Aleksandrovich Chugaev[7] (1873-1922) was already dead, and his younger brother, engineer Nikolay Nikolayevich Ipatiev (1869-1938), from 1921 he stayed in Prague (Czechoslovakia, now the Czech Republic)[8].

At the Berlin conference, which took place on June 16-26, 1930, Vladimir N. Ipatieff met many eminent chemists from different countries all over the world. One of them was an American chemist Gustav Egloff (1886-1955) from Universal Oil Products Company (UOP) in Chicago [12]. He told Engloff that he interested in visiting UOP laboratories in the USA. In September, 1930, he and his wife arrived in New York City, thanks to Egloff's help in obtaining a visas from the American Consul. After his visit to Research Laboratories of the UOP in Riverside (Illinois), and talk with the president of UOP – Hiram J. Halle (1867-1944), he agreed to take a post of the Director of Chemical Research. As he was bound by a 3-year contract with German *Bayerische Stickstoffwerke* (Bavarian Nitrogen), he agreed with Halle that 6 months he will stay in Germany and remaining 6 months in the United States. Then, Ipatieffs returned to Berlin. In May, 1931, both spouses came to the USA again. In addition to working as a research director at UOP Research Laboratories, he also became a lecturer on catalysis in organic chemistry at Northwestern University.

The political situation in the USSR, after leaving the country by Ipatieff, did not improve. In 1934, his close associate organic chemist Grigory Alekseevich Razuvayev (1895–1989) was arrested. A former his student, a geochemist Nikolay Alexandrovich Orlov (1895-1937) was also arrested. In January 1935, many well-known people from the party and government were convicted and soon shot, including Lev Borisovich Kamenev (1883-1936) and Grigory Yevseyevich Zinoviev (1883-1936), with whom he has previously collaborated.

From the last month of the third quarter of 1936, correspondence was conducted between the permanent secretary of the Academy of Sciences of the U.S.S.R, academician Nikolay Petrovich Gorbunov (1892–1938) and Ipatieff about the need to return the scientist to the USSR. The translation of an excerpt of Gorbunov's letter of September 17, 1936, to Ipatieff into English is as follows: "… For about six years now you have been outside the borders of the USSR and are not taking any part in the practical work of socialist construction. You are a citizen of the USSR, a major scientist, a full member of the Academy of Sciences, our country needs you. Therefore, on behalf of the Presidium of the Academy of Sciences, I ask for your direct, clear and frank answer to the following question - do you consider yourself obligated to work fully for your homeland - the Soviet Union, for to enhance his power and prosperity … . If you answer the question posed to you in the affirmative, then you should soon return to the USSR for scientific work. …" [9]. Here is an excerpt from a Ipatieff reply to Gorbunov, translated from Russian into English (letter of 1 December, 1936). "… I must say, firstly, that I

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[4] While wives were usually not allowed to travel abroad with their husbands, Ipatieff received his wife's passport in just three days, stating that he would be a delegate only if his spouse can accompany him because she needs treatment abroad. Until they left Russia, he didn't tell his wife that he did not expect to return to the country [13].

[5] Professor and Doctor of Science, Vladimir Vladimirovich Ipatiev (1897-1955), like his father, was a chemist. He managed the laboratory of the Leningrad Scientific-Research Institute dealing in the processing of crude oil and the production of synthetic liquid fuel. He also lectured at the Forestry Academy and the Leningrad State University [4].

[6] In 1935, Nikolay [Nicolas (d') Ipatieff] died in Africa testing a treatment he had invented for yellow fever. At that time, he worked in the Belgian Congo as the government inspector Industry and Commerce [22].

[7] The father of Lev Aleksandrovich was the teacher Alexander Fomich Chugaev. His mother was Ipatieff's mum, Anna Dmitrievna. Vladimir N. Ipatieff did find out that Lev A. Chugaev is his half-brother in 1907 [16].

[8] On July 17, 1918, in his house in Yekaterinburg the Bolsheviks killed Tsar Nicholas II and his family [17].

can in no way agree with the fact that I do not take any part in the scientific work that has taken place in the USSR over these six years. … It is enough to indicate that … I wrote a book, which, in addition to summarizing my old studies, contains very valuable new material that will be used to great advantage in the USSR. … In addition, I sent all my new studies to Russian chemical journals at the same time as sending their translations to American journals. … It is undeniable that every scientist works not only for his country, but for all mankind. I love my homeland and, making new discoveries, I always thought and think now that all this belongs to her and she will be proud of my work. … I ask you to declare to the Presidium of the Academy of Sciences that I'm not giving up my hope of coming to the USSR, but now the circumstances are such that I actually can't do this. ..." [9].

On December 29, 1936, Ipatieff was deprived the title of the Member of the Academy of Science Of the USSR. In its justification was written, among other, "Refusing to return to work at the Academy of Science, decidedly preferring work in the foreign commercial company, V. N. Ipatiev grossly violates the basic duty of every citizen of the Soviet Union – to work for the good of his homeland" [23]. Ipatieff was expelled from the Academy by sixty-three votes in favor, no one against, and six abstentions [24]. On January 3, 1937, Presidium of the Central Executive Committee USSR in the decision signed by Mikhail Ivanovich Kalinin (1875-1946) and Ivan Alekseyevich Akulov (1888-1939) decided to "deprive Vladimir Nikolayevich Ipatiev of citizenship of the USSR, because he refused to fulfill his duty to his homeland and forbid to cross the borders of the Soviet Union" [25][9].

Vladimir N. Ipatieff did not wait long for American citizenship. On March 11, 1937, he became United States citizen. His wife received such citizenship one month later. On the day of the 70th birthday of Ipatieff, Chicago Section of the American Chemical Society (ACS) organized ceremonious meeting, in which he gave the lecture entitled "Catalysis - chemistry of the future". He in this occasion received greetings from the scientists of 30 countries all over the world, for instance German chemist Friedrich Bergius (1884-1949), American chemist-organic Mozes Gomberg (1866-1947) and Estonian chemist Gustav Tammann (1861-1938).

On December 18, 1939, Ipatieff underwent a serious throat surgery, after which he spoke in a hoarse whisper. His doctor forbade him any public speech. However, this problem did not exist too long, and after a few months after surgery, he was again able to speak at meetings.

Particularly interesting were the celebrations that took place on November 14-20, 1942, on the occasion of Ipatieff's 75th birthday, 50 years of his scientific activity and the Golden Anniversary (50 years of his marriage). In the organized ceremonious meetings, warm greetings he received from Gustav Egloff and representatives of the chemical institutions from various American States. Greeting sent also American chemists: Linus Pauling (1901-1994), Paul Emmet (1900-1985), and Kasimir Fajans (1887-1975).

Between May 28 and June 6, 1951, Ipatieff attended the *Third World Petroleum Congress* in the Hague (the Netherlands). In July 1952, he celebrated the 60th Anniversary of his wedding. There were no any meetings on the occasion of his 85th birthday because he categorically opposed their organization by Northwestern University. He died a few month later, at 07:00, in Saturday on November 29, 1952, and was buried in the Saint Vladimirs Russian Orthodox Cementary in Jackson, Ocean County (New Jersey). Ten days later (on December 9) died his wife Varvara Dimitrievna.

IPATIEFF'S RESEARCH ACTIVITIES. DESCRIPTION OF SELECTED RESULTS OF EXPERIMENTAL STUDIES

The list of Ipatieff's published works includes 399 papers. There are the articles published in Russia and the Soviet Union, among other in the journals *Zhurnal Russkogo fiziko-khimicheskogo obshchestva* (Journal of the Russian Physical-Chemical Society) and *Doklady Akademii Nauk SSSR* (Proceedings of the Academy of Sciences of the U.S.S.R), and many papers published in German, French and American journals [13,26].

Ipatieff's first work was published in 1892 and concerned the chemical investigation of the structure of steel. In the following years, he focused his research in the field of organic chemistry. In two articles from 1897 he described his method of the synthesis of isoprene (2-methyl-1,3-butadiene) and as the first among chemists, correctly explained the diene nature of its structure [5,27,28]. Information about isoprene synthesis by Ipatieff appeared, among other, in the book written by Thomas Percy Hilditch (1886-1965) – British chemist – in 1911 [29], and in 1913 in the book written by another British chemist Benjamin Dawson Porritt (1884-1940) [30].

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[9] Ipatieff's daughter, Anna Vladimirovna (1894-1958) persistently fought for the restoration of the good name of her parents. In 1957, she turned to Kliment Efremovich Voroshilov (1881–1969) for posthumous rehabilitation of her father. In 1990, citizenship and membership in the USSR Academy of Sciences was posthumously restored to Vladimir N. Ipatieff [4].

The studies of catalytic processes in organic chemistry was started by Ipatieff in 1901, independently and simultaneously with French chemist Paul Sabatier (1854-1941) [1,16]. He did a lot of safe laboratory experiments using a rotating autoclave, so-called "Ipatieff bomb", which he designed to conduct studies under pressure of several hundred atmospheres. Such apparatuses, for the first time, were made in 1904 according to the drawings of Ipatieff in a private mechanical workshop by the mechanic *Mal'mstrem* (Malmstrom), and then were made at a mechanical plant in St. Petersburg, which belonged to Richard Langensiepen (1847-1920) [14].

V. N. Ipatieff used various catalysts in his experimental studies. He and his co-workers carried out many different catalytic reactions, among others, the reactions of dehydrogenation, dehydration, hydrogenation, alkylation, destructive hydrogenation, condensation, destructive alkylation, polymerization, selective demethylation, and isomerization. The examples given below relate to experimental studies carried out in 1901-1951.

Based on studies of both dehydration and dehydrogenation of alcohols, carried out in high temperatures under ordinary pressure, Ipatieff stated that depending on the material of the tube in which alcohol was decomposed, he received various products [31]. Dehydration of ethanol to ethylene was his first experimental study carried out in the laboratory of the St. Petersburg's Mikhaylovskaya Artillery Academy in 1901. In this study, he passed vapors of the ethanol through a graphite tube inserted into an iron tube at 600°C. Confirmation of obtaining ethylene in this reaction was that the resulting gas reacted with bromine to form ethylene dibromide (1,2-dibromoethane) [14]. In another study, he passed vapors of the ethanol through a glass tube containing pieces of graphite mass also at 600°C, and the ethanol quickly decomposed into ethylene and water. Propyl alcohol in the same way was dehydrated into propylene [32]. When the vapors of a primary aliphatic alcohol, for instance ethanol, passed through a platinum tube inserted into a wide iron tube, at 780°C the alcohol decomposed and the main reaction product was acetaldehyde [14]. He also found that secondary alcohols dehydrogenate in an iron tubes to ketones [33], and tertiary to olefins [14].

Vladimir N. Ipatieff discovered a new method for the conversion of ethanol to divinyl (1,3-butadiene), during which hydrogen was formed. When passing the vapors of this alcohol at high temperature and ordinary pressure over powdered aluminum as a catalyst, the following reaction take place:

$CH_3 - CH_2OH + CH_3 - CH_2OH = 2H_2O + CH_2 = CH - CH = CH_2 + H_2$ [14,34].

Using a rotating bomb, Ipatieff studied the reduction of benzene by hydrogen under high pressure. He, working with 25 grams of benzene and 2 grams of black nickel oxide (nickel (III) oxide) at 250°C under a hydrogen pressure of 180-186 atmospheres[10](18.238500 to 18.846450 MPa), hydrogenated benzene to hexahydrobenzene (cyclohexane) for one and a half hours [14,35].

The hydrogenation of the citral (3,7-dimethylocta-2,6-dienal) was carried out by Ipatieff at 110°C in the presence of palladium. He found that under a hydrogen pressure of 110 atmospheres (11.145750 MPa), pure decanol (3,7-Dimethyl-1-octanol) could be obtained in four hours [14]. The simultaneous used of nickel oxide and alumina, in another experimental study, allowed him to obtain isocamphane ($C_{10}H_{18}$) from borneol ($C_{10}H_{17}OH$) within 10-12 hours at 215-220°C under a hydrogen pressure of 110 atmospheres (11.145750 MPa). He also mixed 30 grams of camphor ($C_{10}H_{16}O$) with 3 grams of nickel oxide and 1.5 grams of alumina. The hydrogenation of camphor into isocamphane was achieved in 24 hours at 200°C under a hydrogen pressure [14].

For the first time, V. N. Ipatieff and Finish chemist O. Rutala polymerized ethylene in the presence of dry zinc chloride as a catalyst at 275°C under pressure 70 atmospheres (7.092750 MPa). According to the gas product analysis, paraffins (61%), olefins (36%) and hydrogen (3%) were present. The results of study also showed that the liquid reaction product contained pentane and hexane, and some alkenes (hexylene, hepylene, octylene and nonylene) [14,36].

The study on the catalytic synthesis of methane from carbon and hydrogen Ipatieff carried out in the presence of catalyst consisting of nickel and alumina at 500-519°C and under hydrogen pressure of 35 to 60 atmospheres (3.546375 to 6.079500 MPa) [14,37].

For hydrogenation of anethole (1-methoxy-4-(1-prop-1-en-1-yl)benzene), Ipatieff used nickel as a catalyst. This compound was reduced to dihydroanethole (1-methoxy-4-propylbenzene) at 95°C under a hydrogen pressure of 50 atmospheres (5.066250 MPa) within 4 hours [14,38].

For the first time V. N. Ipatieff and his associates carried out alkylation of phenol in the presence of alumina. The phenol was heated with methyl alcohol and alumina in a Ipatieff rotating bomb at 440°C. It was found that at a pressure of up to 200 atmospheres (20.265000 MPa), o-cresol ($CH_3C_6H_4OH$) as a the main product of this reaction was obtained within 24 hours. Neither m-cresol nor p-cresol was found in reaction products [14,39].

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[10] In the article the conversions have been made from atmospheres to MPa as a derivated unit of SI.

As the result of experimental study V. N. Ipatieff and N. Kljukvin were successful in solving the problem of destructive hydrogenation of naphthalene in a rotating autoclave. They, working with 3 grams of catalyst (50% NiO, 50% Al_2O_3) and 40-60 grams of naphthalene at 450-480° under a hydrogen pressure of 60 atmospheres (6.079500 MPa), succeeded in hydrogenating naphtalene in 25 hours. The main reaction product was hydrogen. Small amounts of methane and carbon dioxide were also obtained [14,40].

Vladimir N. Ipatieff and his associates proposed a new method for obtaining xanthene ($CH_2[C_6H_4]_2O$) in a catalytic condensation reaction. This compound was obtained by heating o-cresol ($CH_3C_6H_4OH$) and phenol (C_6H_5OH) in the presence of alumina as a catalyst at 440-450°C under the high pressure [14,41].

V. N. Ipatief and V. I. Komarewsky conducted research that enabled the destructive alkylation of benzene. They used 81.1 grams of benzene and 8 grams of aluminum chloride saturated with hydrogen chloride. The reaction proceeded in a rotating bomb at 125°C within 24 hours [14,42]. The main reaction products were ethylbenzene ($C_6H_5C_2H_5$) and diphenyl ($C_6H_5C_6H_5$). "The formation of these two compounds makes probable the following scheme of the reaction: (a) two parts of benzene combine to form [under the influence of aluminum chloride] diphenyl, liberating hydrogen; (b) a destructive hydrogenation of the benzene occurs during which benzene decomposes, and the *decomposed fragments are hydrogenated* to form ethylene; (c) ethylene *alkylates* the unchanged benzene to form ethylbenzene" [42].

For the first time polymerization of ethylene under pressure of 48.39 atmospheres (4.903325 MPa) at 330°C in the presence of 90% phosphoric acid as a catalyst was studied by V. N. Ipatieff and Herman Pines (1902-1996). Olefins, paraffins, naphthenes and aromatic hydrocarbons were found among the reaction products obtained within eight hours [43].

Studies of the catalytic dehydrogenation of gaseous of paraffins in the presence chromium oxide on alumina as a highly selective catalyst at 500-750°C have been carried out by V. N. Ipatieff and Aristid V. Grosse (1903-1985). It was found that the conversion of paraffins to the corresponding olefins proceeded with a yield of 90-95%. The ethane was converted into ethylene, the propane into propylene, and isobutane (2-methylpropane) into isobutylene (2-methylpropene). A mixture consisting of α-butylene (1-butene), cis-β-butylene (cis-2-butene) and trans-β-butylene (trans-2-butene) was obtained from n-butane [44].

The research of V. N. Ipatieff and Robert L. Burwell, Jr. (1912-2003) has led to the preparation of various ethers. As a result of the passage of an equimolar mixture of benzyl alcohol and methanol over seventy five cubic centimeters of "solid phosphoric acid" in the form of pellets (5 x 7 mm) used as a catalyst at 350°C under pressure of 50 atmospheres (5.066250 MPa), benzyl methyl ether (methoxymethylbenzene) was obtained. They also showed that "solid phosphoric acid" catalyze at 336°C under pressure of 60 atmospheres (6.079500 MPa), the reaction between methanol and ethanol. The product of this reaction was ethyl methyl ether (methoxyethane) [45].

Vladimir N. Ipatieff with Vladimir Haensel (1914-2002) developed the catalytic method of selective demethylation. This method was used to obtain triptane (2,2,3-trimethylbutane), a hydrocarbon with antiknock properties. Triptane began to be used as an aviation gasoline component. Thanks to it, the performance of aircraft engine has improved significantly [46].

The results of experimental studies conducted by Herman Pines, William A. Huntsman, and V. N. Ipatieff showed that alkylation is accompanied by isomerization. For instance, by reacting of 1.2 mole of benzene (C_6H_6) with 0.1 mole of ethylcyclopropane ($C_3H_5C_2H_5$) in the presence of 0.5 mole hydrogen fluoride as a catalyst, at 0-5°C, were obtained the mixture which consisted of about 63% of 2-phenylpentane [$CH_3CH(C_6H_5)C_3H_7$] and 37% of 3-phenylpentane [$C_2H_5CH(C_6H_5)C_2H_5$] [47]. They also showed that the product from the reaction 0.114 mole of 3-pentanol ($CH_3CH_2CHOHCH_2CH_3$) with 1.0 mole of benzene and 1.0 mole of hydrogen fluoride in the same temperature consisted of 56% 2-phenylpentane and 44% 3-phenylpentane [48].

STATEMENTS BY AMERICAN AND RUSSIAN CHEMISTS ABOUT VLADIMIR N. IPATIEFF AND HIS SCIENTIFIC RESEARCH

In 1942-2018, some chemists and historians of chemistry in both the United States and Russia have spoken very positive about Ipatieff and his scientific research. In their eyes, he was not only creator, excellent experimenter, and organizer, but also the great patriot. Below, these statements are quoted.

Frank Clifford Whitmore (1887-1947), professor at the School of Chemistry and Physics of the Pennsylvania State College said in 1942: "Russia has produced three outstanding chemists among its many great ones. These are Lomosoff, Mendeleev, and Ipatieff. Ipatieff has had a far greater influence on world chemistry than his two famous countrymen. He is a chemist who was a pioneer 50 years ago and is still pioneering today" [11].

Ward V. Evans (1880-1957), former chairman of the Department of Chemistry of Northwestern University, on the ocassion of the Ipatieff's eightieth birthday said in 1947: "OCASIONALLY a great research worker is born. Occasionally the world produces a great teacher. Occasionally a great humanitarian appears in the race. Very rarely, almost in defiance of the law of probability, are all these personalities embodied in a single individual. When to this unusual combination is added yet another, the gallantry to endure unheardof hardship and suffering and to rise above it with head unbowed and eyes bright, to carry out at 80 years some of the greatest researches of a lifetime, you have an idea of the man you meet in this Russian scientist whom we now proudly claim as a fellow American—Vladimir N. Ipatieff" [49].

Jacob Joseph Bikerman (1898-1978), head of the Adhesives Laboratory of the Massachusetts Institute of Technology (1956-1964) wrote: "If he were born in America instead of Russia, he probably would become the president of a billiondollar corporation. He emigrated to the United States when he was about 60, learned English at this age, and showed (in the Universal Oil Company) that he was more than a match for American-born rivals. … The first great success was achieved by Ipatiev relatively late because he was trained to be an army officer and, as a chemist, was a self-made man. This success was in the field of heterogeneous catalysis. Other scientists studied and utilized this technique at moderate temperatures and at the atmospheric pressure" [50].

In the 1991 book historian of chemistry Vladimir Ivanovich Kuznetsov (1915-2005) wrote, that Ipatieff was "the originator of the catalysis theory in the high temperatures and pressures, which became scientific basis of the industrial organic synthesis", and also that during the World War I, he was "the organizer of the sulfuric acid and benzene industries in Russia" [8].

The authors of the brochure commemorating the research carried out the "UOP Riverside research and development laboratory" wrote that Ipatieff "was one of only three industrial chemists to receive the prestigious Willard Gibbs Medal of the Chicago Section of the ACS since the award's inception in 1911. Because he played a leading role in the development of UOP's polymerization, alkylation, and isomerization processes, Ipatieff made a major contribution to the development of the high-octane aviation fuel that helped the Allies win World War II" [51].

In the 2017 publication Andrey G. Morachevskiy, professor of St. Petersburg Polytechnic University of Peter the Great wrote: "He laid the groundwork of the innovated heterogenic catalysis in the organic chemistry, he was an excellent experimenter and industrial production organizer. The General-Liutenant, academician, he managed the whole military-chemical industry in Russian in the difficult years of the World War I" [52].

Herman Pines, who was the "student, friend, and the executor of V. N. Ipatieff's will" said in 1967: "You, Russians, cannot even comprehend who Vladimir Ipatieff was. Every hour of his life here, in the United States, every step in his research, he dedicated it all to Russia. His limitless love for his motherland, which I have never seen in any of the emigrants, was the soil on which grew the outstanding results of his scientific work …" [53].

In 2018 publication Christopher P. Nicholas, principal scientist at Honeywell UOP wrote: "Vladimir Ipatieff contributed numerous concepts to catalysis including high pressure, dispersion of metals on supports, and the use of promoters. He also discovered many catalysts and reactions, several of which are still in use today, some 80 years later. His efforts continue to inspire the catalysis community in many ways, including through the Ipatieff Prize administered by the ACS, processes offered by industry, and the teaching of students at Northwestern University" [54].

CONCLUSION

Vladimir Nikolayevich Ipatiff was one of the eminent chemist of the first half of the XX century. He played a huge role in the development of catalysis, first in Russia and then in the United States. He was a pioneer in the study of catalytic reactions at high temperatures and pressures in organic chemistry. The results of his many experimental studies have been published in scientific journals in several countries around the world. He, as an inventor or co-inventor, acquired 174 U.S. Patents.

V. N. Ipatieff became a corresponding member of the Imperial St. Petersburg Academy of Sciences on November 29, 1914. He was elected an academician on January 9, 1916. At that time only two chemists Pavel (Paul) Ivanovich Walden (1863-1957) and Nikolay Semenovich Kurnakov (1860-1941) shared this distiction with him.

Vladimir N. Ipatieff became member of the Göttingen Academy of Sciences in 1922. In 1930, he was elected an honorary member of the *Deutsche Chemische Gesellschaft* (German Chemical Society) [10]. The Russian Institute of Science in Belgrade (former Yugoslavia) elected him an honorary member in 1938. On April 26, 1939, he became a member of the National Academy of Science of the United States of America. He was elected Doctor *honoris causa* of the universities of Munich (1927), of Strasbourg (1928), of Northwestern (1938), and of Sofia (1939) [6,13].

On the American website *Medill Reports Chicago* in the article entitled *NU symposium of honors chemist Vladimir Nikolayevich Ipatieff who helped win World War II* by Lakshmi Chandrasekaran [55] is an information about symposium devoted to Ipatieff's 150th Anniversary, which took place on September 7, 2017. It was organized by *The Center for Catalysis and Surface Science* (CCSS) and the Institute *of Sustainability and Energy* (ISEN) at Northwestern University [56]. Chandrasekaran's article also contains the photograph of Wolfgang Sachtler (1924-2017), CCSS director in 1985-1994, Robert L. Burwell, Jr., and Herman Pines, standing in the front of a big, hanging on the wall on the second floor of the catalysis building, beautiful, color Ipatieff's portrait. On his chest is visible the insignia of Commander of the Legion of Honour (*Commandeur de la Légion d'Honneur).* This is one of the highest honours of the French Republic, which the French Government awarded him in 1916 in recognition of all his work during World War I [10,57].

The Russian Physical-Chemical Society awarded Ipatieff with the Minor Butlerov Prize in 1896. The Ivanov Prize of the Imperial St. Petersburg Academy of Sciences was awarded to him in 1906; in 1920, the Major Butlerow Prize, and in 1927, the Lenin Prize, granted by the Soviet Government for his work on catalysis and high pressure. In 1928, at the Congress of Industrial Chemistry in Strasbourg, he was honored the Berthelot Medal awarded by *La Société de Chimie Industrielle* (The Industrial Chemistry Society) in Paris [10,13,17].

The High Pressure and Catalytic Laboratory at the Department of Chemistry of Northwestern University, estabilished in 1940, was named in honor of Ipatieff [58]. In the same year, he was honored with the Willard Gibbs award, which is granted to the: "eminent chemists, who through years of application and devotion, have brought to the world developments that enable everyone to live more comfortably and to understand this world better" [59]. In 1942, he was awarded with the Honor Scroll award "presented annually by the Chicago chapter of the American Institute of Chemists for distinguished service to the science and profession of chemistry" [60].

The Russian Academy of Sciences on the occasion of the 150th anniversary of Ipatieff 's birth organized two exhibitions in 2017-2018. The first exhibition on-line organized by St. Petersburg Branch of the Russian Academy of Sciences Archive besides an information about the most important events in Ipatieff's life contains photocopies of his and the members of his family personal documents [4]. The second exhibition contained his selected works, which were ranked, among other, in the following categories: general catalysis, alcohols dehydrogenation, alcohols degradation, hydrogenation, and general chemistry. Moreover, chemistry handbook written by Ipatieff in 1902-1909 were shown: *Kurs neorganicheskoy khimii* (A Course of Inorganic Chemistry, 1902), *Kurs organicheskoy khimii* (A Course of Organic Chemistry, 1903), *Rukovodstvo dlya prakticheskich zanyatiy po khimii* (A Guide for Practical Training in Chemistry, 1905), and *Kratkiy kurs khimii* (A Short Course in Chemistry, 1909). Photographic part of the exhibition is available in the Web, still. It contains among other Ipatieff's photographs made in various periods of his life and photocopies of the title pages of the books written by him [61].

The name of this remarkable Russian-American chemist is loudly heard in the chemists milieu in both United States and Russia. There are two awards associated with his name. First "Ipatieff' Prize", is sponsored by the Ipatieff Trust Fund. It is awarded by the American Chemical Society every three years, since 1947, for "the outstanding chemical experimental work in the field of catalysis or high pressure, carried out by an individual of any nationality, who is not over 40 years of age" [62]. Second prize, *Premiya imeni V. N. Ipat'yeva* (The Prize named after V. N. Ipatiev) is awarded by the Russian Academy of Sciences every three years, since 1994. Russian chemists receive this award "for outstanding work in the field of technical chemistry" [63].

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