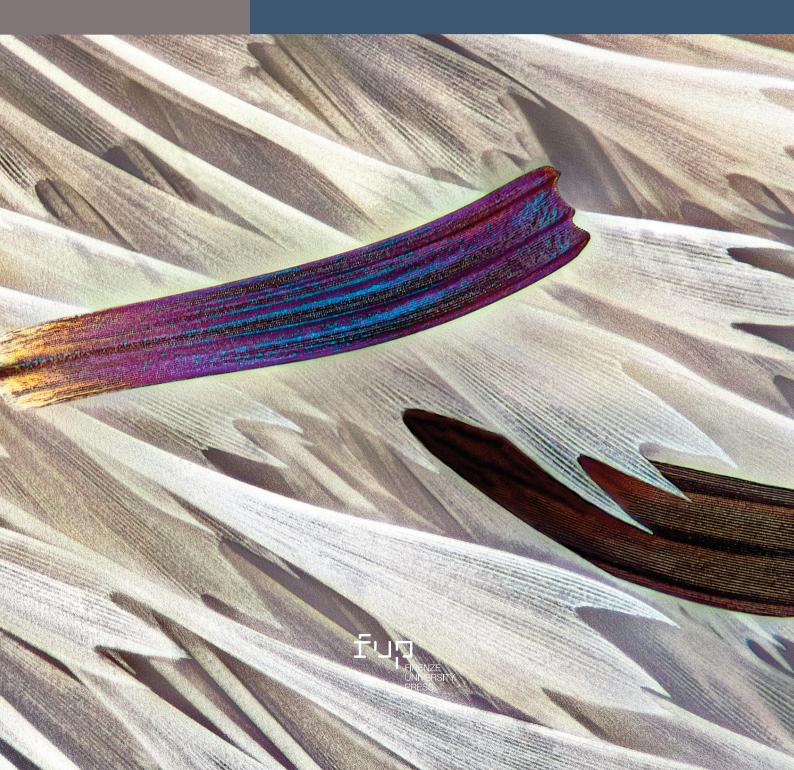
September 2025 Vol. 9 - n. 2



Substantia

An International Journal of the History of Chemistry





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Vol. 9, n. 2 - 2025

Substantia. An International Journal of the History of Chemistry

Published by

Firenze University Press – University of Florence, Italy
Via Cittadella, 7 - 50144 Florence - Italy
http://www.fupress.com/substantia

Direttore Responsabile: Romeo Perrotta, University of Florence, Italy

Cover image: Isolated scales on Madagascan sunset moth wing (*Chrysiridia ripheus*). Technique: Darkfield, Image Stacking, Reflected Light (40X Objective Lens Magnification) by Sébastien Malo (Saint Lys, Haute-Garonne, France). Courtesy of Nikon Small World (15th place, 2024 Photomicrography Competition, https://www.nikonsmallworld.com).

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Editorial

The Invisible Infrastructure of Science: The Starring Role of Librarians and Archivists and a Call for Appreciation

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I recently received a standard 'template e-mail message,' sometimes referred to as a 'canned response' or 'standardized message,' from my University's Interlibrary Loan office: "We have information about an ILL request that you placed: Atti della Accademia nazionale dei Lincei. 24, 850-854, 1915, Title: Autoxidation by light in the terpene series. I and II (English translation), Author: E. Sernagiotto, has been cancelled for the following reason: We have exhausted all possible sources. No library is able to supply this item. Questions and comments regarding interlibrary loan policies and procedures may be directed to us." (I learned later that none of my University's Interlibrary Loan (ILL) Department's partner institutions had a copy of the requested article. I also learned later that, as a result of this particular interaction, my University's ILL Department is developing a policy to handle such instances. "Continuous improvement" is a wonderful lifelong commitment!)

But at that very moment, I was not happy. That's an understatement. I was disappointed because my research had been, at least temporarily, thwarted. Indeed, it was more than that, as I shall relate. It took only a moment via Google search to learn that there are two national libraries in Italy, one being the Biblioteca nazionale centrale di Firenze (in English, the National Central Library of Florence). Of course, we all know of Firenze and the role that this very special city has played in the development and display of human culture and achievement. But additionally, Firenze is the home of Substantia, An International Journal of the History of Chemistry, and of its editorial staff, including its editor, Pierandrea Lo Nostro, a professor at the Università degli Studi di Firenze.

I focused my attention on Firenze. It took only a minute or two on the Biblioteca's website for me to find the link I had hoped to find: "Contact Us." It took only seconds to write a short request seeking their help: Could they provide me with a pdf of Sernagiotto's 1915 publication?

The link to that publication arrived within hours. I had the pdf!

Let me tell you why all of this matters.

Of course, the Biblioteca's response was a wonderful display of international collegiality and professional courtesy. And I repeat: international courtesy. Think of the degrees of separation between the Biblioteca and me. One marker of separation is distance, 4436 miles from Richmond to Firenze. Others are nationality and language. What duty does a national library in Italy have to a Virginian? Further, the librarian/archivist - scientist relationship is another step in separation beyond the scientist - scientist relationship. I could have, and I almost did call Pierandrea to seek his help. An insider's assistance can always smooth the way, and he has previously and generously helped me on professional matters. But I had faith in the system, and I went directly to the Biblioteca. Their immediate and productive response displays, in a most splendid fashion, two qualities about the international science community: first, the collegiality that we generally experience within the scientific community; and second, the commitment of librarians and archivists to users around the world.

Librarians and archivists have long been among my greatest heroes. They truly honor human achievement, by collecting and preserving treasures of the past and providing access to scholars around the world. For me to

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receive such immediate attention from across the globe is an earmark of professional commitment to the highest level, by the Biblioteca nazionale centrale di Firenze.

It is even more than that. It is actively venerating the very culture and achievements that information scientists collect and provide. And for me, the Biblioteca's performance allowed me to fully know of and cite the research of a rather unknown Italian chemist who toiled more than 100 years ago.

These considerations certainly apply to historians of chemistry. There are simply not enough historians to tell *all* the stories of human accomplishment and of human passion. And when we historians or would-be historians choose to tell a story, we must diligently recover and document each researcher's role in that story. (In my case, it is the history of the conversion of acyclic diterpenes to their cyclic analogues in the late 1800s and early 1900s. You've surely heard the names geranial, linalool, limonene, terpineol, menthol, and pulegone.)

Furthermore, I believe that all chemists are historians. Every introduction to a publication, every review article, every reference cited - all of these are history of chemistry. Of course, many of today's historians of chemistry were once experimentalists in days long past. We all share our common legacies, and we all use the history of our science. We also know how very hard it is to do research. We know the kind of resolve one must have to write our manuscripts, deal with journals, editors, and reviewers, and ultimately correct the galley proofs. It takes a very special commitment and follow-through to be a scientist. And that commitment is collected and saved for posterity by our archived books, journals, and patents. These archives make this history available for both scientists and historians today and far into the future. Without the librarians, archivists, and information technology (IT) staff, today's records and those of the past would otherwise remain untouched and unnoticed, perhaps not even collected, forgotten on the dusty shelves of yesteryear or lost forever.

My collection of pdf reprints obtained via the ILL Department at my University for the past nearly 20 years is an even more impressive emblem of their commitment to my research and that of my colleagues. And I have another resource: my university's science librarian who provides specialized support. She urges me to send her my most complex IT problems.

A reader of an earlier version of this manuscript criticized its content as being anecdotal. But what are all of our experiences in doing research other than anecdotal? Just about the time I needed the article from the 1915 Atti della Accademia nazionale dei Lincei, I required a copy of a publication from an 1891 issue of the Proceedings of the Society of German Natural Scientists and Physicians. That

is another rather obscure publication. In that instance, I wrote directly to the information desk at the still-in-existence Society of German Natural Scientists and Physicians, in Bad Honnef, Germany. They forwarded my request to an archivist at the Deutsches Museum von Meisterwerken der Naturwissenschaft und Technik in Berlin. Within hours, the requested article arrived!

More anecdotes? I spent the month of March 2025 in Japan on a short-term fellowship sponsored by the Japan Society for the Promotion of Science. I enjoyed two days with Kenichi Fukui's documents at the Fukui Institute for Fundamental Chemistry at Kyoto University (Figure 1-Left). I also spent an afternoon with the papers and autograph books of Tetsuo Nozoe at the Tohoku University Archives in Sendai (Figure 1-Right). Two months later, for four days in early May 2025, I reviewed documents in the R. B. Woodward papers at the Harvard Archives in Cambridge.

And I would be remiss if I did not highlight my many explorations within the archives of the Science History Institute and Patrick Shea, SHI's Chief Curator of Archives and Manuscripts. In all of these visits, the archivists provided personalized assistance so that my research would be as efficient, productive, and as pleasant as possible. Not a moment of my time was wasted. Anecdotes plus more anecdotes and even more anecdotes make a trend. And that trend is, an open-arms welcome from librarians and archivists around the world. I must add: I am particularly grateful and rather awed by the many new "jewels" that rest happily and eagerly in my collection of future research projects.





Figure 1. (Left) Information technology professionals Dr. Ayumu Saito and Ms. Noriko Kitagawa at the Fukui Institute for Fundamental Chemistry, Kyoto University, March 18, 2025. Photograph courtesy J. I. Seeman. (Right) Seeman holding one of Tetsuo Nozoe's autograph books, Tohoku University, Sendai, March 11, 2025. Photograph courtesy Yoshiteru Maeno, Kyoto University.

How could librarians and archivists know the importance of each of our requests without substantive connectivity with their clients? I posit that we users of libraries and archives around the world should personally thank these information scientists for their work on our behalf and on behalf of our shared scientific and cultural heritage. We probably never, or never enough, directly share with them why this or that request is important in the history of humankind. We can do that, also.

Let me encourage you to connect with your librarians and archivists and share with them the stories of your research. When I do so, as I always do, I can feel their eyes opening wide. Really wide! For example, at an

archive, I bring special documents to the attention of the archivist and explain their uniqueness and their value. I can sense their own appreciation of the documents they curate as well as the research I do and their role in that research. They are, all too invisibly, collaborators in my research. And they also become members of the audience for my research.

So, you can see why librarians and archivists are among my favorite people. And surely, they are some of your favorite people as well. It is important and rewarding to make the effort to interact with, and especially to thank, these sometimes invisible but always invaluable professionals.





Citation: Kragh, H. (2025) Positronium Chemistry: Origin, Development, and Historical Roots. *Substantia* 9(2): 9-19. doi: 10.36253/Substantia-3540

Received: Jun 11, 2025 **Revised:** Jun 28, 2025

Just Accepted Online: Jun 30, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

Positronium Chemistry: Origin, Development, and Historical Roots

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Abstract. Positronium science has for more than half a century been an important research area located somewhere between physics and chemistry. Based upon the study of positrons and the electron-positron atom called positronium, the field was originally part of atomic physics but soon became embraced also by the chemists. In this article I present a first preliminary study of the origin and early history of positronium science with an emphasis on its chemical aspects. It includes a so-called prehistory going back a long time before the discovery of the positron, at a time when the ether was sometimes conceived as consisting of pairs of oppositely charged electrons. Apart from positronium, the intertwined history of muonium – where the electrons are replaced by the heavier muons – is also described. More generally, the paper discusses from a historical perspective how various kinds of exotic atoms, antiatoms and superheavy atoms included, have become parts of the chemical sciences.

Keywords: positronium, muonium, exotic atoms, antimatter, hydrogen isotopes

1. INTRODUCTION

Terms such as 'positronium' and 'muonium' may not be commonly known, but for more than seventy years these exotic atomic systems or quasi-atoms have been studied intensely by a large number of researchers. They form today the basis of a flourishing interdisciplinary research area cultivated mostly by physicists and chemists but also by other scientists. In this essay I outline the development of the field from a historical perspective, paying particular attention to how positronium and like atomic systems migrated from theoretical physics to chemistry. Of course, it is not the only migration of this kind. On the contrary, since the mid-nineteenth century the chemical landscape has changed significantly as a result of new discoveries in physics. Modern positronium chemistry, largely a child of quantum and nuclear chemistry, is as much physical in nature as chemical.

The standard history of positronium science – insofar there is such a history – is to trace the field back to either 1934, when electron-positron atoms were first hypothesized, or to 1945, when the term positronium was coined in the context of quantum physics. However, one can find earlier if only qualitative ideas of negative and positive electrons (not positrons) forming atom-like

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systems. These early and today forgotten ideas, summarized in section 2, may not belong to the history of positronium proper, but at least they belong to its prehistory. The alleged birth of positronium in 1934 is critically evaluated in section 3, to be followed by section 4 dealing with the first decade of the post-World War II development. At that time positronium was not yet recognized to be of interest to chemists, a situation that changed only in the 1960s with the childhood of positronium chemistry (section 5). In section 6, I take a broader and less historical look at positronium, muonium and related quasi-atoms (including antiatoms), briefly discussing their chemical nature and relevance.

Inevitably, the history presented here is selective and highly incomplete. But as I see it, even such a history is preferable to no history.

2. PREHISTORY: ELECTRONS AND ATOMS

Whereas positrons are positive electrons, in a historical context positive electrons (e^+) are not necessarily positrons (\bar{e}). In fact, the idea of light positive unit charges predates the discovery of the positron by more than half a century. Likewise, the idea of atomic systems composed of symmetrical combinations of positive and negative electrons can be found long before positronium was introduced.

As early as about 1870 the eminent German physicist Wilhelm Weber suggested that all matter and ether consisted of oppositely charged electrical particles of the same mass orbiting around each other.² By means of this hypothesis he thought that the chemical atom might in principle be explained. Without using the term 'electron' Weber's speculation was followed up by Karl-Friedrich Zöllner and a few other German physicists. However, it left no noticeable impact on the development that in the late 1890s led to J. J. Thomson's discovery of the (negative) electron. Even before Thomson's celebrated discovery Joseph Larmor proposed an electromagnetic theory based on the assumption of primordial particles which were "quantitatively alike, except that some have positive and others negative electrifications, the one set being ... simply perversions or optical images of the other set." He compared the two kinds of electrons - a term he used - with the chemists' optical isomers, stating that a simple atom or molecule might be "composed of a single positive or right-handed electron and a single negative or left-handed one revolving round each other."3

To the surprise of the physicists, the new electron appeared only as a negatively charged particle with no positive counterpart. And yet, although positive electrons as mirror particles of the negative ones failed to turn up in experiments, for a period of time they were considered as possible constituents of ether and matter.⁴

The British-Australian physicist William Sutherland worked on a variety of subjects, many of them on the borderline between physics and chemistry. Among the research topics he investigated were Brownian motion, viscosity, spectroscopy, the ionic theory of solutions, the structure of water, and the intermolecular forces in liquids and solids.⁵ In a paper of 1899 he suggested that the free ether was made up of elementary particles, each of them composed of a positive and negative electron revolving around their centre of gravity.6 For the neutral ether particle, he coined the name 'neutron' which would later be adopted for a very different kind of elementary particle. "In free æther the positive and negative electron revolving ... round their centre of inertia form what I have proposed to call the neutron, the electric doublet," Sutherland stated two years later.⁷

Possibly without knowing of Sutherland's proposal, in his widely read textbook *Theoretische Chemie* Walther Nernst reintroduced the ethereal neutrons consisting of electron doublets. In agreement with Larmor and Sutherland, he wrote:

The relationship between positive and negative electrons evidently calls to mind the one between optical isomeric twins. It is a question of much importance whether a compound of the positive and negative electrons ($\bigoplus =$ neutron, an electrically neutral massless molecule) really exist; we shall assume that neutrons are everywhere present like the luminiferous ether, and may add that the space filled by those molecules is weightless, non-conducting, but electrically polarisable.⁸

To mention but one more example from the fin-desiècle era, in 1901 young James Jeans examined in mathematical detail a hypothesis similar to the one of Sutherland and Nernst. Jeans considered "an atom as a collection of negative and positive ions [electrons], the negative ions each carrying a charge of electricity of amount –e, and the positive ions each carrying a charge +e."9 The only difference between the two species of electrons was the charge. Moreover, he stated that when a positive electron collided with a negative one, the two would annihilate according to the process

$e^- + e^+ \rightarrow \text{radiation energy}$

Thirty years later, Jeans' hypothetical process would reappear as Dirac's electron-positron annihilation. Without going into further details, it may not be too farfetched to see in these early speculations an anticipation of what much later became known as positronium.

Still in 1906 atoms composed solely of positive and negative electrons was considered a possibility, if not perhaps the most likely one. Among several other atomic models, Oliver Lodge referred to the possibility that

... the atom may consist of a multitude of positive and negative electrons, interleaved, as it were, and holding themselves together in a cluster by their mutual attractions, either in a state of intricate orbital motion, or in some static configuration, kept permanent by appropriate connexions.¹⁰

Although the positive unit charge was soon identified as the hydrogen ion H⁺, eventually called the proton, the 'positive electron' continued to appear in the physics literature well into the 1920s if no longer as a mirror particle of the electron.¹¹

3. MOHOROVIČIĆ'S ELECTRON-POSITRON ELEMENTS

The modern positron was predicted by Paul Dirac in 1931 as the electron's antiparticle. In the same groundbreaking paper, he predicted the existence of antiprotons.¹² Two years later Carl Anderson reported his discovery in cosmic rays of positive electrons, which he called positrons. However, Anderson's discovery was unrelated to Dirac's theory and it was only later in 1933 that the positron was identified with the antielectron. As Dirac realized, this particle would quickly annihilate with a negative electron $(e^+ + e^- \rightarrow 2\gamma)$, a process verified in 1934. When Dirac received the Nobel Prize in late 1933, the positron was widely accepted if not necessarily as an antielectron. With the discovery of artificial radioactivity in 1934, it was understood that positrons are not particularly rare or exotic. In some artificially produced nuclides, a proton transforms spontaneously into a neutron, a positron and a neutrino: $p \rightarrow n + e^+ + \nu$. Dirac ended his Nobel lecture with speculations about antimatter composed of antiprotons and positrons. Perhaps, he suggested, half the stars in the universe were made of matter and the other half of antimatter.¹³

Dirac's speculation inspired an obscure Yugoslavian-Croatian physicist by the name Stjepan Mohorovičić to suggest a series of very light celestial atoms composed solely of electrons and positrons. The simplest of these exotic atoms, an electron and a positron revolving around their common centre of gravity, he called 'electrum'. Although Mohorovičić's paper in Astronomische Nachrichten was ignored for two decades, today it is widely recognized as the pioneering paper in posi-

tronium science. The first reference to it in a research publication dates from 1953 and presently it has received more than 200 citations.¹⁵

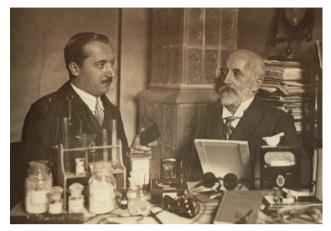


Figure 1. Stjepan Mohorovičić with his father Andrija Mohorovičić. Source: https://cro2.salamander-studios.com/2019/06/03/stjepan-mohorovicic/

The little-known Stjepan Mohorovičić was a productive and versatile but also decidedly unorthodox scientist. Born in Croatia in 1890, he was the son of the much better known Andrija Mohorovičić, the noted geophysicist and seismologist who in 1910 proposed the discontinuity between the Earth's crust and mantle named after him as the Moho discontinuity (Fig. 1). Mohorovičić junior published on a variety of subjects including geophysics, meteorology, fundamental physics, astronomy and philosophy.¹⁶ He was particularly interested in Einstein's theory of relativity which he however rejected as philosophically unacceptable and lacking in experimental support.¹⁷ Like many other anti-relativists in the 1920s he maintained that the absolute ether was indispensable. There is little doubt that his poor reputation among mainstream physicists was a contributing reason why his 1934 paper on electron atoms attracted no interest at all.

Mohorovičić derived the theoretical spectrum of the electrum atom e^+e^- essentially by copying Bohr's treatment of the hydrogen atom from 1913, the only difference being that the heavy proton was now replaced with the much lighter positron (M/m=1836). While in the case of the hydrogen atom the reduced mass

$$m^*=rac{mM}{m+M}=rac{m}{1+m/M}$$

is close to the electron mass m, for electrum it is half this value, $m^* = m/2$. Likewise, while the ionisation energy of a hydrogen atom in its ground state is 13.6 eV, for elec-

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trum it is 6.8 eV. Mohorovičić considered electrum to be a new chemical element, if so far hypothetical, with atomic number Z=1 and atomic weight A=0.0010863 on the H=1 scale. He proposed Ec as its chemical symbol. Because of electrum's large diffusion velocity, the element would have escaped the gravitational field of the Earth, but "the gas could easily be part of the corona of the fixed stars and the astrophysicists should at first look for it in the Sun's corona." To detect the element its characteristic line spectrum would suffice.

Electrum was not the only electron-positron atom considered by Mohorovičić (Fig. 2). He thought of a whole class of such elements, which he called "abaric" meaning non-heavy (from the Greek barys for heavy or weighty). For a few of them he suggested names and symbols, as for 'nobilium' (Nb) consisting of a nucleus of two electrons and four positrons (Z = 2) surrounded by two satellite electrons. The atomic weight of nobilium was thus 0.00436. Another of the abaric elements was 'slavium' with chemical symbol SI and atomic number Z = 3 which he suggested might be identical to the old 'coronium' element hypothesized by earlier chemists and astronomers. The possible existence of coronium was based on an unidentified solar spectral line which was only explained in 1939 as due to the highly ionised iron atom Fe13+.18 By 1934, the hypothesis of coronium as a celestial element was still alive but no longer taken seriously in mainstream science.

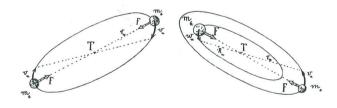


Figure 2. Mohorovičić's drawings in his 1934 paper of electrum (left) and nobelium (right).

Confident that the abaric electron-positron elements were real and would one day be detected, Mohorovičić ended his paper with an appeal to the chemists: "It will be up to the spectroscopists to search for these new elements, not only in the spectra of stars and nebulae but also in discharge tubes at high voltages. Should the predicted elements be confirmed in this way, they would also be of importance to pure chemistry."

Was Mohorovičić's electrum really the same as the later positronium? Did positronium science have its humble origin in his 1934 paper? Although the Croatian physicist clearly imagined an electron-positron atomic system, he did not identify the positron with

Dirac's antielectron. For this reason alone, electrum was not just another name for the positronium system discovered many years later. Had Mohorovičić accepted the antielectron, which he knew of, he would have realized that the two constituents of electrum would rapidly annihilate. But his hypothetical hydrogen-like electrum atom was no less stable than the real hydrogen atom. To phrase it differently, in its spirit Mohorovičić's atom was closer to the fin-de-siècle ether speculations of Sutherland, Jeans and Nernst than it was to Dirac's ideas based on relativistic quantum mechanics. On the other hand, there was the significant difference that while Sutherland and Jeans had ordinary atoms in mind, Mohorovičić thought of a series of entirely different atoms that might exist in parallel with the ordinary ones. I conclude that it is only half a truth to trace positronium history back to Mohorovičić's 1934 paper in Astronomische Nachrichten. The Croatian physicist is an interesting figure in the history of science but to credit him as "the father of positronium" is to go too far. 19

4. FROM ELECTRUM TO POSITRONIUM

Other and perhaps better father figures may be American physicists Arthur Ruark and John Wheeler. In a short note in *Physical Review* dated 13 November 1945, Ruark suggested the name 'positronium' for the simplest electron-positron atom. "I think no physicist will doubt the existence of these unstable hydrogenlike atoms," he opined. As Ruark stated, possibly for priority reasons, he had contemplated the possibility of such an atom for several years: "In 1937 I conceived the idea that an unstable atom composed of a positron and a negative electron may exist in quantities for spectroscopic detection."20 Shortly before he submitted his note, he had learned that Wheeler, by then a wellknown nuclear physicist, had just submitted a longer and more detailed paper on the same topic. However, whereas Ruark's note appeared in print already on 1 December 1945, it took until 11 October 1946 before Wheeler's article on 'polyelectrons' appeared in the Annals of the New York Academy of Sciences.²¹

While both authors unknowingly reproduced some of Mohorovičić's results, such as the size and optical spectrum of the positronium atom, they went much beyond the Croatian physicist by recognizing that the positron was an antielectron and that the atom would therefore decay by annihilation into pure radiation energy. By taking into account the electron's spin – something Mohorovičić had ignored – they realized that the positronium system could exist in two states, one a sin-

glet (para-positronium with antiparallel spins) and the other a triplet (ortho-positronium with parallel spins). While para-positronium decays into two photons, in the case of the ortho form the result is $e^+ + e^- \rightarrow 3\gamma$. For the first state Wheeler calculated a lifetime of the order 10^{-10} s and for the second 10^{-6} s (the presently known values are 1.3×10^{-10} and 1.4×10^{-7} s). Ruark and Wheeler both discussed various means by which the hypothetical positronium might be revealed experimentally but without advocating a definite experiment.

As to nomenclature, Wheeler spoke of 'polyelectron' generically and for the simplest systems he chose the names 'bi-electron' and 'tri-electron.' The associated symbols were P^{+-} and either P^{++-} or P^{+--} . The hypothetical positronium molecule Ps_2 was designated P^{++--} . Wheeler was the first to consider the question of whether a positron can attach itself to an atomic or molecular system and form compounds such as Cl^-e^+ and H^-e^+ . In addition to the suggestion of polyelectrons, Wheeler also considered the polarisation of photons from e^-e^+ annihilation. His remarks on this issue have later been interpreted as "the first clear and transparent written description of what quantum entanglement really is."²²



Figure 3. John Wheeler. Source: Niels Bohr Archive, Photo Collection.

In his autobiography from 1998, Wheeler recalled that for some time he had been fascinated by the idea that everything was built of negative and positive electrons:

I just explored some of the atoms and molecules that could be constructed from electrons and positrons alone, and calculated their properties. The simplest such atom ... is now called positronium, and its properties have since been extensively studied. It has the purity of my early dreaming. Unadulterated by quarks and anything else, its properties can be wholly understood in terms of the electron, the positron, and the photon. Later, I went further, calculating how a large collection of positronium atoms might behave. Liquid positronium should be superconducting.²³

The Ruark-Wheeler positronium was no less hypothetical than Mohorovičić's electrum, but within a few years it metamorphosed into a real entity. Born in Vienna in 1917 to a Jewish family, Martin Deutsch emigrated to the United States where he later became a physics professor at MIT.²⁴ In a series of experiments, he measured the delayed gamma photons emitted by positrons stopped in gases and gas mixtures. Correlating the e^+e^- annihilation rate to the gas pressure, he found in his data convincing evidence for a bound state of the two particles. As he concluded in a brief paper dated 13 March 1951, the data were "proof of the abundant formation of positronium." It took another thirty years until the existence of the negative ion $e^+e^-e^-$ predicted by Wheeler in 1946 was demonstrated experimentally. ²⁶

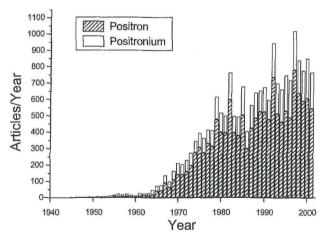


Figure 4. The growth of positron and positronium science. Reproduced from ref. 46, p. 8.

The confirmation that positronium really existed, albeit as an ephemeral atomic system only, was followed

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up by a large number of experimental investigations that placed positronium physics as a new and exciting branch of nuclear and particle physics. In July 1965 the First International Conference on Positron Annihilation was held in Detroit. As shown in Fig. 4, the number of research publications in the new field grew dramatically, in the early period dominated by workers in the USA and USSR. It was in this early period that positronium, conceived as an element, was designated the chemical symbol Ps first appearing informally in a 1959 paper in *Physical Review.*²⁷

Still by the mid-1950s positronium science was almost identical to positronium physics. It was a research area predominantly cultivated by particle physicists with the aim of understanding the fundamental interactions between radiation and matter. But a few physicists realized that since positronium was an atomic system, hence a kind of element, it might just as well belong to the chemical sciences. As two American physicists wrote in an extensive review article:

The formation and decomposition of positronium is related to the properties of the molecules of the surrounding gas; in a sense, it can be regarded as a chemical problem It would seem natural that the work should be continued by chemists, to whom positronium should present the challenge of a new element whose chemical properties have to be classified; and, owing to its extreme simplicity, it may be an element of particular value for the understanding of the mechanism of chemical reactions and for the study of the nature of the chemical bond.²⁸

The article was reviewed in the *Journal of the American Chemical Society* the following year, with the reviewer, the chemist Richard W. Dodson, citing approvingly the above quotation.²⁹ This may have been the first time that the term positronium appeared in a high-ranking chemical research journal.

5. BEGINNINGS OF POSITRONIUM CHEMISTRY

Early workers in what came to be positronium chemistry were physicists or nuclear chemists who were primarily interested in how positrons and positronium interacted with matter in either the gaseous, liquid or solid state. For example, a study of 1959 looked at electrochemical reactions in aqueous solutions such as the reduction process³⁰

$$Cd^{2+} + Ps \rightarrow Cd^{+} + Ps^{+}$$

John Lee, a young Australian scientist, completed in 1960 a Pd.D. dissertation on "The Chemical Behav-

iour of Positronium" which he later developed into an influential monograph co-authored by James Green. Although the title of the book was *Positronium Chemistry*, it was not chemistry in the traditional sense accepted by the majority of working chemists at the time. Correspondingly, in this early phase almost all research on positronium chemistry was published in physics and not in chemistry journals.

The new field was thoroughly interdisciplinary and from the late 1960s onwards it was increasingly cultivated by scientists with a background in the chemical sciences. Articles on positronium began to appear in the Journal of Physical Chemistry and, more frequently, in the Journal of Chemical Physics established in 1932. One of the pioneers was the German-born Hans Ache, a professor of chemistry who contributed with several papers in the mentioned journals. In an introduction of the subject to readers of Angewandte Chemie-International Edition, he described positronium as "the lightest isotope of hydrogen" and "an analog of the hydrogen atom ... in which the proton is replaced by a positron."32 As he added, no doubt correctly, this atom-like system was "probably not so well known" to chemists and yet it was of great value with regard to a number of chemical problems. In a later review article based on a conference held in 1977, he commented on the short history of positronium chemistry:

The area of Ps chemistry was and still is made by scientists trained by physicists. However, despite all the pioneering efforts by these groups, chemists remained rather indifferent to this new atom and it was only during the past five to seven years that chemists of all persuasions have become more and more involved in the chemistry of this exotic atom ... We have successfully finished the first stage and ... we have to direct our attention now to the second stage, a task for which we need the cooperation of chemists in all areas of chemistry reaching from nuclear and radiation chemistry to bio- and enzyme chemistry.³³

Positron and positronium chemistry was not only cultivated by Western scientists but also attracted much interest in the Soviet Union, where the leading authority was Vitaly Goldanski, director of the Institute of Chemical Physics under the USSR Academy of Sciences. In 1968 he published a comprehensive book-length review of positron annihilation and positronium science which he described as "one of the most important branches of contemporary nuclear chemistry ... a tool for investigating the physical and chemical properties of matter." Goldanski was fascinated by the new light atoms, which apart from positronium also included the more recent muonium atom in which the positron is replaced by the 207 times heavier positive muon. He counted both of the

new atoms as isotopes of hydrogen, suggesting that the centre of mass in positronium might count as a kind of immaterial nucleus.³⁵

Although the history of the muon (μ) is very different from that of the positron, muonium history has much in common with the older and better known positronium history. 36 The negative muon μ^- is conventionally called a muon and the positive muon an antimuon. The existence of an atom-like entity with an electron (e^{-}) revolving round a muon (μ^+) was proposed in a paper of 1957 in which the term 'muonium' was also introduced.³⁷ Three years later, the muonium particle was found experimentally by a team led by Vernon Hughes, a respected nuclear and particle physicist at Yale University. In a popular article in American Scientist, he described muonium as a new atom remarkably similar to the hydrogen atom except for its mass and short lifetime. Whereas the reduced mass m^* of positronium is m/2, for muonium it is close to that of the hydrogen atom. Correspondingly, the Bohr radius of muonium is 1.0043 times that of the hydrogen atom, and for the ionization energy the ratio is 0.9957. Hughes briefly suggested that the exotic atom might be of relevance to the chemists: "It seems clear that a substantial field of research in muonium chemistry may be available for study."38 And indeed, within a few years 'muonium chemistry' evolved as a subfield in parallel with the larger and slightly older field of positronium chemistry.³⁹

Muonium looks in some respects like hydrogen, but there is the crucial difference that the first atom only survives for a period of approximately 10^{-6} s before the muon decays into an electron and two neutrinos. This happens to be of the same order as the lifetime of an ortho-positronium atom. But whereas the two components of positronium annihilate, in muonium the instability is caused by the muon's intrinsic lifetime of 2.2×10^{-6} s.

As IUPAC has accepted the chemical symbol Ps for positronium, so muonium has been assigned the symbol Mu. Whereas the first is a particle-antiparticle system, the latter is not. The muonium analogue of positronium would be the bound system ($\mu^+\mu^-$), which is sometimes called 'true muonium.' Alas, this system is as yet hypothetical only. Since muons and electrons both belong to the lepton family of elementary particles, physicists have recently coined the term 'leptonium' as a common name for positronium and muonium. However, it is not much used and 'leptonium chemistry' not at all. (While 'positronium' and 'muonium' are both accepted by the Oxford English Dictionary, 'leptonium' is not).

Paul Percival, a Canadian expert in muonium chemistry, reflected in a paper of 1990 on the nature of the

new field.⁴⁰ Did it belong primarily to chemistry or to physics? As Percival pointed out, from a chemical point of view the properties of the muon are irrelevant as the chemistry is solely determined by the electrons. "Implicit in any definition of muonium chemistry is a demarcation of the boundary between chemistry and physics," he stated. Since no such intrinsic boundary seems to exist, he adopted a pragmatic criterion, namely to "define chemistry as what chemists do." According to Percival:

Muonium chemistry is defined by the activities of the handful of chemistry groups doing experiments at meson factories ... These few researchers cover an amazing breadth of science ... [and] they share expertise in radiation chemistry, molecular spectroscopy, chemical kinetics, molecular dynamics and more.

Before leaving muonium it is worth calling attention to the much heavier but still related atom called *muonic helium* first observed in 1980.⁴¹ This system consists of an electron revolving around an ordinary He-4 nucleus with a negative muon orbiting very close to it. The effective nucleus or pseudo-nucleus (α , μ^-) is thus of charge +1, namely an alpha particle combined with a negative muon. Despite its two protons, muonic helium behaves chemically more like hydrogen than helium. For this reason, it is sometimes considered a heavy isotope of hydrogen.

Positronium science was born in physics and subsequently migrated not only to chemistry and astronomy, but also to biology and medicine.⁴² Although the evanescent electron-positron atoms may seem to be strange creatures, today they are produced routinely and in large numbers also outside the laboratory. In positron emission tomography (PET), a medical technique dating from the 1960s, a radioactive positron-emitting tracer, such as ¹⁸F, is injected into the patient. With a half-life of 110 min the fluorine isotope decays into ¹⁸O and a positron which annihilates with an electron in the body. As a result, gamma photons are produced and these can be detected in the scanning device.⁴³ About 40% of the annihilation processes occurs through the formation of short-lived positronium atoms. With recently invented PET systems it has proved possible to study the photons from positronium annihilation and in this way to construct positronium images of the human brain.44

One gets an impression of the rapid growth of positron and positronium science through a bibliography compiled in 1975 which includes references to 2,449 research articles published in the period 1930-1974. In the introduction to the bibliography, the compiler wrote: "It is apparent that positrons are finding increasing applications in physical chemical measurements, including chemical dynamics and mechanisms."

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Half a century after Deutsch's discovery the annual output of papers related to positron annihilation and positronium chemistry, broadly conceived, was about 800 of which almost half were of a chemical nature. 46 By June 2025 the Web of Science records a total of 6,250 papers with 'positronium' as a topic and 3,147 papers with the term in its title. The corresponding numbers for 'muonium' are 2, 270 and 1,253, respectively. It should be noted that in the more recent literature the terms 'positronium' and 'muonium' often appear under their symbols Ps and Mu. To mention but one example, in a 2006 paper titled "Relativistic Ps- and Ps" the term positronium appears 12 times and that of Ps 68 times. 47

The atoms of ordinary gaseous elements, like hydrogen, form molecules (H₂). As Wheeler briefly suggested in 1946, the same may be the case with positronium forming Ps₂ or P⁺⁺⁻⁻ in his notation. However, the theoretically possible Ps₂ molecule called dipositronium defied observation for a very long time. Only in 2007 did laboratory experiments provide unambiguous evidence that the molecule had been created and in this sense exists.⁴⁸ It also took a long time before the theoretically predicted positronium hydride (HPs) was turned into a reality. Consisting of one proton, two electrons and one positron, the stability of the molecule was predicted in 1951. Forty-one years later a group of physicists at Aarhus University, Denmark, created it by bombarding methane with an intense beam of positrons:⁴⁹

$$e^+ + CH_4 \rightarrow CH_3^+ + PsH$$

As far as the natural occurrence of either free Ps or Ps_2 is concerned, all searches have been negative. As Mohorovičić pointed out back in 1934, it should be relatively easy to detect the entities by means of their emitted optical spectral lines. Later astrophysicists agreed that this was indeed a possibility, 50 but so far there is no generally accepted observation of the spectral signatures from celestial positronium atoms. Nonetheless, astrophysicists and astrochemists have studied in detail the numerous gamma photons emitted by positron-electron annihilation in the interstellar medium and by a variety of stars. As most of these photons are known to have their origin in Ps atoms, these atoms may be said to have been indirectly observed in cosmic space.

6. DIGRESSION ON ELEMENTS, MATTER AND ANTIMATTER

As mentioned, in the early literature positronium was sometimes described as a superlight isotope of

hydrogen. S1 However, other authors have argued that this is a misconception. According to David Walker, "Positronium (e^+e^-) is not a hydrogen isotope. In this species there is no nucleus because the two particles are of equal mass." Walker believed in a light isotope of hydrogen, but this isotope was muonium and not positronium. The majority of scientists undoubtedly agree, if from different arguments, that positronium does not qualify as a hydrogen isotope. Two isotopes have the same number of protons but a different number of neutrons, which is obviously not the case with positronium and hydrogen. Moreover, "isotopes always have similar chemical reactivities [whereas] Ps reacts with molecules very differently from H ... it is inappropriate to consider Ps a light isotope of H." 553

But then, what is an isotope? The current IUPAC definition states that two nuclides are isotopes if they have the same atomic number Z but different mass numbers A. It does not refer explicitly to protons, neutrons or chemical properties. The view of muonium as a hydrogen isotope has been sanctioned by IUPAC which in 2001 recommended names for muonium and the three hydrogen isotopes protium, deuterium and tritium. Despite the absence of a proton, "Muonium ... can be regarded as a light isotope of hydrogen," we are told. 54

The question of isotopy is closely related to the question of whether or not positronium (or muonium) should occupy its own place in the periodic system. If muonium is admitted as a hydrogen isotope, like deuterium and tritium, it already has a place. But what about the non-isotopic positronium? One can simply declare it a non-element outside the periodic system, end of story. The three editors of Principles and Applications of Positron and Positronium Chemistry thought otherwise, namely that the element-like positronium deserved a place in the system. "It should have its own special place in the Periodic Table of the Elements, as the Period 0 (zero), and Group 1, or 1A."55 This is how positronium is placed in a revised and unconventional periodic system, an element preceding hydrogen in group 1 and with an atomic weight of 0.0011. The proposal, the only one of its kind, was politely ignored.

Not only do positronium and muonium have chemical properties, it has also been argued that the same is the case with muonic helium and the μ^+ particle itself. According to two Iranian quantum chemists:

The positively charged muon is similar to the proton from the structural and bonding viewpoint and deserves to be placed in the same box of hydrogen in the Periodic Table ... The same reasoning may be applied to place muonic Helium, as a composite system, also in the box of hydrogen. ⁵⁶

If the positive muon is admitted as a hydrogen isotope – which is not the standard view – it would be another isotope lighter than hydrogen (protium) if not quite as light as positronium.

Although positronium includes an antiparticle, it is not an antiatom in the ordinary sense of the term. The simplest antiatom is a system composed of a positron orbiting an antiproton (H = $\bar{p}e^+$), which physicists at CERN succeeded to create in 1995. Antihelium with two antiprotons, two antineutrons and two satellite positrons has not been detected in either the laboratory or in nature, and nor have heavier antiatoms. Only a few simple antinuclei have been produced, namely (apart from the antiproton) two helium antinuclei He of mass numbers 3 and 4.57 Nonetheless, atomic and even molecular antimatter is theoretically possible and has attracted much attention by physicists, astronomers and chemists (not to mention science fiction authors). An example from the literature is the massive volume New Directions in Antimatter Chemistry and Physics published in 2011.⁵⁸ The term 'antimatter chemistry' turned up in 1994, but it seems to be a hyperbole or misnomer insofar that the field is largely restricted to purely theoretical investigations or to experiments with antihydrogen.

If antimatter consisting of antielements exist, it will have the very same chemistry as ordinary matter. As the Swedish physicist Hannes Alfvén, an advocate of cosmic antimatter, said: "The only difference between water and antiwater is that a mixture of the two would generate tremendous energy."59 In an antiworld the antielements would be organized in a system completely symmetric to the well-known periodic system. A few people have speculated about such an antisystem as an extension of the ordinary one, for example by providing the antielements with negative atomic numbers (Z = -1 for \bar{H} , Z =-2 for He, etc.). Unfortunately, the Wikipedia article on antimatter claims that "a complete periodic table of antimatter" was envisaged by Charles Janet, a French naturalist and amateur scientist, even before Dirac came up with the idea of antiparticles.⁶⁰ Perhaps needless to say, the claim is unfounded.

7. CONCLUSIONS

As shown in this paper, the electron-positron atomic system known as positronium has historical roots that can be traced back many years before the positron was discovered in 1933. The atom, as it is generally called, was hypothesized twice, first in 1934 by Mohorovičić and next in 1945-46 by Ruark and Wheeler. However, the positive charge was only identified as an antielectron in the latter

case. As far as the actual discovery of positronium is concerned, priority belongs to Deutsch's work of 1951. Initially seen as a playground for theoretical physicists, since the late 1950s chemists increasingly studied the exotic and short-lived atom. The early development of positronium chemistry and its place in the scientific landscape is sketched in the present paper. The same is the case with its sister subfield called muonium chemistry.

Some of the general problems concerned with positronium and muonium refer to their status as chemical entities. They are atoms of a sort, but of what sort? If they are atoms, supposedly there are also corresponding elements and like all other elements these should occupy places in the periodic system. Chemists discussed these and related questions early on, with the result that today muonium is widely accepted as an unusual isotope of hydrogen. Despite having distinct chemical properties, positronium is not generally counted as an element. Some of the general questions relating to positronium and muonium are relevant also to other forms of exotic matter including antimatter, superheavy elements, and protonium $(p\bar{p} = p^+p^-)$. These questions have been discussed in the literature from a philosophical point of view,⁶¹ but they are not part of the present paper.

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Citation: Nguyen, T.T., Garrido Sanchis A., Pashley R.M. (2025) Enhanced Desalination in a Hot-Bubble Pilot Plant. *Substantia* 9(2): 21-34. doi: 10.36253/Substantia-3353

Received: Feb 27, 2024 **Revised:** Jun 17, 2025

Just Accepted Online: Jun 19, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

Enhanced Desalination in a Hot-Bubble Pilot Plant

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Abstract. The bubble-column evaporator (BCE) offers a simple, energy-efficient and affordable seawater desalination process based on sub-boiling evaporation by enhancing the efficiency of heat and mass transfer through a constant flow of dense, heated bubbles rising in a solution-filled column. A large-scale hot-bubble pilot plant (HBPP), based on the BCE, was built to implement the thermal desalination process. Several different inlet gases, dry air, helium and combustion exhaust gas, were used in the HBPP to produce purified water from synthetic seawater. The efficiency was improved by using hot combustion gas instead of dry air or helium at the same inlet temperature, thereby reducing the energy consumption.

Keywords: Desalination, hot-bubble pilot plant, helium, combustion gas, dry air

1. INTRODUCTION

Seawater desalination has been widely used on a global scale to address freshwater scarcity resulting from rapid population and economic growth. Desalination techniques can be classified into thermal methods, which mostly involve heating water to its boiling point to generate water vapour, and high-pressure membrane processes in which seawater is filtered through a membrane¹. While membrane processes offer the advantage of separating salt from seawater without the need for high temperatures, they require comprehensive pre-treatment of the feedwater to avoid membrane fouling, together with the use of sophisticated energy-intensive high-pressure pumping systems². The main challenges in seawater desalination include achieving high efficiency, reducing energy consumption, preventing continuous membrane fouling in high-pressure membrane processes² and making the process more economical and environmentally acceptable³.

Bubble-column desalination is an innovative and emerging thermal technology that offers a simpler and more environmentally friendly process. The process is simpler because it does not require expensive membranes or a supply of high-pressure steam, enabling efficient heat and mass transfer at sub-boiling temperatures⁴. The bubble-column evaporator (BCE) is a scaled-down emulation of the natural semi-permeability of the water-gas interface

used for desalinating saltwater through a process resembling the water cycle^{3,4}. To be more specific, the BCE method uses a pre-heated inlet gas to transfer thermal energy to the aqueous solution, resulting in an efficient transfer of mass as water vapour into the rising bubbles created by the gas⁵. These bubbles quickly become saturated with the water vapour⁶ and transport it to the top of the column⁵, where it can be condensed into pure water⁷. The thickness of the water film through which the gas bubbles are sparged is of importance to both evaporation and condensation of the water vapour. However, the estimate of a thin heated solution layer surrounding the hot rising bubbles was developed in order to explain how salts like ammonium bicarbonate could be thermally decomposed at relatively low column solution temperatures⁸. That is because the AB ions cannot penetrate the bubbles, whereas viruses and bacterial cells could be exposed (at least their surfaces) to the hot gases in the bubbles and hence be sterilized9. With the bubble vapour desalination process, we are only interested in water vapour transfer across the gas/water interface and the energy requirement. Hence, the thickness of any heated water layer is not actually relevant to the bubble vapour desalination process.

The bubble column method makes use of a finding dating back to the 1930s, when Russian engineers observed that the introduction of salt into a flotation chamber led to a reduction in bubble size and an improvement in overall efficiency⁵. The presence of certain salts enhances the effectiveness of flotation by inhibiting bubble coalescence¹⁰; dissolved salt at seawater concentrations in the BCE process enables the formation in the column of a substantial packing volume of relatively uniform bubbles with diameters in the range 1-3 mm. This configuration significantly improves the efficiency of evaporation and transportation of saturated water vapour inside gas bubbles¹¹, as high density bubbles will collect water vapour throughout the entire body of the salt solution¹². By comparison, multistage flash distillation (MSF) uses essentially heating surfaces to flash evaporate water. Furthermore, the traditional thermal evaporation via boiling is an irregular process and can result in a higher rate of corrosion of the heating surfaces. In contrast, the BCE continuously produces new surfaces and the inhomogeneity in temperature between the bubbles and the solution catalyses transient high-temperature mass and heat transfer at temperatures significantly below boiling point with a high vapour-collection efficiency¹². Therefore, the bubble column method eliminates the need to boil the solution, thereby reducing inconsistencies and lack of control in the boiling process, and mitigating corrosion risks and scale production⁷. The continuous flow of gas bubbles passing through the salt solution ensures controlled, uniform and very fast (a few tenths of a second) vapour collection up to saturation⁴.

Furthermore, water vapour, but not ions dissolved in the seawater, is continuously transported by the bubbles, so that the BCE process is resilient to highly contaminated feed solutions¹³, with no requirement for feedwater pre-treatment and no high pressures needed¹⁴. In contrast, commercial RO systems require high mechanical pressures significantly above the osmotic pressure of seawater to move pure water through a semi permeable membrane, in a relatively complicated process which produces large volumes of salt concentrate to be discarded out to sea.

Altogether, these factors contribute to an overall efficiency improvement, compared with quiescent systems⁴, making the dynamic bubble column method a promising approach for desalination. However, even though the bubble process is straightforward, our understanding of the physical and chemical principles underlying the BCE remains limited, leaving several aspects yet to be explored and fully elucidated¹⁵.

With the aim of enhancing the BCE process for desalinating seawater, several different inlet gases, air, nitrogen, carbon dioxide and helium, have been tried in a lab-scale BCE. Significantly enhanced evaporation occurred when using helium compared to dry air, an approximately threefold increase at an inlet-gas temperature of 150°C^{5} . This was accompanied by a notable decrease in the apparent enthalpy associated with the vaporization of water ΔH_{ν}^{14} .

These results were in good agreement with those reported by14 for inlet gases (air/helium) at 75°C. The evaporation efficiency with helium was about 3.1 times larger than with air, which indicates the promising potential application of operating a BCE with helium as the inlet gas, even at rather moderate temperatures. The helium could be heated by solar energy or waste vent gas. Rui Wei suggested that the fundamental principle underlying the improved evaporation efficiency with helium is the disruption of the hydrogen bonds in the water by the helium atoms¹⁴. Because of the relatively small molecular size of helium compared with the length of hydrogen bonds, helium atoms can penetrate the hydrogen-bond network and break up the bonds simply by atomic vibration¹⁴. However, accurate estimates of both efficiency and energy cost of the bubble desalination process with sparged helium flow could only be obtained by design and construction of a larger scale system, where the issues associated with vapour water condensation performance can be addressed. In the literature, there does not seem to be any useful follow-on work in papers citing Rui Wei's work. Therefore, for the first time, this study aims to investigate the efficiency of the large-scale hot-bubble pilot plant (HBPP) based on the BCE for helium sparged aqueous salt solutions by comparing the condensation efficiency in a range of different input carrier gases (dry air, He and combustion exhaust gas). The new HBPP has been designed as a large-scale pilot test unit of a possible final commercial plant of BCE, where the issues associated with vapour condensation have been addressed.

Using dry air as carrier gas at an inlet temperature of 275°C to produce hot, dry bubbles has been investigated within a laboratory-scale BCE and resulted in a further 10% improvement in the effectiveness of watervapour collection, suggesting that raising the inlet-gas temperature promotes increased vaporization¹⁶. Surprisingly, the rapid transfer of water vapour across the bubble surface, which occurs after hot, dry inlet air enters the column, did not have an impact on the inhibition of the coalescence of bubbles in salt solutions, compared with the prevention of water evaporation into the bubbles, using the vapour water saturated inlet air¹⁷. It appears that any local concentration enhancement in a thin region of solution around the bubbles, which produces soon after dry bubbles enter the column, has no influence on the film thinning process¹⁷. Another possibility is that both the bubbles and the solution flowing rapidly across the bubble's surface dissipate any significant solute concentration build up¹⁷. Whatever possible explanations for this could be, these lab-scale BCE processes demonstrated a higher energy efficiency, approximately 7.55 kWh/m³ of fresh water, compared with conventional thermal-desalination methods¹⁸. However, weighing the advantages and disadvantages of the use of dry air and humid air, the utilization of air with a certain level of humidity itself requires more energy to heat to a specific temperature, while it has no effect on the air bubble coalescence inhibition due to added salt, which is the basis for the bubble column method of desalination. Hence, optimizing operational factors, such as selecting dry air as an alternative inlet for humid air; using helium as the inlet gas rather than dry air and elevated inlet-gas temperatures would enhance the evaporation efficiency of the BCE process even further⁵ and reduce energy consumption^{14,18}.

The BCE method has recently been implemented in a hot-bubble pilot plant (HBPP) with the aim of developing an industrial-scale, energy-efficient water-treatment technology that increases evaporation efficiency while lowering energy usage¹⁹. In the first reported experiments, the HBPP used either hot air or hot combustion gases for water sterilization²⁰. There was a 37% increase in the evaporation efficiency at an inlet temperature of 120°C using the hot combustion gases, compared to

using air; this enhancement was partly ascribed to the heat that was generated when the water vapour in the combustion gas underwent condensation¹⁹. Furthermore, an analysis of the water condensed from the HBPP confirmed that it met the international standards for drinking-water quality16. Hence, incorporating exhaust gas from combustion processes into the large-scale HBPP is a promising method for seawater desalination with improved evaporation efficiency while producing highquality condensed water. However, to examine whether there is an improvement in the condensation efficiency achieved in the large-scale pilot test unit, a study comparing the condensation performance of the bubble column desalination process when sparging combustion gas with that of other input carrier gases, including dry air and He is lacking.

Hence, this paper focuses on comparing the effectiveness of using dry air, helium or combustion gas as the inlet gas to optimize the working efficiency of the HBPP in desalinating seawater. The effect of different inletgas temperatures on the evaporation performance of the HBPP is also investigated using either helium or dry air.

2. MATERIALS AND METHODS

2.1. Experimental solution

HBPP was operated with a saline solution of known salt concentration to simulate seawater, rather than actual seawater, to ensure the evaporation experiments were conducted under controlled conditions. For each experiment, a solution of 0.5 M NaCl was prepared by adding 585 g of sodium chloride to 20 L of tap water. Tap water was used because the HBPP does not require pre-treatment of the feed solution. After the inlet gas was heated to its target temperatures of 90°C, 120°C, and 147°C, the experimental solution was poured into the solution chamber to initiate evaporation measurements.

2.2. Inlet gases

Experiments were first conducted using air or helium at different inlet gas temperatures, ranging from 90°C to 147°C. The amount of condensed water vapour collected every 5 minutes over a 60-minute period was used to evaluate the effect of inlet temperature on the efficiency of vapour transfer desalination. Subsequently, both air and helium were compared with combustion gas at the same flow rate and temperature. The number of moles of inlet gas per unit time was the same for all the inlet gases.

A 140 L/min flow of dry air at a temperature of 90°C was produced using two Hiblow HP 120 air blowers connected to a silica-gel desiccator (Fig. 1).

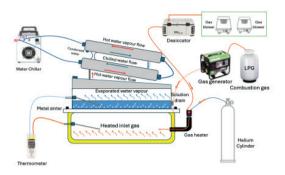


Figure 1. The HBPP setup for using different inlet gases (helium, combustion gas and air) (adapted from ¹⁹)

Dry helium was used directly from gas cylinders (Coregas; purity > 99.999%). The flow rate of dry helium was monitored by a rotary gas meter (FMR DN40 G016) and maintained at 140 L/min. Using dry helium carrier gas, the bubble column desalination process offers a higher overall mass and heat transfer compared with dry air (mentioned in the introduction), with less heat required for the dynamic heat-exchange process from the pre-heated inlet gas bubbles in evaporating the column solution due to its low heat capacity. Both the air and helium were heated by a Lesier LHS 21S gas heater and monitored with a thermometer (Tenmars TM-82N Type K/J).

The steady-state temperature of the column solution was measured at different inlet gas temperatures, after which the air and helium temperatures were adjusted to produce the same column solution equilibrium temperature (54°C) produced by 90°C combustion gas at a flow rate of 140 L/min. Here, we used liquid petroleum gas (LPG) as the combustible source without requiring additional heating equipment or gas pumps, which is emitted from biogas engines and is the byproduct of many industrial processes, such as pig farms, landfills, biogas power plants, and coal power plants. During combustion, the amount of air was carefully controlled to ensure that the LPG was fully combusted in a Greenpower gas generator. The combustion exhaust flow then was connected to the gas chamber as the combustion gas inlet. By assuming that the LPG was a mixture of 50% (by mass) of butane (C_4H_{10}) and 50% propane (C_3H_8) , the chemical formula of LPG was (C_{3.5}H₉). The composition of the combustion gas is the fully combusted products of the LPG and determined by equation (2). Hence, none of small fraction of unburned contaminants would end up in the water condensed from the HBPP.

Since the exhaust gas came with the combustion heat, heating helium that contains water vapor would require significantly more energy than using the combustion gas from the gas generator while as in the case of air, the presence of water vapor would not potentially enhance the system's performance. Hence, the current work introduced dry air and helium into the large-scale HBPP system to reduce the overall energy cost and scientifically determines the optimal operating conditions for the system's efficiency by a comparison with the efficiency of condensation using combustion exhaust gas.

2.3. Hot-bubble pilot plant

HBPP incorporated a metal sinter, and a gas chamber lined with high-performance refractory material. The 0.5 m² sinter, made from 316 stainless steel with Grade 40 porosity, maintained a continuous production of dense bubbles (1–3 mm in diameter). This size range ensured that the evaporated water vapour was completely saturated inside the rising bubbles by the time they reached the top of the column. A porous sinter was placed at the top of the gas chamber to continuously generate a stream of hot, dense, fine bubbles in the bubble column reactor, which transfer and collect heat and water vapour to and from the surrounding solution. Two thermocouples underneath and over the porous sinter monitored the inlet-gas temperature and the column-solution temperature. Figure 2 shows the internal structure of the HBPP.



Figure 2. Structure of the HBPP. **Top left**: gas chamber with refractory material. **Top right**: condensing units. **Bottom left**: water-treatment column with the metal sinter. **Bottom right**: mesh cover (adapted from ²¹).

Insulating the gas chamber with refractory bricks significantly reduced thermal energy loss, thereby improving the pilot plant's performance. The service life of the sinter was prolonged by using heat-resistant material, effective even at temperatures greater than $500C^{\circ 22}$.

The water-treatment reactor, with dimensions 500 mm \times 500 mm \times 250 mm, was placed on the top of the sinter and allowed for the treatment of up to 20 L of solution per batch operation. The solution height (250 mm) was designed to ensure that the ascending hot bubbles became fully saturated with water vapour before reaching the top of the reactor, thereby preventing contamination of the condensation units by foam generated during the process¹⁴. A mesh cover placed on top of the column further ensured that foam could not enter the condensing units.

The condensing units, which collected and condensed the water vapour (Fig. 2, top right picture), consisted of three interconnected shell-and-tube heat exchangers, providing a total surface area of 3m². Chilled water was circulated through each condensation unit, with an industrial water chiller (CW-5000AG) maintaining the water temperature at approximately 24°C. Once the desired inlet gas temperature was reached, 20 L of 0.5M NaCl solution was introduced into the water treatment reactor, marking the start of the experiment (time zero). Evaporation occurred at the surfaces of the hot rising gas bubbles, which ascended to the top of the reactor, where they collapsed and released water vapour that was then condensed. The volume of condensed water was measured every 5 minutes.

3. RESULTS AND DISCUSSION

3.1. *Influence of inlet-gas temperature*

In the current experiments, a continuous flow of hot, dry air or pure helium at varying inlet gas temperatures was used as a carrier gas in the open-to-atmosphere bubble chamber to evaporate water from concentrated salt solutions (0.5M). The effects of substantially increased gas-bubble temperatures on the efficiency of water vapour collection from the HBPP were examined. Shahid¹⁷ found that a significantly higher rate of evaporation was achieved by the use of high inlet-gas temperatures. The findings are consistent with the notion that a significant degree of supersaturation within the bubbles can be obtained at high bubble temperatures.

This is possibly due to the combined effects of hightemperature inlet gases and supersaturated conditions, which enhanced the performance of the BCE process for thermal desalination⁴ by increasing the rate of vapour transfer²³. In fact, a continuous flow of hot, dry air bubbles at 275°C was used to improve the water vapour collection rate by approximately 10% compared to the vaporisation expected from equilibrium vapour pressures¹⁷. This study further confirms the enhanced desalination in the large-scale HBPP due to the positive effects of high bubble temperatures on the efficiency of vapour transfer.

Since the effect of increased inlet gas temperature on the intervening liquid film trapped between colliding bubbles is negligible within the range of 150–275°C^{17,23}, it may not play a critical role in preventing these bubbles from combining, even at temperatures below 150°C, as suggested by the film drainage model⁴. This suggests that local heating in the adjacent solution, caused by inlet gas temperatures below 150°C, does not significantly alter film viscosity and, therefore, does not clearly dominate the rate of vapour transfer.

Another way to assess the impact of high-temperature inlet gas on heat and mass transfer processes in desalination is through the bubble evaporation layer model⁴. In this model, the presence of a thin heated solution layer surrounding the hot rising bubbles is used to explain how the performance of BCE increases with increasing inlet-gas temperatures: water molecules are moved into the heated layer around the surface of the bubbles and hence carried away.

However, for desalination, the primary focus is on water-vapour transfer across the gas-water interface and the energy required for this process. The thickness of any heated water layer is not actually relevant to this process, although it is a function of steady-state column temperature⁴. In fact, the gas-water interface drives the evaporation process and transportation of saturated vapour, which produces drinking water from seawater in a continuous flow evaporative bubble column operating below the boiling point. This means that a higher surface area of the gas-water interface correlates with improved heat and mass transfer efficiency⁴.

Nonetheless, the heat from a hot, dry bubble entering the column is passed to the transient hot water layer surrounding its surface to cause water evaporation⁴. As the bubble approaches a steady state, the water film formed around the rising bubbles cools to the equilibrium temperature of the column solution when hotter bubbles flow into the HBPP. As a result, this hotter layer has a stronger influence on changes within the solution, particularly on water evaporation. Even if the same heated gas-water interfacial area is created with hotter gas bubbles, the higher heat transfer coefficients in the HBPP system enhance evaporation efficiency, while the column temperature remains well below the boil-

ing point⁴. This supports the view that enhanced water evaporation appears to increase with gas temperature, as shown in the following sections.

3.1.1 Air as the inlet gas

Figure 3 shows boxplots of the average volume of water collected every 5 minutes at different temperatures using air as the inlet gas.

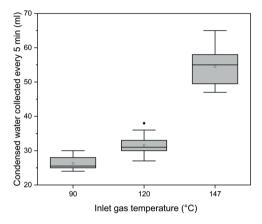


Figure 3. Average volume of condensed water collected every 5 minutes from the NaCl solution at different inlet-gas temperatures using air as the inlet gas.

The results show a clear trend: the volume of water collected increased as the inlet-air temperature increased in the range of 90–147°C (one factor ANOVA in SPSS; F= 1256; *df* (5, 59); *p* < 0.0001; Dunnett T3 test, 95% CL). This indicates that evaporation is strongly dependent on inlet-air temperature. Moreover, since the efficiency continued to increase, the optimal inlet-air temperature must be higher than the highest temperature here, 147°C. At high inlet-gas temperatures, the HBPP exhibited strong desalination performance because of the rapid mass and heat transfer at the interface between the solution and the hot gas bubbles. When the inlet-air temperature rose, the temperature at this interface also increased; more heat was exchanged between the hot air bubbles and the surrounding solution to reach a new dynamic equilibrium, and the bubbles collected a greater volume of water vapour.

It should be noted that not all the heat supplied by the heated inlet air was transferred to the column to produce saturated vapour in the bubbles²³. Also, assuming perfect thermal insulation of the bubble column, the expected equilibrium temperature can be directly calculated from the inlet-gas temperature using the steady-

state thermal-energy balance equation developed in a bubble column (Equation 1 in 18). Hence, with the inlet air at higher temperatures, the column solution constantly attained a higher temperature than that expected at steady-state operating conditions²³. This led to a higher vapour transfer mass (as calculated from the observed column temperature) in comparison to the observed total transfer mass. However, it is interesting that, in all the experiments carried out with the inlet-air temperatures of 150-250°C, the observed vapour transfer was found to be higher than that expected for the column operating at steady-state conditions²³. These results suggest that, although the balance between the heat supplied and the heat required for vaporisation was not achieved at high inlet-air temperatures, an enhanced water transfer rate was still observed with increasing air temperature²³.

In the current study, the 'expected' rate of water vapour production was calculated by multiplying the saturated vapour density carried in an air bubble ($\rho_v(T_e)$ in g/m³; see Table 1) at equilibrium for every 5-minute interval of the 60-minute runs by the airflow rate in the water treatment column/reactor (140 L/min) over each 60-minute run²⁴.

Table 1. Expected and experimental water transfer rates compassion using HBPP for 60 min bubbling run with 140 L/min airflow rate (adapted from ⁵)

Inlet air	Column	Water vapour	Expected	Measured
temp. (°C)	solution	density	water vapour	volume of water
	temp. (°C)	(g/m^3)	carryover	evaporated
		(adapted from	(mL), A*	(mL), B*
		Fig. 2 in ⁵)		
90	42.6	59.80	41.9	26.29
120	54.3	103.48	72.4	31.54
147	55.1	107.74	75.4	54.50

Across the range of inlet air temperatures from 90 to 147°C, the calculated water vapour carryover—measured from the point when stable water condensation performance was observed—was higher than the actual amount of condensed water produced by the BCE commercial prototype (Table 1). Therefore, while higher water transfer rates per unit volume of air into the rising bubbles were clearly achieved by increasing the inlet air temperatures (Table 1), due to the substantial increase in steady-state water vapour density data⁵, it is likely that full condensation of the water vapour was not achieved in this study. Additionally, heat loss from the hot inlet gas flow may not have been effectively prevented during the gas transmission process.

In earlier works, the bubble column was weighed to obtain the accurate water-vapour loss, indicating

that water was not condensed^{17,23}. For instance, increasing the temperature of air bubbles from 150 to 250°C raised the weight of water vapour removed from the aqueous NaCl solution from 6.2% to 8.3%, exceeding the expected water vapour carryover rate²³. Moreover, Shahid¹⁷ reported that a continuous flow of hot, dry air at 275°C resulted in approximately 10% higher water vapour collection efficiency than expected from equilibrium vapour pressures. However, in the current work, though condensation took place in the larger scale pilot test unit, the efficiency of water vapour collection was much less than expected, around 50 - 60 % of the expected amount (Table 1). This suggests that the condensation unit requires further optimization to increase the water-vapour saturation levels in the bubbles for seawater desalination.

On the whole, although hot air bubbles at temperatures ranging from 90 to 147°C passing into the column at a flow rate of 140 L/min did not increase the water vaporisation over the expected volume of water evaporated at steady-state conditions, the initial results reported here still support the view that increasing the inlet-gas temperature further improves the water-vapour collection rate.

3.1.2 Helium as the inlet gas

It is well known that the equilibrium water-vapour density in bubbles of any gas is only a function of the liquid-water temperature and is independent of whether the solution is boiling or not¹⁹. In other words, the amount of equilibrated water vapour contained in the bubbles is the same as that collected in boiling bubbles at the same solution temperature¹⁴. Consequently, an increase in inlet gas temperature is expected to enhance the amount of water vapour carried by the bubbles for both air and helium¹⁷.

For this reason, the same setup was used for helium as for air, with the results in Fig. 4. When the helium temperature was increased from 90°C to 147°C, there was a significant and linear increase in the evaporation efficiency (one factor ANOVA in SPSS; F = 731.8; df (2, 16); p < 0.0001; Dunnett T3 test, 95% CL). These findings are in agreement with those reported by ^{19,23}, which show that, by increasing the inlet-gas temperature, the amount of condensed water vapour increased accordingly. Interestingly, despite the lower water vapour density with helium at 75°C¹⁴, the evaporation efficiency was similar to that observed with helium at 150°C⁵, due to its superior ability to disrupt hydrogen bonding among water molecule clusters¹⁴. Wei and Pashley¹⁴ found that at a heated helium inlet temperature of 75°C, the actu-

al solution weight loss measured by a balance over a 30-minute run was approximately 3.1 times higher than the expected loss, which was calculated by summing the evaporated water weight loss per minute based on the corresponding vapour pressure at the actual column solution temperature. Similarly, at a helium inlet temperature of 150°C, the actual weight loss measured was approximately 3.3 times higher than the theoretical weight loss⁵. These results indicate that when using helium as a carrier gas, variations in inlet temperature have a relatively minor impact on evaporation efficiency. This means that operating a BCE with moderately heated helium gas inlet can still significantly facilitate the evaporation efficiency¹⁴.

However, the results in Table 2 for helium obtained in the industrial-scale BCE, i.e. HBPP show that the amount of water evaporated in the bubble column reactor was only marginally higher than the calculated theoretical water-vaporisation rate based on the observed column temperature.

Table 2. Desalination efficiency with inlet helium temperature (adapted from ⁵).

	Column solution temp.	vapour density	Expected water vapour	Measured volume of water	Vaporisation efficiency [B*/A*]
('C)	(°C)	(g/m^3)	carryover	evaporated	
			(mL), A*	(mL), B*	
90	40.5	54.15	37.9	35.14	0.9
120	52.5	95.16	66.6	73.25	1.1
147	53.5	99.23	69.5	106.00	1.5

In particular, at an inlet gas temperature of 147°C, there was an observed increase of a factor of 1.5, which was the highest vaporisation efficiency among all the tested inlet temperatures. This value is significantly lower than the vaporisation efficiencies reported for the labscale BCE, where helium demonstrated 3.3 times higher efficiency than theoretical values⁵. Besides, helium was found to have 0.9 and 1.1 vaporisation efficiency at the lower temperatures of 90°C and 120°C, respectively.

In this calculation, it is important to note that vaporisation efficiency was determined by dividing the volume of evaporated water measured during the runs, B^* , by the expected water transfer value based on the actual column temperature, A^* . Table 2 presents the measured total volume transferred using hot helium bubbles at temperatures ranging from 90°C to 147°C B^* , and the expected volume at steady state A^* , at a flow rate of 140 L/min.

The significantly higher carryover of water vapour by helium gas observed by ^{5,14} was not observed in this

BCE commercial prototype. This discrepancy may be attributed to the fact that the bubble column reactor was not well insulated with refractory material to control the heat loss of the hot inlet gas flow during the evaporation process. Also, the condensation system may be insufficient, resulting in incomplete condensation of the collected water vapour.

In conclusion, the initial experiments were conducted using the same flow rate and inlet temperature for both air and helium. However, different steady-state temperatures were observed in the column solution due to the differing heat capacities of helium and air, which affect heat transfer for solution evaporation at the same inlet temperatures. An increase in evaporation efficiency was observed with higher inlet gas temperatures for both gases, as shown in Figs 3 and 4.

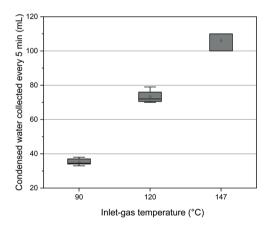


Figure 4. As for Fig. 3 but using helium as the inlet gas.

In subsequent experiments, the inlet-gas temperature was adjusted to achieve the same steady-state temperature in the column for both air and helium. This approach allowed for the use of the steady-state column solution temperature to estimate the expected water vapour carryover for each gas, facilitating a direct comparison of their performance.

3.2. Influence of inlet-gas type

3.2.1 Helium and air

Different gases exhibit varying evaporation efficiencies due to their distinct effects on the mass and heat exchange processes between the bubbles and the surrounding salt solution. The faster equilibrium was reached in the movement of water vapour into the bubbles, the quicker the bubbles saturated with water

vapour and the higher the evaporation efficiency. A comparison of the volumes of condensed water collected using air and helium as the inlet gas at an equilibrium temperature of 54°C is shown in Fig. 5.

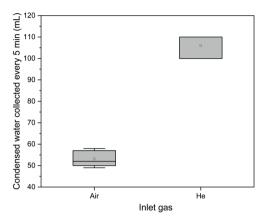


Figure 5. Average volume of condensed water collected every 5 minutes from the NaCl solution with the inlet gas air or helium at 54°C.

To enable a comparison between air and helium as inlet gases, the inlet-gas temperature was adjusted to achieve the same steady-state solution temperature in the HBPP. The theoretical evaporation rate at the steady-state solution temperature was calculated by multiplying the equilibrium water-vapour density (g/m³) by the corresponding flow rate. As the rotary gas meter used to measure the helium flowrate was also used to measure the flow rate of air, a correction factor for the flow rate was needed. The flow rate of air produced using the two air blowers (Hiblow HP 120) was measured by the rotary gas meter (FMR DN40 G016) as 260 L/min. The flow rate of air into the solution was measured by the meter at about 150 L/min.

It is well known that data for equilibrium water vapour density as a function of liquid water temperature is the same for all gases, including helium and air¹⁴. Thus, the saturated water-vapour density in a helium atmosphere matches that in an air bubble at the same solution temperature. As a result, the theoretical amount of water vapour collected using the same flow rate is the same for both air and helium.

This equivalence allowed a direct comparison of the water-vapour collection performance of the two gases at the same steady-state solution temperature. The volume of condensed water collected was multiplied by the specific heat capacity of each gas to calculate the relative evaporation efficiency of $H(T_e)$ of helium and dry air at an equilibrium temperature T_e using

$$H(T_e) = rac{V_h}{V_a} imes rac{C_p(air)}{C_p(He)}$$

where $V_{\rm h}$ and $V_{\rm a}$ are the average volumes of water produced (mL) over the 5-minute periods at the temperature T_e (K) using helium and dry air, respectively, and C_p (air) and C_p (He) are the corresponding specific heat capacities (J/molK) at this temperature.

At around 54°C, the HBPP using helium achieved an evaporation efficiency 2.8 times higher than that of air (Table 3).

Table 3. Relative evaporation efficiency, helium vs dry air.

Equilibrium temp./°C		Condens vapou		Relative evaporation efficiency He/Air
Air	He	Air	He	
53.7	53.5	53.1	106	2.8

Note: Condensed water vapour is the average amount collected every 5 minutes in a 60-minute run. The relative evaporation efficiency was calculated from Equation (1) with the specific heat capacity of air 29.2 J/molK, and of helium 20.8 J/molK.

These results align with those reported by ^{5,14} for a lab-scale BCE sparged with dry air or helium into an aqueous solution at a solution temperature of either 25°C¹⁴ (3.1 times) or 45°C⁵ (3.3 times). The difference in evaporation efficiency may be attributed to the inefficiency in condensing the water vapour collected in the larger-scale HBPP.

The improved evaporation efficiency with helium was further confirmed using statistical analysis. The evaporation efficiency for both gases was found to follow a normal distribution at 54°C, so the independent t-test was used. The null hypothesis assumed that the evaporation efficiency remains the same, regardless of the type of gas used, whereas the alternative hypothesis was that the evaporation efficiency is different for each gas. The analysis provided strong evidence (95% CL) that the efficiency of evaporation was higher with helium than with air at 54°C (t = -14.8, df = 5.59, p < 0.0001), which agreed well with results obtained from a laboratory-scale BCE^{5,14}.

According to Wei and Pashley¹⁴, the superior performance of helium as an inlet gas can be attributed to its small molecular size and stable atomic configuration. Its smaller molecular size allows for greater penetration into the water surrounding the bubbles compared to larger air molecules. Evidence for this has been shown in²¹. This greater penetration disrupts the local hydrogen bonds, aiding evaporation^{5,14}. Helium's atomic structure might also enable it to trap gas-phase water molecules in its lattice structures over a wide range of pressures

and temperatures, thereby promoting enhanced evaporation at lower temperatures and reducing the thermal energy needed for desalination²⁵. Additionally, the superior thermal conductivity of helium increases the heattransfer coefficient, further enhancing the evaporation process¹⁴. Wei and Pashley¹⁴ pointed out that bubbles produced with helium have a higher density than air bubbles at the same flowrate. The formation of more and finer bubbles, along with the inhibition of bubble coalescence by the salt in the column solution, enhances the rate of heat and mass transfer between the hot bubbles and the solution, thereby increasing the evaporation rate of water molecules.

Energy consumption

In the context of large-scale desalination using the HBPP, energy consumption is also an important factor to assess the efficiency of the process. Hence, an estimate of the energy using helium in the HBPP for desalination at an equilibrium solution temperature of 54°C was calculated as follows.

The specific heat capacity per unit weight of helium gas C_p^g (He) = 5.19 J/gK or 20.8 J/molK. Helium at 147°C gave an equilibrium solution temperature of about 54°C with a relative evaporation efficiency compared to air, of about 3 (Table 1).

Consider a helium bubble with an average diameter of 1.5 mm. Assuming it to be spherical, the average volume can be found using the standard formula

$$V = rac{4 imes\pi}{3} imes \left(rac{1.5mm}{2}
ight)^3 = 1.77mm^3 = 1.77 imes 10^{-9}m^3$$

The average mass of helium bubble therefore will be (considering a density of 0.178 kg/m^3) =

$$1.77 \times 10^{-9} \ m^3 \times 0.178 \frac{kg}{m^3} = 3.16 \times 10^{-7} g$$

- a rough estimate for a mm-sized helium bubble in water. Next, the volume of a helium bubble leaving the top of the reactor at 54°C = 327 K was calculated using:

$$V^{\, '} = rac{n {
m R} T_e}{P^{\, '}} = \, rac{rac{3.16 imes 10^{-7} {
m g}}{4 \, rac{{
m K}}{
m mol}} imes rac{8.314 \, {
m J}}{{
m K.mol}} imes 327 \, {
m K}}{1 \, {
m atm}} = 2.15 imes 10^{-9} \, {
m m}^3$$

The amount of heat (and work) required to heat this volume of helium is given by the difference between room temperature (around 20°C) and the inlet helium temperature (around 147°C) multiplied by the specific heat capacity of helium (5.19 J/gK)⁵, that is,

$$[C_p^g~({\it He})_{\times}\,{\rm m_{He}}_{\times\,\Delta T^*]} = 5.19~{\rm J/gK} \times 3.16 \times 10^{-7}~{\rm g} \times (147-20)~{\rm K} = 2.08 \times 10^{-4}~{\rm J}.$$

At this temperature, the saturated water-vapour density carried in a bubble of any gas, $\rho_{\nu}(T_e)$ is about 101.9 g/m³ ⁵. Therefore, the total amount of water vapour transferred into the helium bubble is

$$101.9 \text{ g/m}^3 \times 2.15 \times 10^{-9} \text{ m}^3 = 2.19 \times 10^{-7} \text{ g}.$$

As observed in this current work, there was a 1.5 times increase in water vapour produced with helium at 54°C compared to the theoretical water-vaporisation rate (Table 2) for 1000 L of condensed water recovered from the saline solution (0.5 M NaCl) in HBPP; the process therefore requires:

$$\frac{1000\,L\times\,10^{3}g/L}{2.19\times10^{-7}g\times1.5}~\times~2.08\times10^{-4}~J_{~=6.33\times10^{8}~J}$$

that is 1 kL of condensed water is 633 MJ/kL, which is the energy cost per kL of water produced by using helium at 54°C within HBPP.

It is very important to use solar heating to preheat the seawater and thus making the bubble vapour desalination process viable and competitive with MSF, in terms of the energy demand. By comparison, the highest-energy-consuming commercial boiling method uses 67 kWh/m³ or about 240 MJ/kL (1 kWh = 3.6 MJ)²6. Furthermore, the thermal-energy recovery such as that used in multi-stage flash distillation reduces the energy demand by over 90%, to values as low as 100 MJ/kL²6. In comparison, most of the energy demand (633 MJ/kL) calculated for the HBPP/He method is not, currently, recycled on condensation of the water vapour, and is not used to heat the saltwater feed.

Overall, present results show that although there is an improved helium carryover of water vapour compared with a dry air inlet at the same equilibrium temperature, the energy required to evaporate the same amount of water calculated for helium achieved by HBPP is higher than that required in the worst commercial boiling method²⁶. Hence, the HBPP/He method could only be viable with thermal-energy recovery or by using solar heating.

3.2.2 Combustion gas, helium and air

Figure 6 shows the volumes of condensed water collected using dry air, combustion gas or helium as the inlet gas, all at 90°C.

Combustion gas produced the largest amount of condensed water, followed by helium and air (F = 81.49; df (2, 33); p < 0.0001; Dunnett T3 test, 95% CL), in agreement with previous studies^{16,19}. This was, at least in part, because of the amount of water vapour in the combustion gas, calculated using Equation (2).

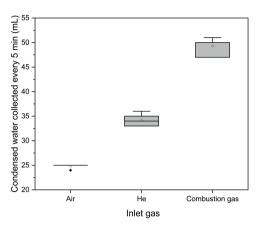


Figure 6. Average volume of condensed water collected every 5 minutes from the NaCl solution with dry air, combustion gas or helium, all at an inlet temperature of 90°C.

In this work, the combustion gas was produced by the combustion of LPG $(C_{3.5}H_9)$ in the gas generator without additional heating¹⁹:

$$C_{3.5}H_9 + 5.75O_2 + 22N_2 \rightarrow 3.5CO_2 + 4.5H_2O + 22N_2$$
 (2)

Equation 2 shows that water vapour is produced in the combustion process and is therefore present in the inlet gas. As a result, when the net amount of water vapour evaporated was calculated, this extra water vapour had to be taken into account.

Additionally, with combustion gas as the inlet gas, the total energy heat transferred by the gas bubbles includes the exothermic heat from the hot water vapour in the combustion gas¹⁹. That is to say that the hot inlet combustion gases do not use the heat to evaporate pre-existing water vapour as they already come with a great percentage of hot water vapour, making it greater than the heat supplied by the other heated gases. The condensation of this water vapour releases additional heat to evaporate the column solution¹⁹:

$$Q_w + \Delta T' \times C_p (T_e) + \Delta p = \rho_v (T_e) \times \Delta H_v (T_e)$$
(3)

Here, Q_w (J/m³) is the exothermic heat transferred from the water vapour contained in the combustion gas inlet but has not been used to evaporate the solution; C_p (T_e) (J/m³K) is the specific heat capacity of the inlet gas at the equilibrium solution temperature; ΔT (K) is the temperature difference between the gas entering and the gas leaving the column; Δp (J/m³) is the hydrostatic pressure difference between the inlet gas flow and the atmosphere. The term ρ_v (T_e) (mol/m³) on the right-hand side is the vapour density at the equilibrium solution tempera-

ture and ΔH_{ν} (T_e) (J/mol) is the enthalpy of vaporisation of the column solution. Equation (3) shows that, with combustion gas as the inlet gas, the calculation of the total heat transferred by the gas bubbles must take into account the heat released from the water vapour in the combustion gas¹⁹.

The saturated water-vapour density depends on the solution temperature but not whether the solution is boiling or not¹⁴. A higher equilibrium temperature of the water in the reactor was observed for combustion gas compared to helium and air (Fig. 6). Furthermore, since the inlet combustion gas contained hot water vapour, CO₂ and N₂ (Equation (2)), it had more degrees of freedom and a higher heat capacity, which resulted in a column-solution temperature (56°C) higher than helium (40°C), a less complex gas molecule (Fig. 7).

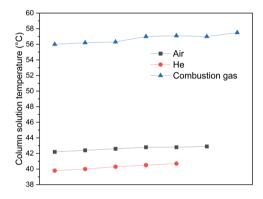


Figure 7. Temperature of the NaCl solution every 5 minutes with the inlet gas air, combustion gas or helium, all at 90°C.

Additionally, due to the exothermic liquefaction reaction of the hot water vapour contained in the combustion gas (Equation 2), a higher column solution temperature was achieved with combustion gas (56°C) compared to dry air (43°C) (Fig. 7). This exothermic heat energy can be determined from the heat released during the condensation of vapour to liquid at 90°C and the subsequent cooling of the 90°C liquid water to 56°C in the column solution (Fig. 7), as shown in ¹⁹. Furthermore, since the combustion gas temperature (90°C) was similar to that of the other gases, no additional heating was required.

Hence, using combustion gas as the inlet gas in the HBPP offers two advantages: first, it leverages the high heat capacity of the heated water vapour it contains, enhancing heat transfer between the hot combustion gas bubbles and the solution; second, it utilizes the heat generated by the combustion process to evaporate the solution without requiring additional heating.

Furthermore, the utilization of combustion gas in a single-stage bubble column desalination process at a relatively low temperature would be a viable option compared with the typical multiple-effect evaporation system operating under vacuum. By comparison, a multiple-effect evaporation system operating under vacuum heats saltwater under a reduced pressure to depress the boiling point, and then a small proportion of water vapour is boiled off and condensed in a series of 'multi stages' process. Substantial energy is required to initiate boiling of the saltwater feed. However, the nature of the bubble vapour desalination process itself means that there is no need to boil the water. In this process, the water vapour content immersed and equilibrated in the bubbles at temperatures significantly below the boiling point is almost identical to that in bubbles carried over by boiling at the same temperature. Furthermore, the water vapour is not only collected on the surface of the liquid as used in the multiple-effect evaporation but is transferred throughout the entire body of the salt solution. Hence, the bubble vapour desalination is a more effective method in terms of energy requirements and is viable when combined with an available source of waste industrial heat, such as from pig farms. The results obtained in this study on the enhanced water recovery with combustion gas are in agreement with those reported by 16,19.

Latent heat of vaporization of water

To further understand the mechanism by which combustion gas enhances water evaporation efficiency in the desalination process of the HBPP large-scale pilot test unit, the latent heat of vaporisation $\Delta H_{\rm v}(T_{\rm e})$ of the column solution was determined in relation to changes in the steady-state equilibration temperature within the combustion gas atmosphere. This was achieved by applying a steady-state thermal energy balance between the combustion gas and the surrounding salt solution, assuming that the vapour pressure of water at this temperature is known. It should be noted that in this energy balance, the $\Delta H_{\rm v}(T_{\rm e})$ term accounts for the expansion of bubbles as they absorb water vapour, while the corresponding reduction in gas volume is represented by the $C_{\rm p}(T_{\rm e})$ term²⁴.

By using the same steady state thermal energy balance developed in a bubble vapour desalination process, the calculated results of the enthalpy of water vaporization ($\Delta H_{\rm v}$) in an aqueous salt solution sparged by other input carrier gases (dry air and helium) have been reported and are shown in Table 4. In this energy balance formula, only the steady state equilibration tem-

perature of the bubble column, temperature of the inlet gas and the hydrostatic pressure across the column need to be measured to determine the heat of vaporization for water.

Regarding the use of combustion gas, assuming that 1 mol of combustion gas ($C_{3.5}H_9$) consists of a mixture of 3.5 mol CO_2 , 4.5 mol H_2O , and 22 mol N_2 (Equation 3), the specific heat capacity per unit weight of the combustion gas at the reactor's equilibrium temperature is given by

$$\begin{array}{c} C_p^g(T_e) = \frac{n_{\mathrm{CO}_2} M_{\mathrm{CO}_2} c_p(\mathrm{CO}_2) + n_{\mathrm{H}_2\mathrm{O}} M_{\mathrm{H}_2\mathrm{O}} c_p(\mathrm{H}_2\mathrm{O}) + n_{\mathrm{N}_2} M_{\mathrm{N}_2} c_p(\mathrm{N}_2)}{m_{\mathrm{CO}_2} + m_{\mathrm{H}_2\mathrm{O}} + m_{\mathrm{N}_2}} = \\ 3.5 \; \mathrm{moles} \times 44 \frac{g}{\mathrm{mol}} \times \frac{0.844\mathrm{J}}{\mathrm{g.K}} + 4.5 \; \mathrm{moles} \times 18 \frac{g}{\mathrm{mol}} \times \frac{4.18\mathrm{J}}{\mathrm{g.K}} + 22 \; \mathrm{moles} \times 28 \frac{g}{\mathrm{mol}} \times \frac{1.04\mathrm{DJ}}{\mathrm{g.K}}} \\ 3.5 \; \mathrm{moles} \times 44 \frac{g}{\mathrm{mol}} + 4.5 \; \mathrm{moles} \times 18 \frac{g}{\mathrm{mol}} + 22 \; \mathrm{moles} \times 28 \frac{g}{\mathrm{mol}} \times \frac{1.04\mathrm{DJ}}{\mathrm{g.K}} \\ = 1.3 \; \mathrm{J/gK}. \end{array}$$

This value remained fairly constant over a wide temperature range of 0–100°C. It must be converted into the heat per unit volume of combustion gas released from the reactor, $C_p(T_e)$, expressed in units of J/m³K.

The specific heat of combustion gas $C_p(T_e)$, in units of J/m³K is given by the specific heat per unit weight of combustion gas $C_p(T_e)$, in units of J/gK multiplied by the vapour density carried in the combustion gas mixture at equilibrium $\bar{\rho}_v$, in units of g/m³.

To calculate the vapour density $\bar{\rho}_v$, the molar mass (M) of the combustion gas mixture is calculated using the mole of gas compositions in mixture, that is

$$M = \frac{3.5\,\mathrm{moles} \times 44\frac{\mathrm{g}}{\mathrm{mol}} + 4.5\,\mathrm{moles} \times 18\frac{\mathrm{g}}{\mathrm{mol}} + 22\,\mathrm{moles} \times 28\frac{\mathrm{g}}{\mathrm{mol}}}{3.5\,\mathrm{moles} + 4.5\,\mathrm{moles} + 22\,\mathrm{moles}} = 28.37\frac{\mathrm{g}}{\mathrm{mol}}$$

Using the ideal gas equation, the vapour density carried in the combustion gas $\bar{\rho_v}$ is given below:

$$\bar{\rho_v} = \frac{PM}{RT_e} = \frac{101325 \frac{J}{m^3} \times 28.37 \frac{g}{mol}}{8.314 \frac{J}{mol K} \times (56+273.15) \text{ K}} = 1050.32 \text{ g/m}^3$$

This converts the heat capacity per unit weight of combustion gas mixture to the heat capacity per unit volume:

$$C_p(T_e) = C_p^g(T_e) \ge \bar{\rho_v}$$
1. 3 J/gK x 1050.32 g/m³ = 1365.416 J/m³K.

The saturated water vapour density, $\rho_{\nu}(T_e)$, at equilibrium is provided in references ^{4,5}. At a column temperature of approximately 56°C, its value is 112 g/m³. Assuming no pressure difference in the combustion gas between the point just before it entered the sinter and the atmospheric pressure at which it passed through the reactor, the hydrostatic pressure difference across the sinter and water column would be $\Delta P = 0$ J/m³.

This assumption is reasonable, as the HBPP operates under atmospheric pressure conditions. These calculated

values were used to determine the enthalpy of vaporisation of water with combustion gas inlet, given by

$$\Delta H_{\rm v}(T_{\rm e}) = \frac{\Delta T \times C_p(T_e)}{\rho_v(T_e)} = \frac{(90-56){\rm K} \times 1356.416 \; \frac{\rm J}{\rm m^3 K}}{112 \; \frac{\rm g}{\rm m^3}} =$$

414.50 J/g (or 7.46 KJ/mol)

at a column temperature of around 56°C. In the bubble column reactor, the corresponding values of $\Delta H_{\rm v}$ in a helium or air atmosphere are approximately 15.50 kJ/mol and 13.75 kJ/mol, respectively, when the HBPP operates at steady-state equilibration temperatures of 40°C and 43°C (Table 4).

Table 4. Calculated heat of vaporization using the energy balance formula

Inlet gas	Air	Helium	Combustion gas
T_e (°C)	43	40	56
$C_p(T_e)$ (J/gK)	1.0	5.19	1.3
$\rho_{\nu}(T_e)$ (g/m ³)	61.0	52.97	112
$\Delta H_{\nu}(T_e)$ (kJ/mol)	15.50	13.75	7.46

A significant drop in the calculated $\Delta H_{\rm v}$ values correlated with the observation of an increased condensation efficiency of water vapor from the salt solution suggest that the use of combustion gas as inlet gas within HBPP can facilitate the evaporation process more promising than helium. The decreased effective value of $\Delta H_{\rm v}$ reported for the HBPP sparged with pre-heated helium inlet gases into the aqueous salt solution also indicates the superior performance of helium in decreasing the energy required at promoting the evaporation of the same amount of water via the mechanism proposed, compared with dry air.

Overall, the $\Delta H_{\rm v}$ values obtained for different inlet gases sparging under equilibrium column conditions confirm that heated combustion gas significantly enhances the efficiency of water evaporation in the HBPP. This improved performance is likely due to a reduction in the effective value of $\Delta H_{\rm v}$ for water.

4. CONCLUSIONS

The HBPP was developed as a small-scale industrial implementation of the BCE method. Three different gases were used for the inlet gas. Increased inlet-gas temperatures resulted in increased evaporation efficiency, primarily due to the increased heat transfer from the gas bubbles.

The HBPP performed better with helium as the inlet gas than with dry air at a solution temperature of 54°C; the evaporation efficiency with helium was 3 times greater than with air, similar to that observed with helium in a

laboratory-scale BCE at solution temperatures of either 25°C ¹⁴ or 45°C ⁵. The HBPP achieved the energy consumption using helium at a solution temperature of 54°C of around 633 MJ/kL and could only be competitive with thermal-energy recovery or the use of solar energy because even in the commercial boiling method using the most energy (MSF), the energy demand can be reduced by over 90 % to 240 MJ/kL using energy recovery.

Combustion gas at 90°C produced a greater amount of condensed water vapour in the HBPP than helium and dry air, without requiring additional heating. The enthalpy of water vaporisation in a combustion gassparged aqueous solution was calculated using the energy balance equation for an upscaled BCE system. These findings suggest that the HBPP holds potential for development into a simple and efficient commercial seawater desalination process, particularly when utilizing gases derived from the combustion of waste materials.

CRediT authorship contribution statement

Thi Thuy Nguyen: Conceptualization, investigation, data curation, formal analysis, methodology, writing – original draft, writing – review editing. Adrian Garrido Sanchis: Conceptualization, investigation, supervision, writing – review editing, funding acquisition. Richard M. Pashley: Supervision, writing – review editing.

Declaration of competing interest

The authors declare that they do not possess any identifiable financial conflicts of interest or personal relationships that might have appeared to impact the findings presented in this paper.

Data availability: Data will be made available on request.

Acknowledgements

This study was funded by Australian Pork Limited (APL), grant number APL2018/0074. Dr. Peter McIntyre is gratefully acknowledged for his assistance in manuscript editing.

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Citation: Murphy, M.A. (2025) The Emergence and Evolution of Atom Efficient and/or Environmentally Acceptable Catalytic Petrochemical Processes from the 1920s to the 1990s. *Substantia* 9(2): 36-50. doi: 10.36253/Substantia-3100

Received: Nov 8, 2024

Revised: Apr 15, 2025

Just Accepted Online: May 14, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

The Emergence and Evolution of Atom Efficient and/or Environmentally Acceptable Catalytic Petrochemical Processes from the 1920s to the 1990s

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Abstract. The emergence and evolution of "Green / Sustainable Chemistry" began decades earlier than the 1990s. Beginning in the 1920s and 1930s, atom efficient catalytic processes for producing simple organic compounds started to be discovered and commercialized. In the 1940s and 1950s, oil refining processes using new catalytic methods dramatically increased the carbon efficiency of and usable variety of downstream products produced by oil refining processes, and simultaneously and dramatically decreased the waste residues and the pollution they produced. After World War II, new catalytic processes for producing a wide variety of increasingly atom efficient and/or "environmentally acceptable" downstream petrochemical products proliferated. This article will briefly recount multiple examples of those pre-1990s evolutionary developments in the petrochemical industries which produced new and highly atom efficient or environmentally acceptable catalytic processes for producing multitudes of petrochemical products that both changed modern societies, and also evolved toward the modern conceptions of "Green / Sustainable Chemistry".

Keywords: Green Chemistry, Green Engineering, History, Atom Economy, E-Factor, Environmental Quotient, Catalysis, Interdisciplinary Research, Evolution, Industry, Sustainability

1. INTRODUCTION

Since the late 1990s, widely published but wildly incomplete "narratives" about the origins of "Green Chemistry" have widely propagated in the English-speaking Academic and Governmental literature, and also in the English-speaking trade and popular press, to the effect that "Green Chemistry originated during the 1990s from the efforts of the US Government, US EPA and Academia", and/or from the "12 Principles of Green Chemistry" pub-

lished in 1998,"1,2,3

Over the last several years this author (who conceived (in 1984) the BHC Ibuprofen Process that won one the earliest US Presidential Green Chemistry Challenge Awards, in 1997 ⁴), has thoroughly documented and argued that "Green Chemistry" was in fact a narrow subset of, and evolved from and renamed, the much earlier and much broader international, interdisciplinary, and initially Industrial "Pollution Prevention" efforts during the 1970s and 1980s ^{5, 6}.

However, even the purposely environmentally oriented industrial "Pollution Prevention" efforts of the 1970s and 1980s were preceded by the semi-independent emergence of multiple examples of increasingly "atom efficient"^{7,} and/or "environmentally acceptable" ^{8, 9, 10} catalytic Industrial processes for producing commodity petrochemicals, beginning in the 1920s.

2. EARLY ATOM EFFICIENT PETROCHEMICAL PROCESSES

The early industrial organic chemistry of the 1800s, typically based on treating chemicals isolated from coal with stochiometric reactants and/or reagents, was not environmentally friendly. Oil drilling and refining (by simple distillation) began in the 1850s but was also not environmentally friendly. But after cars and airplanes were invented in the early 1900s and their uses exploded, demand for more and better petroleum products also exploded. This article will focus on the early inventions, emergence and continuing evolution of increasingly environmentally friendly petrochemical processes and products, beginning in the 1920s, and then continued to emerge and evolve, well into the 2000s.

2.1. Early Industrial Organic Chemistry

As many have noted, prior to WWII most home heating was based on wood or coal, and lighting in the city streets was based on coal gas (flammable mixtures of carbon monoxide, hydrogen, and other gases produced by coal gasification). Most organic chemicals were

¹ See Anastas, PT., and Warner, J. C., (1998)

derived from the coal tar byproduct of coal gasification. As Sheldon has described 8,10, industrial organic chemistry began with William Henry Perkin's 1856 serendipitous synthesis of "Aniline Purple" dye, via chromic acid oxidation of a mixture of aniline and toluidine's (derived from benzene and toluene isolated from coal tar), to form one of the first synthetic dyes for fabrics. That industrial process, like most of the synthetic organic reactions and industrial processes that followed over the next 100 years, typically employed multiple stoichiometric reagents comprising inorganic heteroatomic groups, groups which ultimately produced stoichiometric quantities of unwanted waste products and pollution in the environment, and too often continued the use of such inherently waste and pollution generating methods in the fine chemical and pharmaceutical chemical industries for decades. Change began in the 1920s however, when industrial chemists and engineers began to invent and develop catalysts capable of inducing "atom economical" and/or "environmentally acceptable" organic reactions that did not produce stoichiometric quantities of wastes, hazardous or otherwise.

2.2. "Atom Economy" and "Environmental Acceptability"

The concepts of "atom economy" and "environmental acceptability" were first described in the peer-reviewed scientific literature in the early 1990s by Trost¹¹ and Sheldon¹², though both men conceded that the use of "atom economical" catalytic reactions had already been in commercial use in the commodity chemicals industry for decades.¹³ Trost's Abstract had simply defined "atom economy" as the "maximum number of atoms of reactants appearing in the product". Slightly later, Sheldon similarly described "atom utilization" as "the ratio of the molecular weight of the desired product to the sum of all the materials (excluding solvents) used."

Sheldon then defined another concept related to "atom economy", i.e. the "kg of waste to kg of desired product", which is now known as the "Environmental Factor" or "E-Factor".^{8,13} The "E-factor" concept has since become a very well-known and widely used metric in Green Chemical research, for both contemplating conceptual chemical reactions, and also for evaluating the final commercial processes.

Sheldon also pointed out that simply calculating the total quantity of chemical waste for a given reaction or final process was not adequate, and that the "nature" of

² See Anastas, P.T. and Beach, E.S., (2009)

³ See Linthorst, J.A. (2010)

⁴ Murphy, M.A, (2018)

⁵ Murphy, M.A., (2020)

⁶ Murphy, M.A., (2021)

⁷ Trost, B.A., (1992)

⁸ Sheldon, R.A., (1992a and 1992b)

⁹ Murphy, M.A., (2023)

¹⁰ Murphy, M.A., (2025a)

¹¹ See Trost, B.M., (1991)

¹² See Sheldon, R.A., (1992a) and (1992b).

¹³ See Murphy, M.A., (2023)

the wastes, i.e. the toxicities and/or dangers of the particular materials should also be considered, and then articulated a general concept of "unfriendliness". Sheldon admitted the concept of "unfriendliness" is difficult to precisely define and is "debatable and will vary from one company to another, being partly dependent on the ability to recycle a particular waste stream". As will be seen below, these generic concepts were not new to the industrial chemists of the time, but Sheldon was certainly correct to articulate his concepts in the peer-reviewed literature, give them a name, and point out the importance of those concepts to those Academics unfamiliar with them.

Sheldon also formulated and published another yet broader concept and terminology to include the importance of considering both the "E-Factor" and "unfriend-liness", by formulating a conceptual "equation" relating both the E-Factor and "unfriendliness" and used the "equation" to define a new terminology for "environmental acceptability".

While Sheldon's conceptual definition for "environmental acceptability" was not genuinely mathematical (because of the difficulties in rigorously defining "unfriendliness"), it can serve as a useful "conceptual framework" for contemplating the environmental impact of either a new chemical reaction, or a new commercialized process based on that chemical reaction.

As will be seen below in many examples, chemists in the commodity chemicals industry had already been quietly using these concepts, to discover, develop, and commercialize "atom economical" and/or "environmentally acceptable" petrochemical processes for about five prior decades. Furthermore, in 1992 Sheldon pointed out, and has continued to point out since, the importance of catalytic reactions to develop commercial processes that produce little waste and thereby achieve good "atom economy", "E-Factors", and "environmental acceptability".

To document that point, in Table 1 of his (1992a) publication Sheldon listed multiple already commercialized "Environmentally Acceptable" catalytic processes for making a variety of large volume commodity petrochemicals. Included on Sheldon's list were existing processes for making terephthalic acid, styrene, methanol, formaldehyde, ethylene oxide, acetic acid, phenol, propylene oxide, acrylonitrile, and vinyl acetate monomer.

Below, we will provide more details about most of the already "Environmentally Acceptable" products and processes listed in Sheldon's Table I and provide additional examples of the downstream products and polymers produced from those early "building block" petrochemical products. Those examples will illustrate the long-term evolutionary processes that began and then progressed for decades before the 1990s.

3. EARLY "ENVIRONMENTALLY ACCEPTABLE" ORGANIC PRODUCTS AND PROCESSES

The use of catalysts to invent, develop, and commercialize increasingly "atom efficient" and/or "environmentally acceptable" processes in the international oil refining and/or commodity chemicals ("Petrochemical") Industries began in the 1920s after WWI, about 100 years ago. For an even more detailed and technical description of Industrial Organic Chemistry as of the 1990s, see Weissermel and Arp (1997).

3.1. Methanol Synthesis

The following short summary of the history of methanol and its production and uses is based on the detailed description provided by D. Sheldon (2017). Methanol was a component of embalming fluid used by the ancient Egyptians, produced by the destructive pyrolysis of wood. The pure compound was first isolated by Robert Boyle by distillation in 1661, but the pure compound only became available in commercial quantities in the 1920s, after WWI. Mixtures of carbon monoxide and hydrogen were readily available from coal gasification, via treatment of hot coal with steam. In 1923 BASF commercialized a catalytic process developed by Mathias Pier (see U.S. Patent #1,569,775) using an ironfree Zinc Chromite catalyst previously developed Alwin Mittasch.

$$CO + 2 H_2$$
 $CO + 2 H_2$
 $CO + 2 H_3OH$
 $CO + 2 H$

$$CO_2 + 3 H_2 \longrightarrow CH_3OH + H_2O$$
 (II)

$$CO + H_2O \longrightarrow CO_2 + H_2$$
 (III)

Scheme I, Methanol Synthesis

The methanol synthesis reaction, Equation 1, Scheme I, is perfectly atom economical on paper, but practice was considerably more difficult for about four decades. The BASF process required very high pressures and temperatures to achieve the equilibrium state illustrated by the three reactions in Scheme I. All three reactions are exothermic, but entropically disfavored, and under those harsh conditions only small conversions to methanol were obtained. Accordingly, multiple passes over the catalyst were required, as were large and energy and high capital cost recycle streams, so the BASF process could hardly be called "Green" by today's standards. But the BASF process did provide commercial quantities of methanol for the first time, which allowed for the development of many downstream uses, such as the formaldehyde synthesis process discussed below.

Major improvements followed in the 1950s and 1960s. Oil drillers began to capture natural gas that had previously been vented or flared, which provided a cheap source of methane. Methane can be reacted with very hot steam over supported Nickel catalysts to make synthesis gas (mixtures of CO and H₂) reasonably cleanly, atom efficiently, and very economically (see Scheme II, Eqn 1). Some of the CO can also react with water to make CO₂ and H₂ (the well-known "Water-Gas Shift Reaction, Scheme II Equation 2, and see also Scheme I Equation III). This "Methane Reforming" process can produce syngas mixtures very efficiently and is also used to make most of hydrogen used in modern Industrial processes (such as ammonia synthesis).

$$CH_4 + H_2O \xrightarrow{\text{Ni}} CO + 3H_2$$
 (I)

$$CO + H_2O \qquad = \qquad CO_2 + H_2 \qquad (2)$$

Scheme II

Engineering and equipment issues are very important in both the synthesis of the syngas and in the methanol synthesis reaction, as described in detail by Sheldon (2017). In 1963 Davies and Snowdon of ICI applied for patents (see U.S. Patent #3,326,956) that described catalysts comprising copper, zinc, and chromium which dramatically improved conversions, and lowered pressures (30-120 atm) and temperatures (200-300 C), at a methanol selectivity of 99.5%, an industrial scale production process that can reasonably be called "Green". Refinements in both the catalysts and engineering / process design and equipment have continued since. In 2022,

global methanol production was estimated to be 111 million metric tons.

3.2. Formaldehyde Production and Uses

Formaldehyde is ubiquitous in Nature and in biological systems at low concentrations but was first conclusively identified by August Wilhelm von Hofmann in 1868 after passing air / methanol mixtures over incandescent platinum. Pure formaldehyde is a colorless gas with a pungent odor, but it has many condensed and/or aqueous physical forms depending on its degree of hydration and/or polymerization.

$$CH_3$$
-OH + 1/2 O_2 $Catalysts$ CH_2 =O + H_2 O

Very small-scale production via air oxidation began in Germany in the 1880s for use in embalming and preservatives, and then slowly spread and grew with time. Early catalysts used supported silver, but modern air oxidation processes typically use supported combinations of iron and molybdenum (or some other) oxides. The reaction is very exothermic, and heat and mass transfer issues are important to the results, and the N₂ gas from the air serves as a diluent to keep the reacting gases from reaching flammable conditions. Modern industrial processes achieve methanol efficiencies approaching 95%, but because formaldehyde is odiferous and considered a human carcinogen and a risk to workers exposed to higher concentrations over long periods, careful engineering and control of the purification, distillation and transport processes is important.

In 1907, Dr. Leo Baekeland, a Belgian chemist, invented a hard and moldable phenol-formaldehyde resin called "Bakelite", which many regard as the first synthetic polymer. Today the biggest use for formaldehyde is in binding wood products such as plywood, particle boards, and fiberboards, using urea-formaldehyde, melamine modified urea formaldehyde, or phenol-formaldehyde. There are ppm levels of formaldehyde emissions from those wood products, and they are subject to governmental regulations in most countries, but their use enables inexpensive production of otherwise "Green" wood products. In 2022, formaldehyde production volumes were estimated to be 23 million tons.

3.3. Ethylene Oxide

In 1931, Theodore Lefort, a French chemist, filed a French patent application for the air oxidation of eth-

ylene to produce ethylene oxide, (which was eventually granted in many countries, see US Patent #1,998,878).

$$H_2C = CH_2 + 1/2 O_2$$
Supported Ag
 $H_2C = CH_2 + 1/2 O_2$
Ethylene Oxide ("EO")

LeFort's air oxidation was perfectly atom economical on paper, and was commercialized in 1936 by Union Carbide, and initially had a Real-World selectivity to Ethylene Oxide of about 70%. The reaction is extremely exothermic, and technical details such as support, catalyst pellet characteristics, and reactor design and operation are all very important. Today, after evolutionary improvements, the selectivity to Ethylene Oxide is about 90%, and worldwide production was estimated to be about 32 million tons in 2022.

EO is an easily liquifiable gas, and moderately toxic. Most of the EO is hydrolyzed to make ethylene glycol, which is primarily used to make polyethylene terephthalate polyester, and as anti-freeze. Due to the high reactivity of EO, it is also used to efficiently make a wide variety of other downstream commercial products, many of which are non-toxic, bio-compatible and bio-degradable.

4. USE OF CATALYSTS FOR "GREENER" OIL REFINING

Prior to WWI, oil refining was conducted by simple atmospheric distillations of crude oil, primarily to produce kerosine for lighting and heating purposes. Before WWII, most industrial organic chemicals were derived from coal. But starting just before WWII, and over subsequent decades, multiple inventions and/or improvements in the oil drilling and refining industry occurred which steadily increased the proportion of salable products produced and decreased the amount of waste residues from oil refining. Those evolutionary developments were both economically and environmentally beneficial, though economic motivations may have been primary. This author previously described these developments in more detail¹⁴, but will very briefly recount some of them here, because they dramatically increased the supply and decreased the price of several small downstream organic compounds that soon became feedstocks for increasingly "Green" petrochemical products and processes.

In the 1920s, French engineer Eugene Houdry experimented with natural zeolite clays as catalysts for

cracking heavy coal oil waste residues, to provide lighter hydrocarbons useful as fuels, and Houdry developed a method for regenerating the quickly fouling zeolite catalysts. In 1930, Houdry moved to the U.S. and began collaborating with the Socony Vacuum and Sun Oil companies, to use the zeolite catalysts to crack heavy residues from the distillations of crude oil.

In 1937, a commercial "Houdry" cracking unit using a fixed bed catalyst opened at a refinery in Pennsylvania and dramatically increased the production of highoctane gasoline-range hydrocarbons from the heavy waste residues, as well as other valuable small hydrocarbons such as ethylene, propylene, and butanes and butenes. Several other "Houdry" fixed-bed cracking units were built before the U.S. entered WWII. Then in 1942 Houdry and Standard Oil of New Jersey opened a new fluidized bed cracking unit using zeolite catalyst powders that eliminated the need to shut down the cracking units for catalyst regeneration, and also dramatically decreased the amount of waste residues from oil refining. The "Houdry" high-octane aviation fuels gave US pilots a significant power advantage over Axis airplanes during the War and then proved very valuable for gasoline blending after the War as demand for high octane gasolines rose dramatically, especially when lead additives were banned from gasolines in the 1970s.

Furthermore, in 1950 Houdry filed a patent application for a catalytic converter for automobile exhaust gases, which oxidized the residual hydrocarbons in exhaust gases to CO_2 and $H_2O!$ See U.S. Patent #2,647,521, and Figure I from that patent below.

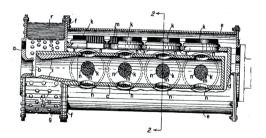


Figure I from US Patent #2,674,521, "Catalytic Converter for Exhaust Gases"

Houdry's catalytic converter contained supported noble metal catalysts for air oxidizing the unburned hydrocarbons. Unfortunately the lead additives in gasolines during those times quickly fouled the precious metal oxidation catalysts, so Houdry's converters were not used in commercial practice until the 1970s when lead additives were banned from gasolines. Neverthe-

¹⁴ See Murphy (2020), Murphy (2021), Murphy (2023), and Murphy (2025a)

less, this author would nominate Eugene Houdry for the hypothetical title of "World's First Green Engineer"!

Also during and after WWII, oil refineries continued to develop additional new processes that chemically manipulated the organic compounds found in oil, to increase the yield of useful and salable products, decrease the waste residues, and improve the economic results.¹⁵ Those new processes included 1) catalytic "alkylation" of propylene, butenes, and pentenes with isobutane, to form highly branched and high octane heptanes, octanes, and nonanes for gasoline blending; 2) catalytic reforming processes which convert napthas from early oil distillations into branched alkanes and aromatics; 3) catalytic hydrocracking which converts heavy distillation fractions (diesels, kerosines, and heavy gas oils) to lighter and more valuable napthenes and paraffins, and other gasoline-range hydrocarbons; and 4) olefin metathesis, which is sometimes used to upgrade low molecular weight olefins to higher molecular weight olefins. As a long-term result of these long-term evolutionary developments in oil refining, in 1992 Sheldon estimated that oil refineries were only producing about 0.1 kg of waste products per kg of useful and salable products.16

But importantly for purposes of this paper, the evolution of catalytic cracking processes in oil refineries also generated large quantities of small organic building block molecules, such as ethylene, propylene, butenes, etc., which would stimulate the development and evolution of many downstream petrochemical products and processes, as discussed below.

5. THE POST-WAR EVOLUTION OF ATOM EFFICIENT AND/OR ENVIRONMENTALLY ACCEPTABLE PETROCHEMICAL PRODUCTS AND PROCESSES

After WWII, the oil refining and organic chemical industries began to boom worldwide, as the international economies rebounded. The growing and cheap availability of small organic molecules from the proliferating oil refineries motivated research for new uses of those small organic molecules, and multiple inventors in multiple countries began to invent, develop, and commercialize a growing number of new petrochemical products made by new catalytic processes that were atom efficient and/or environmentally acceptable on paper, though considerable evolution was needed in some cases in order for those processes to become genuinely "Green" in Real-World practice. We describe some major examples below.

5.1. Olefin Hydroformylation

In 1938, Otto Roelen of Ruhrchemie was investigating Fisher-Tropsch reactions of CO/H₂ mixtures, as potential a source of synthetic fuels for Germany, and reacted ethylene with CO/H₂ at several thousand psig in the presence of heterogeneous Cobalt catalysts. Aldehydes were produced, and Roelen investigated further¹⁷. Despite the physical and political difficulties of WWII, Roelen and Ruhrchemie managed to build a small functioning plant to hydroformylate ethylene to n-propional-dehye (at pressures well over 3000 psig), and then in a second step catalytically hydrogenated the propionaldehyde give n-propanol.

Both the two catalytic reactions shown above were perfectly Atom Economical on paper and gave good Real-World yields. After the War, the US "commandeered" Roelen's original 1938 German patent application, see US Patent #2,327,066. Roelen apparently believed the Cobalt catalyst was heterogeneous, but in 1960-1961, Heck and Breslow of Hercules Corporation identified HCo(CO)₄ as the active homogeneous catalyst and explored the mechanism of the hydroformylation reaction. ¹⁸

Many uses of hydroformylation have subsequently evolved and been commercialized to make a variety of important industrial products.¹⁹ The biggest volume application is the hydroformylation of propylene to make n-butyraldehyde (see equation below). The annual production volume of n-butyraldehyde was estimated to be 7 million tons per year in 2017.

When a substituted olefin is hydroformylated, the carbon monoxide insertion can potentially occur at either end of the double bond, to produce either the "n"-aldehyde or an "iso"- aldehyde. In many (but not all) applications, the n-aldehyde is more commercially valuable. The propylene hydroformylation to give n-butyralde-

¹⁵ See Leffler, W.L., (2008), Murphy (2020), and Murphy (2021)

¹⁶ See Sheldon (1992a) and Sheldon (1992b)

¹⁷ See Cornils et.al., (1994)

¹⁸ See Heck and Breslow, (1961)

¹⁹ See Zhang et. al., (2022)

hyde was first commercialized by BASF / Ruhrchemie in 1960, using $HCo(CO)_4$ catalyst, at pressures well above 3000 psig. Unfortunately, the "n/iso" isomer ratio was only about 3:1, so the Real-World cobalt catalyzed propylene hydroformylation was not yet particularly atom efficient, or "environmentally acceptable".

But in the late 1960s, Shell added trialkyl phosphines to the Cobalt catalysts, which significantly lowered the required pressures, increased the activity and stability of the Cobalt catalysts, and improved the n/iso ratio, to about 7:1. Shell and some other companies still use the Co/PR₃ catalyzed processes to manufacture some higher molecular weight aldehydes.

In 1968, Evans, Osborne, and Wilkinson of Imperial College of London described the use of Rh-triphenylphosphine complexes as catalysts for the homogeneous hydrogenation of olefins, and then the propylene hydroformylation reaction²⁰, part of the work that won Wilkinson a Nobel Prize in 1973. In the 1970s Union Carbide (and other companies) rapidly commercialized the Rhodium / Triphenylphosphine catalyzed processes for propylene hydroformylation, which operate at much lower pressures (400 psig) than the Cobalt processes and produce much better n/iso ratios around 12:1. The Rh/ PPh₃ catalyzed processes are also continuous and operate without added organic solvents, the product aldehyde (and a hydrocarbon oil that slowly builds up from condensation and hydrogenation of the aldehydes) are the only solvents. In this author's opinion, those processes had evolved into economically successful, truly atom efficient, and environmentally acceptable commercial petrochemical processes by the 1970s.

But further evolution of hydroformylation processes continued. In 1976, Emile Kuntz of Rhone-Poulenc developed a process for hydroformylation of olefins using Rhodium / tri-sulfonated triphenylphosphine catalysts dissolved in water, see US Patent #4,248,802. In 1984 Rhone Poulenc and Ruhrchemie commercialized a process for making n-butyraldehyde in which the catalyst is dissolved in water, and the sulfonated watersoluble phosphines have since been used for a variety of other catalytic processes. In the 1980s, researchers at several corporations explored and commercialized hydroformylation processes using sterically hindered bidentate phosphite complexes which produce very high n-iso ratos.¹⁹ Readers will hopefully recognize the longterm evolutionary changes in hydroformylation chemistry which eventually resulted in "Green" commercial processes, decades before the 1990s.

An interesting spin-off from Wilkinson's work on

Rh / phosphine complexes occurred when William S. Knowles of Monsanto modified Wilkenson's Rhodium catalysts to employ optically active bi-dentate phosphine ligands²¹ and subsequently used them to invent a commercial process for making l-Dopa by asymmetric hydrogenation, see U.S. Patent #4,005,127. Knowles work was the first commercialization of the use of asymmetric metal complexes as catalysts for organic reactions, work for which he shared a Nobel Prize in 2001 with Ryöji Noyori and K.B. Sharpless (for their subsequent uses of metal complexes with optically active ligands as catalysts for many other asymmetric hydrogenation and epoxidation reactions).

5.2. Processes for Making Acetic Acid and Its Derivatives

Acetic Acid has been known and used by humans since Antiquity, in the form of fermented vinegars. It was first synthesized in pure form in 1845 by Hermann Kolbe. Before WWII, pure acetic acid was available on small commercial scales, by hydrolysis of calcium carbide, or from treatment of "pyroligneous liquor" from charcoal production with inorganic bases, processes which produced stoichiometric salt wastes. Around 1913, researchers at BASF discovered a Cobalt / Iodide catalytic process for making acetic acid by "methanol carbonylation", the reaction shown below, but the methanol feedstock was not yet available in commercial quantities, and the required pressures were very high.

$$\begin{array}{c} \text{CH}_3\text{-OH} & \begin{array}{c} \text{CO} \\ \\ \hline \\ \text{Catalyst}, \\ \\ \text{H}_2\text{O} \end{array} & \begin{array}{c} \text{O} \\ \\ \text{H}_3\text{C} \end{array} & \begin{array}{c} \text{OH} \\ \\ \text{OH} \end{array}$$

$$\text{Methanol} & \begin{array}{c} \text{Acetic Acid} \end{array}$$

After commercial quantities of methanol became available in the 1920s, several companies began to investigate the reaction, and it was piloted at British Celanese in 1925, but the lack of sufficiently corrosion-resistant metals delayed commercialization for decades.²²

However, after WWII, the oil-drilling and refining industries boomed, as did the use of oil cracking technologies. N-Butane became cheap and plentiful, and in the early 1950s several companies (including Celanese, Union Carbide, Standard Oil, Eastman, Huls, and AKZO) commercialized plants for cobalt catalyzed air oxidation of n-butane, which produced acetic acid as

²¹ See Knowles and Sabacky, (1968)

²² See Wagner, F., and LookChem online Chemical Encyclopedia

²⁰ See Evans, Osborn, and Wilkenson, (1968)

a major product, accompanied by smaller amounts of several other low molecular weight organic oxygenated organics.⁴ Those catalytic processes were certainly not atom efficient, and they emitted considerable gaseous carbon dioxide and carbon monoxide, but they did eliminate the stoichiometric production of inorganic salt wastes that had been produced by prior processes. The complex mixture of oxygenated organic products required an energy-intensive separation by complex distillation processes, but nevertheless remained economically viable until the 1990s, when they finally became both technically, economically, and environmentally obsolete.

The price of ethylene and propylene were also decreasing dramatically, and many companies began to research potential applications. In 1956 Schmidt, Hafner, and Jira at Wacker Chemie discovered the "Wacker Process" for the air oxidation of ethylene to produce acetaldehyde²³, using a homogeneous Palladium / Copper / HCl catalyst, dissolved in water solvent (see equation below).

The "Wacker" catalyst solutions were however extremely corrosive, so commercialization was delayed until corrosion-resistant alloys became available several years later. The Wacker oxidation of ethylene was followed by a catalytic air oxidation of the acetaldehyde (over supported transition metal catalysts) to give acetic acid. Both these reactions are perfectly atom efficient on paper, and the Real-World yields are high, so together the two reactions represented a highly economically attractive and atom efficient and environmentally acceptable process for making acetic acid. Multiple plants were built by several companies in the 1960s, and they remained economically competitive until the 1990s.

Meanwhile, the development of corrosion-resistant alloys in the 1950s also enabled commercialization of methanol carbonylation processes for producing acetic acid, already briefly mentioned above. In 1960, BASF built a small plant for manufacturing acetic acid by methanol carbonylation, catalyzed by CoI₂. But the methanol selectivity was only about 90%, the carbon monoxide efficiencies were only about 70%, the required pressures were over 9,000 psig, and considerable byproducts were produced.²² Two more plants were eventually built, but the Cobalt-catalyzed methanol carbonylation

process was only marginally economically competitive with and/or "Green" as compared to the Wacker process.

Methods for methanol carbonylation improved dramatically in 1968, when Paulik, Hershman, Coeur, and Roth of Monsanto invented a new homogeneous Rh/I-catalyzed methanol carbonylation process, see US Patent #3,769,329. The Monsanto Process was continuous, required only about 400 psig pressure, gave greater than 99% selectivity to acetic acid (based on methanol), gave carbon monoxide efficiencies in the low 90% range, and used the product acetic acid as solvent. Therefore, the Monsanto process constituted a new highly efficient, economically superior, and "Green" process for making acetic acid. Monsanto built a first plant in 1970, then licensed the process to Celanese (who built a plant in 1975), and later also to British Petroleum.

Although it was little recognized or understood for years, the acetic acid solvent used in the original "Monsanto" processes also had to contain at least about 8 mole % of water, in order to prevent rhodium precipitation during the isolation of the acetic acid product. The high water content also promoted a water-gas shift side reaction that significantly lowered the carbon monoxide efficiencies.

During the 1970s, multiple companies attempted to adapt the "Monsanto" Rh / I catalysts to carbonylate methyl acetate to produce acetic anhydride, in the complete absence of water, as shown in the equation below. But those early efforts were not commercialized because of poor rates, rhodium catalyst instability, and the formation of tarry byproducts.

But in the early 1980s, Larkins, Polichnowski, Tustin, and Young of Eastman Chemical developed a successful catalytic carbonylation of methyl acetate to acetic anhydride, which was commercialized in the mid-1980s at Eastman's plant in Kingsport Tennessee. The secret to Eastman's success (in the absence of water) was the addition of lithium iodide co-catalyst and deliberate inclusion of a modest partial pressure of $\rm H_2$ in the carbon monoxide feed, see U.S. Patent #4,374,070. The new Eastman process for acetic anhydride was nearly perfectly atom economical on paper, and in practice, and was a commercial success.

In 1983, a small team at Celanese in Corpus Christi Texas, aware of the Eastman work and patents, successfully and dramatically lowered the water content

²³ See Jira (2009) and U.S. Patent #3,080,425

required for commercial "Monsanto" methanol carbonylation, from 8 mole % to about 2 mole %, by the addition of lithium iodide and re-optimization of some other process variables.²⁴ The benefits from this "low water" methanol carbonylation were excellent Rh catalyst activity and stability, a large increase in plant capacity, lowered purification costs and energy usage (because of the much reduced water loads) and a significant increase in carbon monoxide efficiency (because of much lower rates for byproduct production via the water-gas shift side reaction). That even more efficient and Environmentally Acceptable Celanese "AO™" methanol carbonylation process was commercialized at Clear Lake Texas in the late 1980s, and two more Celanese plants were subsequently built and further improved. Furthermore, this author was working (on a part-time basis) on the early Celanese AO™ product team at the time (1984) he first conceived the BHC Ibuprofen Process (which used a carbonylation reaction for its final key step) that won one of the first U.S. Presidential Green Chemistry Challenge Awards.²⁵

The innovations at Celanese did not stop later innovation and evolution at Celanese's competitors. In August 1994, Garland, Giles, and Sunley of BP Chemicals Ltd filed for a patent (see U.S. Patent #5,672,743, and Jones (2000)) for a methanol carbonylation process using Iridium / Ruthenium catalysts, which also runs under "low water" conditions. Several commercial BP plants for manufacturing acetic acid using Ir / Ru catalysts are now in commercial operation internationally. Global acetic acid production was estimated to be 18 million metric tons in 2018.

This author hopes that readers will recognize the evolutionary process that eventually produced the modern and highly atom efficient and "Green" acetic acid technologies actually began in 1913, followed by a long-term sequence of unpredictable evolutionary improvements carried out by a series of largely independent inventors and companies, wherein each improved on the technology of their predecessors and/or competitors.

Acetic Acid has many commercial uses, but the largest is the production of vinyl acetate monomer ("VAM"). It was discovered in 1912 by Fritz Klatte, who reacted acetylene with acetic acid in the presence of mercury salts, and who discovered VAM could be polymerized (sometimes violently) in the presence of various radical initiators. See U.S. Patent #1,241,738. For decades VAM was produced commercially by variations of Klatte's method, but when ethylene from petroleum cracking processes became cheap and available, a new method of synthesizing VAM was discovered and commercialized

by a number of companies, i.e. by catalytic air oxidation of ethylene and acetic acid over supported Palladium catalysts, as illustrated by the chemical equation below.

The continuous catalytic oxidation process uses atmospheric oxygen as a cost-free oxidant and converts it to water. Some over-oxidation of the ethylene to CO_2 occurs in practice, and Real-World efficiencies are in the range of 80-90%, and VAM is relatively non-toxic to humans. Accordingly, the VAM production process can be considered favorably "environmentally acceptable". Global production volume for VAM was estimated at 9 million tons per year in 2023.

VAM is used to prepare a wide variety of polymers and copolymers. VAM can be homo-polymerized in solutions, water suspensions, and/or emulsions to form polyvinyl acetate emulsions ("Wood Glue"). Polyvinyl acetate is bio-degradable and is used in a wide variety of film and packaging applications, including the production of plywood and particle boards. Polyvinyl acetate production volumes were estimated to be 3.4 million metric tons in 2020.

Polyvinyl acetate can be hydrolyzed under basic conditions to produce polyvinyl alcohol ("PVA"), with the liberation of acetic acid, which can be recovered and recycled. PVA is a water-soluble and bio-degradable polymer with many uses in adhesives, papermaking, textiles, coatings, 3D printing, food and pharmaceuticals, wound dressings, and contact lenses, and for making water-soluble polymer blends. Worldwide production volumes are estimated to be about 650,000 tons per year.

VAM is also widely co-polymerized with other vinylic monomers, including ethylene and various acrylic acid esters, often for use in paint and coatings applications. Hopefully readers will recognize that the commercial availability of VAM has resulted in the evolution of a large downstream family of useful and relatively environmentally acceptable polymeric materials and products.

5.3. Ziegler-Natta Olefin Polymerization

The 1963 Nobel Prize in Chemistry was awarded to two bitter competitors, Karl Ziegler of the Max-Planck-Institut für Kohlenforschung (coal research), and Giulio Natta of the Institute of Technology in Milan Italy, for their discoveries related to the polymerization of ethyl-

²⁴ See Smith et.al., (1987)

²⁵ See Murphy (2018)

ene and propylene to high molecular weight polyethylene and polypropylene respectively, polymeric plastics which are still produced today in massive commercial quantities worldwide.

To oversimplify an interesting and complex story (told more fully on the website of the Max Planck Institute²⁶, and by Sivaram (2017)), Ziegler and Natta both had prior relationships and research agreements with the Italian company Montecatini. Ziegler (who had a bent toward Academic research) and his graduate students pursued a tortuous multi-year research effort directed toward the catalytic polymerization of ethylene to produce high molecular weight polyethylene. In the Fall of 1953, Ziegler and his graduate students discovered an increasingly effective series of catalysts comprising mixtures of Group IV metal chlorides (especially TiCl₄) and aluminum alkyls, which successfully polymerized ethylene being bubbled through a solvent in a canning jar and produced 400 grams of (dry) high molecular weight polyethylene. Ziegler and his students rapidly submitted a German patent application (Patentschrift No. 973,626) for the polymerization of ethylene.

Natta, aware of Ziegler's catalysts and patent applications through both formal and informal channels, was inclined towards the practical applications of Scientific research, and began investigating use of Ziegler's catalysts for the polymerization of propylene and other substituted (and prochiral) olefins. To oversimplify, Natta's work led to the discovery (and ultimate commercialization) of stereoregular, crystalline, isotactic polypropylene, as well as the recognition of its crystalline, helical structure. Montecatini submitted a patent application naming Natta an inventor for the polypropylene polymerizations, without notifying or consulting Ziegler.

Over 40 years of bitter patent litigations resulted between the Max Planck Institute, Montecatini, and several other major petrochemical companies. The litigations were eventually won by the Max Planck Institute on the basis a "first-to-invent" feature of American patent law that is now legally defunct. In 2022, global production of polyethylene was estimated to be 110 million metric tons, and the global production of polypropylene was estimated to be 79 million metric tons.

Years afterwards, Ziegler compared his research path to "a hiking tour through a new country...but one on which one never did know just where the journey was really headed. For decades, I never even remotely thought that my path would also include technological successes." Now we recognize that the Ziegler-Nata polymerization reactions are atom efficient, and there-

²⁶ See Max-Planck-Gesellschaft website, (2014)

fore "Green" in some respects. But it also seems safe to assume that neither Ziegler nor Natta foresaw the huge technical and economic importance of their discoveries, or the ecological problems that result from the lack of bio-degradability of the huge volume of the commercial polyolefin plastics we now produce and use, an issue which we still struggle with today.

5.4. Acrylic Acid, Acrylic Esters, Methods for their Production, and Their Polymers

Acrylic acid was first prepared in 1847 by air oxidation of acrolein. The polymerization of acrylic acid and its esters was first reported in 1901 in a PhD thesis entitled "Polymerization products of Acrylic Acid" by Otto Röhm. In 1907 Otto Röhm and Otto Hass founded a German company to manufacture leather products, but in the 1920s Röhm began new research efforts directed toward polymers, especially polymers derived from acrylic acid, methacrylic acid, and their esters. In 1927, Röhm & Hass commercialized its first product, which used an acrylic polymer layer sandwiched between glass layers to form a shatter-proof glass, and in the 1930s commercialized PLEXIGLAS which used a polymethylmethacrylate layer between the glass sheets. The many commercial applications of acylates and methacrylates grew rapidly thereafter.

Until the 1950s, acrylic acid was typically produced by various methods from acetylene, which was typically produced from calcium carbide, which in turn was produced from coal, an expensive and dirty process that produced many waste salts and products. In the later 1950s, as the supply of propylene from refinery catalytic crackers increased and the price dropped, many researchers and/or companies began to investigate methods for the air oxidation of propylene to produce acrylic acid.²⁷ Although many variations of processes and catalysts have been reported since, modern commercial processes for producing acrylic acid from propylene typically operate continuously in two stages, as shown by the chemical equations below:²⁸

$$\begin{array}{c} \text{CH} \\ \text{H}_2\text{C} \\ \text{CH}_3 \\ \text{Propylene} \end{array} \begin{array}{c} + \text{O}_2 \\ \text{Catalyst 1} \\ \text{Steam} \\ \text{Acrolein} \end{array} \begin{array}{c} \text{CH} \\ \text{H}_2\text{O} \\ \text{H} \\ \text{Acrolein} \\ \end{array} \begin{array}{c} + 1/2 \text{ O}_2 \\ \text{Catalyst 2} \\ \text{Steam} \\ \text{Acrylic Acid} \end{array} \begin{array}{c} \text{CH} \\ \text{OH} \\ \text{Acrylic Acid} \\ \end{array}$$

In the first stage, air is used to oxidize propylene to acrolein, in the presence of a first supported catalyst and

²⁷ See for example Campbell et.al., (1970)

²⁸ See for example Turton, R., "Acrylic Acid Production via the Catalytic Partial Oxidation of Propylene"

significant excess of steam (which acts as a moderator which also dilutes the gas mixture to below flammable limits) while oxidizing the propylene and reducing the oxygen to produce water as a non-toxic byproduct. Then in a second stage, conducted over second supported catalyst, another half mole of oxygen is injected which further oxidizes the acrolein to acrylic acid. A small amount of over-oxidation occurs, producing relatively small amounts of CO₂ and acetic acid byproducts. The hot 2nd stage product gas mixture is then immediately quenched by absorption into liquid water, and thereby easily separated from the gases. The aqueous acrylic acid is then extracted from the quench water into an organic solvent, and the organic phase is separated by distillation, to isolate the acrylic acid product and recycle the solvent. An instructive process flow diagram can be found in Turton's article.

Acrylic acid monomer is toxic but is biodegradable in both air and water. The chemical oxidation reactions are not technically atom efficient (because of the water byproduct produced), but they are economically attractive and reasonably environmentally acceptable. Multiple companies use these oxidation processes commercially, and the global acrylic acid production volume was estimated to be about 8 million metric tons in 2022.

Acrylic acid monomer is used in many polymer and co-polymer applications, including superabsorbent polymers, cosmetics, skin care, and in adhesives, coatings, and sealants. Many acrylic acid esters are made and sold commercially, the choice of the particular alkyl group for the ester being dependent on the particular polymer or co-polymer application. The biodegradability of the polymer products depends on the characteristics of the particular polymer or copolymer.

5.5. Acrylonitrile

Acrylonitrile was first synthesized in 1893 and is produced today by the Sohio Process developed in the 1950s²⁹, via catalytic amoxidation of propylene with sizeable excesses of air, ammonia, and steam.

$$\begin{array}{c} + O_2 + NH_3 \\ \text{(in excess)} \\ - CH_3 & \hline \\ - CH_3 & \hline \\ - CAtalyst \\ Steam & \hline \\ - CH_2 & \hline \\ - CH_2 & \hline \\ - CH_3 & \hline \\ - CH_3$$

The Sohio process is carried out continuously in a single reactor over a bismuth phospho-molybdate catalyst, for short residence times. It is believed that the first step of the reaction is the oxidation of propylene to acrolein (similar the acrylic acid processes discussed above), and that the acrolein condenses with the ammonia (in an equilibrium step) to form an imine of the acrolein, which is then further oxidized in-situ to produce the highly valuable acrylonitrile monomer. Some overoxidation also occurs, to produce substantial amounts of acetonitrile and hydrogen cyanide co products, which are also purified and sold commercially. Unfortunately, large excesses of ammonia and steam are required, and the process produces large gaseous and aqueous waste streams and high energy usage. Because the acrylonitrile monomer and hydrogen cyanide co-products are highly toxic, the current "Sohio" catalytic process can hardly be termed either atom economical or environmentally acceptable.

The acrylonitrile monomer is however very valuable commercially for producing polyacrylonitrile and multiple kinds of co-polymers, including styrene-acrylonitrile, acrylonitrile-butadiene-styrene, acrylonitrile-styrene-acrylate, and acrylonitrile-butadiene. The acrylonitrile is also a useful intermediate for making some types of nylons. The global annual production volume of acrylonitrile was estimated to be 8.6 million tons in 2022.

Various researchers have been investigating potentially "Greener" methods for producing acrylonitrile, including from bio-mass starting materials such as glycerol, but those methods are not economically competitive as yet.

5.6. Styrene

Styrene was first isolated in 1839 by Eduard Simon and occurs in nature at low concentration levels. Although other modern processes exist and still operate, most styrene is derived from a continuous catalytic reaction over zeolite catalysts between benzene and ethylene to form ethylbenzene. The ethylbenzene is then thermally dehydrogenated over potassium promoted iron oxides in the vapor phase.

The dehydrogenation of ethylbenzene was discovered in the 1930s and was used during WWII to produce

²⁹ See American Chemical Society, (2007), "The Sohio Acrylonitrile Process"

styrene for making styrene-butadiene rubber during the War. Styrene production expanded dramatically after WWII and continued to grow and evolve afterwards. In modern processes, ethylbenzene and steam are passed over potassium promoted iron oxide catalysts at temperatures over 600 K, at low pressures, to produce equilibrium mixtures of styrene and H₂. These processes have been recently described in considerable detail by Behr.³⁰ Although operation at high ethyl benzene conversions is possible, byproduct formation causes most modern plants to operate at lower conversions, using steam injection through multiple reaction stages, to produce conversions of 50-70% with recycle of unreacted ethylbenzene, but at overall yields of 88-95%. Behr provided worthwhile process flow diagrams.

The dehydrogenation of ethylbenzene to produce styrene is reasonably atom economical, but requires significant energy expenditure, and the benzene and styrene are both considered to be human carcinogens and toxic. The production process is nevertheless conducted on a large commercial scale. Global styrene production was estimated to be about 37 million tons in 2022.

Styrene is a low-cost monomer used in many polymer / co-polymer / plastic applications for packaging, construction, household goods, transportation and safety products and military applications. It is worth noting that the very first U.S. Presidential Green Chemistry Award, in 1996, was given to the Dow Chemical Company, for an invention entitled "100 Percent Carbon Dioxide as a Blowing Agent for the Polystyrene Foam Sheet Packaging Market". See U.S Patent #5,250,577 to Gary C. Welsh, filed August 2, 1989.

Polystyrene is non-toxic but non-bio-degradable, though some polystyrene products can be recycled under some circumstances. The biodegradability and/or recyclability of the many co-polymers made from styrene vary depending on the exact nature of the copolymer and its particular application. The recyclability and/or lack of biodegradability of many polymers and copolymers is of course these days a major issue and/or research topic in modern "Green" chemical research in the petrochemical industries.

5.7. Terephthalic Acid Production

Terephthalic Acid is a major industrial product used for condensation with glycols to produce polyesters. The predominant process for producing terephthalic acid was discovered by Saffer and Barker of Mid-Century Corporation in the mid 1950s, see U.S. Patents #2,833,816 and #3,089,906. In this process, p-Xylene provided by reforming processes in refineries is continuously air oxidized to terephthalic acid in acetic acid solvent containing cobalt, manganese, and bromide ions as catalysts, see the equation below. On paper the reaction is not perfectly atom economical but is reasonably environmentally acceptable, because water is the only stoichiometric co-product and the terephthalic acid is biodegradable by microorganisms.

p-Xylene Terephthalic Acid

The Mid-Century process was developed and commercialized in the late 1950s in collaboration with Amoco and ICI, using the highly corrosion resistant alloys that became commercially available then. In practice, excess atmospheric O₂ reactant is used, and some minor over and under oxidation occurs, but the conversion of p-Xylene is reportedly around 98% with about 95% selectivity to terephthalic acid. A significant quantity of the acetic acid solvent does get combusted to CO₂ and H₂O during the process and must be replenished. Accordingly, the Mid-Century / Amoco process is reasonably environmentally acceptable, but research work continues to develop improved and/or "Greener" methods. ³¹ It has been estimated that the global production of terephthalic acid was 84 million metric tons in 2022.

The biggest uses for terephthalic acid is polymerization with various glycols to form polyesters. By far the biggest use is condensation polymerization with ethylene glycol to make polyethylene terephthalate ("PET"). The first synthesis of high molecular weight PET suitable for polymer application was in 1941 by J.R. Whinfield and J.T. Dickson of the Calico Printer's Association of England (see Canadian Patent Application CA 490196). PET polymers and processes for making them were developed and commercialized by DuPont in the early 1950s.

In most commercial processes, terephthalic acid is heated with ethylene glycol and the water produced by the polyesterification is removed by distillation, so the process is not technically atom efficient, but it is reasonably environmentally acceptable. A minority of commercial processes use a multi-step polymerization procedure in which the terephthalic acid is first esterified with

³⁰ See Behr, (2019), "Styrene Production from Ethylbenzene"

³¹ See Tomás, Bordado, and Gomes (2013) and Lapa, Luisa, and Martins (2023)

methanol to eliminate water and make and isolate dimethyl terephthalate. The dimethyl terephthalate is then polymerized with ethylene glycol in a two-step polymerization procedure. Global production of PET was estimated to be about 25 million metric tons in 2022.

PET is widely used in food and drink packaging applications, textiles, electronic components, and many other applications. PET polymer is not very bio-degradable but is readily recycled to reusable resin in situations where the PET waste can be economically separated from the other materials in a waste stream.³² It is also sometimes possible to economically depolymerize PET with methanol or ethylene glycol to produce high quality monomers that can be re-polymerized.

6. EVOLUTION IN THE CHEMICALLY RELATED INDUSTRIES, "GREEN CHEMICAL" RESEARCH, AND BROADER SOCIETIES

The historical examples described above demonstrate that after WWII, decades before the words and "Principles" of "Green Chemistry" were coined, many oil and petrochemical companies and their scientists and engineers (working in interdisciplinary teams with many different motivations) invented and commercialized multiple atom economical and/or environmentally acceptable catalytic processes for making low-priced but high-volume commodity petrochemicals.

After WWII, in the 1950s and 1960s, the Societies and/or economies in many countries recovered and then boomed, as did oil drilling and refining in response to booming demand for fuels. Economic recovery and the political and strategic imperatives of the developing Cold War dominated many Societies' concerns, and the understanding of ecological issues was still rudimentary. Technical, economic, and political motivations certainly outweighed environmental concerns during those years, but the discovery and development of efficient catalysts provided the technical tools /means that enabled much more efficient conversion of oil into low cost and readily available organic building block molecules, and growing profits, even though the companies and their scientists, and engineers kept many of their strategies, motivations, and technical details secret.33 The building block molecules were then used generate a widening and evolving downstream network of petrochemical products and polymers. Those atom efficient catalytic processes and resulting products improved people's lives in many ways, though little direct attention was being paid to environNevertheless, a wide variety of other motivations were also important in many individual cases, and they varied tremendously with time, the country, the company, and the individual people and circumstances. At least some of the industrial scientists and engineers involved had some internal environmental motivations, as was clear from Houdry's 1950s invention of a catalytic converter for exhaust gas emissions.

Other smaller segments of the chemically-related industries, including fine chemicals and pharmaceuticals, also did much to improve people's lives, but most continued to use the reactions of traditional organic chemistry that inherently produced stoichiometric wastes and/or pollution. In those industry segments, the proportion of waste produced per pound of product was orders of magnitude higher, but did not have much economic impact in the absence of environmental regulations, with the result that the environmental issues were neglected by many for many years by many companies in those industry segments. Similarly, in many down-steam consumer products industry segments, the economic costs of waste disposal were modest and were mostly ignored for decades by too many companies.

But things began to change rapidly in the 1960s and 1970s as Society, the chemical industries, and the resulting pollution, grew rapidly ³⁵, The Environmental Movement grew quickly in reaction against the pollution, and politicians in many countries also reacted. Legally inspired "Command and Control" environmental statutes and regulations were passed by the governments in many countries which dictated "end-of-the pipeline" methods for controlling and treating the wastes that were being created. But as the international industries attempted to implement the legally mandated "end-of-the-pipeline" controls, the industries quickly encountered poor effectiveness and spiraling costs, especially as the emission limits were lowered.

In the 1970s, in response to the rise of the Environmental Movement and "Command and Control" statutes, many industrial inventors in many countries began to work to creatively improve their individualized pollution problems. Those sorts of individualized solutions first coalesced into an organized "Pollution Prevention" (and publicized) program at the 3M Corporation in 1975, led by Dr. Joseph T. Ling, and those semi-independent efforts coalesced into a "movement" of very broad scope and approaches in 1976, at a United Nations

mental issues. Environmental regulations were typically lax and there was little immediate cost if toxic products, waste and/or pollutants were released into the biosphere.

³² See Joseph et.al., (2024)

³³ See Murphy (2025 b)

³⁴ See Sheldon (1992a), (1992b), and Murphy (2023)

³⁵ See Murphy (2018), (2020) and (2021)

multi-disciplinary seminar entitles "Non-Waste Technology and Production" published in 1978.³⁶

Then in the 1980s many additional companies in many countries began to adopt the explicitly environmentally conscious 3M approaches and began to quietly commercialize many such "Pollution Prevention" projects, aided by slowly growing support from many national governments in the 1980s and 1990s.

Then, as this author has previously argued, the predominantly Academic / Governmental "Green Chemistry Movement" of the 1990s and 2000s evolved out of, but was only a narrow subset of, the earlier mostly industrial Pollution Prevention efforts of the 1970s and 1980s.

Furthermore, the importance of the mostly parallel and semi-independent emergence of modern biotechnology, not addressed by this paper, has clearly and rapidly accelerated and evolved, especially in recent years. But it also appears that much remains to be done to evolve both the "chemical" and "bio-technological" and downstream consumer products and achievements toward better economic and environmental outcomes.

This author believes that it is important to recognize the evolutionary nature of the long-term historical developments described here, and in this author's prior papers. In particular, this author has previously argued that:³⁷

...Real-World Industrial "Green Chemistry" emerged as a holistic final outcome from an extremely varied and complex set of parallel evolutionary "random tinkering" sub-processes that began about the time of World War II, and that evolutionary process accelerated in the 1970s That overall evolutionary process was the product of very complex interactions of very many internal and external events, carried out by many human investigators from multiple disciplines and countries, who were individually driven by many different goals, motivations, influences and input factors, including customer / societal needs and desires, economics, the environment, the legal / statutory / regulatory pressures, as well as the constantly evolving state of the underlying sciences of Chemistry, Biology, and Engineering, over decades. Many of the resulting individual inventions were also the direct product of individual human creativity, thought, and logic, as aided by intercommunications between the investigators, as well as the constraints of the laws of Nature, local circumstances, and elements of chance.

While contemplating such broad and long-term evolutionary phenomena, it seems worth re-considering a comment by Professor Giuseppi Bruni (the teacher and mentor of Guilio Natta), who said that "the only difference between theoretical (fundamental) and industrial (applied) problems is that the latter is more difficult to resolve because you have to take into account lot of factors that you can neglect in the former."

Fortunately, in the last 10 years or so, the "Green Chemistry Movement" appears to be evolving and broadening back again, to encompass the much earlier, broader, international, and interdisciplinary concepts of "Pollution Prevention", "Sustainability", "Systems Thinking", and/or a "Circular Economy". ³⁸ In this author's opinion, those broader, international, interdisciplinary, and evolutionary approaches will be an important key to successfully addressing and resolving the sometimes conflicting needs and contributions of individuals, Industry, Society, the Economy, the various branches of the Sciences and Engineering with the Environment.

In 1997, Professor Jared Diamond of UCLA published his Pulitzer Prize winning book, "Guns, Germs, and Steel - The Fates of Human Societies." Diamond explored the influence and effect of very many external physical, biological, technological, and social factors on the evolution of, and births and deaths of multiple human societies, from many causes over thousands of years, beginning with the pre-historic hunter-gatherers, then up to the modern technological age. Surely, we should all occasionally take the time to consider and learn about and from all those factors and history, during our current and future attempts to further harmonize Man's constantly evolving technologies with the still growing population and its needs, and with the physical, biological, and cultural constraints of the Earth and its ecosystems.

Mark A. Murphy Ph.D., J.D. is a retired industrial chemist and patent attorney, writing "Pro-Bono." He thanks his many prior colleagues from Science, Engineering, and Law, and the authors of the references cited herein, and his wife Mary Bertini Bickers (a woman of many very unusual talents in her own right) for her many forms of support. The opinions stated in this article are solely those of the author and were not induced or financially supported in any way by any other person, business, or legal entity.

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Citation: Casu, B.P., Tatini D. (2025) The Work of Carlo Garosi: a Parallel History of the Discovery of Tritium. Substantia 9(2): 51-57. doi: 10.36253/

Substantia-3436

Received: Dec 12, 2024

Revised: Jun 03, 2025

Just Accepted Online: Jun 11, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

The Work of Carlo Garosi: a Parallel History of the Discovery of Tritium

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Abstract. The advent of "New Physics" at the beginning of the XX century ignited a transformative era for Nuclear Physics, characterized by a dramatic growth of its knowledge and boundaries. The existence of isotopes, the discovery of neutrons and the advancement of experimental techniques all conjured groundbreaking discoveries, where experimental physicists were at the forefront of developments. The discovery of tritium, the hydrogen isotope of mass number 3, is among the most sought-after results in the 1930s, and we present evidence of how Carlo Garosi, an Italian pharmacist, made significant yet unacknowledged contributions in 1936. By recognizing the importance of the Oliphant, Harteck and Rutherford experiment of 1934, Garosi correctly identified the heavy atom discovered as an isotope of hydrogen. This paper begins with the recapitulation of both the philosophical and scientific roots of his theory, showing how he critically engaged with older theories, such as Prout's 19th-century atomic theory, and integrated more recent works from international sources in original ways. Garosi proposed a unique interpretation of the Periodic Table, engaging in a critical review of the notion of how Helium is a result of the fusion of 4 Hydrogen atoms, and he explains the progression from one chemical element to another in terms of interactions among hydrogen, deuterium and tritium. By revisiting this seemingly peripheral event, we underscore its broader significance as a testament to the resilience and ingenuity of scientists journeying amid rising geopolitical tensions.

Keywords: Isotope, Nuclear Physics, Hydrogen, Helium, Periodic Table, Chemical Elements

1. INTRODUCTION

In 1934 at the Cavendish Laboratory in Cambridge, in series of experiments involving heavy water and heavy hydrogen Mark Oliphant, Paul Harteck and Ernest Rutherford observed an anomalous emission of protons, neutrons and other weak group of particles by bombarding deuterated ammonium chloride, ammonium sulphate and orthophosphoric acid with deuterons (or diplons, the chosen name at that time). As reported in their letter to the Editor of Nature [1]:

While it is too early to draw definite conclusions, we are inclined to interpret the

results in the following way […] It seems more probable that the diplons unite to form a new helium nucleus of mass 4.0272 and 2 charges. This nucleus apparently finds it difficult to get rid of its large surplus energy above that of an ordinary He nucleus of mass 4.0022, but breaks up into two components. One possibility is that it breaks up according to the reaction $D_1^2 + D_1^2 \rightarrow H_1^3 + H_1^{11}$.

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This is the first experimental evidence of the existence of tritium [2], the hydrogen isotope with a mass number of 3. Unfortunately, they were not able to isolate it, and as they stated [1]:

While the nuclei of H_1^3 and He_1^3 appear to be stable for the short time required for their detection, the question of their permanence requires further consideration.

A few months later, in a work published in the Proceedings of the Royal Society of London [3] Oliphant, Harteck and Rutherford reported a new series of experiments that provided further confirmation of the existence of an hydrogen isotope of mass 3. They proposed the following reaction:

$$_{1}D^{2} + _{1}D^{2} \rightarrow _{2}He^{4} \rightarrow _{1}H^{1} + _{1}H^{3}$$

assuming that the first step in the reaction between two diplons is the formation of an excited helium nucleus. Then, on a very short timescale, the high-energy helium breaks up into a proton and a hydrogen isotope of mass 3. From energy and range calculations, paired with the analysis of the oscillograph deflections magnitude, the authors concluded that [3]:

It seems clear that the production of this isotope of hydrogen of mass 3 in these reactions is established beyond doubt. The mass of the $_1H^3$ atom is consistent with its possessing a stability of the same order as $_1H^2$. The possible existence of this isotope has been discussed by several writers and although a careful search has been made no evidence of its presence has been found. It seems probable, however, that it could be formed by the process we have considered in sufficient quantity to be detected ultimately by spectroscopic or positive-ray methods.

The conclusive evidence of the existence of tritium (this name was originally proposed by Harold Urey, George Murphy and Ferdinand Brickwedde in 1933 [4]) was provided in 1939 by Luis Alvarez and Robert Cornog, who converted a cyclotron into a mass spectrometer dedicated to detect species with mass number 3 [5]. In a series of experiments conducted at the Radiation

Laboratory in Berkeley they were able to demonstrate the stability of He^3 and the radioactivity of H^3 . It is curious to note that in his initial investigations Rutherford made a serious mistake by considering tritium as the stable species and helium-3 as the radioactive one [3]. He firmly defended his idea and sought to convince other eminent scientists, like F.W. Aston, the inventor of the mass spectrometer, until the discovery of Alvarez and Cornog compelled him to revise his stance. This is the official historical reconstruction of tritium discovery. But there is another interesting story about its identification, that runs parallel to the experiments of Oliphant, Harteck and Rutherford.

2. AN INDEPENDENT STORY

This alternative story begins in the small town of San Quirico d'Orcia, an ancient village in the countryside of Siena, en route on the Via Francigena, the old pilgrimage axis between Canterbury and Rome. The year is 1938, Italy is ruled by the Fascist dictatorship, and the ghosts of a new war in Europe are looming over the future. The regime decisions have long set aside the Italian scientific community from its counterparts in Europe and beyond, and lack of funds, small scientific institutions, and isolationism have thwarted the progress in the new branches of physics, especially nuclear physics. However, a genuine interest propels the debate among a community which is not restricted only to academia. This larger audience, albeit geographically far from the vanguard, avidly follows the latest developments.



Figure 1 Photo of Carlo Garosi, courtesy of Venera Dibilio Impallomeni.

Carlo Garosi [San Quirico d'Orcia, 05/07/1883 - Florence, 22/12/1954], a pharmacist in San Quirico d'Orcia, is part of this community. Figure 1 is a photography of him, courtesy of his descendants. The con-

¹ We reported the original notation used by the authors for the nuclear charge number and the mass number.

nections between pharmacy and chemistry, both on historical and scientific grounds, are well known, and it is not surprising that a member of the order kept up with the news. The Authors had the opportunity to work with Garosi's personal archive. The archive has not been properly indexed yet, and a conservation effort is required to allow the scientific community to access it. Garosi subscribed to many publications, and he was also the author of a number of articles ([6] - [10]), on national magazines like "Chimica. Rivista Mensile per la Diffusione della Cultura Chimica"2, published by the "Istituto Italiano di Storia della Chimica"³ on the topic of fundamental components of matter. In July 1937 Garosi begins the publication of his magnum opus ([11] - [14]), where he recollects all the evidences - mainly theoretical - supporting the existence of an elementary constituent, tritium, two years before the experimental confirmation by Alvarez and Cornog [5]. Figure 2 shows the typewritten edition of his paper. Garosi proved to be a fine expert of chemistry, reviewing and building on a theory that dates back to 1815.

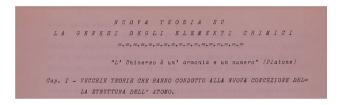


Figure 2 Header of the first page of 1937 original typewritten edition of "The New Theory of the Origin of the Chemical Elements"; the quote is supposedly from Plato: "The universe is number and harmony", translation by the Authors.

2.1. An Old Theory Resumed

William Prout (1785–1850), an English chemist, noting how element masses seemed to be multiples of the hydrogen weight, hypothesized in 1815 that all the nuclei were constituted of fundamental entities, called protyles, the hydrogen nucleus [15] [16]. His theory showed some serious flaws [12], because of "anomalies" such as chlorine of atomic weight 35.45, and it was definitely abandoned following the discovery of the neutron by Chadwick in 1932 ([18] - [20]). However, the concept of isotope allowed Garosi to update Prout's theory, and in 1937 he published an article "Teoria sulla genesi degli

elementi chimici^{n_4} [11], in which he claimed the development of a comprehensive theory that linked all existent chemical element to a combination of H^1 , H^2 or H^3 .

2.2. Prout's Hypothesis

A quick review of the original theory is needed before we introduce Garosi's advancements. William Prout was an English physician at a time when the borders between chemistry and physiology were neither established nor understood. His major scientific achievement was the discovery of urea in urine [21], and its composition, alongside the discovery of hydrochloric acid in gastric juices of animals [22]. His scientific interests spanned from urinary and digestive pathologies to atomic theory. During his time the debate between vitalism and a materialistic and mechanistic view took a turn toward chemistry and a quantitative approach to physiology. Being interested into the chemical composition of organic fluids, he approached the matter studying meticulously the weight of the compounds involved in his analysis. His hypothesis suggests that hydrogen might be the foundational "brick" of all elements, whose atomic mass would be an integer multiple of hydrogen's, that Prout names protyle, a Greek name from prot-, proto, and hyle, substance. This idea contributed to the scientific discussions about the atomic theory, but failed to explain anomalies such of chlorine and other elements, and was later discarded.

3. CARLO GAROSI'S ORIGINAL WORK

3.1. Genesis of a Theory

The scientific environment at Garosi's time is very different from the one Prout experienced. Quantum Mechanics and General Relativity have made their appearance on the global stage, and they have quickly become mainstream, although not unchallenged [23]. Differences in the established atomic weight were now explained also through concepts such as energy binding, and the development of mass spectroscopy won the Nobel Prize for F. W. Aston in 1922, with the discovery of isotopes. An echo of Prout's hypothesis reverberates through the motivation of Aston's prize [24]:

[...] for his discovery, by means of his mass spectrograph, of isotopes, in a large number of non-radioactive elements, and for his enunciation of the whole-number rule.

² "Chemistry. Monthly Journal for the Promotion of Chemical Culture", translation by the Authors

³ "Italian Institute for the History of Chemistry", translation by the Authors

⁴ "Theory on the Origin of Chemical Elements", translation by the Authors

The discovery of neutron by Chadwick in 1932 [19] complicated things, although its status within the atomic nuclei was uncertain. In this early stage of nuclear physics, where the influence of experiments was quickly rewriting how physicists were supposed to develop hypothesis, Carlo Garosi completed his reorganization of the table of elements. His hypothesis is shaped by two main general principles, which are interesting to highlight the philosophical roots of his work:

- Unitary principle: Garosi draws inspiration from the "alchemic tradition", particularly its philosophical assertion that all matter originates from a single, unified source and transforms into diverse elements through processes of change. This concept is encapsulated in the phrase "The whole is one", which he prominently cites at the beginning of his paper⁵. This principle serves as a foundation for his interpretation of the genesis and progression of chemical elements;
- Evolutionary principle: through his work, Garosi applies a synthesis of evolution and Aristotelian principles, trying to frame evolution as depending on "intelligent design from within" and "environmental pressure from outside", and applying this scheme to both biology and chemistry: chemical elements are both "prone" to react with different compounds based on their properties and also because of the environment they happen to exist in, due to time and other factors.

These two principles account for the idea that:

- a. all the elements ought to originate from a single one,
 and:
- b. all the elements are linked to one another trough

common characteristics resembling genetic links in living organism.

It is unclear if Garosi is trying to mix ancient, prescientific, theories with modern ones, or borrowing their prestige to support his claims; drawing inspiration from old and new paradigms is nonetheless a feature that seems crucial to understand his work.

3.2. From Hydrogen to Uranium

As a reminder that a strong component of his theoretical work is actually rooted in experimental physics, Garosi begins with a review of the nuclear physics since the observations of Becquerel in 1896, mentioning the discoveries of Marie and Pierre Curie about radioactivity, to point out that helium nuclei, as byproduct of alpha decay, belong to the atomic nuclei of every chemical element heavier than hydrogen. His attention therefore focuses on the relation between the first two elements of the Periodic Table. He disagrees with the idea that helium is originated from the fusion of 4 hydrogen nuclei, and instead proposes a different interpretation, based on the hypothesis of the existence of three isotopes of hydrogen, each one heavier than the preceding of exactly one unit of atomic weight. The first twenty elements of the Periodic Table are analyzed in terms of atomic number and atomic weight: his first observation was of an alternating regularity between the elements. Leaps between them seemed to happen regularly in terms of 1 or 3 atomic weights: 3 from Hydrogen to Helium, 1 from Sodium to Manganese, then 3 from Manganese to Aluminium. With the exception of Beryllium, Nitrogen, and Argon, he devised a recurrent pattern between the first twenty elements:

He notes two other patterns: a) the conservation of parity between atomic number and atomic weight, i.e. elements with even atomic number would have even atomic weight too, and b) the difference of 16 units in the atomic weights of homologous elements, for instance between Oxygen (16) and Sodium (16 + 16 = 32). All these findings helped him explaining the deviations of Beryllium, Nitrogen, and Argon in terms of undiscovered isotopes: Beryllium-8, Nitrogen-13, and Argon-36. The elements on the Table then progress like:

⁵ Translation by the Authors; the original is "Il tutto è uno," Garosi, Nuova Teoria sulla Genesi degli Elementi Chimici, pg. 1

⁶ "Se per EVOLUZIONE S'INTENDE, come mi sembra doversi intendere, QUEL FENOMENO PER IL QUALE UNA DATA ENTITA' SOTTO L'AZIONE DI UNA INTELLIGENTE SPINTA INTERNA, ED IN STRETTA DIPENDENZA DALLE CONDIZIONI AMBIENTALI, SI SVILUPPA, ATTRAVERSO ARMONIOSE TRANSIZIONE RARA-MENTE APPARISCENTI, IN FORME VIA VIA PIU' COMPLESSE, si deve ritenere che vi soggiaciano anche gli Elementi chimici", Garosi, ibid.; all caps from the original work. In English (translation by the Authors): If by EVOLUTION we mean, as it seems we should, THAT PHENOMENON BY WHICH A GIVEN ENTITY, UNDER THE INFLUENCE OF AN INTELLIGENT INTERNAL IMPULSE AND IN CLOSE DEPENDENCE ON ENVIRONMENTAL CONDITIONS, DEVELOPS THROUGH HARMONIOUS TRANSITIONS THAT ARE RARELY CONSPICUOUS, INTO INCREASINGLY COMPLEX FORMS, then it must be considered that even chemical elements are subject to it.

Deuterium and Tritium, along with Hydrogen, take part in the formation of isotopes, as reconstructed in the graph above: $He_4^2 + H_3^1 \rightarrow Li_7^3$ originating the correct Lithium isotope in accordance with the rule of 1 or 3 steps between elements, while the two isotopes of Beryllium, Be_8^4 and Be_9^4 , are generated by $Li_7^3 + H_1^1(hydrogen) \rightarrow Be_8^4$ and $Li_7^3 + H_2^1(deuterium) \rightarrow Be_9^4$.

While noticing that the rules of alternation of 1 and 3 steps between elements do not seem strictly enforced across the Table, he applies the other symmetries to Helium. Garosi therefore suggests the existence of five isotopes⁷:

$$H+H o He_2$$

$$H+D \rightarrow He_3$$

$$H+T$$
 or $D+D o He_4$

$$D+T o He_5$$

$$T+T
ightarrow He_6$$

We can see how Garosi is aware of using predictions as test bench of his theory, and this is fairly clear with Helium-6: the isotope itself has been discovered in 1936 [25].

Garosi also proves to be fully aware of the developments in nuclear physics, reviewing its hypothesis to include the presence of positron, theorized by P. Dirac in 1928 and discovered in 1932 by C. D. Anderson [26]: the proton is constituted by a neutron and a positron, together, to explain the presence of neutrons within the nucleus. Carlo Garosi is able to use his hypothesis to compute a more accurate value for the energy belonging to the process of Helium synthesis, testing, although indirectly, the consistency of his formulation. The hypothesis enables Garosi to redefine some basic concepts such as atomic weight, atomic number, isotope, incorporating the new experimental evidences - prov-

ing that he is well within the contemporary milieu - and ordering them, following general principles of simplicity, symmetry, logic. In doing so, Garosi masters correctly the mix of theoretical considerations and experimental evidences that defines the formulation of a scientific theory [11]. He is also able to draw predictions from that, postulating the existence of some isotopes and transuranic elements that will be indeed discovered in the following years [27].

4. CONCLUSION

Demonstrating a keen understanding of the evolving field, Garosi correctly recognized the 1934 experiment by Oliphant, Harteck, and Rutherford as the first evidence of tritium, a claim he made with conviction in 1936 [11]. Albeit limited, by political and geographical boundaries, Garosi successfully proved to be able to build a genuine scientific theory. It is also possible that his conclusions had some influence on the work of Enrico Fermi: in a private letter from 1938, Gino Testi⁸ — one of the founders of the Istituto Italiano di Storia della Chimica and editor of the journal "Chimica"informed Garosi that Aroldo De Tivoli9 was interested in his research on the origin of the chemical elements and requested a copy of the 1937 manuscript. Professor De Tivoli was assistant director of the Laboratorio Fisico della Sanità Pubblica¹⁰ (formerly Ufficio del Radio¹¹), the official institution that provided financial and logistical support to Enrico Fermi's research team, the so-called Via Panisperna group¹². Probably Garosi's theories cir-

⁷ We will use Garosi's own notation, where H denotes Hydrogen, D as Deuteron, and T as Triton, the last two being the nuclei of each isotope; his notation for the isotope weight is also in use.

⁸ Gino Testi [Catanzaro 02/07/1892 – Rome 21/06/1951] graduated in pure chemistry and worked as a senior official at the Ministry of Finance until his retirement around 1948. He focused primarily on industrial chemistry and the history of chemistry, taught as a private lecturer at the University of Rome, and was among the founders of the Italian Society for the History of Chemistry. A World War I veteran, he also played a key role in the preservation of rare books and documents. Among his most successful works is the *Dizionario di alchimia e di chimica antiquaria* (1950). He contributed to various academic journals and was active in several academic societies.

⁹ Aroldo De Tivoli [Buonconvento (Siena) 14/07/1888 – Florence 25/04/1972] served as assistant in the Central Office for the Preservation of the Standard Chorister at the Regio Istituto Fisico (Royal Institute of Physics) in Rome between 1922 and 1924. In 1924, he became Giulio Cesare Trabacchi's assistant at the Laboratorio Fisico della Sanità Pubblica, located at the Via Panisperna Institute. He taught mathematics for chemistry and natural sciences students in Rome (1928–1933), then he became lecturer in experimental physics (1935–1938) and mathematics (1938–1944). He also contributed several definitions to the Enciclopedia Italiana.

¹⁰ "Public Health Physics Laboratory", translation by the Authors.

¹¹ "Radium Office", translation by the Authors.

 $^{^{12}}$ See: https://brunelleschi.imss.fi.it/nobel/iviapanisperna.html and https://media.accademiaxl.it/pubblicazioni/ScuolaFermi/st4.html#4

culated among Fermi's collaborators and may even have reached Fermi himself. The original letter is shown in Figure 3, while the English translation from the Authors is reported below:

Dear Doctor [Garosi]13,

It seems I owe you several replies! My apologies — renewing subscriptions and dealing with related invoices are depriving me of the few minutes of happiness I have. The journal is printed. It will be shipped, I hope, on Tuesday, and you will receive the usual package.

Right after that, I will have the other two episodes printed. I don't know if I told you that Prof. De Tivoli, one of the assistants of His Excellency Fermi, was interested in your work and that of Palmeri. I gave him the 1937 issue as a gift immediately, but then he never followed up.

Our Institute is still waiting for the decree from the Ministry of Home Affairs. As soon as possible, you will receive the diploma. The clichés turned out excellently. Thank you for your opinion on Cerasoli.

I don't know who Bentuzzi is, but I believe he is a doctor. My wife thanks you for your wishes and concern. We finally realized it is a pregnancy — after 11 years of marriage! Let's hope everything goes well. With warm regards, I extend my greetings to your wife and daughter.

Greetings Gino Testi

Much more remains to be done, beginning with the personal archive of Carlo Garosi. Currently under the care of Venera Dibilio and Carlo Impallomeni, his direct relatives, the archive is an extraordinary opportunity to cast a light on an under-looked part of the Italian scientific community. The conspicuous amount of papers, letters, documents, magazines, and more, is a window on the stories of those local personalities and institutions that, far from the centres of the country, successfully established a proper research activity. This material needs to be indexed, organized and made fully available to others. The work of Carlo Garosi could become a case study for how the genesis and the acknowledgment of a scientific idea is far from a linear process.

Figure 3 Private letter from Gino Testi to Carlo Garosi. From Garosi's personal archive, courtesy of Venera Dibilio Impallomeni.

ACKNOWLEDGMENTS

The authors would like to thank Venera Dibilio Impallomeni, Sandro Tatini, Tiziana Fantauzzo and Marzia Tatini for their help with the translation of the 1938 correspondence between Garosi and Testi.

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Citation: Dei, L. (2025) Chemistry and Literature: Disciplines in Dynamic Equilibrium. *Substantia* 9(2): 59-73. doi:

10.36253/Substantia-3435

Received: Nov 26, 2024 **Revised:** Mar 31, 2025

Just Accepted Online: Apr 17, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

Chemistry and Literature: Disciplines in Dynamic Equilibrium

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Abstract. This article examines the complex and multifaceted topic of the link between chemistry and literature. Instead of scouring the literary works of the various epochs in search of links with chemical thought or reasoning only on those literary works that are clearly imbued with chemistry (Primo Levi first and foremost, but also Gadda, Calvino and Sinisgalli in Italy, or, in the world arena, Sacks, Hoffmann, Goethe, Wells), a different approach is proposed, a third way that moves from a suggestive hypothesis of chemistry and literature as very different disciplines, but in constant dynamic equilibrium. To illustrate this thought and point of view, a number of themes are identified that are of fundamental importance in both chemistry and literature, albeit with profoundly different implications. The themes are events and their why and how, the before and after, that is, time and its irreversible arrow, the interpretation of the present, reality and unreality, questions and answers, and the value of discovery. In six separate paragraphs, these themes are analysed with significant and original references to discoveries and innovations in chemistry combined with reflections on works of international literature, attempting to highlight consonances and dissonances between chemistry and literature and arriving at a synthesis that identifies how chemistry and literature have behaved, over the centuries, like two planets revolving around the same sun of culture and knowledge, sometimes moving apart, sometimes coming closer together.

Keywords: History of Chemistry, Chemistry Discoveries, Literature, Scientific and Humanistic Culture, Knowledge Contamination.

1. INTRODUCTION

Reflecting on the link between chemistry and literature¹ is an arduous and complex undertaking that can be approached in basically two ways: by scouring the literary works of the various epochs in search of links with chemical thought² or by reasoning only on those literary works that are manifestly imbued with chemistry³ (Primo Levi first and foremost, but also, Gadda, Calvino and Sinisgalli in Italy, or, in the world arena, Sacks, Hoffmann, Goethe and Wells as typical examples). In both cases, the risk of concluding that, regardless of the approach, no suture or integration can be established due to the inherent, abnormal distance between the two disciplines is highly probable. The attempt that I am proposing in this meditation on such apparently antithetical univers-

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es of knowledge is to try to take a third way, which starts from an intriguing hypothesis of the electronic engineer Ludovico Ristori, very shrewd and particularly open to the contamination of knowledge. In an article he published on the 'Scienza in Rete' (Science on the Net) website, entitled Scienza e letteratura, discipline in equilibrio dinamico (Science and literature, disciplines in dynamic equilibrium),⁴ he begins by asking whether science and literature are opposing worlds, or entities that interact dynamically, finding different equilibriums depending on historical moments and protagonists. Dichotomous opposition, then, or correspondence, albeit dynamic and articulated in a kind of interpenetration? On this basis, Ristori develops his reflections by bringing arguments and positions of the critics in favour of one or the other hypothesis and finally concludes with these words.

We can, therefore, say, with an image, that science and literature can be seen as two planets revolving around the same sun. Objects in permanent equilibrium, coming closer at certain times and moving away at others. Each with its own specificities, however, because, as Battistini notes⁵ in his article *Nuovi licei: l'avventura della conoscenza (New high schools: the adventure of knowledge)*, if 'it is deforming to ignore common traits, as if humanity proceeds in its knowledge by watertight compartments, equally deforming is to believe that one can erase all differences, making them trivial or, worse, pretending they do not exist'.^{4,6}

The considerations here obviously also apply to the relationship between chemistry and literature, chemistry being a branch of science. Since the differences are obvious and less interesting, in my opinion, than the convergences, I will try to impress the reader with some thoughts about the common traits. It will be inferred, moreover, that from the analysis of common traits, differences and even dichotomies and antinomies will naturally arise, paradoxically demonstrating the evocative power of assonances, proving the essential need for contemporary humans to keep the rudder straight towards a unitary vision of knowledge and culture. I have chosen to revolve this reflection around a few fundamental themes in chemistry and literature, albeit with profoundly different implications. These are the six themes: events and their 'why' and 'how', the 'before' and 'after', which means time and its irreversible arrow, the interpretation of the present, reality and unreality, questions and answers, and the value of discovery. For each one, I will try to illustrate the common traits, which, of course, at the same time reveal substantial differences, going along with Ristori's intuition about disciplines neither opposing nor interpenetrating but differing in their depths, albeit in constant dynamic equilibrium.

2. THE EVENTS: THE WHY AND THE HOW

The events are certainly the starting point for chemistry and literature. And when I speak of events, I mean this in the widest sense of the term: things that happen in the widest possible sphere. In nature, of course, this is the main realm of scientific investigation, but also in human history, personal history and thus in the psyche of those who witness what is happening around or within them. A fine popular science book by Italian physicist Andrea Frova is entitled Perché accade ciò che accade (Why what is happening happens)6,7 and tells how science has managed to answer this question in an extraordinary variety of cases. And, of course, answering the question of why what is happening happens also often means creating the conditions to predict what has not yet happened. Therein lies the enormous conceptual strength of the framework of modern science, namely its predictive power. The story is told8 that Tsar Peter the Great was aware of the importance of culture and education in combating superstitions and beliefs: he was convinced that eclipses had to be explained to the people so they would not regard them as miracles. Something that is known before it happens cannot be considered miraculous. "That which is foretold ceases to be a miracle" is the most concise and acute representation of one of the most fascinating sides of scientific thinking: its power of predictability. Chemists, as all scientists, are strongly attracted to the nature of phenomena and why they manifest themselves in a certain way. They may be moved by an eclipse, a rainbow or a sunset, the blue colour of the sky, i.e. by how the event manifests itself, but undoubtedly it is the why that fascinates and disturbs them. They want to understand why, on a certain day, at a certain time, in bright sunlight, that fantastic lamp, goes out for a short time or why the bright yellow sickle is hidden in the night. Literature, even when it takes its cue from the same natural phenomena, is attracted by the how, by the emotions aroused: what does it matter to know why what is happening happens, if I then take pen and paper and describe how it happens and how the happening reverberates within me, I find the right and best words to share with the world not a formula, but a sensation, an emotion, a psychological mark? Let's read Mario Luzi on the eclipse of the moon in the poem Non andartene ^{6,9} (Do not go):

Do not go, do not leave the eclipse of you behind in my room He who seeks you is the sun, does not pity your absence. The sun finds you even in random places where you passed, in the places you left and in those where you have inadvertently been it burns and equates to nothingness all your fervent day. Yet it was, it was none of its hours is thwarted.

Or Emily Dickinson:¹⁰

Sunset at night is natural, But sunset in the dawn Reverses Nature, Master, So midnight due at noon,

Eclipses be predicted And Science bows them in, But so one face us suddenly -Jehovah's watch is wrong.¹⁰

But also, Italo Calvino's amusing and brilliant definition in *The Cosmicomics*:^{6,11} "As for eclipses, with Earth and Moon stuck together the way they were, why, we had eclipses every minute: naturally, those two big monsters managed to put each other in the shade, constantly, first one, then the other." To end with Erri De Luca, who, in his book *Sulla traccia di Nives* (On the Trail of Nives), with much insight, makes us literally reflect on the fact that the 'why' of what happens, even in the remote pre-scientific world, has prevailed over the 'how' of what happens and its emotional-psychological implications.

The human species has felt the respiratory need to widen its bronchi and trespass beyond the edges of its assigned existence. This need was more important than organising itself into social communities. The numbers that allow the calculations of the heavens precede the legislatures; Pythagoras comes before Pericles and Plato. The discovery of the cycle of comets and eclipses precedes the polis. The rules of the triangle appear before politics. 6.12

In this dichotomous viewpoint, science, i.e. the reasoning intellect, versus literature, i.e. emotion-sensation, Ristori dwells on "a strong argument for those who support the thesis of the opposition, namely the supposed difference in purpose." He adds,^{5,6} "Literature would be different precisely because of its tension to deny and tran-

scend the rigidities and limitations of scientific reasoning. Giacomo Leopardi is considered one of the main authors to support this, based on statements by the poet from Recanati such as 'the heart remakes life that the intellect destroys." Apart from the fact that recently Gaspare Polizzi¹³ has punctually argued that even the second Leopardi, that of 'cosmic pessimism' and mistrust of science, in reality, does not represent signs of a break with scientific thought, but rather a disillusionment with a certain way of doing science. We could even venture, with the examples that follow, that, in reverse, in literature, the heart remakes in its own way the life that the intellect constructs!

Continuing on the theme of the events that arouse the interest and curiosity of *Homo chemicus*, I would like to bring to the fore a topic that engaged 19th-century chemistry and physics for about half a century from the early 1800s:¹⁴ we are talking about the phenomenology associated with electricity, magnetism and also, albeit in a still rudimentary way, the relationship between these two branches of physics and chemistry and light, in the studies of Faraday, Ampère, and Ørsted, mainly.

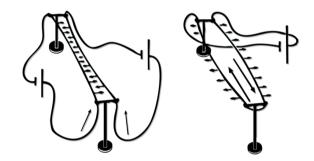


Figure 1. Ampère discovered that wires carrying an electric current exert forces towards each other.

Aspects related to attractions/repulsions between electric charges and between magnetic poles were topics that engaged the chemists and physicists of the time to a great extent, starting with the Italians Luigi Galvani and Alessandro Volta. The events that intrigued and aroused curiosity were essentially related to the fact that electrical phenomena influenced magnetic ones and vice versa and, above all, the resounding novelty of the mechanics of moving bodies concerned with action at a distance (see Fig. 1). For the first time, it had to be understood why it happens that two bodies – for example, a magnet and a copper wire in which electricity flows, or the needle of a compass in the vicinity of a wire in which an electric current flows (see Fig. 2) – interact at a distance even if I create a vacuum, i.e. remove the air.

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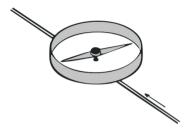


Figure 2. Ørsted discovered that a current-carrying wire deflected the needle of a compass. This stimulated Faraday's work in electromagnetism.

Science works by analysing experiments and looking for causal links. Thus, it came to be understood that moving a magnet close to a copper wire would generate current in the wire, or, in reverse, running current through a wire coiled around an iron nail would turn the nail into a small magnet.

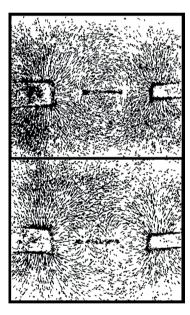


Figure 3. A favourite experiment of Faraday's to illustrate the reality of lines of force was to sprinkle iron powder on a sheet of paper beneath which a magnet was placed. On gently tapping the paper, the iron particles 'revealed' the lines of force.

The way was open for electric motors, dynamos, and turbines generating enormous electrical energy by rotating huge magnets wrapped in copper coils. What makes these magnets rotate? From a trivial bicycle wheel to make light in the headlamp, one arrives at mighty turbines set spinning by water rushing down from a reservoir or by immense volumes of expanding water vapour produced by huge boilers fuelled by coal,

gas, and oil fuels not to mention those events that show that chemical reactions can generate electricity, thanks to what we will later call batteries and which will make the fortune of the element lithium. Or that the opposite can happen, by using current and its associated electrical energy, ad hoc chemical reactions can take place to plate metal objects of little value with thin lavers of silver or gold. Such events are being investigated and dissected in those years. Scientists seem obsessed with why what is happening happens and especially with the fact that electricity and magnetism make each other feel at a distance. Michael Faraday performed the famous experiment of the magnet that, at a distance, with air, but also without it, manages to orient iron powder in a geometrically well-defined way (see Fig. 3).15 He imagined, with an idea far removed from reality, that there is a mysterious force field around that magnet that only comes into action if I make it interact with iron filings.

And what does this have to do with literature? Let's try and find out. Roughly at the same time, two great writers are attracted by completely different events: of the social type or concerning customs and psychological interiority - in short, they are attracted by human stories. Unlike chemists, in their literary inventions, they do not question why what is happening happens. They merely describe how it happens, but the literary invention is not science fiction, unreal. It mirrors the becoming of society that moves relentlessly and inexorably around them. I am referring to Flaubert's Madame Bovary¹⁶ and Tolstoy's Anna Karenina.¹⁷ Again, this action is at a distance, sparking love and passion. But there's something else. An ambiguous morality permeated the society of the time: the celebration of male conquests in which the man's mistress, preferably bejewelled, enhanced the prestige of the man himself and, at the same time, the stigmatisation and condemnation of the 'lost woman'. Adultery was permitted exclusively to women of the upper classes but only if discreetly concealed; otherwise, if publicly revealed, strongly deprecated.¹⁸ And what captures these stirrings in society if not literature? Not only does it capture them, but it also filters, distils, and then crystallises them into a novel, which stands there as an eternal mirror of an era, transcending it and making it timeless. And just as in scientific research, the immense experimental work and interpretation of data is condensed into a law, an utterance, an equation, a formula, so too in the case of literature, beyond the hundreds of pages of which the novel is composed there are gems, the distillation into words rather than numbers, like this masterful and crystalline passage from Madame Bovary.

But a woman is forever hedged out. By nature, both flexible and sluggish, she has to struggle against the weakness of the flesh and the fact that, by law, she is dependent upon the others. Her will, like the veil fastened to her hat by a string, eddies in every wind. Always she feels the pull of some desire, the restraining pressure of some social restriction.¹⁹

The beauty and originality of the image of the contrast between "passionate desire and restraining pressure painted in the veil of a hat fastened by a string that eddies in every wind" is unique and lends the narrated story authenticity and credibility, making it convincing. Aristotle wrote in Poetics: "A likely impossibility is always preferable to an unconvincing possibility." This means that for the purposes of a story, an impossible but plausible and convincing thing is preferable to an unconvincing possibility. And that is indeed how literature is: we read avidly, we get excited, but at the same time, we murmur to ourselves: 'What an impossible story, it just doesn't make sense, that's not how it happens', but our eyes may be moist because evidently the story is credible, authentic and has convinced us.

Similarly, Tolstoy's Anna Karenina, a novel published in instalments between 1875 and 1877, paints a fresco in which an entire society is mirrored in the evolution of social conventions, tradition, turmoil, changes in customs, in the patchwork of feelings of hypocrisy, jealousy, faith and fidelity, carnal desire, passion, and in the turmoil of the changes that will characterise the coming decades regarding the role of the family, marriage, society, progress, all revolving around the Anna-Vronsky-Levin-Kitty quartet.²¹ Again, Tolstoy is interested in the 'how' of events, which he perceives and transfigures into high literature. The conclusion for the woman is dramatic, with the epilogue of suicide on a par with Emma; Tolstoy dedicates a memorable page to this. And here we again discover that trait common to chemistry and literature of condensing the sum of events into a limited space, again chemistry answering the why, literature immortalising with a lapidary juxtaposition of words the how. This is how Tolstoy reveals to us the 'how' of those moments before suicide.

That familiar gesture brought back into her soul a whole series of girlish and childish memories, and suddenly, the darkness that had covered everything for her was torn apart, and life rose up before her for an instant with all its bright past joys. But she did not take her eyes from the wheels of the second carriage.²²

The literature could have stopped here, as the passage foreshadowed the outcome. The 'literary creator' knew what he would narrate; he knew what would hap-

pen; he just had to bring it to life and shape it with ink on paper. We can imagine him hesitating and thinking about what the world would be like if Tolstoy had stopped there, if that second bandwagon had suddenly halted its course. Without a last word, we would have had a much poorer humanity in the years to come. Instead, Tolstoy goes on and continues his narration. And so it was that Anna made the insane gesture, and that train, that station, that ironworker became legend. The act of suicide is not the most important thing, as it was already foretold. Tolstoy is interested in that moment that radicalises Anna's life, bringing it to a conclusion.

And the light by which she had read the book filled with troubles, falsehoods, sorrow, and evil, flared up more brightly than ever before, lighted up for her all that had been in darkness, flickered, began to grow, and was quenched for ever.²²

The connection between the candle's flame and life juxtaposed with death as its ultimate extinction is resounding, on a par, to my mind, albeit in a completely different way, with that madly visionary intuition of the electric and magnetic field evoked by Faraday.

The years of the great discoveries around electricity and magnetism, as well as the beginning of profound changes in customs that were immediately grasped by literature, are also years in which chemistry encounters events that concern a hypothesised but still totally unknown world, the sub-microscopic world of atoms and molecules, a reality that will produce an extraordinary revolution in scientific thought generating quantum mechanics. But isn't the dilemma of the unknown the theme of Moby Dick?²³ One of the peculiar characteristics of chemistry is the constant quest to find solutions, to undress the unknown and to clothe it with intelligible meanings. In this prodigious and noble purpose, an obsession can also lurk, even before we realise the possibility of finding the right clothes that make the unknown known. This characteristic, typical of chemical research, finds a sublime transfiguration in the relationship between Ahab - the chemist obsessed with chasing the why of his phenomena - and the so-called white whale - actually a sperm whale - representative of the unknown. Alongside fear and terror, there is awe, diversity, and the emotions that characterise the progress of science, which, in a way, is also a fantastic and fascinating adventure novel. The voyage of the Pequod is both an allegory of the condition of human nature and, at the same time, represents a bit of a compelling parable of nineteenth- and twentieth-century science, ready to take off towards seemingly unattainable destinations full of,

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at times dramatic repercussions. When we think of the prodigious discoveries in the field of nuclear energy – truly the deepest unknown – and Hiroshima and Nagasaki, we can only sum up the bewilderment and despair with Starbuck's invocation of Ahab: "Moby Dick seeks thee not. It is thou, thou, that madly seekest him!"²⁴

The intention of the above examples was to show this first common, and in many ways different, aspect that characterises science and literature, namely the *why* or *how* of what happens. The final measure and stigma of this trait in chemistry and literature can be found in a passage from Stendhal's *The Red and the Black*.²⁵

Yes, monsieur, a novel is a mirror which goes out on a highway. Sometimes, it reflects the azure of the heavens, sometimes the mire of the mud pools on the way, and the man who carries this mirror in his knapsack is forsooth to be accused by you of being immoral! His mirror shows the mire, and you accuse the mirror! Rather, accuse the main road where the mud is, or rather the inspector of roads who allows the water to accumulate and the mud to form.²⁶

Not only is the novel a mirror, but chemistry, too, is a mirror reflecting on the blue of the skies and the mud of the quagmires. Literature tells us how blue and wonderful the sky is and how ugly and brown the mud is; chemistry only explains why the sky is blue and the mud brown. Ugly and wonderful do not pertain to it.

3. BEFORE AND AFTER, OR THE IRREVERSIBLE ARROW OF TIME

We now come to the second aspect: the before and after, the irreversible arrow of time. The discoveries and achievements of chemistry in its evolution and progress always determine that our humanity changes profoundly before and after a chemical discovery, not least because of the impact chemistry has had on everyday life, especially in the last 150-200 years. Chemical discoveries from Lavoisier to the present day, the infinitely small, electricity, magnetism, light and electromagnetic radiation, the DNA double helix, drugs, thermodynamics, and quantum mechanics, have dramatically altered humanity's relationship with the world around it and thus determined a before and an after. When I refer to the irreversible arrow of time, I mean to scientifically connote the usual and well-known statement: 'There is no going back'. I could give thousands of examples of this 'before and after' of a strikingly different chemical discovery. Still, I will choose two that are perhaps among the most easily understood and suggestively dense. Photography²⁷ and cinematography²⁸, on the one hand – I am talking about the nineteenth and twentieth centuries – and recording sound sources, on the other – around 1935.

$$Ag^{+}Br^{-} + h\nu \rightarrow Ag^{+} + Br + e^{-}$$

 $e^- + lattice trap \rightarrow [e/trap]^-$

$$Ag^+ + [e/trap]^- \rightarrow Ag^*(LI)$$

$$2Ag^{+}$$
 close to $[Ag^{*}(LI)]_{clusters} + (C_{6}H_{4})(OH)_{2} \rightarrow 2Ag_{(s)}(RI) + (C_{6}H_{4})O_{2} + 2H^{+}$

Not reacted
$$Ag^+ + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-}$$

Scheme 1. The main reactions involved in the photographic process: LI = latent image, RI = real image.

The watershed between before and after is here truly striking. To fix instants of life and make them eternal or to cast images, sounds and then moving dialogues on a white sheet represent a resounding break of symmetry in the evolution of *Homo sapiens*. Not to mention the recording on magnetic tape - the first device was made by Telefunken in 1937²⁹ - which, for the first time in human history, made it possible to preserve sound sources and no longer just documents, books, paintings, sculptures, drawings and then photographs. Again, chemistry enables the miracle of photography and cinematography, thanks to the reactions shown in the diagram Scheme 1. Humanity's relationship with the world around it changes radically: the senses of hearing and sight expand the acoustic and visual range to an enormous extent, the unthinkable just a few years before is seen and heard. Stories are no longer confined only to the world of literature and books; they burst into everyday life, obviously in an uncontrolled and increasingly uncontrollable manner. Music, a fleeting art of choice intimately connected to the irreversible arrow of time, can be set in minute magnets and be heard again tomorrow, a year from now, decades from now, or centuries from now. Those who, like the writer, were born in the second half of the 20th century, have the good fortune to have experienced decades of extraordinary scientific breakthroughs, becoming eyewitnesses to this before and after in numerous fields: before and after increasingly refined and powerful drugs, before and after noninvasive diagnostic techniques for our health, before and after the internet, mobile phones and the personal computer, before and after mobility on a planetary scale. But also, as the law of counterpoise has it, before and after the rapidly changing climate.

Well, something similar also happens with literature. Let us see in what sense. People's relationship with themselves, the world around them, and their fellow human beings before and after reading a great work of literature is strikingly different, irreversibly so. We are no longer the same after reading Dostoevsky's Crime and Punishment³⁰ or Kafka's The Metamorphosis³¹. Their literary works have affected our psyche similarly to the quantum mechanics revolution, the Copernican revolution, or eventually Darwinism, have had, not on the individual, but on the whole of humanity. Here is the difference: chemistry, with its waves of innovation, bathes the whole of humanity, and when the water recedes, life starts again, profoundly changed. Literature performs a similar flood, however, not only on the level of humanity as a whole, but also on the level of individual readers: certainly, the individuals come out better off. On humanity it remains to be seen whether the after is better than the before, and this applies to both literature and chemistry. Why did I choose Dostoevsky and Kafka to demonstrate this crazy change in our understanding of the world that their works induce in us, an irreversible metamorphosis like that of Gregor Samsa? To realise what I mean by the after being irreversibly different from the before following the reading of these two literary masterpieces, focus on the two incipits and the two endings of both stories that anticipate the dramas of the contemporary person.

On an exceptionally hot evening early in July, a young man came out of the garret in which he lodged in S. Place and walked slowly, as though in hesitation, towards K. bridge. He had successfully avoided meeting his landlady on the staircase. His garret was under the roof of a high, five-storied house and was more like a cupboard than a room. The landlady who provided him with garret, dinners, and attendance, lived on the floor below, and every time he went out, he was obliged to pass her kitchen, the door of which invariably stood open. And each time he passed, the young man had a sick, frightened feeling, which made him scowl and feel ashamed.³²

Raskolnikov feels a morbid and vile sensation of which he is ashamed, leading him to twist his face into a grimace. Morbidity, cowardice, and shame: three strong themes are introduced, but still, everything seems to be shrouded in an atmosphere in which neither crime nor punishment hovers. We shall now read Kafka.

As Gregor Samsa awoke one morning for uneasy dreams, he found himself transformed in his bed into a gigantic insect. He was lying on his hard, as it was armour-plated, back, and when he lifted his head a little, he could see his dome-like brown belly divided into stiff arched segments

on top of which the bed-quilt could hardly keep in position and was about to slide off completely. His numerous legs, which were pitifully thin compared to the rest of the bulk, waved helplessly before his eyes.³³

Here, the drama is presented immediately with unprecedented, bursting and minute reality: the theme of metamorphosis is clear and manifest in just a few lines. As if Kafka had read *Crime and Punishment* and thus did not need the development present in the Russian novel, but instead entered immediately *in medias res*, precisely forged by the metamorphosis of the student-murderer Rodja. The evolution of the two novels, obviously completely different in scope and content, nevertheless contains the essence that will make them archetypes of the existential dramas of the man to come. And if the beginning is the *before*, equally dazzling are the two endings, the *after*.

But that is the beginning of a new story—the story of the gradual renewal of a man, the story of his gradual regeneration, of his passing from one world into another, of his initiation into a new unknown life. That might be the subject of a new story, but our present story is ended.³⁴

There is a *before* and an *after* in Raskolnikov, too, as well as in us readers, and in between is that terrible ordeal of suffering, the real punishment, not the seven years of imprisonment, which will be another story. And we are irreversibly changed by the first story, which leaves an indelible mark on us as soon as it is finished. Kafka, in his own way, is even more tragic; alienation admits of no redemption and so he concludes.

They grew quieter, and half unconsciously exchanged glances of complete agreement, having come to the conclusion that it would soon be time to find a good husband for her. And it was like a confirmation of their new dreams and excellent inventions that at the end of their journey, their daughter sprang to her feet first and stretched her young body.³⁵

And here, too, the beginning and finale establish this before and after with the nectar of the literary masterpiece in between. Gregor "was lying on his hard, as it was armour-plated, back," while his sister, after the metamorphosis and the drama of her brother's exit metamorphosed into an insect by self-annihilation, "sprang to her feet first" from the tram seat where she is with her parents, "stretching her young body", also ready for new life, but not Gregor, he has no rebirth, total alienation has led him to self-destruction. I hope I have given you a sense of why these two literary works do change us irreversibly and why the after can never be like the before.

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4. THE INTERPRETATION OF THE PRESENT

Before and after stand for the past and the future, but chemistry and literature are also very much concerned with the present. Chemistry seeks to interpret phenomena that present themselves to it and that concern all matter and its incredible transformations; the more obscure they are, the more exciting and exhilarating the challenge. For example, at the end of the 19th century, a phenomenon undermined present-day theories: blackbody radiation. Without going into detail, the problem of that present was to interpret how a blackpainted furnace, with a small hole connecting it to the outside, was able to absorb all the radiation coming from outside and at the same time emit it when properly heated. The blackbody was like the inside of a church, in which the small hole is the door ajar: light enters, but looking at the door from outside, you can only see black, as all the light bounces back into the walls and almost nothing comes out. 36,37 If we were able to heat the church to a high temperature, however, we would see the light coming out, first red-hot (from the Latin rubens, i.e. reddening, a derivation of rubere, i.e. being red) and then white-hot or "incandescent" (from the Latin candescĕre, i.e. whitening)! Unlike the church, the furnace can be heated, and this is what happens: the blackbody lights up: radiation visible to the naked eye comes out of the little hole and becomes red, then orangeyellow and then all the colours together, i.e. white, the higher the temperature. The type of light, red or white, correlated to the blackbody's temperature. Furthermore, the curves obtained all had a single-peak shape, moving towards smaller and smaller wavelengths but still tending to zero at both very small and large wavelengths. This could not be properly explained with the theories known at the time. A scientist, Max Planck, decides to face the situation and solves it, as Heinlein so aptly put it, by denying the obvious and accepting the impossible:36,38 Indeed, he formulated a theory (see Eq. 1: Given B the spectral radiance, l, the wavelength, T, the temperature in Kelvin, h, the Planck constant, c the light velocity, k the Boltzmann constant) that accounted for the experiments, but totally upset old paradigms. In particular, energy no longer presented itself for certain phenomena as a continuous function, but as a discrete one, i.e. transmitted in packets, what would later be called quanta. Here, then, is the present experienced and ultimately interpreted by science with a revolution of thought that marks a milestone in its history.

$$B_{\lambda}(\lambda,T) = (2hc^2/\lambda^5) \cdot [1/(e^{hc/\lambda kT} - 1)] \quad (1)$$

And what is the present in literature? It is society, customs, politics, living conditions, inner drives, and how all this flows into human psychology. New physics challenges old paradigms. Roughly at the same time as the quantum-mechanical revolution in chemistry and physics, at the turn of the 20th century, Italo Svevo and Thomas Mann did the same in their field of literary creativity. Let us see how. As with the quantum-mechanical revolution, two themes burst into the history of literature that somehow deny the obvious and accept the impossible, as Heinlein suggested for advances in physics. This time, the present shows up with the double face of the blackbody of the unconscious and the crisis and decadence of the European bourgeoisie. Let us not forget that these two great writers are coeval with the birth and development of Freud's psychoanalysis. For the first time in the history of thought, Freud attempts to establish correlations between the vision of the unconscious, i.e. the symbolic representation of real processes and its components, with the physical structures of the human mind and body. These theories will find partial confirmation in modern neurology and psychiatry. The unconscious is the huge iceberg block that lies hidden inside the sea, containing the essence of our human being: emotions, dreams, fantasies, creativity, instincts, impulses, and intuition. The two writers, therefore, totally immersed in the present, distil it into literary works, bringing about a real revolution in the novel's history. Ervino Pocar, 39, in his introduction to the Italian edition of The Magic Mountain in 1965, vividly captures precisely the immersion in the present. He writes that *The* Magic Mountain

is a faithful, complex, comprehensive portrait of Western civilisation in the first decades of the 20th century and, in its enchanting fusion of prose and poetry, of scientific vastness and refined art, is perhaps the most magnificent book written in the first half of the century.^{6,40}

The theme of illness, which dominates the entire novel, is only apparently the lung disease treated in the sanatorium. In reality, the illness is essentially mental and moral: the great drama of 20th-century humanity that the writer feels, perceives and condenses in his work.

On the one hand, the reflection on the moral illness of the bourgeoisie of Western civilisation. On the other hand, the mental illness of the individual self of Zeno's conscience. It is, therefore, no coincidence that *The Magic Mountain* was published in 1924, barely a year after the release of the novel *Zeno's Conscience*.⁴¹ On the subject of illness, Svevo's vision shifts from society to the individual:

Unlike other sicknesses, life is always fatal. It doesn't tolerate therapies. It would be like stopping the holes that we have in our bodies believing them wounds. We would die of strangulation the moment we were treated.⁴²

The revolution is thus accomplished in literature as well. This inexplicable blackbody of the unconscious, investigated and eviscerated, opens up new visions of the self and, more generally, of the existential crisis that is beginning to appear in the face of the Western world: a society impoverished of all values. It would be Albert Camus who, a few decades later, would receive this baton and carry it forward. The analogy with the break made by quantum chemistry also extends to how these two scientific and literary revolutions relate to the pre-existing. Quantum chemistry does not disregard the value of classical physics and chemistry, which continue well to describe an extremely conspicuous harvest of natural phenomena; it simply complements them when dealing with the infinitely small.

Similarly, Svevo and Mann represent a further development, marking a definite break with the past, in the history of world literature. They also stand alongside the giants of world literary history who continue to represent eternal and universal themes. Svevo and Mann of the present scrutinise and re-interpret the drama of humanity grappling with the anxieties of living, as well as of the relations between peoples and nations: everything that literature intuits and crystallises in two works mentioned that have become milestones, will manifest itself with incredible and crude harshness in the tragic landfalls during the nascent century.

5. REALITY AND UNREALITY

If the theme of the present is, as we have seen, a significant one in trying to demonstrate the dynamic equilibrium in which chemistry and literature oscillate, equally rich in intriguing and interesting aspects is the reality/unreality pair. That chemistry, and more in general science, is concerned with reality is almost a tautology, but beware, it can often be the case that it is a reality explained through models and theories that are far removed from reality, at least from that reality linked to sensory perception. A reality, we might venture, explained in a quite unrealistic way. Think of the postulate of the existence of atoms and molecules, the discovery of x-rays and elementary particles, and the very 'unreal' theoretical construction of quantum mechanics, which then gives rise to real objects (the laser, for example). Or even to evolutionary theory, apparently very 'unreal' at its formulation and perhaps for some even afterwards! Not to mention relativity and the dissolution of the concept of time in physics with a theory far removed from what common sense identifies with reality. It is said that Einstein liked Charlie Chaplin so much that he addressed this exclamation to him: "What I most admire about your art, is your universality. You don't say a word, yet the world understands you!" And Chaplin's wonderfully shrewd response about the distance from reality and common sense of Einsteinian theories: "True. But your glory is even greater! The whole world admires you, even though they don't understand a word of what you say."43,44 As can be seen, to dismiss chemistry as a discipline that deals with reality while ignoring all unreality is very simplistic.

All great chemical discoveries give rise to a reality that is often presented as profoundly unreal at the time of discovery. The example of x-rays is paradigmatic. 45-52 The physicist Konrad Röntgen realised in 1895 that near a glass tube in which he was conducting electrical discharges, totally obscured by tin foil and black cardboard and therefore invisible from the outside, there was a substance that normally fluoresces with a yellow-green colour when illuminated. The room where he did the experiment was completely dark because the aim was to test whether light was coming from those tubes. He was so surprised to see luminescence from that substance: who had turned it yellow-green? To the eye, nothing could be seen coming out of the glass tube; it was covered with black cardboard, so even if light had formed inside, it could not have come out. Röntgen repeated the experiment many times, always with the same result: the fluorescent substance only glowed when he produced electrical discharges inside the tube, but nothing could be seen coming out of it. There was, therefore, an element of objective reality: the fluorescent screen lit up. But then again, this reality coexisted with the unreality that no light ray came out of the tube, as it was totally 'wrapped' in black cardboard. He then imagined something unreal, which he could not in any way prove, namely, that mysterious, invisible rays were coming out, able to pass through the black cardboard. Such rays, when hitting the screen substance nearby, made it glow. Since they were mysterious and unknown - and, I would add, as such, very unreal - he named them after the unknown in mathematics, namely x. So far, a discovery by chance; now comes the genius that makes unreality realistic. Let's see how. Between the tube that emitted the mysterious rays and a photographic plate, he first placed a closed wooden box with the metal weights of a scale inside, then the barrel of his rifle and finally his wife's hand. And what kind of real68 Luigi Dei

ity emerged incontrovertibly? Three fundamental applications that would change the world. The three developed plates revealed the clear shapes of the small brass weights for the precision scales inside the closed box; an imperfection inside the gun barrel, invisible from the outside, of course; the skeleton of his wife's hand with a clear image of her metal ring. 45-52 The road to metal detectors, quality control of metal artefacts, and radiographic medical diagnostics was paved. He had discovered that x-rays were very penetrating, and that only sufficiently heavy atoms could block them. So, calcium and phosphorus from the bones stopped the x-rays and did not blacken the plate, while the soft matter in our bodies made of carbon, hydrogen, oxygen and nitrogen could easily be passed through. We can conclude, not surprisingly, that the brilliant German physicist made unreality realistic. French poet, essayist, playwright, dramatist, writer, librettist, director, and actor Jean Cocteau, to whom Marcel Proust wrote: "I crack with jealousy to see how in your extraordinary pieces on Paris you are able to evoke things that I have felt and have only been able to express in a very feeble way,"6, 53 gave a beautiful definition of cinema, which goes like this. "Vive la jeune Muse Cinéma, car elle possède le mystère du rêve et permet de rendre l'irréalité réaliste."54,55 (Long live the young Muse Cinema, since she possesses the mystery of the dream and allows for the rendering of realistic unreality)6. Well, if Röntgen made the unreality of x-rays realistic with his ingenious experiments, literature also responds perfectly to this definition that Cocteau adopted for the cinema.

To illustrate this theme of the reality/unreality relationship in literature, I will give three examples: Orlando Furioso, late 19th-early 20th-century verism and naturalism, and science fiction literature. In Astolfo's journey to the moon to recover Orlando's lost wits due to Angelica's betrayal, there is the distillation of this continuous contrast between unreality and reality.⁵⁶ After having visited Hell, Astolfo reaches the summit of the Earthly Paradise on the back of a hippogriff, and here he is welcomed by St John the Evangelist, who then escorts him to the moon aboard Elijah's chariot and acts as his guide. A classic, phantasmagorical imaginative apotheosis - today, we would say science fiction - a condensation of images manifestly dripping with unreality, yet full of fascination. But at the same time, as prodigious as it is unreal, this journey becomes an opportunity to blame the reality of man's folly in wasting time in pursuit of and thus losing his wits over vain illusions. Still, it also allows the author to polemise against a petty reality, that "of service lost in court" 56a ("servir de le misere corti"), a subject that also recurs in other works by Ariosto, that of deploring real human miseries with these fantastic, fairytale-like flourishes results from brilliant creativity and literary mastery. Lost sense is the ingenious gimmick of linking unreality to reality, "a body moyst and soft" ("un liquor suttile e molle") that gives an account, when lost, of numerous, real human miseries.

On the other hand, the theme of reality in literature was to characterise French naturalism and Italian verism, with the two great writers Emile Zola and Giovanni Verga. Reality becomes an obligatory theme: it is spoken of almost in terms of a theoretical manifesto. And if in French naturalism, perhaps for the first time, science and literature go almost hand in hand, in the verism of Verga and Capuana, the positivist influence of Comte dissolves. Reality is analysed and described not in the same way as a scientific investigation, as seen in some of Zola's novels, but with lyricism and attention to human passions and even, in this antinomian to French naturalism, with distrust in scientific progress, which is pessimistically indicated as responsible for a modernisation that makes the condition of the less well-off classes ever more miserable. In both cases, however, reality becomes not only a relevant theme but also a pretext and a cue to bring the nameless into the limelight, be they the fishermen of Aci Trezza or the miners of Germinal. It is the reality of outcast men and women, with a spasmodic focus on certain things that become almost iconic. Two striking examples: Providence,⁵⁷ the Malavoglia's fishing boat, and Lison,58 the locomotive from La bête humaine (The Beast Within).

Two different ways of making the real the focus of literary invention. At the same time, as we have seen happen with science during the quantum-mechanical and relativistic revolution, a literature was born in England and France that made the unreal, the so-called scifi, its focus: Jules Verne⁵⁹ and Herbert George Wells.⁶⁰ Verne lived between 1828 and 1905, Wells between 1866 and 1946; Zola between 1840 and 1902 and Verga between 1840 and 1922. As you can see, reality and unreality in literature elbow to elbow: just to give you an idea, Verne published between 1863 and 1905 his 54 novels in the collection Voyages extraordinaires (among which the best known, Around the World in 80 Days, From the Earth to the Moon, Twenty Thousand Leagues Under the Sea), in 1895 Wells published The Time Machine, I Malavoglia was published in 1881, Mastro don Gesualdo in 1889, Germinal in 1885 and La bête humaine in 1890. In short, truly a literary apotheosis of reality and unreality!

6. QUESTIONS AND ANSWERS

We now come to the fifth and final theme, since the sixth, namely the value of discovery, will be more of a final coda, a kind of homage to science and chemistry on the part of literature. Questions and answers. Chemistry has been constantly asking questions and searching for answers since time immemorial; not only since the advent of modern chemistry born in the 18th century but also before, when pre-chemistry was only a philosophy of nature. A typical example of chemical questions and answers distilled in literature several centuries before the advent of modern science is Lucretius' De rerum natura.61 Nature itself, with its phenomenology, is often a natural experiment that poses questions. The rainbow, the blue sky and white clouds, lightning, light, fire and heat, wind and much more ask to be explained, silently manifesting themselves spontaneously and available to our heuristic activity as Homo sapiens. The question I choose, as an example is: what is wind? Lucretius' literary answer already contains the scientific notion we know today for wind, i.e., the volume of a gaseous mixture moving more or less rapidly from higher pressure to lower pressure areas. "Wherefore again and yet again I say | That winds have hidden bodies, since they rival | In character and action mighty rivers | Possessed of bodies plain for all to see."62 The molecules that make up the gaseous atmosphere in which we are immersed are the *invisible* moving *bodies*, just like other molecules, visible and touchable, that move due to the difference in level in the great rivers. Modern science would establish the primacy of the experimentum with its reproducibility and the introduction of mathematicalgeometric formalism. But the experimentum is ultimately designed and executed to answer one or more questions. A wonderful example of a chemical question and answer sublimated into a literary passage comes from Primo Levi. In an article in the Italian newspaper La Stampa about 'Signs on Stone', later published in the volume Other People's Trades,63 Levi describes what can be seen on the pavements when walking around Turin. After discussing the signs caused by the bombings of the Second World War, Levi inserts a brief warning ("Other signs are less sinister and more recent"). He abruptly poses a question that has no answer, highlighting an apparently irremediable contradiction in our technological civilisation. Why is it that "the effort made to establish the excellence of a particular material's resistance and solidity can often lead to serious difficulties when it comes to eliminating the material itself after it has fulfilled its functions?"64 And from this unanswered question comes the amazing and astounding literary example of chewing gum leaving precisely those less sinister and more recent signs on stone.

The demand for a gum which resists, which changes form without being destroyed, and can undergo the torment of mastication, which consists in pressure, heart, humidity and enzymes, has resulted in a material which stands up only too well to trampling, rain, frost and the summer sun. [...] Alongside more obvious and trivial elements, these are the signs one sees on the pavement when the soul clings to it like a chewing gum, because of sloth, laziness or fatigue.⁶⁵

This is one of the many passages that justify Primo Levi's selection as the best science writer of all times.

Literature, too, is full of questions and answers, or lack of answers. The quintessence of this can be seen in the famous 'to be or not to be, that is the question'. Moreover, Federico Bertoni very shrewdly writes in the afterword to the Italian edition of *The Red and the Black*.

At the end, close the book, look back and you will see some fundamental questions take shape. What things are worth living for? Do genuine passions exist in a hopelessly corrupt and prosaic world intoxicated with vanity and careerism? Can one act with vital fullness without being paralysed by thought or an abstract must-be? Is it art imitating life, or perhaps, as Oscar Wilde put it, life imitating art? How can one act sensibly in a dull world, impervious to any inner strength? Can one look for a key in novels without getting trapped in the imaginary, without exhausting one's passions in a delirium of suspended actions that do not catch up with reality and history? In the end, Julien acts. He shoots and condemns himself to ruin. He exits his novel and finishes it as he pleases. Who knows whether that gesture is the point of coincidence with itself or yet another mystification in which the truth is always behind, a little further away?^{6,66}

On these probably unanswered questions, and on all the others that almost always characterise the legacy of a literary work, it is worth mentioning, finally, the illuminating reading of the chapter *Pasternak and the Revolution* in Italo Calvino's *Why Read the Classics*?⁶⁷ At one point, Calvino asks himself, after a careful reading of the novel, "*Who is this Zhivago*?"⁶⁸ And the non-answer he gives is intriguing: at the centre of the novel is, in fact, the story of Lara, rather than that of Doctor Zhivago:

[...] Lara's life is in its linearity a perfect story of our time, almost an allegory of Russia (or the world), of the possibilities that have gradually opened up to her (or it), or which were all presented to her (or it). ⁶⁹

But Pasternak's novel also questions us on the big issues of history, nature and how humanity is in it with its *doing*. The writer's answer is defiant pessimism about this *doing* of humanity. Nature cannot be changed but only understood with science – why what is happening

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happens – and with poetry, suggesting *how* what is happening happens. History, then, is made neither by great individuals nor by nameless little ones: "It moves like the plant kingdom, like the wood changing in springtime, [...] as a solemn coming into being, transcending man." If Pasternak asks questions and suggests answers according to his feelings, he nevertheless leaves the field open, precisely by the answers he gives, to reflections and consequent responses of an opposite sign. We are back, then, to the great tradition of the Russian epic, which, not surprisingly, will feature in the motivations for the Nobel Prize in 1958.⁷¹

7. THE VALUE OF DISCOVERY

I feel at this point that I should conclude this study and reflection on chemistry and literature and the dynamic equilibrium that from time to time brings them closer together or pulls them apart, but always in orbits having a common universal centre of gravitation, by evoking the last point that I have called the value of discovery, which for chemistry is obviously a must. Chemistry is a continuous discovery and, at the same time creates more mysteries to be unravelled. It is not trusting one's senses, it is always doubting that one is in the right and assuming even absurdities, overcoming any prejudice or belief. As we have seen, it is denying the obvious and accepting the impossible. The 'icing on the cake' of this reflection on chemistry and literature comes precisely from the homage that literature pays to the value of the discovery; whether it be that of America or an important new molecule, it matters little. Its value is exalted a few moments before the discovery, in the knowledge that Columbus and the great discoverer chemists, in the end, do not really know what great things they have discovered, and the value lies in the path that brought them a step closer to the finish line, that is, in the adventure of living. The great Dostoevsky, with his astonishing novel *The Idiot*, 7² reveals to us the intimate and profound value of discovery.

Oh, you may be perfectly sure that if Columbus was happy, it was not after he had discovered America, but when he was discovering it! You may be quite sure that he reached the culminating point of his happiness three days before he saw the New World with his actual eyes when his mutinous sailors wanted to tack about and return to Europe! What did the New World matter after all? Columbus had hardly seen it when he died; in reality, he was entirely ignorant of what he had discovered. The important thing is life-life and nothing else! What is any 'discovery' whatever compared with the incessant, eternal discovery of life? ⁷³

It is worth recalling, at the end of this zigzag between chemistry discoveries and literary inventions, a passage from a witty article by Cesare Garboli that appeared in the Italian newspaper *Il Corriere della Sera* on 7 March 1977 entitled *Questo poeta è uno scienziato* (*This poet is a scientist*)^{6,74}.

After all, what did we learn from Montale? Like all true poets, Montale is a scientist. He does not send messages but discovers and legislates. It was Montale who expressed in poetic terms the true, great discovery of the century that our life is 'quantum', intermittent, discontinuous, between being and non-being.^{6,74}

Perhaps that dynamic equilibrium between the two planets, chemistry and literature, which revolve around the same sun of culture and knowledge, sometimes moving apart, sometimes coming closer together, is summed up precisely in this iconic and almost desecrating juxtaposition of poetry and science.

8. ACKNOWLEDGEMENTS

The author would like to thank Prof. Gino Tellini, curator of the cycle of Seminars "Lights and Shadows of Modernity" and Dr. Aureliano Benedetti, President of the Fondazione Biblioteche dell'Ente Cassa di Risparmio di Firenze, organiser of such cycle of Seminars for the kind invitation to deliver the lecture "Science and Literature"; thanks also to Prof. Simone Magherini, Editorial Director of the journal Studi Italiani, for the kind permission to translate in English and re-edit the article published in the journal mentioned above, XXXV, issue 2, July-December 2023, pp. 67-94. The author also expresses his gratitude to Sonia Torretta for the very accurate and careful translation of the article from Italian to English and to Lucia Cappelli, Librarian at The British Institute of Florence, for her kind assistance. Figures 1, 2 and 3 are a graphic reworking by the author of three figures (14, 15 and 24) taken from ref. 14. The financial support of the Fondi d'Ateneo per la Ricerca from the Department of Chemistry 'Ugo Schiff' of the University of Florence is gratefully acknowledged.

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Citation: Atikah, A., Habiddin, H., Nazriati, N., Basimin M.D. (2025) Students' Mental Model in Understanding Chemical Bonding and Its Correlation with Chemistry Mindset. *Substantia* 9(2): 75-82. doi: 10.36253/Substantia-3476

Received: Apr 30, 2025

Revised: Jun 17, 2025

Just Accepted Online: Jun 19, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

Students' Mental Model in Understanding Chemical Bonding and Its Correlation with Chemistry Mindset

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Abstract. This study aims to describe the mental models of secondary school students and examine their relationship with the chemistry mindset. The research involved 122 secondary school students in the 10th, 11th, and 12th grades. Data were collected using a structured descriptive assessment and a chemistry mindset questionnaire. Students' mental models were categorized according to Kurnaz and Eksi's indicators, covering initial, synthetic, and scientific models. Meanwhile, the Chemistry Mindset Instrument employed the framework established by Santos et al. and categorized as fixed and growth mindsets. Pearson's coefficient measures the correlation between the mental model and the chemistry mindset. This study finds that many of the students' mental models fall into initial and synthetic categories, with only a small number in the scientific category. The proportion of students with the synthetic model peaks in the formation of ions at 63.11%, in the initial category of covalent bonding at 54.92%, and in the scientific category of coordinate covalent bonding at 18.85%. Furthermore, this study indicates a weak relationship between the mental model and the chemistry mindset. Students' confidence during chemistry class influences this issue. Therefore, teachers are expected to select appropriate learning models to enhance students' achievement and mindset toward chemistry.

Keywords: fixed mindset, growth mindset, model and modelling in chemistry, non-cognitive factor, visual representation

1. INTRODUCTION

Chemistry concept comprehension will be successful when students can relate to three levels of representation: macroscopic, submicroscopic, and symbolic. However, these levels often become obstacles for students, as submicroscopic representations consist of complex concepts and abstract phenomena that are invisible to the naked eye [1]. Due to their abstract nature, chemistry concepts are often represented through models and modeling [2].

Some chemistry educators have attempted to define the terms "model and modeling." A model represents ideas or a simplification, description, or conception of a particular phenomenon, including systems, processes, situations, and mathematical terms [3]. The effort to describe and construct those models into observable procedures is known as modeling [4].

A mental model is an internal depiction formed when a student encounters a problem. This model can be stored in long-term memory and applied when the student receives a similar task [5]. In simpler terms, a mental model is an individual's view or representation of an object, concept, system, or other phenomenon [6], that is constructed within memory and has been of interest in the areas of cognitive science and science education [7]. Mental models are also described as visualization and understanding that students conduct to elaborate on ideas or notions from previously learned phenomena. Therefore, it can be considered an internal depiction created by an individual while understanding and applying a concept or phenomenon.

In chemistry, the mental model is often explained as an understanding of students toward three levels of chemistry representation [8]. It is related to students' understanding of a concept, which can significantly influence students' academic achievement. Students with a good mental model demonstrated a good understanding [9]. The result of this study can be used as a reference for teachers to understand the difficulties, comprehension, and misconceptions experienced by students [8] and utilize to design a suitable learning model [9]. Students who can already specify their mental model can adapt to their learning style. Therefore, students must possess a model and ability while learning chemistry to help them understand and communicate chemistry [11]. In our previous study, it was confirmed that the identification of students' mental models is essential for chemistry learning [12]. Chemical bonding is a challenging topic for many students. A survey conducted on many secondary school students in Indonesia demonstrated a lack of knowledge and an unscientific understanding of the topic [13] impliying insufficient mental models.

Mental Model and Chemistry Mindset

Some experts classify students' mental models into several categories, including scientific, synthetic, and initial models [13]; scientific, phenomena, symbol, and inference characteristics [14]; macroscopic, submicroscopic, and symbolic [8]; No Response (NR), Specific Misconception (SM), Partially Correct (PC), and Scientifically Correct (SC); referent, relation, syntax, result,

and sensemaking process [15]. Among these categories, this study applies the categorization proposed by Kurnaz and Eksi [13], as it provides comprehensive criteria and a fair scoring system to analyze mental models based on descriptive responses and visualizations performed by students. Because the nature of mental models is complex and variable, analyzing mental models requires comprehensive data gathered from students in the form of pictures, writings, and verbal explanations [16].

A scientific mental model represents a perception that aligns with the nature of concepts recognized by the scientific community. A synthetic model partially aligns, while initial models do not align with the accepted understanding in the scientific community. The criteria for these categories are specific to each chemistry concept. For example, regarding molecular polarity, the attributes of students' mental models—whether scientific, synthetic, or initial—depend on their understanding of molecular geometry and its effect on the resultant vector of bonding moments around the central atom. For this reason, this platform is adopted in this study due to its relevance to the need for enhancing students' understanding of chemistry.

Kurnaz and Eksi [11] stated that a person's mental model can be revealed through the expression or action that reflects their comprehension of a particular concept. That is why each student will have a unique mental model, as they hold different scientific perspectives on a phenomenon. Several factors contribute to the unique mental model possessed by each individual, including formal instruction (teacher explanations), textbooks, language, social environment, and student intuition [14]. Additionally, factors that influence the development of mental models include age, scientific thinking skills, and learning experiences. The older an individual is, the more complex the mental model will be; in other words, it will be a more scientific mental model [17]. According to previous studies, student grade level also affects the development of their mental models. Students in the third year of secondary school will have a better mental model than first- or second-year students.

Apart from the mental model, the drive from students themselves, including mindset, motivation, and other non-cognitive factors, is the most prominent factor to promote student success in chemistry [18], [19]. Mindset theory describes a belief system that varies depending on context, specifically concerning how much intelligence can be changed through effort [20]. Mindset is one of the non-cognitive factors that determine students' academic achievement. It refers to a way of thinking, self-efficacy, and goal orientation [21] that enables individuals to obtain, process, investigate, interpret, and

elaborate on the phenomena they experience. Mindset is categorized into two main types: a fixed mindset and a growth mindset. A fixed mindset is held by students who believe that human intelligence and ability cannot be changed or developed. In contrast, a growth mindset is characteristic of students who believe that intelligence is a trait that can be cultivated and enhanced through effort and guidance from a tutor. Students who learn chemistry will adopt a specific mindset known as the chemistry mindset. Chemistry mindset refers to a way of thinking or an individual belief about one's ability to manipulate chemistry intelligence through effort [22]. In subjects with a highly demanding context, such as chemistry, students' perceptions regarding their ability to enhance their intellect and mindset likely exert a greater influence on their academic performance [23]. The chemistry mindsets of students may forecast their behavioural reactions to obstacles encountered in a chemistry course [20]. Therefore, understanding students' mental models and mindsets will help chemistry educators deliver effective chemistry instruction. In addition, a fixed mindset is contagious [24], therefore, knowledge of the mindset could assist teachers in preventing the spread of the unexpected mindset.

Research objectives

Efforts to address students' challenges in learning chemistry primarily focus on cognitive aspects, such as intelligence. In particular, chemistry is regarded as a technoscience that merges scientific inquiry with technological objectives [25]. Therefore, this study examined non-cognitive aspects, including mental models and a chemistry mindset, which also contribute to students' proficiency in chemistry. This study aimed to describe students' mental models and chemistry mindsets in chemical bonding. The correlation between the students' mental models and chemistry mindsets was also investigated.

2. RESEARCH METHOD

This study involved 122 tenth, eleventh, and twelfth-grade public secondary school students in Malang, East Java, Indonesia. Mental model indicator from Kurnaz & Eksi [14] was utilized to measure students' mental models using short-answer questions covering elements of stability, the formation of ions, ionic bonding, covalent bonding, coordinate covalent bonding, and metallic bonding. When answering the mental model questions, students were required to generate a visual representa-

tion (picture) in response to the verbal answer they provided. Therefore, the assessment of students' answers was measured from the two aspects (scientific reasoning & pictorial relevance). Content analysis, using the parameters in Table 1, was employed to uncover students' mental models.

Table 1. Mental Model Rubric

Criteria	Mental Model Category
Robust scientific reasoning & relevant pictorial representation.	Scientific
Partially scientific reasoning and partially pictorial representation; Partially scientific reasoning and relevant pictorial representation; Robust scientific reasoning and partially pictorial representation;	Synthetic
No answer; No picture; irrelevant pictorial representation	Initial

Meanwhile, the chemistry mindset questionnaire from Santos et al [26] was applied to measure students' chemistry mindset. A 1-10 scale semantic differential was implemented to categorize students' chemistry mindset. The growth mindset is associated with the scale of 6 to 10, while the fixed mindset corresponds to scores below 6. This attitude research instrument requires respondents to articulate their attitudes concerning two opposing adjectives [27]. Meanwhile, Pearson correlation analysis was used to determine the relationship between the mental model and the chemistry mindset. This correlation test was carried out after the prerequisite tests (normality and homogeneity) were met.

3. RESULT & DISCUSSION

Description of Students' Mental Models Across Cohorts

Figure 1 depicts the percentage of students with a specific mental model for the tenth, eleventh, and twelfth grades. It illustrates a particular development of mental models tailored to grade level. The figure indicates that the initial mental model, representing the lowest level, is most prevalent among 10th-grade students. This is also the highest initial level across the three cohorts, comprising more than half. The number of students with a synthetic model in this cohort is lower than that of the initial model. However, the number of students demonstrating the scientific model, which is the most expected, is very low, at below 5%. This suggests that most 10th-grade students still lack a sufficient mental model.

The 11th-grade students demonstrated a similar trend to the previous cohort. The number of students

with initial and synthetic mental models in this cohort is almost the same, with the latter being slightly higher. The number of students with scientific mental models is slightly higher than in the 10th grade, but the difference seems insignificant. All in all, this cohort's slightly higher mental model status still does not seem promising.

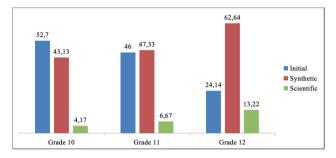


Figure 1. Number of students with the mental model level for each cohort

The twelfth-grade students demonstrated a superior mental model status compared to the other two cohorts, as evidenced by the number of students with scientific mental models (13.22%), which doubled that of the others. The number of students with an initial mental model for this cohort is also relatively small, with less than a quarter. It is revealed that the mental model of twelfthgrade secondary school students is more advanced than that of tenth and eleventh-grade students. It can be used as evidence that an improvement in scientific thinking skills will accompany a student's higher grade level. As stated in a previous study, better scientific thinking skills are a result of student mental model improvement [16]. Learning experiences also contribute to the development of a student's mental model. This implies that students' physical maturity may influence their mental models. This is following the previous study's finding that the older the individual, the closer their mental model is to a scientific mental model type [28]-[30]. The third-grade student who has already studied chemistry for three years has more experience and exposure to chemistry teaching, which may help them formulate chemistry concepts into a more scientific mental model [30].

Description of Students' Mental Models Across Topics

Students' mental models in this study are explicitly described for each topic (Table 2). The data were obtained from all cohorts combined. The table indicates that the highest scientific mental model was observed in coordinate covalent bonding, with nearly one-fifth of the total students. A significant number of

students also demonstrated an understanding of scientific mental models in ionic formation and bonding. Meanwhile, almost none of the students exhibited a scientific mental model in covalent and metallic bonding. Unfortunately, most students are in the synthetic or initial mental model for all topics. This implies the need to consider this issue in chemistry teaching in an appropriate manner. A similar study conducted in Indonesia involving prospective chemistry teachers in the school chemistry topic demonstrated comparable results with medium average scores [31], suggesting initial or synthetic models.

Table 2. Number of students with the mental model level for each topic

Sub-Topic	Scientific (%)	Synthetic (%)	Initial (%)
Element Stability	4.10	43.44	52.46
Ionic formation	9.84	63.11	27.05
Ionic Bonding	7.38	52.46	40.16
Covalent Bonding	0.82	44.26	54.92
Coordinate Covalent			
Bonding	18.85	42.63	38.52
Metallic Bonding	0.00	45.90	54.10

The insufficiency of students' mental models must be considered because it also reflects their understanding of relevant chemistry concepts. Figure 2 presents an example of a student's initial mental model regarding the stability of elements. For clarity, the figure is reconstructed from the original manual drawing. The students' responses indicate a lack of understanding of element stability, as shown by their inability to correctly write down element configurations, grasp how elements achieve stability, and accurately describe electron configurations.

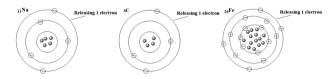


Figure 2. Initial Mental Model on Element Stability

Figure 3 provides an example of a synthetic mental model experienced by 63.11% of students in the context of ionic formation. Like the previous figure, *it is also reconstructed from the original manual drawing*. The figure illustrates the misconception or unscientific understanding regarding ionic formation by depicting a Lewis structure that represents a covalent bond instead of an ionic one. Another unscientific understanding identified

in this context is the assumption that the radii of Cland Cl are the same. These two samples confirm the linear relationship between the insufficient students' mental models and their difficulties in understanding chemical bonding. Another example of unscientific understanding associated with the low mental model level is drawing the Lewis structure for HCl; some students considered a double bond between H and Cl.

$$Mg^{2+} + 2Cl \longrightarrow MgCl_2$$

$$xMgx + 2 Cl \longrightarrow Cl Mg Cl_2$$

Figure 3. Example of Synthetic Mental Model

Meanwhile, those with a scientific mental model also have a strong scientific understanding of the concept. They understand that the cation radii are always smaller than that of the neutral atom due to the strong interaction between the proton and the outer electron after releasing one electron. Conversely, for a similar reason, the anion radii are always larger than those of its atom. Students with this mental model also provide an accurate drawing of the Lewis structure. These findings suggest the need to enhance students' mental models in order to improve their understanding of chemical bonding and other chemistry concepts. This finding aligns with a previous study that found an unscientific understanding of atomic spectra led to the formation of an unexpected mental model [32]. In a broader perspective, some variables, including prior knowledge, motivation, and learning environment, could affect students' mental models [33].

Description of Students' Chemistry Mindset

Students' chemistry mindset was measured using the instrument of Santos et al [26]. Table 3 describes the indicators of students' chemistry mindset. The mindset is measured using a semantic differential ranging from 1 to 10. Table 3 demonstrates the average value of students' chemistry mindset, which is 6.41. It reveals that students in secondary school tend to have a developing mindset, also known as a growth mindset. Students with a growth mindset will always try to increase their intelligence. They are likely to face challenging tasks by using new strategies that will lead them to successful academic achievement [22].

Table 3. Student Chemistry Mindset Average for Each Question

No	Question	Chemistry Mindset Average
1	My problem-solving skills in chemistry	6.39
2	My ability to understand concepts in chemistry	6.54
3	My ability to apply chemistry knowledge	6.20
4	My ability to comprehend chemistry content	6.39
5	My ability to visualise chemical structure and process	6.29
6	My ability in reasoning and logical thinking in chemistry	6.66
7	My overall chemistry intelligence	6.43

Table 3 also shows that the distribution of students' chemistry mindsets across all indicators is equal. The average score of students' chemistry mindset is 6.41, which tends to fall in the growth mindset. This is in line with the work of Wichaidit [18], the majority of secondary school students in Thailand demonstrated a growth mindset, with almost 70% exhibiting this attitude and only a small portion showing a fixed mindset. Although the score indicates a positive result with a value greater than 6, students' chemistry mindsets still need empowerment to reach the peak point of 10. Students may still consider chemistry a challenging subject. Strengthening this aspect in chemistry students is essential because students' perceptions about their capacity to enhance their intelligence, mindset, presumably, exert a greater influence on their academic performance in demanding educational settings, such as chemistry [26].

Correlation Between Students' Mental Model and Chemistry Mindset

The aforementioned explanation implicitly mentioned that students' mental models correlate positively with the chemistry mindset. The dominant students' mental model at the initial and synthetic levels is relevant to the students' chemistry mindset status, with an index of 6.41. The statistical test using Pearson's Correlation, presented in Table 4, confirms this.

Table 4 presents the correlation test with a value of 0.288, indicating a positive correlation between the mental model and chemistry mindset. However, the correlation index reveals that this correlation falls into a weak category [35]. The correlation result is supported by the observation that students with strong mental model criteria do not always possess a good chemistry mindset. Conversely, some students with a low mental model

can still demonstrate a good mindset in chemistry. This weak correlation could also be influenced by other factors, such as students' prior knowledge and the nature of chemistry concepts. As stated in a different study, the effectiveness of mindset intervention depends on its ability to convince participants to alter their mindsets [19]. In our effort to find relevant studies, research uncovering the relationship between students' mental models and chemistry mindsets is lacking. This fact strengthens the novelty of this study.

Table 4. Mental Model and Chemistry Mindset Correlation

		Mental Model	Chemistry Mindset
Mental Model	Pearson Correlation	1	.288**
	Sig. (2-tailed)		.001
	N	122	122
Chemistry Mindset	Pearson Correlation	.288**	1
	Sig. (2-tailed)	.001	
	N	122	122

Similar studies report on the correlation between mental models or chemistry mindsets and other aspects. Demirdogen & Lewis [20] stated that the theory of mindset suggests that students who possess a growth mindset will achieve higher academic success compared to those with a fixed perspective. This hypothesis aligns with the existing data; however, the changes observed are minimal. The relationship between self-efficacy and formative outcomes was fully mediated by masteryapproach and avoidance goals. However, Mindset was not found to predict formative scores, either directly or indirectly through goal orientations [21]. An interesting finding is reported from the study in the USA [36] who found that a growth mindset positively predicted achievement only among students from economically more privileged families, not among those from less privileged ones. Meanwhile, another study reported that educators with a fixed mindset were more likely to implement performance-oriented instructional strategies, emphasizing interpersonal comparisons. In contrast, those with a growth mindset tended to prefer mastery-oriented instructional approaches, focusing on the enhancement of individual skills [37].

Regardless of this weak correlation, effort is required to promote students' mental models and chemistry mindset. Amalia et al. [8] was successful in improving student mental models by applying the cognitive apprenticeship learning model. Moreover, a student's mindset can be transformed into a growth mindset with high learning motivation. This serves as a nudge for teachers to adjust their learning processes effectively, ensuring that the student's mental model and chemistry mindset align in the same direction. Some alternatives to enhance the student's mental model and chemistry mindset include applying learning models that improve conceptual understanding and boost student motivation.

4. CONCLUSION

The study revealed that most students' mental models were classified as initial and synthetic, with only a few categorized as scientific. When the mental models were compared across the three cohorts, the twelfthgrade students' mental models outperformed those of the tenth and eleventh-grade students. The number of students with a scientific mental model in this cohort reflects this. The result is unsurprising considering that the twelfth grade has experienced more chemistry teaching than the other two cohorts. Meanwhile, on average, students' chemistry mindset is 6.41, indicating a tendency towards a growth mindset. However, the effort to strengthen the mindset is still substantially required. A weak relationship exists between students' mental models and their chemistry mindsets. This weak relationship complicates the ability of these variables to predict one another. However, support for students' mental models and chemistry mindsets is expected to serve as an alternative means of improving their understanding of chemistry. Chemistry teaching should deliver not only a focus on cognitive factors but also non-cognitive factors such as chemistry mindset, chemistry identity, motivation, and a positive attitude towards chemistry. Following the study by Ronnel et al [36], it is crucial to analyze the interaction between mindsets and socioeconomic circumstances to understand students' motivation, engagement, and achievement.

AI-ASSISTED TECHNOLOGY STATEMENT

While preparing this work, the authors used Grammarly to enhance language clarity and detect and correct certain misspellings. After utilizing this tool, the authors reviewed and edited the content as needed and took full responsibility for the publication's content.

ACKNOWLEDGEMENT

We would like to thank all the members of H-CERG (Habiddin—Chemistry Education Research Group) for their assistance in data collection and analysis, as well as the Faculty of Mathematics and Natural Sciences at Universitas Negeri Malang.

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Citation: Maar, J.H. (2025) Victor Meyer (1848-1897) Chemist. *Substantia* 9(2): 83-98. doi: 10.36253/Substan-

tia-3439

Received: Feb 21, 2025

Revised: Jun 27, 2025

Just Accepted Online: Jun 30, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

Victor Meyer (1848-1897) Chemist

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Abstract. Victor Meyer (1848-1897) is one of the great organic chemists of the second half of the 19th century. While his extensive experimental work in Organic Chemistry and Physical Chemistry is well known among chemists, little is known about his personal life and his professional career. The aim of this article is to contribute to filling this gap by presenting not only his research activities (aliphatic nitro compounds, oximes, thiophene, aromatic compounds containing iodine, stereochemistry, vapor density determination, pyrochemistry), but also details of his academic career in Zurich, Göttingen, and Heidelberg, as well as his personality and personal life, until his tragic end.

Keywords: Victor Meyer – History of Chemistry – Organic Chemistry – Thiophene – Nitro Compounds – Stereochemistry – Vapor Density.

There are brilliant personalities who, like luminous meteors, pass through the world. Human existence in all its forms and developments is not unfamiliar to them; yet they follow their own path, unconcerned with the world's turmoil everywhere, leaving their marks only to return to the Universe after a rapid victorious run.¹ (Richard Ernst Meyer)

INTRODUCTION

The laconic title of this article is symbolic: we know from Victor Meyer that he was a chemist, and that he made some important discoveries. Rarely we find a chemist who claims not to know Victor Meyer (1848-1897), given the great number of his important discoveries, especially in Organic Chemistry and in Physical Chemistry which are attributed to him. There is hardly a textbook that does not mention him several times, and there are also no Histories of Chemistry that do not give him space, sometimes briefly, due to the importance of his works. There is no chemist or researcher of a related science who does not know Victor Meyer's works. But it is difficult to find a chemist or someone interested in Chemistry who knows something about the life of Victor Meyer, doubtless one of the most important organic chemists of the second half of the 19th century and, in the opinion of Michael

Engel, "the most versatile chemist of his time." ² Besides the obituaries following his tragic and unexpected death, such as those by Georg Lunge (1839-1923)³, Carl Liebermann⁴, Paul Jacobson (1859-1923)⁵, Otto Nikolaus Witt (1853-1915)⁶, or Heinrich Biltz (1865-1920)⁷, among others, all from 1897, there is an extensive and detailed biography written by his brother Richard Emil Meyer (1846 Berlin -1929 Braunschweig), professor at the Polytechnic of Braunschweig, "Victor Meyer - Leben und Wirken eines deutschen Chemikers und Naturforschers" Leipzig 1917, published in the series "Grosse Männer" by Wilhelm Ostwald (1853-1932)8. In 1908, Richard Meyer had already published a 214-page article on his brother⁹ in the *Berichte*. The prophetic final sentence of the Lunge's obituary of Victor Meyer was fully confirmed: "his name will be eternally and greatly honoured in the Histories of Chemistry."10 In London, in 1891, at the jubilee of the Chemical Society, Sir Jocelyn Thorpe (1871-1940), a former student of Victor Meyer, delivered a Memorial Lecture in honour of his master¹¹. Outside Germany, there were an anonymous note in Nature, in 1897, a very short obituary in the American Journal of Chemistry (today the J. Am. Chem. Soc.), and in 1916 a biographical article by B. Horowitz¹². There is also a recent biographical paper by Aleksander Sztejnberg $(2022)^{13}$.

FAMILY, ORIGIN, EDUCATION

Victor Meyer was born in Berlin on September 8, 1848, the son of Jacques Meyer (1816-1892), a manufacturer and merchant of fabrics, from a non-orthodox and non-practicing Jewish family, originally from Inowroclaw, in the Hohensalza district, in the then Prussian province of Posen, and of Bertha Meyer (1822-1895) (no familial relation). The couple had four children: Richard, a chemist and professor at the *Technische Hochschule* of Braunschweig; Victor, subject of this article; Otto, who went into commerce and later managed his father's company; and Clara, who married the sculptor Johannes Pfuhl (1848-1914) (a bust of V. Meyer [1902] by Pfuhl is in the Auditorium of Heidelberg University).

In 1858, Richard and Victor, despite their age difference, were enrolled at the *Friedrichwerdersches Gymnasium*, a traditional school in Berlin, founded in 1681 by the "Great Elector" Frederick William, and closed in 1944. In 1865, Victor completed the course and the final examinations, which granted him access to the university. The young man's interests were manifold, spanning both, the exact sciences as well as the arts and humanities. He devoted more time than usual to the study of

physics and of mathematics (chemistry was not taught at the Gymnasium), but was also engaged with literature, writing poetry; during festivities hold at the Gymnasium he participated in the performance of an anonymous humorous play (in the role of a female character, Pauline Lucca [1841-1908], at the time one of the most famous opera singers; the theatrical experience made him consider becoming an actor). With so many interests, it was difficult to him to choose a university course. His father preferred chemistry: a chemist would be important in his textile industry, and his brother Richard had been studying chemistry in Heidelberg since 1863. At his parents' suggestion, he visited his brother in 1865, was charmed by university life, laboratory work, and new discoveries (in Heidelberg, Bunsen and Kirchhoff had invented shortly before, in 1859, the revolutionary analytical technique of spectroscopy). The visit to his brother was decisive: Victor decided to study chemistry.

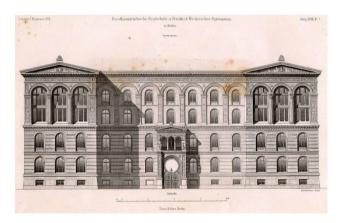


Figure 1 Friedrichswerdersches Gymnasium, building from 1871/1875, drawing by Richard Bohn, 1878, from Zeitschrift für Bauwesen, year 28, 1878, ed. G. Erbkam. (public domain).

Still very young, his parents tried to "keep him at home" for a little longer. "At home," he attended a semester of chemistry at the University of Berlin, where he attended in 1865 August Wilhelm Hofmann's lectures. Later that same year, he transferred to Heidelberg, where he could study with the 'greats': Bunsen, Kirchhoff, Helmholtz, H. Kopp, Erlenmeyer. Heidelberg attracted many students at the time, not for the casinos in nearby Wiesbaden and Baden-Baden, as was said jokingly, but because of the excellence of the faculty and the minimal bureaucracy at the University, and where a thesis in Latin was no longer required. He earned his doctorate under Robert Bunsen (1811-1899) in 1867, at the age of 19. Bunsen appointed him his assistant and tasked him with the systematic analyses of mineral waters, a subject that allowed him to show the extreme accura-

cy and precision of his work. Intending to improve his skills also in Organic Chemistry, he went in 1868 to the Gewerbeschule (Trade School) in Berlin, founded in 1824 and the precursor of the Technische Hochschule of Berlin (1879), where he stayed until 1871. The school was then directed by Adolf Baeyer (1835-1917) and held a great prestige. At that time, Carl Graebe (1841-1927) and Carl Liebermann (1842-1914), who in 1869 isolated the dye alizarin from the root of madder (Rubia tinctorum L.), also worked there. A strong friendship arose between Baeyer and Meyer, which lasted until Meyer's death. At the Technische Hochschule, Meyer had the opportunity to demonstrate his rigorous work, his competence in teaching, and his ability to disseminate new chemical knowledge in lectures delivered to an audience of physicians, lectures which later were published. His first publication from Baeyer's laboratory was a paper on the synthesis of aromatic carboxylic acids from sulfonic acids and formates¹⁴, which became significant in Organic Chemistry (1869). He also studied the structure of chloral hydrate¹⁵, discovered by Liebig (1832) and introduced into therapy as a hypnotic in 1869 by Oscar Liebreich (1839-1908). He further researched, among other subjects, disubstituted benzene, dibromobenzene¹⁶, and proposed a then not accepted formula for camphor¹⁷. Jacobson notes that the diversity of subjects did not allow for a prediction of a future research line but showed already his multiplicity of interests¹⁸.

In 1871, he concluded his thesis for Habilitation at the University of Berlin, "Untersuchungen über die Constitution der zweifach substituirten Benzole"19 (Studies on the Constitution of Doubly Substituted Benzenes). But fate had other plans for him. Hermann von Fehling (1812-1885), professor at the Technische Hochschule of Stuttgart, asked Baeyer to recommend a professor for a second chair of chemistry created at the Polytechnic. Baeyer had no doubts: the candidate was Victor Meyer. Meyer moved to Stuttgart in 1871. He collaborated in the planning of a new laboratory, and there he discovered aliphatic nitro compounds²⁰ in 1872. His stay in Stuttgart was short-lived. In 1872, the chair of Chemistry at the Polytechnic of Zurich became vacant, with Johannes Wislicenus (1835-1902) moving to the University of Würzburg, replacing there the suddenly deceased Adolf Strecker (1822-1871), who had held the chair since 1870.

VICTOR MEYER IN ZURICH, 1872-1884

Karl Kapeller (1816-1888), President of the Swiss Confederation's Council of Education, and in that capacity also of the Polytechnic of Zurich, always sought (and succeeded) in transforming the *Eidgenössische Technische Hochschule* into one of the leading research centres in Europe. He saw in the hiring of Victor Meyer the future presence of a great professor and researcher²¹, succeeding Wislicenus, who was a professor there from 1860 to 1872, and Georg Städeler (1821-1871), professor from 1854 to 1870.





Figure 2 Above: The Zurich Polytechnic, shown is the building by Gottfried Semper (1893-1879), photograph ca. 1880 by an unknown photographer. Baugeschichtliches Archiv, Zurich Polytechnic (public domain). Under: The Zurich Polytechnic after Gustav Gull's (1858-1942) reform, 1915. (Photograph by Thomas Maar).

Several researchers from the University of Zurich, like Weith and Merz, used to do their research at the laboratories of the Polytechnic. The University of Zurich (founded 1833) was a cantonal institution and had less resources than the Polytechnic, maintained by the Swiss confederation. There was no laboratory at the university until 1864, when the Polytechnic received a new laboratory and the old one was transferred to the university.

From Meyer's perspective, however, there was initially not as much optimism and prospects for a prom-

ising future. Upon arriving in Zurich, then a city with approximately 70,000 inhabitants, he felt that he was not well received, encountering indifference and little receptivity from the local population. He arrived with certain reservations. Swiss chemist Adolf von Planta (1820-1895), a student of Liebig and assistant to Kekulé, who resided in Reichenau Castle in the Grisons canton and maintained a laboratory of agricultural chemistry at the Polytechnic of Zurich, wrote to Meyer: "For a Swiss, a chemist who introduces even a single improvement in cheese making is worth more than a chemist authoring 1000 theoretical articles." Meyer admired the work ethic of Swiss people, their continuous activity in production, but, perhaps recalling Planta's observation, he lamented that everything was done having profit in mind²². Those familiar with the history of Switzerland's chemical and pharmaceutical industries would not consider the observation entirely misguided.



Figure 3 Victor Meyer (1848-1897) in Zurich. Photograph by unknown author. Courtesy Oepser Collection for the History of CHemistry, University of Cincinnati.

Regarding his new work environment, the Polytechnic, founded in 1854, operated in a spacious building of magnificent architecture constructed from 1858 to 1864 by the German architect Gottfried Semper (1803-1879), known for the Dresden Opera and the *Burgtheater* in Vienna. The current appearance of the historic building is due to the renovation completed in 1915 by

Gustav Gull (1858-1942). Meyer initially was met with some kind of reservation and suspicion by colleagues and assistants. Exceptions were the professors Wilhelm Weith (1846-1881), later his close friend and confidant, and Victor Merz (1839-1904), born to Swiss parents in Odessa, a student of Liebig in Munich (1861/1862). Merz was actually a professor at the University of Zurich, but collaborated with the Polytechnic. The initial distrust had its reasons: Victor Meyer, an *Ordinarius* (= full professor), was only 23 years old, younger than most of his future students. But Kappeler was convinced of Meyer's competence, and Victor took up his position in Zurich om June 6th 1872.

Initially settled in the house that had belonged to Wislicenus, located in the *Vogelsangstrasse*, in Oberstrass, the northernmost outskirts of the city, Victor Meyer adapted himself gradually to the new context, thanks to his conciliatory and calm temperament, his readiness to help others, his multiple interests, and his hospitality. The apparent indifference of the local population soon disappeared, so that his intellectual and artistic demands led him into the circle around poet and novelist Gottfried Keller (1819-1890), the greatest Swiss writer in German language. At the Polytechnic, quickly emerged a high-level research and teaching group. In a confidence to his brother, Victor Meyer said that the twelve years he spent in Zurich were the happiest of his life.

Attaining academic and financial stability, Victor Meyer married in 1873 in Berlin Hedwig Davidson (1851-1923), his childhood friend and daughter of Moritz Davidson (1812-1852), a doctor in Posen (now Poznań, Poland). The couple had five daughters, three born in Zurich: Else, born in 1874 and deceased at the age of seven from septicemia, a heavy blow to Victor and likely one of the causes of his future depression; Grete (1875-19), who married the painter Fritz Widmann (1868-1937); and Hildegard (1879-1965), married to Kurt Stieler (1877-1963), an actor and theatre and film director, from whom she separated in 1922, moving to the Riviera, where she became known as Hilde Stieler, remembered as an expressionist painter and poet ("Der Regenbogen", Berlin, 1918).

During his long stay in Zurich, Victor Meyer conducted extensive research in Organic Chemistry and in Physical Chemistry. As we have seen, his scientific contribution however began much earlier, in Baeyer's laboratory in Berlin and at the Polytechnic of Stuttgart. A more detailed description of Meyer's scientific work will be presented later on in this article.

After establishing himself, Meyer returned to work in Zurich, initially revisiting two themes he had already

been studying. Since Kekulé presented his benzene formula in 1865, it became important to determine how substituents are positioned in disubstituted benzene compounds (ortho, meta, para), and Meyer participated in these experimental studies, alongside with the independent studies of Wilhelm Koerner (1839-1925) in Giessen (1860) and of Peter Griess (1829-1888) in England. A theme started in Stuttgart, the reaction of alkyl iodides with silver nitrite, obtaining aliphatic nitro compounds, was studied in detail, demonstrating that for an experienced chemist, a simple theme such as aliphatic nitro compounds can lead to a range of new discoveries²³. Meyer soon noticed the isomerism between aliphatic nitro compounds and organic nitrites, the acidic nature of the -CH₂- group adjacent to NO₂, a way to differentiate primary, secondary, and tertiary nitro compounds (1875, reaction with nitrous acid), "nitrolic"24 and "pseudo-nitrolic"25 acids, the behavior of hydroxylamine against nitrous acid, the formation of alkyl-aryl azo compounds. The increased reactivity of the methylene group CH₂ adjacent to the nitro group NO₂ led him to investigate whether there was also increased reactivity of the CH₂ adjacent to other groups such as carboxyl, CO, or -CH₂CH₂COOH etc. Thus, he arrived at nitroso compounds, such as nitrosoacetic acids (nitrosation, substitution of a hydrogen atom by a nitroso group, 1873/1874).

Two other important discoveries by Victor Meyer in Organic Chemistry date from his Zurich period, both in 1882: oximes²⁶, in partnership with his student and collaborator Alois Janny²⁷, and thiophene. Oximes are formed by the reaction of aldehydes and ketones with hydroxylamine, resulting in aldoximes and ketoximes. Oximes were important "derivatives", and hydroxylamine (discovered by Lossen in 1865) is a reagent in "classic" organic analysis. Ketoximes were the subject of studies on isomerism. Acetoximes were the topic of Janny's doctoral thesis (1883). An important oxime synthesized by Meyer and Janny in 1882 was dimethylglyoxime, introduced into Analytical Chemistry (nickel detection) in 1905 by Lev Chugaev (1873-1922)²⁸.

The story of the discovery of thiophene²⁹ is anecdotal. A reaction used by Victor Meyer in his classes to qualitatively detect benzene was Baeyer's "indophenin reaction", in which benzene would produce a blue color reacting with a mixture of isatin and sulphuric acid. At an occasion the reaction failed, and it was necessary to find a reason: another compound similar to furan, which was called thiophene, should accompany benzene. With Traugott Sandmeyer (1854-1922), the precision mechanic whom Meyer converted to his assistant and professor, he began to investigate a synthesis for thiophene.



Figure 4 Traugott Sandmeyer (1854-1922), Victor Meyer's collaborator. Photograph, ca. 1910, anonymous. Courtesy Oesper Collection for the History of Chemistry, University of Cincinnati.

Amidst his successful advances in Organic Chemistry, in 1876 Meyer became suddenly interested in a topic from Physical Chemistry: the determination of the vapour density of a volatile liquid or of a liquid easy to vaporize. Determining vapour density allows the determination of molecular mass. The procedure is simple: the volume of a precisely known mass of a volatile liquid is determined, and by the general gas law, the molecular mass of the substance under study could be calculated. To perform the measurements, Meyer constructed a very simple apparatus (1876), consisting of a tube for evaporation, which ends at the bottom in a bulb containing a heating liquid (water for substances that evaporate below 100°C). In this tube is placed another tube containing the liquid to be evaporated. Then the entire device is hermetically sealed. At the top of the heating tube, a gas burette measures the volume of gas formed³⁰. There are many modern variants of this simple "Meyer apparatus," which has since become widely used in laboratories.

Meyer's successor in Zurich was Arthur Hantzsch (1857-1935), a doctoral student of Johannes Wislicenus. Hantzsch became a professor in Würzburg in 1893, and in Leipzig from 1903 to 1927, invited by Ostwald to succeed Wislicenus, deceased in 1902.

VICTOR MEYER IN GOTTINGEN, 1884-1889

Amidst his numerous activities in Zurich and the planning, in collaboration with Professor Georg Lunge, of a new laboratory, Victor Meyer received an irresistible offer to assume the chair of Chemistry at the University of Göttingen, vacant following the death of Hans Hüb-

ner (1837-1884), who had succeeded Friedrich Wöhler (1800-1882) in 1882. This opportunity offered a return to researching and teaching in his homeland, but presented a difficult choice, as Meyer was perfectly adapted to life in Zurich and to his work at the Polytechnic. After a period of rest on the Riviera, due to increasing health problems, Meyer accepted the offer.

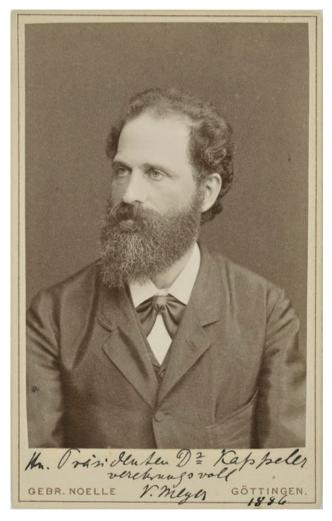


Figure 5 Victor Meyer in Göttingen. Photograph, by Gebrüder Noelle, 1886. Archives of the Library of the Zurich Polytechnic. (public domain).

He arrived in Göttingen in 1885, coming directly from the Riviera, adapting rapidly to the academic, social, and cultural environment of the city. His health was the only concern. In Göttingen, the last two of the couple's five daughters were born: Elisabeth (1885-1940), who married Carl Willmans (1875-1945), a professor of psychiatry in Heidelberg, and Irmgard (1888-1942), married to jurist and judge Guido Leser (1883-1942). Guido

Leser and Irmgard Leser committed suicide in Berlin, in October of 1942, to avoid their deportation to the concentration camp of Theresienstadt.

At the Institute of Chemistry in Göttingen Meyer found a group of assistants, including Ludwig Gattermann (1860-1920), Rudolf Leuckart (1854-1899), and Karl von Auwers (1863-1939). From Zurich, he brought Traugott Sandmeyer as an assistant for a year, to continue his research on thiophene. Their first task was to complete researches which that were underway in Zurich; in 1883, Meyer and Sandmeyer synthesized thiophene from acetylene and sulphur³¹. Over the course of 20 years, with various collaborators, Meyer researched thiophene and its derivatives, resulting in many unsuspected discoveries³². This early example not only represents exhaustive study (with the resources available at the time) but also signifies a growing specialization in Organic Chemistry, necessary for fully understanding a subject, but potentially stifling the chemist's creativity. All these studies on thiophene culminated in 1888 with the publication of the book "Die Tiophengruppe."

Another ongoing research project was the determination of vapor density, which was completed with the participation of Sandmeyer and Gattermann. They conducted vapor density determinations at very high temperatures (pyrochemistry), wherein molecules such as Cl₂ or Br₂ were converted into atoms. Victor even speculated: could we not fragment atoms if we achieved sufficiently high temperatures? The pyrochemical studies, including those from Zurich, were conducted in collaboration with Carl Langer (+1935). In 1885, Meyer and Langer published the book "Pyrochemische Untersuchungen." In 1888, Meyer began planning a new laboratory, next to the Wöhler's historical laboratory (1860), later demolished. The new laboratory had a chimney 20 meters high, for pyrochemical experiments.

Meyer did not get to use his laboratory, as an invitation from Heidelberg came. The laboratory was completed by Otto Wallach (1847-1931), Meyer's successor in Göttingen, and Nobel Prize winner in Chemistry in 1910 for his systematic study of terpenes.

VICTOR MEYER IN HEIDELBERG, 1889-1897

The fame of the University of Heidelberg in the 19th century was largely due to the activity of Robert Bunsen (1811-1899) as a professor from 1852 to 1889, when he retired. Bunsen himself recommended Victor Meyer, his former doctoral student, as his successor. Once again, Meyer did not decide immediately, as he was well-established in Göttingen. Before making a decision, he spent

some time in Bordighera, on the Italian Riviera, where he encountered Baeyer, Emil Fischer, Otto Wallach, and researchers from other fields. Finally, on the third invitation, to the dismay of the University of Göttingen, Meyer accepted.

From Göttingen he brought five assistants with him to Heidelberg: Paul Jacobson, Paul Jannasch (1841-1921), Karl von Auwers (1863-1939), Ludwig Gattermann (1860-1920), and Robert Demuth³³. From Göttingen, he brought also Emil Knoevenagel (1865-1921) and E. Ney. Many of these assistants and doctoral students of Meyer later became professors (Gattermann in Freiburg, Knoevenagel in Heidelberg, Leuckart in Göttingen).

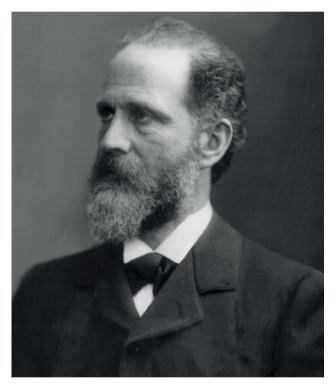


Figure 6 Victor Meyer in Heidelberg. Photograph, F. Langbein & Co., 1890. Archives of the Heidelberg University (public domain).

Despite already being well-known for his discoveries, Meyer continued to engage in intense activity in Heidelberg. Initially, he still focused on the determination of vapor density, but later he turned exclusively to topics in Organic Chemistry. Initially, he dealt with the positioning of substituents in aromatic compounds, then with two new themes: aromatic compounds containing iodine and stereochemistry. Although already existed methods for introducing iodine into an aromatic ring, the systematic study of aromatic compounds containing iodine promoted by Victor Meyer and his collaborators

from 1892 to 1894 represents a thorough investigation of these compounds: iodobenzene, iodosobenzene, iodoxybenzene, iodonium salts, iodobenzoic acid, iodosobenzoic acid, and iodoxybenzoic acid.

The second major theme was stereochemistry, a term coined by Meyer in Göttingen in 1888. Abandoning the idea of a 'point-like' atom and considering that the atom has volume and dimensions (1890), the empirical aspect entered into problems related to the spatial structure of chemical compounds, for example, in "steric hindrance" (1894), a concept developed in parallel with Carl Adam Bischoff (1855-1908), who was then a professor at the Polytechnic of Riga. An example of this "steric hindrance" is as follows: benzoic acid easily reacts with alcohols to form esters; however, 2,4,6-trimethylbenzoic acid does not react because the volume occupied by the three methyl groups prevents the approach of the alcohol. For a time, this effect was called 'Meyer's rule'. Meyer also observed, with Auwers (1890), that there can be hindrances to free rotation (Beschränkte Drehbarkeit) of single bonds - C - C -. 34 Meyer thus pioneered the study of 'steric hindrance' and was the first to present van't Hoff's theory of the tetrahedral carbon in the university lectures.

Victor Meyer's successor in Heidelberg was Theodor Curtius (1857-1928), a doctoral student of Kolbe in Leipzig (1882), a notable researcher of nitrogenous organic compounds, who held the position until his retirement in 1926.

THE PUBLICATIONS

Victor Meyer wrote easily, and due to his great interest in literature, elegantly about non-chemical subjects. In chemistry, his first book dates to his time in Zurich, co-authored with Frederick Pearson Treadwell (1857-1918), professor of Analytical Chemistry, titled "Tabellen zur Qualitativen Analyse" (Tables for Qualitative Analysis, 1884, Bern, 8th edition 1918). His most important work was a new textbook on Organic Chemistry, "Lehrbuch der Organischen Chemie", 5 volumes, co-authored with Paul Jacobson (1859-1923), published in 1883. Regarded as the best text on the subject since Kekulé's famous work (7 volumes, 1859/1887), it went through several editions following Meyer's death, overseen by Jacobson. A new edition appeared in 2023. In 1888, Meyer published "Die Thiophengruppe" (The Thiophene Group), an early example of the specialization that would later dominate chemistry. "Pyrochemische Untersuchungen" (Pyrochemical Investigations), with Carl Langer, dates from 1885. This was followed in 1890 by "Ergebnisse und Ziele der Stereochemischen

Forschung" (Results and Objectives of Stereochemical Research) and the pamphlet "Chemische Probleme der Gegenwart" (1890, Chemical Problems of the Present), spanning just 42 pages. The literary character and elegant writing style are evident in "Aus Natur und Wissenschaft" (From Nature and Science, Heidelberg, 1882) and in the account of a holiday trip, "Märztage auf dem Kanarischen Archipel" (March Days in the Canary Archipelago, Leipzig, 1893).

THE TRAGIC END

The end of the great chemist was tragic. Already in his Zurich days, his - imperceptible - sensitive temperament led to frequent episodes of depression, a persistent insomnia, and after each semester, extreme exhaustion from his intensive work pace. Vacations and trips revived him, but the cycle repeated each semester. It is supposed that doctors prescribed him large quantities of medications. Bromine and chlorine vapours, along with exposure to other reagents, must also have seriously affected his health. Exhaustion from overwork, severe neurasthenia, chronic insomnia, recurring depressions, fear of losing his mental faculties - all led to his suicide on the night of 7-8 August 1897. Returning from a party, he retired to his room, requesting not to be disturbed until morning. When the door was forced open, he was found dead, still in his party attire, with a vial of cyanide in his hand. In the pocket of his jacket was found the formidable long poem "Sturz und Erhebung" (Fall and Ascent), written by Meyer himself in 1884/1885, which begins³⁵:

"Wer bist du
Schecklich blickender Dämon,
Drohende Furie, die in das Herz mir
Bohrend dringt mit glühender Spitze,
Dass ich des Nachts vom weichen Lager
Aufschnelle – bebend, bedeck mit Angstschweiss,
Das Auge trocken, stier, todsuchend der Blick?
Wehe mir, ich kenne dich!
Verzweiflung ist dein Name,
Entsetzen dein Hauch!"

Or, translated into English:

"Who are you,
You, terrible oppressive demon
Of threatening fury that in the heart
Penetrates me with burning spear,
As soon as at night on my soft bed
I shudder – trembling, covered in the sweat of fear,
Dry eye, fixed gaze seeking death!

Woe is me, I recognize you! Despair is your name, Horror your breath!"

An example of how little was known about Victor Meyer appears in the obituary published in the American Journal of Chemistry: "It is generally believed that the indirect cause of his death was overwork. He was repeatedly warned to conserve his strength, but his innate desire to be active was uncontrollable³⁶." This is only part of the truth. Victor Meyer was buried in the Bergfriedhof, in Heidelberg, in the presence of Bunsen, Baeyer, friends, and a representative of the Grand Duke of Baden. In 1885, Victor and his wife converted to Christianity, not for religious conviction, but to facilitate social and academic advancement. Victor Meyer was a member of the Academies of Berlin and Munich, the Leopoldina Academy, the Scientific Societies of Göttingen and Uppsala, and received the Davy Medal from the Royal Society in 1891 for his method of determining vapor densities at high temperatures. From the Grand-Duke of Baden he received the title of Geheimrat (privy councillor). He served as president of the German Chemical Society in 1897.

HIS STUDENTS

Victor Meyer had many students, in Zurich, in Göttingen and in Heidelberg, but surprisingly few of them reached prominent positions, despite the renown of Heidelberg University at the time and the very high level of Victor Meyer's research. Many of his doctoral students as well as collaborators in his numerous research projects no longer appear in texts on the History of Chemistry, except perhaps in histories of local interest - a matter we do not know. Among his compatriots, there are a few exceptions, chemists who had respectable careers, perhaps the most notable is Traugott Sandmeyer (1854-1922) in Zurich, remembered to this day for the Sandmeyer reaction (1884). Also mentioned are Emílio Noelting (1852-1922), professor at the School of Chemistry in Mulhouse, a dye specialist (originally from the Dominican Republic, son of a German merchant); Casimir Wurster (1864-1913), known for "Wurster's red"; in Göttingen, Heinrich Biltz, Emil Knoevenagel (1865-1921), Ludwig Gattermann (1860-1920); in Heidelberg, Max Bodenstein (1871-1942) and Karl von Auwers (1863-1939), who already had a doctorate with Hofmann, all frequenters of the History of Chemistry. Victor Meyer had many English and North American students, but few have a particular interest in the History of Chemis-

try; others pursued activities in related fields. Among the English students, Sir Jocelyn Field Thorpe of the Imperial College London (teacher of Sir Christopher Ingold [1893-1970], establishing a link between the Imperial College, a fuel specialist; John Joseph Sudborough (1869-1963), professor at the Indian Institute of Technology in Bangalore (1911/1926) and author of a textbook on Organic Chemistry (1912); among the North Americans, Forris Jewett Moore (1867-1926) of the MIT, Francis Benedict (1870-1957), who became a nutrition specialist, and Francis Despard Dodge (1868-1942), an specialist in essential oils. With Wilhelm Michler (1846-1889), assistant and eventual substitute for Victor Meyer in Zurich, Meyer's influence reached Latin America: after a trip to Buenos Aires and southern Brazil in 1881, Michler was a professor at the Polytechnic School of Rio de Janeiro (1881/1889)³⁷, studying fats and vegetable oils.

VICTOR MEYER'S SCIENTIFIC WORK

Judging by the mere enumeration of the topics addressed by Meyer in his research, one cannot perceive the extent of his work in Organic Chemistry. It is a characteristic of the astute researcher to foresee, like in a chess game, the next steps of his work. Victor Meyer's immense scientific output in just over twenty years of academic life allows us to assess the loss his premature death was to science.

Aliphatic Nitro Compounds ("Nitroparaffins")

Aromatic nitro compounds had been known since 1835, when Eilhard Mitscherlich (1794-1863) obtained nitrobenzene by nitration of benzene. This compound was of enormous importance in the history of Organic Chemistry, as Nikolai Zinin (1812-1880) obtained aniline by reduction of nitrobenzene (1842). Aniline, through the formation of diazonium salts (1858, Peter Griess, 1829-1888) leads to azo compounds and dyes, and by Sandmeyer's reaction to a variety of substances, being a key piece in organic synthesis. For example, in 1875 Victor Meyer obtained, with his student G. Ambühl, the first aromatic-aliphatic³⁸ compound, benzene-azo-nitroethane, C₆H₅-N=N-CH₂CH₂-NO₂. Aliphatic hydrocarbons, however, cannot be nitrated: nitric acid fragments the carbon chain.

In 1872, at the Polytechnic School of Stuttgart, Victor Meyer and his collaborator Stüber³⁹ developed a process to obtain aliphatic nitro compounds, a substitution reaction: they treated amyl iodide with silver nitrite (AgNO₂) and obtained a compound with the formula

 $C_5H_{11}NO_2$, which Meyer named nitropentane (Meyer's reaction). That same year, Hermann Kolbe (1818-1884), in Leipzig, obtained nitromethane using the same process, but unlike Meyer, he lost interest in the subject and published his work three months later. Meyer continued to explore the topic for 20 years, from various angles⁴⁰. For example, he quickly recognized the isomerism between aliphatic nitro compounds and organic nitrites. After Conrad Laar (1853-1929) defined the concept of tautomerism in 1885, and with Meyer discovering the acidic nature of the hydrogen atom adjacent to the NO_2 group, it was realized that aliphatic nitro compounds are tautomers of nitronic acids, discovered by John Ulric Nef (1861-1915) in 1894 (Nef reaction⁴¹) (and apparently already in 1893 by Dmitri Konovalov [1856-1929]).

Victor Meyer's research group continued to study nitro compounds in Göttingen and Heidelberg. In 1875, they developed a method to differentiate primary, secondary, and tertiary⁴² nitro compounds. Primary nitro compounds form a red solution of nitrolic acid with nitrous acid in ether, turning red in basic medium; secondary nitro compounds form a blue solution of a nitronitroso compound (pseudonitrole) with nitrous acid; tertiary nitro compounds do not react under these conditions.

The discovery of oximes

Hydroxylamine was a frequent reagent in Meyer's hands. In 1882, with Alois Janny, he discovered oximes through the reaction of hydroxylamine with aldehydes and ketones, forming aldoximes and ketoximes, respectively⁴³. Oximes feature a C = N bond, which gives rise to geometric isomerism, studied in 1887 by Ernst Beckmann (1853-1923) in Leipzig. The rearrangement of ketoximes to lactams⁴⁴ was termed by Victor Meyer as the "Beckmann rearrangement" in 1886.

Thiophene

As we saw earlier, the history of the discovery of thiophene is anecdotal. In his classes, Victor Meyer used to demonstrate a qualitative detection of benzene with Baeyer's "indophenin reaction", where benzene would turn blue with a mixture of isatin and sulphuric acid. In one class, benzene did not turn blue; it was a highly pure benzene obtained from the decarboxylation of benzoic acid, whereas the benzene typically used was extracted from coal tar. Initially it was thought that an "activated benzene" caused the colour, but a rigorous analysis led to the discovery of a new heterocyclic compound, simi-

lar to pyrrole and furan, which was named thiophene. Meyer and Sandmeyer developed a synthesis for thiophene in 1883, starting from acetylene and sulphur.

Still in the field of thiophene, Meyer attempted to synthesize a thiophene homologue containing five carbons ("pentathiophene"), starting from thiodiglycol, but without success: he obtained bis(2-chloroethyl)sulphide in 1886⁴⁵. This compound was not new; it had been synthesized in 1860 by Frederick Guthrie (1833-1886), and the study of its toxicity cost Albert Niemann (1834-1861) his life. Known as "mustard gas", it became the infamous chemical warfare agent 'yperite' used during World War I by the Germans in Ypres (1917) and by the Allies in Cambrai (1918). Its chemotherapic activity was discovered in the 1940s (Alfred Gilman, [1908-1984]). In total, Victor Meyer and his collaborators published 106 articles on thiophene, in five years of research (1883/1888), supplemented by 25 articles from other research groups, such as the Volhard-Erdmann synthesis, starting from sodium succinate and P₂S₇. Jacob Volhard (1834-1910) was a professor in Halle, and Hugo Erdmann (1862-1910) was his student, later professor in Halle and at the Berlin Polytechnic. With all this material, Victor Meyer published his book "Die Thiophengruppe" in 1888 in Braunschweig.

Aromatic Compounds Containing Iodine

The introduction of iodine into aromatic rings became easier with the Sandmeyer reaction. There were earlier, much more difficult methods, developed by Heinrich Hlasiwetz (1825-1875) and Paul Weselsky (1828-1889), (1869)⁴⁶, by Kekulé, and by Paul Schutzenberger (1829-1897) in 1862. From 1892 to 1894, in Heidelberg, Victor Meyer studied, with a group of students, still unknown compounds - aromatic compounds containing iodine: iodobenzene, iodosobenzene, iodoxybenzene, and iodonium salts, iodobenzoic acid, iodosobenzoic⁴³ acid, and iodoxybenzoic acid. Of all these compounds, iodosobenzoic acid had the greatest consequences for the study of Organic Chemistry ⁴⁷.

It is interesting to observe how experimentation at that time led to a logically grounded chemical reasoning, despite apparent contradictions 48 . For example, Meyer and his collaborator W. Wachter observed that adding nitric acid to o-iodobenzoic acid resulted in a compound containing no nitrogen, and the determined formula $C_8H_5O_2I$ suggested an oxygen atom bonded to iodine. This fact was the starting point for several studies conducted over several years. The resulting acid, $C_8H_5O_2I$, has oxidizing power: heating it with HCl releases chlorine, treating it with KI in acidic medium releases

iodine, and the ortho-iodobenzoic acid is formed again. It can conclude that oxygen is combined with iodine, which becomes trivalent. The formula for iodosobenzoic acid is then, in our notation $C_7H_5IO_3$.

The low stability of this structure led several researchers to suggest not confirmed cyclic formulas.

Six years earlier, in 1886, Conrad Willgerodt (1841-1930), at the University of Freiburg, obtained the first polyvalent aromatic compound containing iodine, (dicloro)iodobenzene, C₆H₅ICl₂ in today's notation, obtained by adding chlorine to iodobenzene⁴⁹. Willgerodt continued to study this subject and in 1892 obtained iodosobenzene, C₆H₅IO,⁵⁰ from the above compound. Willgerodt also studied meta- and para-iodosobenzene, but their properties differed greatly from those of the ortho-derivative. This "territory invasion" sparked a brief controversy between Meyer and Willgerodt. Meyer acknowledges Willgerodt's priority in the discovery of (dicloro)iodosobenzene and would also concede priority for iodosobenzene if it were not for the differences in properties of the compound obtained by Willgerodt, which leads him to dispute these results⁵¹.

Victor Meyer and Christoph Hartmann continued this research, synthesizing in 1893 iodoxybenzene acid⁵² from iodosobenzoic acid:

$$C_6H_4$$
 $I = O$ C_6H_4 IO_2 $COOH$ $COOH$

Experiments conducted in collaboration with Chr. Hartmann led to a new group of compounds, iodonium salts (analogous to ammonium and sulfonium salts) ⁵³: treating iodosobenzene successively with sulfuric acid, KCl, and other reagents, the following sequence is obtained:

$$C_6H_5IO \rightarrow C_6H_5I + C_6H_4IO_2 \rightarrow (C_6H_5)_2$$
-I-OH

Stereochemistry

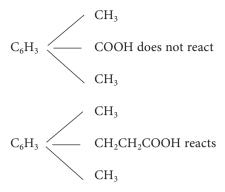
Victor Meyer's last comprehensive research theme was stereochemistry. He coined the term "stereochemistry" himself in 1888. Starting from 1894, his investigations revolved around what would later be called "steric hindrance". Meyer was a pioneer in studying

stereochemical effects on reaction mechanisms, and along with van't Hoff and Wislicenus, he elevated stereochemistry to a scientific status, advocating for the three-dimensional structures of organic compounds. Carl Adam Bischoff (1855-1908), a professor at the Polytechnic of Riga, was a partner in these investigations. Even before his systematic studies on steric hindrance, Meyer observed in 1890, with his collaborator Karl von Auwers (1863-1939), that there were restrictions on free rotation around a single C-C bond due to the presence of bulky substituents (Beschränkte Drehbarkeit)54. Decades later, these studies led to conformational analysis, a subject researched by Sir Derek Barton (1918-1988) and by Odd Hassel (1897-1981), who were awarded the Nobel Prize in Chemistry in 1969. Interestingly—or perhaps not-neither Barton nor Hassel mentioned the pioneer Victor Meyer in their respective Nobel Lectures, as if current knowledge did not rely on prior discoveries...

But let us start with the early experiments by Victor Meyer's team, which involved aromatic carboxylic acids, many of which were then still unknown and had to be synthesized; the property studied was the higher or lower yield in their esterification⁵⁵. A multitude of compounds and reactions led to the "ester law" or Meyer's Law⁵⁶, which enabled not only the determination of structures but also the production of very specific compounds.

Meyer observed that benzoic acid yields 92% ester during esterification, whereas mesitylbenzoic acid yields only 9%. This was attributed to the presence of three methyl groups in the latter case, which hindered esterification; however, durylbenzoic acid, an isomer of mesitylbenzoic acid, yielded 90% ester. Thus, the different ester yields were due to another factor. Polyaromatic carboxylic acids entered the scene: pyromellitic acid (1,2,4,5-tetracarboxybenzene) forms four esters, while the isomer prehnitic acid (1,2,3,4-tetracarboxybenzene) forms only two esters. The reason for the lack or low yeld of certain esterifications was the large volume of groups in the ortho position to the carboxyl group, considered in three dimensions: CH₃, and carboxyl itself⁵⁷. Many other aspects can be considered: mesitylcarboxylic acid forms minimal amounts of ester, but mesitylacetic acid forms esters easily⁵⁸.

There are many more situations explained by stereochemistry, but a detailed exploration of these situations is not within the objectives of this article. Nonetheless, it should be mentioned that esterification occurs when the carboxyl group is distant from bulky groups that hinder the reaction.



Also in the formation of keto-oximes can occur steric hindrance, among other reactions examined by Victor Meyer and his collaborators.

Determination of Vapor Density

By measuring the vapor density of substances, it is possible to determine their molecular mass, and various methods existed for this purpose. The first to use vapor density comparisons to determine molecular weights was Jean-Baptiste Dumas (1800-1884) in 1826, for liquids and solids that were easy to evaporate. Due to many uncertainties about atoms and molecules, this method initially did not attract much attention. It allowed the determination of vapor density for substances with boiling points below mercury's evaporation point. Dumas's method was improved by Henri Etienne Saint-Claire Deville (1818-1881) and Louis Joseph Troost (1825-1911), for temperatures up to 1400°C, by Carl Graebe and others, to allow for the determination of vapor density of substances with higher boiling points.

Victor Meyer developed a method to determine vapor density, and consequently molecular mass, at high temperatures. The idea is simple: determine the volume of a precisely known mass of a volatile liquid without losses, and using the general gas law, calculate the molecular mass of the substance under study. To determine vapor density, Meyer constructed an apparatus, also very simple. An evaporation tube ends at the bottom with a bulb containing a liquid heating bath (water for substances that evaporate below 100°C). Inside the tube, another tube contains the exact amount of liquid to be evaporated. The entire device is hermetically sealed. At the top of the heating tube, a gas burette is attached to measure the volume of gas formed⁵⁹. There are many modern variants of this simple "Meyer apparatus," which became widely used in laboratories. Meyer intended to work above the boiling point of sulphur (444.6°C) and used mercury or Wood's metal (an alloy of Bi, Pb, Cd, and Sn)⁶⁰ as the heating material.

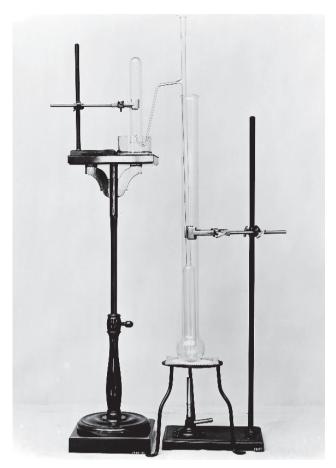


Figure 7 Victor Meyer's Apparatus for vapor density determination. Courtesy Wellcome Foundation, London.

Widely used in its time, the method was later replaced by others, such as tonometry, cryoscopy, and ebulliometry.

Pyrochemical Investigations

Pyrochemical investigations (at high temperatures) are somewhat a continuation of determining molecular masses by measuring vapor density, initially focusing on "substances for which molecular mass determination was of great theoretical importance." These substances were essentially inorganic substances and elements with structures not yet definitively established. The first substance analysed was phosphorus pentasulfide, P₂S₅: the vapor density was determined at high temperatures and in a nitrogen atmosphere. Determining the formula for indium chloride, InCl₃, allowed for the correct placement of indium (an element discovered in 1863 at the Freiberg School of Mines by Ferdinand Reich and Theodor Richter) in the periodic system⁶¹. Other substances studied included⁶²: Sn₂Cl₂, ZnCl₂, Fe₂Cl₆, Sb₄O₆, CdBr₂.

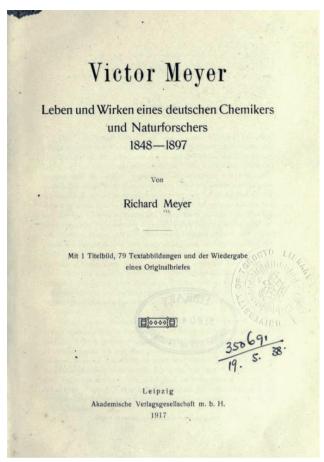


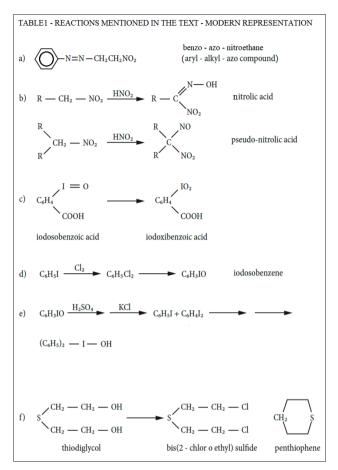
Figure 8 Frontispiece of Victor Meyer's biography, 1917, by his brother Richard Meyer (1846-1926)

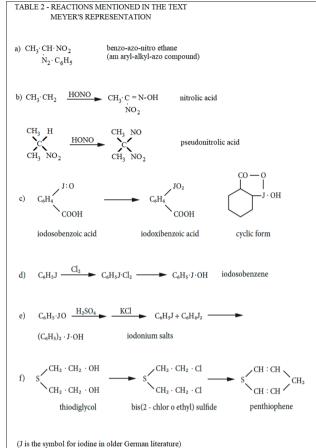
Many doubts were thus clarified. The dissociation of the iodine molecule, I_2 , was also studied, a subject definitively clarified by Max Bodenstein (1871-1942) in the context of photochemistry.

The determination of molecular masses by measuring vapor density was initiated by Victor Meyer in Zurich in 1876, then interrupted, resumed in Göttingen (construction of a special laboratory), and in Heidelberg. The innovation introduced in Heidelberg was working at two temperatures: vaporization at very high temperatures and measuring density at room temperature. Meyer and Heinrich Biltz published a historical account (1889)⁶³.

Other Investigations

The investigations discussed above do not exhaust Victor Meyer's interests in Organic Chemistry and Physical Chemistry. In high-temperature chemistry, there is the study of partial combustion of gases and many publications that do not fit into Meyer's major





research projects, which Richard Meyer in his biography calls *Verschiedenes* (= various), without going into greater detail⁶⁴. We will also not delve into more details, although some interesting topics are mentioned, such as: a synthesis of phenylhydrazine from diazonium salts⁶⁵ (1883), obtaining and studying the properties of 2-nitroethanol⁶⁶ (1890), or, contrary to van't Hoff and Baeyer, confirming that the carbonyl group in glucose is aldehyde and not ketonic (1880).

CONCLUSION

The extensive experimental work of Victor Meyer did not, for the most part, arouse much interest in the researcher Victor Meyer himself. Yet, his numerous works, carried out in just over twenty years, allow him to be listed alongside names like Wurtz, Friedel, Kolbe, Claisen, Curtius, Wislicenus, Butlerov, and others, who, in the typology of Thomas Kuhn, are categorized as "normal" scientists. These individuals were extremely

productive but did not spark "small revolutions" in the *corpus* of Organic Chemistry, unlike Laurent, Gerhardt, Liebig, Wöhler, Kekulé, Hofmann, or Baeyer. Many reasons could be pointed out to explain the lack of interest in Meyer as a character, but in all cases, he would remain an exception. Of simple origin, with a calm and conciliatory temperament, interested in literature and music, and a lover of walks and travels—much like many other chemists of his time—Victor Meyer remains an exception.

Even though the human side of scientists deserves respect and consideration, it can be said that Meyer's work has remained and continues to be relevant, aside from some details that escape those who do not master the German language, in which he published all his research. The best way to conclude his biography is to recall a passage from his pamphlet "Current Chemical Problems," which demonstrates his precise understanding of the evolution of Chemistry. After discussing the relatively recent origin of Chemistry (for him, at the end of the 18th century—a common view at the time and

still today) and Kant's opinion about Chemistry (not a "true science" because it lacks mathematization), he outlines the great advances in Chemistry:

"...the admirable successes of atomic theory and structural doctrines; the synthesis of the most complicated organic compounds; the beneficial multiplication of our pharmaceutical arsenal; the total restructuring of our industrial activity; the planned mode of production, which a renowned technologist called the obtaining of 'gold from waste.'"

It is a hymn of praise to Chemistry in front of scientists who rely exclusively on Mathematics and Physics⁶⁷.

SOME WORDS ABOUT RICHARD MEYER (1846-1926)

We would not have so many details about the life, personality, and scientific production of Victor Meyer if it were not for the extensive biography dedicated to him by his brother Richard Meyer. As Richard was also a chemist, it was easy for him to explain Victor's research

projects, from the various places where he worked. Out of familial respect, the final aspects concerning Victor's illness and tragic death are not explored in the biography, which remains pragmatic and impersonal, despite the abundance of letters and documents dissected in it.

Richard Emil Meyer was born in Berlin in 1846. He studied Chemistry at the University of Berlin with Heinrich Rose, Gustav Magnus, and Franz Leopold Sonnenschein (1817-1879), a specialist in Analytical Chemistry and forensic chemistry, in whose laboratory he conducted his experimental studies. In 1865, he transferred to Heidelberg, where he was a student of Kirchhoff, Kopp, and Helmholtz. Finally, he defended his doctoral thesis in Göttingen under Hans Hübner in 1868: a study on the element indium, discovered a few years earlier. Before becoming a professor of Chemical Technology (1889-1918) and Chemistry (1899-1918) at the Polytechnic of Braunschweig, he was a professor of Physics and Chemistry at a cantonal school in Chur, Switzerland, and defended his Habilitation in 1886 with Baeyer in Munich. He researched various subjects (fluorescein and fluorescence, phthaleins, acetylene polymerization) and dedicated himself to scientific dissemination and the history of Chemistry. He passed away in Braunschweig in 1926⁶⁸.

SOME WORDS ABOUT HILDE STIELER (1879-1965)

Hildegard, the third of Victor Meyer's five daughters, was born in Zurich on March 29, 1879. With a talent for music and poetry, she studied piano in Munich, where she met the actor Kurt Stieler (1877-1963), whom she married in 1902, and subsequently accompanied him in his performances in Leipzig and Berlin. Since 1917, she published her first expressionist poems in the expressionist and socialist magazine "Die Aktion" and in other magazines. She separated from Stieler in 1922 (divorce in 1926), and went to live with the painter Erich Klossovski (1875-1949) in Paris and later on the Riviera, in Saint-Cyr-sur-Mer and in Sanary-sur-Mer, where she passed away. Through marriage to the former monk and Dutch writer Robert de Witt, she acquired Dutch citizenship. She left volumes of poetry ("Der Regenbogen"), 1919; "Die Edelkomparsin von Sanary" (2007, translated from French; encounters with Rilke, Alma Mahler, Aldous Huxley, Thomas Mann), novels, and paintings in the expressionist style. Thus, the love for literature always demonstrated by Victor survived for many decades through the pen of his daughter. Here is one of Hilde Stieler's expressionist poems, "Weihe"69 (= Consecration):

WEIHE

Mitten im Lärm von Allen, die lügen im Lachen und im Reden.

Unvermutet ward mir das Geschenk eines Lächelns voll Zartheit und Güte.

Ich will nicht mehr Gott im Flammenbusche suchen.

Nicht im Sehnen nach fragwürdigen Wunder nutzlos vergehn.

Nein, ich will fortan Gottes Offenbaren darin erkennen.

Das mir im Dunkel ein Auge lächelt.

Or, in the English translation:

Amidst the noise of everyone who lies while smiling, and talking,

Unexpectedly there came to me the gift of a smile full of gentleness and kindness. I no longer want in the burning bush to seek for God. Not on the pursuit of doubtful miracles disappear without purpose...

No, I want now the presence of God to recognize when in the darkness looks at me a smiling eye.

FINALE

The reader may find it strange that this article, which presents the pragmatism of empirical results and the disguised logic of each set of experiments, ends in verses. However, upon reading the verses carefully, we observe that they complement the epigraph of the article. Yes, the footprints of one's own path transubstantiate into personal feelings before metaphysical entities—concrete footprints and sensitive stances. There is no absolute separation between the empirical, the rational, and the sensitive, and the whole of our biography also shows this continuity in a certain way. The daily life of the scientist discussed here was filled with poetry and expressiveness, and as soon as the opportunity arose to reveal them, they appeared—even in the long term and after a long time...

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Citation: Chioccioli, M. (2025) An Investigation into the Role and Importance of Three-Dimensional Representations through an Analysis of Late 19th and Early 20th Century Chemistry Textbooks. *Substantia* 9(2): 99-109. doi: 10.36253/Substantia-3430

Received: Mar 27, 2025

Revised: Jun 15, 2025

Just Accepted Online: Jun 19, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

An Investigation into the Role and Importance of Three-Dimensional Representations through an Analysis of Late 19th and Early 20th Century Chemistry Textbooks

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Abstract. Graphic representations of three-dimensional structures play a pivotal role both in academic research and chemical education. Nevertheless, their deceptive simplicity can lead school and even university students to an incorrect understanding of these representations that are central for both organic and inorganic chemistry. A deep knowledge of their symbolic meaning is, indeed, essential to avoid a meaningless learning of the discipline. Two important historical examples, the three-dimensional representations of tetrahedral carbon and the geometry of metal complexes, are discussed in this paper. More in detail, this work investigates the way in which these three-dimensional formulae were received and presented in school and university textbooks published in the late 19th and early 20th centuries, before the introduction of techniques of structural investigation such as X-ray crystallography. Given the difficulty of finding all textbooks published in that period worldwide, the creation of a freely accessible database is also encouraged. Generally underestimated in historical investigations, old chemistry manuals are, in fact, essential to understand how the discipline has been taught in the past.

Keywords: three-dimensional representations, symbolic level, chemistry manuals, tetrahedral carbon, metal complexes.

As soon as humans started using signs and symbols to represent the natural world, they pushed beyond the limits of that world. Elizabeth Kolbert, The Sixth Extinction: An Unnatural History, 2024.

INTRODUCTION

A fundamental problem in the field of teaching and learning chemistry is well exemplified by the so-called Johnstone's triangle, an influential content model in chemistry education (Figure 1). $^{1, 2, 3, 4}$

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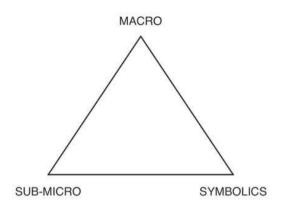


Figure 1. The Johnstone's model, also referred to as *Chemistry triangle*.

Alex Johnstone (1930-2017), one of the most highly regarded chemistry educators⁵, highlighted that the difficulty of achieving a meaningful understanding of chemistry often arises from the non-clear distinction between the three levels on which chemical knowledge is based: the macroscopic level, the sub-microscopic level and the symbolic level.* As he pointed out: «It is psychological folly to introduce learners to ideas [of chemistry] at all three levels simultaneously. Herein lies the origins of many misconceptions».6 Johnstone's triangle remains at the core of chemical education. However, other authors, such as Peter Mahaffy, Jesper Sjöström and Ingo Eilks, have expanded this model over the years, by pointing out that it lies at the basis of a more complex tetrahedral structure of chemical knowledge. According to these more recent didactic models, such a tetrahedron highlights other important aspects that should be taken into consideration in chemistry education, such as human and social aspects.7, 8, 9, 10, 11

Three-dimensional graphic representations of chemical structures are especially relevant to chemical education, due to their contextual reference to both the symbolic and sub-microscopic vertices of Johnstone's triangle.

The symbolic is the level at which chemists use graphs and drawings to convey their mental image of the structure of a chemical compound, while the submicroscopic level refers to the actual spatial arrangement of atoms, molecules, electrons etc. and their behaviour. The third level, the macroscopic one, is related to observable properties of substances. A distinctive feature of this area of research is the fact that graphic illustra-

tions, relating to the symbolic level, were introduced by chemists long before the advent of experimental techniques that enabled a deep understanding of the submicroscopic level of matter.

Chemistry has an intensely visual character¹² and Nobel laureates Roald Hoffmann and Pierre Laszlo pointed out that chemical structures are in some ways trademarks of a chemist's profession, even if their deceptive simplicity can be misleading.¹³ In general, students find it difficult to understand the correct meaning of these graphic representations and the connection they have with the microscopic level.¹⁴

In this paper, I focus my attention on the symbolic meaning of three-dimensional representations, trying to understand when they first appeared in chemistry manuals and what sense was attributed to them. I have analysed both graphic representations of tetrahedral carbon, an important topic in the field of organic chemistry, and those of metal complexes, a central aspect in inorganic chemistry. The first step of this work was to find old chemistry manuals from the late 19th and early 20th centuries; this was done by exploring public and private libraries, as well as digital sources. 15, 16, 17, 18, 19 Subsequently, some of the most well-known and widespread manuals of that period were selected and analyzed (see Appendix), on the basis of the presence in the text of a reference to the subjects discussed in this paper, following a chronological approach. Special attention was also devoted to Italian manuals. Thirdly, conclusions were drawn relative to four main issues:

- the speed with which textbooks have incorporated the findings of chemical research;
- the educational role of graphic representations of chemical structures;
- the meaning attributed to these drawings and their relationships with the reality of matter;
- the usefulness of graphic representations as means for reasoning and interpreting empirical evidence.

This work does not claim to be truly exhaustive, given the vastness of the subject and the difficulty of exploring all the manuals published internationally in that period. In addition to this, sometimes the same edition of a manual was published in several languages, with the addition of new contents.

TETRAHEDRAL CARBON

van't Hoff and Le Bel's Independent Proposals

At first, I focus my attention on the first graphic representations of tetrahedral carbon. In 1874 the Dutch chemist, Jacobus Henricus van't Hoff (1852-1911) and the

^{*} Johnstone defined the nature of chemistry as follows: «I believe that it exists in three forms which can be thought of as corners of a triangle. No one form is superior to another, but each one complements the other. These forms of the subject are (a) the macro and tangible: what can be seen, touched and smelt; (b) the sub-micro: atoms, molecules, ions and structures; and (c) the representational: symbols, formulae, equations, molarity, mathematical manipulation and graphs».⁶

French chemist, Joseph Achille Le Bel (1847-1930), while working independently, made a proposal for the structure of the tetrahedral carbon that was decisive in enabling the rationalization of optical activity, meaning the rotation of the plane of polarised light, in organic compounds. ^{20, 21, 22} The two young scientists, in a way, had the ability to imagine a three-dimensional microscopic world, before the advent of any instrument that permitted the exploration of the ultimate structure of matter.

In his doctoral dissertation, summarized in a pamphlet printed in Dutch in September 1874²⁰, van't Hoff introduced three-dimensional representations of tetrahedral carbon, referred to as asymmetric carbon atom. The text was later translated into French and published in the Archives Néerlandaises des Sciences Exactes et Naturelles.²¹ An abridged version of this work was published in March 1875 in the Bulletin de la Société Chimique de Paris.²³ The first edition of van't Hoff's most famous volume, in which his hypothesis of asymmetric carbon was treated in greater detail, was first published in French in May 1875 under the title of La Chimie dans l'espace²⁴, later translated into German in 1877 with some additions.²⁵ In the German edition there is a preface by the German chemist Johannes Wislicenus (1835-1902), one of the earliest and strongest supporters of van't Hoff's hypothesis. On the other hand, Wislicenus himself in 1873 had reached very similar conclusions²⁶ and his ideas seem to have inspired van't Hoff's theory. After this book, van't Hoff's ideas were more widely disseminated.²⁷ This text went through several editions and about 10 years later, in 1887, it was republished in French under the title Dix années dans l'histoire d'une théorie²⁸ and in 1891 in an English version, under the title Chemistry in Space.²⁹ In this new edition of the text, van't Hoff himself underlines that the presence of his hypothesis in the most popular chemistry textbooks of the time is the most tangible proof of the fact that the theory of asymmetric carbon is spreading rapidly. The English edition says (p. 19): «A more conclusive sign of approval still, it appears to me, is to be found in the fact that the theory in question now forms part of elementary chemical teaching, and is to be found enunciated in the most widely used textbooks». van't Hoff made extensive use of perspective drawings of asymmetric carbons in his publications and prepared even cardboard tetrahedral models which were sent to well-known chemists to help them visualise the relationships between various physical isomers, the chemical compounds which are now known as *stereoisomers*.

Le Bel proposed, independently, a tetrahedral structure for carbon atoms in compounds showing optical activity, but as a result of purely geometrical considerations on molecular symmetry and following a more abstract reasoning. His aim was to find a general rule

that enabled predictions of the existence of optical activity in chemical compounds on a structural basis. Le Bel's paper was published in French in November 1874²², but unlike van't Hoff he didn't use three-dimensional drawings or models to illustrate his ideas.

At first, the idea of a tetrahedral carbon didn't meet with a cordial reception amongst chemists. ³⁰ As time went on, however, van't Hoff's proposal of asymmetric carbon atom has become widespread in chemistry and had the greater impact on the subsequent development of stereochemistry, in comparison with Le Bel's. It has been argued by Grossman³¹ that it could be due to different reasons. First of all, it was much easier to understand and assimilate and van't Hoff was a well-known chemist who made significant contributions to other fields of chemistry, while Le Bel was not so famous in the scientific community. In addition to this, van't Hoff's structural ideas were much more useful for determining the number of isomers of a particular compound, an important endeavour at that time.

Chemistry Textbooks and First Graphic Representations of Tetrahedral Carbon

Starting with the quotation above from the 1891 van't Hoff *Chemistry in Space*²⁹, I have found that in some manuals of that period, that have been examined (see Appendix), only a reference to the theory of asymmetric carbon appears in the text but no three-dimensional representations are present. I have focused my research on textbooks where, in addition to a textual reference, there are graphic representations of tetrahedral carbon.

In chronological order, among the first textbooks with three-dimensional representations, there is one written by Carl Schorlemmer (1834-1892), a German chemist nicknamed the red chemist**, who from 1874 was Professor of Organic Chemistry in Manchester. The first edition of *The Rise and Development of Organic Chemistry* was published in 1879. Schorlemmer was very interested in the history of chemistry and his manual is a masterpiece on the history of organic chemistry. In this textbook, he refers to the Le Bel and van't Hoff hypothesis of atoms in space (p. 96) and uses three-dimensional representations of tetrahedral carbons.

As far as chemical representations are concerned, in the text the author uses the expression *graphic formulae*, with reference to bidimensional graphs representing the position of the atoms in one plane, and *glyptic formulae* to describe three-dimensional drawings and solid models.

^{**} Schorlemmer was known as the red chemist because of the close friendship that bound him to both Karl Marx and Friedrich Engels.

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He explains that (p. 67): «For lecture and class illustration, solid diagrams are often used, consisting of wooden balls of various colours, to represent the atoms, having holes for the insertion of connecting rods, which Kekulè first proposed. These representations are called glyptic formulae». These glyptic formulae are employed in the manual to show the structure of the succinic acid, where carbon atoms are linked via single connections, and to provide a possible explanation for the isomerism between fumaric acid and maleic acid, two organic compounds containing double linked carbon atoms (Figure 2). This is the kind of isomerism we refer to as geometric isomerism or cis-trans isomerism; using a modern terminology, the fumaric acid is the trans isomer, while the maleic acid is the cis one (Figure 3). The author underlines that these formulae in space, containing one or more asymmetric carbon atoms, have been introduced by van't Hoff. In these three-dimensional drawings, a carbon atom is represented as a tetrahedron, its four combining units being represented by the angles. Hydrogen atoms (H) and carboxyls (CO₂H) are the units linked to the carbon atoms via single linkages. A single connection between carbon atoms is represented by a common vertex, while double connections are represented by two tetrahedrons with one edge in common.

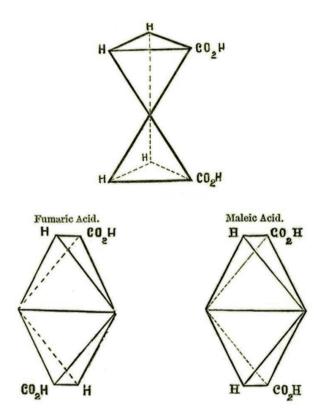


Figure 2. Three-dimensional representations of succinic acid (above) and fumaric acid and maleic acid (below) as found in Schorlemmer's manual (p. 97).

Figure 3. Representations of the two geometric isomers, fumaric acid and maleic acid, according to modern conventions.

The solution of the structural enigma concerning maleic and fumaric acid could be an interesting example of what has been previously mentioned in relation to the Johnstone triangle and the pre-existence of the symbolic level in the field of three-dimensional representations. In fact, van't Hoff's structural hypothesis, exemplified by the graphic structures present in Schorlemmer's manual (Figure 2) referred to a purely theoretical and symbolic level and had been proposed to account for unexplained relations existing between maleic and fumaric acids. It predated the work of Wislicenus, published in 1887³⁴, where the German chemist presented some experimental observations that could be taken as strong proof of the correctness of the geometrical formulae assumed for maleic and fumaric acids. With this publication, in a way, Wislicenus gave the final impetus on the acceptance of the theory of tetrahedral carbon.³⁰ In the Schorlemmer manual (p. 98), there are also two-dimensional formulae where asymmetric carbons are marked with a circle (Figure 4) and not with an asterisk as we are used to seeing them nowadays.

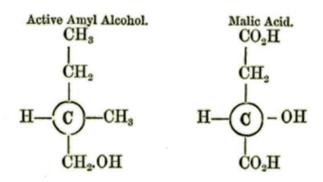


Figure 4. Asymmetric carbons as highlighted in Schorlemmer's manual.

A few years later, another fundamental textbook was published in English by Henry Enfield Roscoe (1833-1915) together with Schorlemmer. Roscoe was a British chemist and had worked under the supervision

of Robert Bunsen (1811-1899) at Heidelberg.³⁵ He was Professor of Chemistry at Owens College in Manchester and Schorlemmer was his assistant there. A Treatise on Chemistry was a textbook for tertiary students and for a long time was considered a standard for teaching chemistry. Four different volumes of this text have been published over the years. Volume III is on The Chemistry of the Hydrocarbons and their Derivatives, or Organic Chemistry; Part I of this volume was published in 1881³⁶ while Part II was published in 1884.³⁷ The two authors use a historical approach both in presenting organic compounds and their discoveries as well as chemical theories and their evolution, adding interesting citations even from Pliny the Elder. In Part I, there is a reference in the text to the hypothesis of the assymetric [sic] carbon atoms (p. 127) and there are two examples (amyl alcohol and malic acid) where these carbon atoms are circled, as previously said referring to the manual of Schorlemmer. In Part II of this volume we can find the same graphic representations already present in Schorlemmer's manual. After presenting van't Hoff's hypothesis of considerable probability, these spatial formulae are used for representing succinic acid and to explain the isomerism between fumaric and maleic acid (p. 216). A reference to tetrahedral structures is also made in the text for the tartaric acid isomers (p. 237).

Two similar manuals with three-dimensional representations of asymmetric carbons appeared in the United States. Ira Remsen (1846-1927), the author, was an American chemist, professor at John Hopkins University and the founder of the American Chemical Journal.*** Remsen is also remembered for the fact that in his lab, the Russian chemist Constantin Fahlberg (1850-1910) produced the chemical compound that was later known as the artificial sweetener saccharin. The first manual was published in 1885 and is about organic chemistry³⁸, while the second is perhaps Remsen's most famous text, entitled The Principles of Theoretical Chemistry.³⁹ The textbook published in 1885, An Introduction to the Study of the Compounds of Carbon; or, Organic Chemistry, presents (p. 164) graphic structures for two tetrahedrons, mirror images of each other (Figure 5). In the text, the author explains these drawings by saying: «Let us suppose that in a carbon compound one carbon atom is situated at the centre of a tetrahedron, and that the four atoms or groups which it holds in combination are at the angles of the tetrahedron as represented in figure».

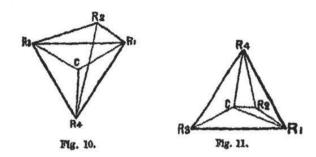


Figure 5. Graphical representations of tetrahedral carbon as found in Remsen's manual published in 1885.

The first edition of the other Remsen manual, *The Principles of Theoretical Chemistry*, was published in 1877, but in this volume there is no reference to van't Hoff's hypothesis. The second edition of the manual was published in 1883. In this second edition there is a reference in the text to the hypothesis of the asymmetric carbon atom, referred to as *a suggestion*, but there is no graphic representation. The first three-dimensional representations of tetrahedral carbon appear in the third edition, published in 1887³⁹, for the *physical isomers* of lactic acid and tartaric acid (p. 284).

Moving on to an analysis of the manuals published in Italian, a reference textbook for the first threedimensional representations of tetrahedral carbon is the Sestini-Funaro. The two authors are the Italian chemists Fausto Sestini (1839-1904), Professor at the University of Pisa, and Angelo Funaro (?-1927). This text was very popular in Italian secondary schools and was published in numerous editions between the late 19th and early 20th centuries, the last one being in 1921.40 In fact, this manual is known outside Italy because Primo Levi (1919-1987) cites it as the school text he used during high school, in the Hydrogen chapter of his book The Periodic Table.41 The edition of interest is the sixth edition, published in 1901, where, in a note added to the main text, there are two mirror images of a tetrahedron (Figure 6) used to show the physical isomers of lactic acid (p. 321).40

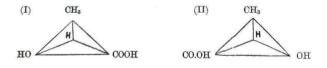


Figure 6. Representations of the two *physical isomers* of lactic acid as found in Sestini-Funaro's manual (1901).

^{***} This journal ran until 1913 and then was absorbed by the Journal of the American Chemical Society.

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Meaning of graphic representations in these manuals

These textbooks, analysed in the present work, are very interesting from an epistemological point of view because authors tend to reflect on the meaning and usefulness of these representations.

In his 1879 manual³³, Schorlemmer points to the objection made by some eminent chemists to the possibly misleading use of these solid diagrams, named glyptic formulae (p. 67). Students, in fact, could take these representations as real objects, while they are not, and «it might lead the pupils to believe that atoms had that shape, or were thus arranged in space, and connected by material bonds». In order to support this statement, he adds: «In fact a dunce, when asked to explain the atomic theory, answered, "Atoms are square blocks of wood, invented by Dr. Dalton."» At the same time, the author underlines the usefulness of these three-dimensional representations in explaining experimental features of chemical compounds; in fact, he underlines that: «Graphic and glyptic formulae [...] are of value for illustrating the different constitution of numerous compounds having the same percentage compositions, but very different properties». In this context, he is referring to different types of isomers. It is important to emphasise that both these aspects, meaning the symbolic value of these representations and their usefulness in an educational perspective, should be taken into consideration even today when using three-dimensional models in a classroom to avoid erroneous learning.

Roscoe and Schorlemmer, in part I of the Volume III of their manual published in 1881³⁶, emphasise the same aspect, that is to say the usefulness of these representations that have only a hypothetical meaning. The authors, in fact, caution readers against a structural interpretation of these three-dimensional formulae (p. 128): «graphical formulae cannot represent the arrangement of the atoms in space, about which, in fact, nothing is known. These rational formulae possess a somewhat similar meaning to the parallelogram of forces in mechanics. They simply serve to give us a notion of the attraction which the single atoms in the molecule exert upon one another».

In the 1885 manual on organic chemistry³⁸, Remsen adds a reference to the purely speculative and theoretical value that was attributed at the time to the van't Hoff hypothesis and, more generally, to the spatial representations of chemical compounds. It says, in fact, that (p. 164): «At present, it is hazardous to indulge in speculations regarding the relations of the parts in space, and, while the hypothesis which is to be explained briefly is ingenious and interesting, the student should be careful

not to be carried away by it. He should remember that it is only a thought». On the other hand, in the absence of data obtained with experimental techniques, these three-dimensional representations are actually only conjectures and hypotheses that move on a purely symbolic plane and useful tools for interpreting empirical evidence.

A further reflection on the value to be attributed at that time to the Le Bel and van't Hoff hypothesis and to its application to cyclic compounds (made by the German chemist Adolf von Baeyer (1835-1917) in 1885⁴²), is made by Remsen in the third edition of its *The Principles of Theoretical Chemistry*.³⁹ He draws readers' attention to the absolute uncertainty that existed at that time; in fact, the text says: «What value to attach to such considerations at present it is difficult to say. In this, as in so many other cases in which our knowledge is imperfect, we can only wait until further work shall have furnished us with more facts» (p. 285). In any case, he underlines that this hypothesis was extremely useful to «account for some cases of isomerism which cannot otherwise be explained».

METAL COMPLEXES

Werner's Hypothesis

Another field that was investigated in the present work is that of three-dimensional geometries of inorganic complexes, initially proposed by the Swiss chemist Alfred Werner (1866-1919), Professor at Zurich, in his original paper of 1893⁴³, and their first appearance in chemistry manuals. The two cornerstones of Werner's theory are the introduction of the coordination number, i.e. the maximum number of chemical species that can bind to the central metallic element, and the spatial geometry of inorganic complexes. In the 1893 paper, Werner proposed the octahedral geometry (he himself used the term Oktaeders) for complexes with coordination number 6 and, for those with coordination number 4, a kind of geometrical arrangement with four bonds in a single plane which now is referred to as square planar. Initially, Werner's ideas were accepted with scepticism in the scientific community, but they began to circulate quickly in textbooks. Werner himself wrote in 1905 a fundamental book on inorganic chemistry where he explained the basis of his coordination theory: Neuere Anschauungen auf dem Gebiete der Anorganischen Chemie.44 This book had a great influence on teaching inorganic chemistry and on the theory of coordination in the early 20th century.⁴⁵

Chemistry Textbooks and First Graphic Representations of Metal Complexes

All the same, it is important to point out that a reference to Werner's work on the ammonia complexes of cobalt and platinum, albeit in footnotes, can already be found in the first edition of a manual written by George Samuel Newth (1851-1936), a British chemist and lecturer at the then Royal College of Science in London. 46 This volume was published in 1894, only a year after Werner's initial proposal. However, no edition of this manual, among the eleven I have consulted, reports a representation of the three-dimensional structures of metal complexes.

The first three-dimensional representations of metal complexes can be found in a series of books where Werner himself had been asked to write or revise sections dedicated to these types of compounds. One of these manuals is The Elements of Stereochemistry by the German chemist, Arthur Rudolf Hantzsch (1857-1935). Hantzsch graduated in Chemistry from the University of Würzburg under the supervision of Johannes Wislicenus. He was a Professor at Zurich Polytechnic (now ETH Zurich) and he had a great influence on Werner during his studies there. There were three first editions of this manual in as many languages: a German edition published in 1893⁴⁷ and the two editions of interest, the 1896 French edition⁴⁸ and the 1901 English edition.⁴⁹ In these latter two editions of the manual, there is a section on the stereochemistry of metal complexes by Werner himself, The Stereochemical Isomerism of Inorganic Compounds. Here, it is possible to find graphic representations of both octahedral and planar square geometries (Figure 7). It is worth pointing out that these two figures are taken directly from Werner's original paper of 1893.⁴³

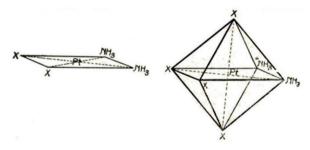


Figure 7. Three-dimensional representations of metal complexes as found in the 1901 English edition of Hantzsch's manual (p. 198).

Another text of this series is the above-mentioned manual by van't Hoff on stereochemistry. In 1898 a second English edition of *Chemistry in Space* was published under the title *The Arrangement of Atoms in Space*, with an appendix on *Stereochemistry among Inorganic Sub-*

stances by Werner.⁵⁰ This book is much more extensive than the previous 1891 English edition and, in addition to Werner's appendix, contains a section on the stereochemistry of nitrogen compounds. In the section on metal complexes there are numerous three-dimensional representations both for octahedral and planar square geometries. There is also a reference to an article published by Werner and the Italian chemist Arturo Miolati (1869-1956) in 1893, with experimental data relating to the measurement of the *molecular conductivity* of solutions of metal complexes, which helped to confirm the theory of coordination.⁵¹ This kind of experiment, performed in aqueous solution, is now called *ionic conductivity* and relates to the number of ions in solution.

A third manual of this group is Holleman's text-book, *Textbook of Inorganic Chemistry*, which has been a reference manual for teaching inorganic chemistry for a very long time, as proved by the various editions of the text translated into different European languages. Arnold Frederick Holleman (1859-1953) was Professor of Chemistry in Groningen, in the Netherlands. The first edition of this textbook was published in Dutch and dates back to 1898.⁵² Other editions of the volume were published in German, the first in 1900⁵³, in English in 1902⁵⁴, and in other languages.

The first three editions of this manual have been consulted, both in German and in English. From the very first edition of the text, there is a paragraph dedicated to the ammonia complexes of the metals of the eighth group. In this section, a mention is made to Werner's work and his hypothesis, but without any reference to the three-dimensional geometry of these complexes. The third English edition, partly rewritten and approved directly by Werner himself with regard to the ammonia complexes of metals, was published in 1908. In this edition there are graphic representations of octahedral complexes (p. 487). These structures are reported as support for the only structural hypothesis that would explain the existence of stereoisomerism for metalammonia compounds. In the third German edition published in 1905 there are no graphic representations.

Another interesting manual on stereochemistry, with no contribution from Werner, but where there are three-dimensional representations of metal complexes, was written by Alfred Walter Stewart (1880-1947), a British chemist and writer of several chemistry textbooks and detective novels. The first English edition of this manual was published in 1907.⁵⁵ In this edition, at the beginning of the chapter on the stereochemistry of cobalt complexes (p. 270), there is a reference to Werner's work and the author underlines that: «It seems possible only to sketch the outlines of his work, as up to the

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present there does not appear to be sufficient accumulation of material to allow more than this to be done». This statement by Stewart sounds a bit odd, as Werner had published at least 5 papers on metal complexes by 1906. The author continues by underlying the hypothesis of two sets of valences, designated as *principal valencies* and *auxiliary valencies*, and the text reports images of three-dimensional structures of both octahedral complexes of cobalt and planar square complexes of platinum. In the manual we can also find a reference (p. 274) to the geometrical motives underpinning the idea of the octahedron as the only possible arrangement of ammonia complexes of cobalt. It says, in fact: « Now six points can be thus symmetrically arranged in space if they are placed at the corners of a regular octohedron [sic]».

Among Italian manuals published in the early 20th century, even for metal complexes the reference manual is the Sestini-Funaro. From the seventh edition on, this text is edited by Quirino Sestini (1872-1942), Fausto's son. Until the ninth edition of this text in 1909, no reference is made to Werner's complexes. From the tenth edition of the manual, published in 1912, graphic representations of metal complexes with octahedral and planar square geometries appear in the text for the first time. These graphic representations are present in the chapter *Complex Compounds of the Metals of the VIII Group* and represent the first that have been so far found in Italian manuals.

CONCLUSIONS

Several conclusions can be drawn from the present research. First of all, it is possible to conclude that the period of time between the original proposals by van't Hoff, Le Bel and Werner and the first appearance of three-dimensional representations in textbooks, is relatively short. This is despite the fact that the means of communication used at the time were not as fast and efficient as those today.

Secondly, from a didactic point of view, it is important to stress that these three-dimensional structures, as presented in the manuals studied, are useful and essential tools for visualising the differences between distinct types of isomers. This property, in a way, evokes the importance of visual aspects in enhancing learning of complex chemical concepts. However, while underlining the usefulness of graphic formulae, some authors warn against a structural interpretation of three-dimensional representations, i.e. they caution against an excess of realism applied to the sub-microscopic level.

This statement leads directly to a third conclusion about the epistemic value of these drawings, which are described in these textbooks as hypothesis, ideas and conjectures. These structures are useful attempts to construct scientific explanations referred to a level of reality, such as the microscopic one, that at the time was not accessible experimentally. On the whole, it is necessary to point out that, with reference to Johnstone's triangle, the clear distinction between the symbolic and the microscopic level should be kept in mind in today's teaching of chemistry if we want to pursue the goal of a truly meaningful learning of the discipline. In fact, even if today we have access to accurate data on the microscopic world, the representations remain purely symbolic, because they refer to a world which cannot be represented in a realistic way, by virtue of its dynamic and quantum mechanical nature.

Finally, it is important to remember the crucial role played by these graphic structures as useful tools for explaining empirical evidence which could not otherwise be explained. One of the most relevant examples was the application of the structural hypothesis put forward by van't Hoff to the solution of the enigma concerning the then unexplained relationships between maleic and fumaric acid.

To sum up, given the difficulty of exploring all manuals published in that period worldwide, the creation of a freely accessible database where everyone could add references to chemistry textbooks with three-dimensional structures would be very interesting. This could help the construction of a sort of map showing how rapidly these fundamental concepts of chemistry spread in different languages and therefore were accessible to secondary school and university students.

ACKNOWLEDGEMENTS

The author expresses his gratitude to Elena Ghibaudi (University of Torino) for her valuable suggestions; to Judith Guttridge (Castelfranco Piandiscò - AR) for her in-depth revision and correction of the manuscript. The author is also pleased to thank the four unknown referees for their very useful advice.

APPENDIX: TEXTBOOKS EXAMINED IN ALPHABETICAL ORDER

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Holleman, A. F. *Leerboek der anorganische Chemie*. 1st Dutch Edition, 1898. First and subsequent editions have been consulted in different languages.

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Citation: Massi, L., da Silva Lima G. (2025) Science Communication as *Praxis*: Analysis of 'The Periodic Table' by Primo Levi. *Substantia* 9(2): 111-120. doi: 10.36253/Substantia-3441

Received: Mar 31, 2025

Revised: Jun 17, 2025

Just Accepted Online: Jun 19, 2025

Published: Sep 15, 2025

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Data Availability Statement: All relevant data are within the paper and its Supporting Information files.

Competing Interests: The Author(s) declare(s) no conflict of interest.

Research Article

Science Communication as *Praxis*: Analysis of 'The Periodic Table' by Primo Levi

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Abstract. This article is an analysis of the book "The Periodic Table", which derives from Primo Levi's praxis. This is an attempt to highlight the reason for the communicative practice and subject-object relationship involved in his book's production. The analysis was based on both praxis categories and the subject/object opposition unit emerging from historical and dialectical materialism. Accordingly, we mobilize and advocate for a science communication concept based on the sense of praxis that is not limited to the discursive aspects of this production type. Based on the sources' selection carried out in the collection of "Centro Internazionale di Studi Primo Levi", this book can be the very result of Levi's transformative praxis, which was driven by a liberating human development substantiated by science. Science outspread as transformative praxis in Primo Levi's work and in the subject/object relationship observed it. Human development was the reason for his practice, and it was driven by a liberating perspective, by outspreading a science that could help expanding the concept of world and society. This reason is linked to his biography and activities, which play a potential humanizing role in relationships man set with nature and society. The present article sought to broaden the understanding of SC as praxis based on a case study and to stand against a narrow view of SC and the superficial reasons often linked to it.

Keywords: Science and literature; science communication; *praxis*; Primo Levi; The periodic table.

CONTEXT

The Science Communication (SC) literature advocates for overcoming the classic Public Understanding of Science (PUS) or the Public Perception of Science model. These models identify gaps in scientific knowledge and their likely overcoming by making scientific facts available to the general public. 1.2,3,4 This traditional discursive context perspective seems to be associated with SC as scientific discourse translation. 5 According to Dahlstrom and Ho,

SC researchers have migrated to the Public Engagement in Science and Technology (PEST) model, which takes scientific controversy as focusing and widespread mechanism. This model makes it easier to discuss the risks and benefits of public policies substantiated by social values and technological information. Furthermore, many important models featuring SC have been created and are still cited.

The new SC perspective is in compliance with the understanding of science as culture. The metaphor to explain the scientific culture is the act of climbing a mountain; in other words, one must become increasingly involved in science and in making it worth the effort. Therefore, SC should be a popular culture aspect, just as storytelling, narratives, rituals and collective meaning-making processes, so stories about science should not be written differently from how other stories are created. From this perspective, Van Dijck analyzed Snow's classic text to advocate for the overcoming of the paradigm that separates science from culture in order to head towards a "(Multi)cultural Practice of Science Communication".

Lima and Giordan understood scientific culture as a set of scientific values, knowledge, beliefs and technological practices forming the human heritage by overcoming the discursive dimension.⁵ Therefore, understanding science as part of culture can be better observed in light of Lima and Giordan's ideas.^{2,3,5}

Despite these new directions and potentials, Halpern and Rogers highlighted the persistent and problematic association between science and its outspreading, and between science and art.⁶ Some authors anchored in the perspective of science as culture and narrative advocate for using Science Fiction (SF) as SC topic, because, more than scientific ideas validity, the internal logic of fiction is what really matters.⁷ However, Lima and Giordan addressed the relevance of differentiating the scientific reference from the expanded scientific culture SC is part of, and it can include narratives.⁵ According to several authors, narratives seem to engage in, and convince more than, isolated scientific facts, besides leading to scientific careers, without distorting science and scientists' perception.^{3,7,8,9,10}

There are differences in both the compositional structure and main elements structuring scientific and everyday language symbolic forms ⁵. While scientific language is ruled by codetermination relations between scientific concepts in the search for a stable and monological meaning, everyday language is based on likely meanings expressions can have; thus, it is substantiated by polysemy. An appropriate form and content organization is needed in order to accomplish scientific communication and technological culture outspread. Not every

fictional narrative has the potential to help outspreading science, unless it is produced for this specific purpose and to mobilize appropriate materials, strategies and tools to do so. Furthermore, the discursive analysis is not enough to capture these potentials.

Primo Levi's texts are an example of narratives produced to promote SC11. According to Lima and Giordan, they are close to the most appropriate scientific culture form, since these fictional narratives or essays acknowledge science as historically determined human production made up of complex social relationships.⁵ Levi was an Italian Jewish chemist who became a writer after surviving Auschwitz concentration camp. He wrote books in several genres throughout his life, most notably autobiographical texts with memoirs of concentration camp experiences or as chemist working in laboratories. The present article is an analysis of the autobiographical book "The periodic table", whose chapters are named after a chemical element. The reported story associates the named element with specific fragments of his life. The other books introducing the same autobiographical aspect are 'If his is a man' and 'The truce', both focused on the Lager tragedy. In "The periodic table" only chapter 'Cerium' talks of his experience in a concentration camp.

Dahlstrom and Ho discussed the likely ethical implications of adopting narratives to outspread science by highlighting an external realism observed in fictional narratives.¹ They also pointed scientists' almost unethical behavior of not taking advantage of these potential narratives to outspread science. Reinsborough even stated that natural and social scientists should be involved in producing narratives, because they are more informative to the public than scientific research results.⁹ William Wilson, back in 1851, already advocated that fiction should be a vector for popular science.

The Scottish poet William Wilson issued a brief manifesto for a new genre of "science-fiction" in 1851, but it proved premature, although Wilson's chosen book, "The Poor Artist' by Richard Henry Horne; or, Seven Eye-Sights and One Object (1850), is a good illustration on how scientific knowledge can inform and transform Nature's imagery.⁷

Acknowledging the difficulty in articulating art and science, as well as SF potential in SC as part of scientific culture, allowed observing the potential of Primo Levi's life and work to explore such associations. ^{6,12} His book "The Periodic Table" was awarded as best science book of all times by the Royal Institution of Great Britain, which is one of the oldest and most prestigious sci-

entific institutions. It was founded in London, in 1799, and is dedicated to outspread and apply new scientific ideas and scientific education to the general public.^{13,14} According to Gordon, this award does not refer to scientific competence, nor does it point out a broader understanding of science by this institution (if one bears in mind its diversity of works), as proposed by Cerruti, but points towards its origins linked to popular science and SC.^{13,15} He highlighted literary writers among competitors, such as Bertold Brecht, and writerscientists like Darwin, Watson and Dawkins. All these authors produced hybrid works that have balanced science, narration, history, ethics or science politics, and modernity.

Many authors state that this award refers to the quality of a given work in spreading out science and in integrating science to art. However, they did not identify the authors of these works as science communicators and avoided classifying those works in this genre. 16,17,18 Assumingly, classifying a book as SC would diminish its literary and author's value, because, according to these authors, despite the work's informative character, it is secondary to literary intentions. 16,17 Therefore, although this particular author is a chemical narrator, his fantastic vicissitudes connected to scientific research refer to the true art of short stories, rather than to its outspread.18 Although "The Periodic Table" has been awarded as the best science book of all times, it has been more often analyzed as autobiography than as SC work. Authors who deny this book as SC, such as Di Meo, classify it as a book about the scientific practice of a chemist, that highlights a narrow view of scientific-knowledge outspreading, which is limited to major scientific facts, canonical knowledge, he also sees it as disconnected from life.16 According to this author, Levi did not write SC because he addressed anachronistic or marginal content and practices, rather than discussed major scientific topics. Di Meo stated that the approach by Levi would only be of interest to a historian of science.16 He argued that, other than producing SC, Levi writes about the association among scientific practice, life and individuals' general conduct.

Gordon's analysis is an important exception, since he rebuilt SC presence in Levi's story.¹³ He stated the need for studies acknowledging this aspect in order to fully understand Levi's communicative power, as well as the charm, curiosity and pleasure emerging from his work¹³. Philip Ball, who was Nature's editor and is an important science communicator, reinforced that this is "the best book ever written about chemistry" and suggests naming a new chemical element "levium".¹⁹ Amidst this dispute, it is necessary understanding that

"The Periodic Table" is a work of scientific communication given the reasons substantiating its elaboration. This interpretation will be introduced in the herein described analyses.

The general aim of the present article was to analyze the book "The Periodic Table" as product of Primo Levi's *praxis*. Its specific goals lie on analyzing the reason for Primo Levi's communicative practice in the book and on the subject/object relationship involved in his work's production process.

Praxis is the conscious activity of the subject based on the theory/practice inseparability. Therefore, praxis means an intentional action carried out by human beings, so a science communicator activity is driven by SC concepts and goals. The need for understanding SC as praxis arises from interpreting the totality of such an activity. This praxis cannot be summarized as discursive simplification, because it also implies recognizing a discourse source that does not always exist. The entire science and technology field form its references, not just its discourses. This field includes practices, agents, stories and, of course, discourses. Therefore, SC interpretation as simplification or discursive translation²⁰ accounts for only capturing one dimension of this complex human activity.

Understanding it as *praxis* is an attempt to overcome limits imposed by the division of labor, which is herein understood as theoretical and practical work. According to the Marxist theory, *praxis* is the dialectical unit bringing together theory and practice. This interpretation derives from observations, according to which, the theory alone is incapable of transforming reality if, at the same time, it is not intertwined with human activity. Practice without theory, in its turn, is an alienated practice, whose reasons and execution means are obscure throughout human activities. It is clear, however, that degrees of overshadowing can vary, and it determines different alienation levels.

Understanding SC as *praxis* implies recognizing that the association between subject and object is dialectic. Therefore, by understanding and changing the object, the subject also changes. According to the Marxist theory, subject and object are mutually historically produced. This association is also mediated by the human society, which determines the social being. This association in "The Periodic Table" shows Primo Levi as subject and scientific culture as object, and the book is their product. By bearing in mind that it is essential understanding the subject who produces the *praxis* in order to understand *praxis* itself, the second analytical section is an investigation about both Primo Levi and his relationship with the scientific and technological culture (the book theme).

METHODOLOGY

The analysis corpus emerged from a search in the collection of "Centro Internazionale di Studi Primo Levi", mainly on OPAC Primo Levi database, which comprises several sources by, and about, Primo Levi. In addition to the digital search carried out by research internship students, the physical collection of "Centro Internazionale" was also accessed and the selected material was read in full. The search was based on the following meshes: "Il sistema periodico" on "ricerca libera" (free search) and "accesso tematico" (thematic access), which led to approximately 600 results. The material was physically selected and consulted. Only publications presenting a straight reference to "The Periodic Table" as SC material were selected for the study, which also included literary analyses, interviews with Primo Levi and book excerpts. Interviews with Primo Levi about the book were included because it is essential understanding the praxis and assessing the author's own awareness of his practice.

The analysis was based on reading the book, on interviews available in the book by Poli and Calcagno, and on The Complete Works of Primo Levi. 22,23 It was done to help better understanding how Primo Levi's praxis was expressed in his book. The analysis followed historical and dialectical materialism categories, mainly the praxis category, as proposed by Marx and summarized by Vázquez.²¹ This category centrality is justified by contributions from Lima and Giordan, who defend SC as praxis. 5 Based on Marx's contributions to the study, the goal was to understand the activity to produce "The Periodic Table", based on need/reason, since this is the very foundation of any working process. Furthermore, the subject/object relationship analysis was substantiated by the materialist dialectic, and contradiction (unit of opposites) was the main aspect assessed through it.

The aim of the present article was to articulate the theoretical foundation during the analysis itself due to writing-style reasons, because this integration helps better understanding the references and the analysis itself.

SCIENCE OUTSPREAD AS TRANSFORMATIVE PRAXIS IN THE WORK BY PRIMO LEVI

Primo Levi is very clear about the reasons leading to his work. This "duty of clarity" is associated with his experience in Auschwitz and with his role as testimony writer, and it was extrapolated to his work as science communicator. According to him, all individuals must feel responsible in order to become human again,

after Auschwitz.²⁴ Martin understands that "the central imperative of this individual responsibility is communication" as "linchpin of liberty".²⁵

If one understands that the aim of Levi's work is to help forming responsible human beings, it is interesting observing his intention to address the scientific and technological culture by emphasizing the need for a free society. Science relevance to form a dignifying society can also be noticed in the report about reasons leading him to write "The Periodic Table", namely: showing that every human experience deserves attention, even in case of careers like factory technician, which is tiring and difficult, because it consists of facing and solving problems, just as many other human experiences.²² This clarity of purpose in writing about science points towards the awareness of a transformative *praxis* in Levi's work.

Marx explains that labor is a product of human needs and Leontiev broadens this understanding by stating that all activities require a motive. ^{26,27} This is a universal feature of human activities: food production satisfies the need for eating, clothes manufacturing fulfills humans' need for protecting themselves from the weather, art production satisfies the need for interacting with the world from multiple human perspectives.

Therefore, according to our interpretation, the Marxist category can be mobilized to infer that "The Periodic Table" had human development as its motive; this was the need guiding Primo Levi's work, although he never declared himself as Marxist. Levi takes scientific and technological culture as object contributing to human development. He designed and triggered a series of actions and means to change scientific and technological culture in order to develop his interlocutors by writing the book. The clear reason substantiating Levi's activity highlights that the teleological projection process (intellectual anticipation of the produced work), the actions taken and the adopted meanings are intrinsically connected to each other, and it points out his transformative praxis aimed at seeking to outspread science by heading towards human freedom and non-oppression. The following excerpt was taken from the Silver chapter and introduces this dimension of Primo Levi's work in a unique way:

I told him that I was in search of events, mine and others', that I wanted to put on display in a book, to see if I could convey to the uninitiated the strong and bitter flavor of our occupation, which is a particular case, a more strenuous version, of the occupation of living. I told him that it didn't seem right to me that the world knew everything about how the doctor lives, the prostitute, the sailor, the assassin, the countess, the ancient Roman, the conspirator, and the Polynesian, and nothing about how we trans-

muters of matter live; but that in this book I would deliberately ignore grand chemistry, the triumphant chemistry of enormous facilities and dizzying profits, because that is collective and therefore anonymous work. I was more interested in stories of solitary, unarmed, pedestrian chemistry, on a human scale, which with few exceptions had been mine: but it was also the chemistry of the founders, who worked not in teams but alone, amid the indifference of their times, for the most part without gain, and who confronted matter without helpers, with their brains and their hands, with reason and imagination.²³

It shows the author's clear and explicit intention to socialize the chemist's trade. This craft is not immersed in the human world, and it requires dealing with stories, concepts, and scientific and technological practices. Levi seeks to broaden his interlocutors' education by seeking to socialize this knowledge, so that they can come to understand the chemist's work. Understanding how to communicate science as *praxis* implies acknowledging that the object (scientific and technological culture) is turned into a process. This transformation derives from the subject/object relationship (in this case, the interaction between Primo Levi, and scientific and technological culture), which must consider the process (work) and the product planned to be objectified (book).²⁷

It is clear that the SC production content is essential, although it is not limited to the scientific-concept approach, as often observed in many SC practices. In addition to SC concepts, as they are currently referred to, Levi stated (in an interview compiled by Poli and Calcagno) that he intended to discuss an important scientific profession, although summarizing his sense of responsibility for outspreading science, as he felt indebted to his profession, which many see as mysterious, arid and suspicious.²² He introduced a whole collection of chemical stories in his book, as well as the contrast between man and matter. In another interview, he stated:

In this book, I have tried to bring to light the nobility of my work, its educational and formative value. [...] the relation between man and matter in the book is ambivalent. Matter is maternal, even etymologically, but it is also inimical. The same goes for nature. And in any case, man too is matter and is thus in conflict with himself, as all religions have acknowledged. Matter is also an education, a genuine school for life. Fighting against it, you mature and grow. In the course of the struggle, you win and you lose. At times, matter seems astute, at others obtuse, and there is no contradiction because the two different aspects coexist.²⁸

In addition to the clear reasons for his activity, this sequence of references by Primo Levi highlights his vision of science scope and social function, which were acknowledged by other authors who have analyzed his work.^{13,15} These writers also pin pointed the need for science to understand the universe, to understand ourselves, the individual and social development of mankind, and how the specificity of chemists' work relates to this whole universe of information.

Levi's understandable and integrated understanding of science, in combination to his clear reason for communicating science, is far from alienated scientific and technological culture practices. Sometimes, the reason for communicating scientific and technological culture in modern society is based on inaccurate, tautological or singular justifications, such as those given to scientific culture due to scientific production growth, to science complexity or even to make science popular, and to personal or corporate enrichment. None of these justifications essentially embodies a social need. They are particular reasons that, although assumingly relevant in certain cases, do not capture the essence of outspreading scientific and technological culture, which is herein understood as element contributing to individual and collective development, which takes place through science and technology appropriation aimed at human emancipation - this reason is close to Primo Levi's statements.

It is important emphasizing that not all human practices should be interpreted in singular terms, but as reflections of existing social relationships. Therefore, both alienated and transformative/emancipatory practices aimed at achieving science outspread correspond to existing social forms and relationships.

From the Marxist perspective, capital is the main cause of alienated practices. The work process makes workers distant from their product, because their activity is determined by the salary setting the relationship among the producer, the capitalist and the product. On the other hand, transformative/emancipatory practices are based on fighting oppression. Marxism allows inferring that Levi's practice emerges from his experience with oppression and fight for freedom. This same condition, in association with the defense of science, consolidated his reasons for, and commitment to, science communication.

These bases have supported Primo Levi's writing of "The Periodic Table", and they were also expressed in his reasoning about the process to write the text available at 'The Complete Works of Primo Levi'. Two brief excerpts from this book are provided below. The first one shows the process to overcome the interest in the chemistry profession due to technical procedures, given his passion for relating his social-practice work to his second text in order to deny the book as treatise on chemistry and as autobiography:

I was in love with my work from the first day, although in that phase it was nothing but the quantitative analysis of rock samples: attack with hydrofluoric acid, precipitate iron with ammonia, precipitate nickel (how little! a pinch of pink sediment) with dimethylglyoxime, precipitate magnesium with phosphate, always the same, every blessed day: in itself, it wasn't very stimulating. But both stimulating and new was another sensation: the sample to be analyzed was not an anonymous manufactured powder, a quiz that appeared out of nowhere; it was a piece of rock, guts of the earth, extracted from the earth by the force of an explosion. And, little by little, from the data of the daily analysis, a map emerged, a portrait of the subterranean veins. For the first time, after seventeen years of school, of aorists and Peloponnesian wars, the things I had learned began to be useful to me. Quantitative analysis, so stingy with emotions, as heavy as granite, became lively, true, and useful when inserted in a serious and concrete job. It could be used: it was set in a plan, a tile of a mosaic.29

It is, or would have liked to be, a micro-history, the history of an occupation and its defeats, victories, and sufferings, such as everyone wishes to recount when he feels close to the end of the arc of his career, and art ceases to be long. [...] So it happens, then, that every element says something to someone (something different to each individual), like the valleys or beaches visited in youth. We must perhaps make an exception for carbon, because it says everything to everyone; that is, It is not specific, just as Adam is not specific as an ancestor, unless you can find today (why not?) the chemist-stylite who has devoted his life to graphite or diamonds.³⁰

The second excerpt shows the contradiction between the science approach and the scientist - science moves between errors and successes, i.e., it is a non-linear science production.

Furthermore, the first excerpt also points out a non-fanciful view of the scientific work. It even highlights how discouraging some tasks in science production can be. However, it also emphasizes the charm of understanding nature, since it establishes associations between particular and general elements - rock dust is no longer seen through its own features, but through its association with the social practice, itself. It pinpoints social practices ability to integrate and give meaning to the produced scientific knowledge, another fact that shows Primo Levi's transformative *praxis*.

The aim of this approach lies on critically (not fanciful) making sense of and on understanding how science drives the contribution to the liberating development Levi has clearly shown. This reason manifested itself in the analyzed case, not only in the writing process, but in the very product of it (the book), which was written amidst a transformative *praxis*.

Accordingly, it can be said that Primo Levi has both practical awareness and awareness of the praxis he carried out. This statement is made explicit in his book and in his interviews. Such an idea is based on the fact that we understand awareness as our capacity to understand the world through subjective reflections about the objective reality generated by subjects, based on their activities in the world. Practical awareness can be understood as articulation between understanding the process and the intentional chain of actions to teleologically achieve the ends planned at the beginning of the activity. 21,27 Therefore, practical awareness is observed at the beginning of, and throughout, the production process in order to intervene in the course to objectify his book "The Periodic Table". Awareness of praxis, in its turn, refers to the fact that the entire action process is known by the subject who carries it out.21 Batista clarified that awareness of praxis, the reflective plane (reflective awareness), is only achieved by overcoming spontaneous viewpoints (common awareness). Only, then, it is possible to consciously gather thoughts and actions.³¹

ON THE SUBJECT/OBJECT RELATIONSHIP IN PRAXIS TO ELABORATE "THE PERIODIC TABLE"

Primo Levi's practical awareness and awareness of *praxis* can be observed in his interviews about "The Periodic Table" and in the analysis of his work. The conscious articulation of the book's form and content seeks to outspread the scientific and technological culture. Assumingly, this is the aim of the book, if one bears in mind its target, namely: forming humans through science.

It is important highlighting that scientific and technological culture mastery was elementary condition to write "The Periodic Table". These two elements guided the objects of Primo Levi's productive activity.

It was necessary to dialectically understand the unit of opposites established between subject (Primo Levi) and object (scientific and technological culture) at the time to write the book, since the interpenetration of opposites was essential to objectify his work. The process of having the object penetrating the subject derived from the subject's appropriation of the object, and it resulted from the individual's activity in the world and from its ability to produce a subjective image of the object, based on the highest degree of verisimilitude possible, within historical limits. Subject penetration in the object, in its turn, resulted from the subject's activity in the object to transform it into something different from what it was before the subject's conscious action. Each of these situations will be addressed separately in order to clarify the analysis.

Primo Levi made it clear in an interview that he was fully aware of the object of his activity. He even compared it to the repertoire of other writers who did not master chemistry. He did so, because chemistry was his raw material, his core topic, mainly in "The Periodic Table".22 Although clarity about the object of the activity was important, it did not imply the appropriation of it. Levi's appropriation of the scientific and technological culture resulted from his life story. He was already encouraged for and showed interest in science since childhood. Cesare, Levi's father, was an engineer and voracious reader who used to give his children books as gifts.²³ His book collection included many books on popular science, books translated from the Anglo-Saxon and European tradition of popular science, including some books printed by the Royal Institution. Later on, Levi was awarded with the herein mentioned prize by this same istitution.¹³ He included two popular science books in his work: "La ricerca delle radici", where he highlighted passages and authors that had most influenced his writing and led him to choose chemistry as career, in addition to reasons linked to the fascist context experienced at that time.²⁴ The cases shone light on the popular science work by Sir William Bragg, 'The Architecture of Things', since it inspired Levi to become a chemist.32

There is a brief Levi autobiography in "The Periodic Table", and it includes some fictional elements, besides the main aspects of his life.³³ Levi had Jewish origin; he was born and lived most of his life in Turin. He chose the scientific career, although he had a broad humanistic education, which was highlighted in the book 'Le ricerca delle radici'. He understood that chemistry was less contaminated by the fascist ideology observed in his formative years. He graduated with the highest institutional honors and was one of the best students in his course, although his diploma disclosed his "Jewish origin". He had difficulty in completing mandatory internship disciplines and getting jobs, because he graduated at a time when racial laws were tightened in Italy. He stated in some interviews that he would possibly have become a researcher if he had not been captured and imprisoned in Auschwitz in 1943, at the age of 24. He survived the camp thanks to a series of "fortunate circumstances"23, including the fact that he understood German, was a chemist and worked in the laboratory. That is why he was less exposed to the cold and to heavy manual labor. It was very hard for him to return to Italy. He described his time in Auschwitz and his return to Italy in his books 'Is This a Man?' and 'The Truce', which were the first two works of his career as writer, although he was initially only acknowledged as testimonial author. He worked as chemist in paint and varnish factories until his retirement at the age of 56, and this activity was defined as technical by him. He registered a patent (in this sector) and kept on writing alongside his work in the factory, besides intensifying his writings after his retirement. He published more than 10 books in different genres, such as poetry, science fiction, novels, short stories and essays. The book "The Periodic Table", from 1975, gave him the status of writer. In addition to the broad chemistry expertise shown in his training and performance in the industry, it is important highlighting the "Periodic Table" analyses carried out by scientists focused on scientific concepts, which showed Primo Levi's exceptional conceptual mastery, as observed in several book chapters by Magro and Sambi.³³

If, on the one hand, Primo Levi's appropriation of the scientific and technological culture expressed the object's penetration into the subject of the activity; on the other hand, the subject penetration (Levi) into the object (scientific and technological culture) was the very product of his own activity (book), which was in compliance with the need it was created for. Therefore, Levi's penetration into the scientific and technological culture takes place as the book is consumed by many interlocutors, as well as contributes to human development, from a liberating perspective.

The aforementioned liberating perspective is disclosed in the book by the precise articulation between science and social practice, or between science and human life. Scientific and technological culture is not substantiated by sensory effects, by 'showing the extraordinary and inaccessible world of science and technology'. Yet, Levi integrated science to life. An exceptional example of it is clear in the chapter "Carbon", where Levi describes the story of a carbon atom (generated through a cosmic process, but intentionally ignored by the author), which begins from the composition of a limestone rock. The molecule this carbon atom bonds to is transformed after human action in the limestone production process. This atom is carried by the wind, dissolved in the sea, converted into organic matter, recombined to other atoms countless times, and so on, after existing through the chimney. It goes on, up to the time when, after a series of cycles, it was found in Levi's body and contributed to placing the final period to "The Periodic Table".

This integration between science and social practice, or between science and life, crosses the whole book, and it points out that they are one of the main ways through which the author understood science. This science is not limited to verbal or mathematical formulations, but is observed in human reality and takes part of his world-

view. Levi describes the objective of writing the book to a fellow undergraduate in an excerpt from the previous chapter (Silver) and asks him to share a story of this same nature with him, so it could be included in his book:

I told him that I was in search of events, mine and other's, that I wanted to put on display in a book, to see if I could convey to the uninitiated the strong and bitter flavor of our occupation, which is a particular case, a more strenuous version of the occupation of living. I told him that it did not seem right to me that the world knew everything about how the doctor, the prostitute, the sailor, the assassin, the countess, the ancient Roman, the conspirator, and the Polynesian live, and nothing about how we transmuters of matter live; but that in this book I would deliberately ignore grand chemistry, the triumphant chemistry of enormous facilities and dizzying profits, because that is collective and, therefore, anonymous work. I was more interested in stories of solitary, unarmed, pedestrian chemistry, on a human scale, which with few exceptions had been mine: but it was also the chemistry of the founders, who worked not in teams but alone, amid the indifference of their times, for the most part without gain, and who confronted matter without helpers, with their brains and their hands, with reason and imagination.³⁴

Levi referred to a chemistry type linked to the human race. He highlighted its role in society by mentioning the great chemistry and by making other references to social practices throughout the book, while overshadowing the professional dedicated to chemistry. Here, once again, it is clear that scientific concepts are not Primo Levi's exclusive object; the subjects of science must appear in communications about science. Certainly, the approach to chemists in "The Periodic Table" was Levi's way to penetrate the scientific and technological culture. This is even clear in his own words when he stated, in an interview, that one of the best compliments he had ever received came from some young people who wrote to him and said that if chemistry was what he described, they would like to become chemists.²²

FINAL CONSIDERATIONS

The aim of this article was to analyze the book "The Periodic Table" as a product of Primo Levi's *praxis*. It was done as attempt to highlight the reason for his communicative practice in the book and the subject/object relationship involved in his production process. Science outspread as transformative *praxis* in Primo Levi's work and in the subject/object relationship in the *praxis* to elaborate "The Periodic Table", disclosed his practical

awareness and awareness of *praxis*, as it can be seen in excerpts from his book.

According to Levi, human development was the reason for his practice, and it was driven by a liberating perspective, by outspreading a science that could help broadening the concept of world and society. This reason is linked to his biography, both because he had lived traumatic experiences in Auschwitz and because he had worked as chemist. He acknowledged these activities as potential humanizing role in the relationship man establishes with nature and society. This same formative and professional trajectory provided him with great conceptual and scientific expertise, which stands out in his work and is acknowledged by other authors.

Despite the elements explained in the current analysis and the fact that "The Periodic Table" has been awarded as the best science book of all times, it has not been analyzed as SC work. It is partly so, because of a narrow view heading towards scientific-knowledge outspreading. Therefore, one of our main remarks in the current article is that it feels like we could identify two opposite ways of conceiving SC or of providing simplistic explanations for scientific contents by using linguistic and multimedia resources or by introducing science as a way to conceive the world through its practice and culture. Levi's way represents the second and broadest SC perspective. The aim of the present study was to broaden SC understanding as praxis based on a case study and to stand against this narrow view of SC and the superficial reasons often linked to it. The herein adopted perspective is part of discussions carried out by other authors who believe in overcoming the PUS and PEST models and in heading towards a broader understanding of scientific culture, although it remains deeply anchored in science itself. 1,2,3,4

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FUNDINGS

The study was partly financed by São Paulo Research Foundation (FAPESP), Brazil. Process Number 2023/12333-6. Partly financed also by Minas Gerais Research Foundation (FAPEMIG), Brazil. Process Number APQ-02477-24.



Substantia

An International Journal of the History of Chemistry

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