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Joseph Achille Le Bel (1847-1930): from Pechelbronn Oil to Asymmetric Carbon

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Abstract – In 1874, Joseph-Achille Le Bel (1847-1930) was assistant to Charles-Adolphe Wurtz at the Faculty of Medicine in Paris. A young polytechnician and heir to the family company operating the oil fields in Alsace (France), he had worked on a method for the distillation of the pyrogenic products of petroleum that led him to the discovery of a mixture of amylenes. From his analysis of the mixture, he obtained two amyl alcohols, one active, the other not.

This marked the beginning of his questioning of the relationship between the rotatory power and the structure of the molecule. Chemists working in Wurtz's laboratory predicted the possible isomers of organic substances by applying the principles of the new so-called structural chemistry, and then confirmed their existence by experiment. In November 1874, as part of his research, Le Bel published a new and clear explanation of molecular asymmetry in its relation with rotatory power, a property that Pasteur had discovered in 1848.

Two months earlier, in September 1874, Jacobus Henricus van 't Hoff had published an article defining what he called asymmetric carbon and its correlation with rotatory power. Although Le Bel and van 't Hoff were working as colleagues in Wurtz's laboratory at the time, they always maintained that they had not exchanged ideas. The context of Wurtz's school was therefore the source of a discovery ready to blossom. Le Bel worked all his life on the stereochemistry of substances, in particular on the asymmetry of nitrogen and the molecules of life, thereby confirming the validity of the principles that he had laid down in 1874.

Keywords: Joseph-Achille Le Bel, amyl alcohol, asymmetric carbon, rotatory power, stereochemistry

Riassunto – Nel 1874, alla pubblicazione del suo fondamentale articolo, Joseph-Achille Le Bel (1847-1930), era assistente di Charles-Adolphe Wurtz presso la facoltà di medicina di Parigi. Giovane allievo dell'École Polytechnique ed erede dell'impresa di famiglia di sfruttamento dei giacimenti petroliferi di Pechelbronn, in Alsazia (Francia), aveva sviluppato un metodo di analisi dei prodotti pirogenici derivanti dalla distillazione del petrolio, che l'aveva portato alla scoperta di una miscela di amileni. Dal trattamento della miscela, Le Bel ottenne due alcol amilici, uno attivo e l'altro no, che riuscì a separare grazie a una serie di distillazioni frazionate successive, guidate dal potere rotatorio. Fu l'inizio della sua riflessione sulla relazione tra il potere rotatorio e la struttura molecolare.

I chimici che lavoravano presso il laboratorio di Wurtz applicavano i principi della nuova chimica cosiddetta strutturale per stabilire, in particolare, i possibili isomeri dei composti organici esaminati, confermandone poi sperimentalmente l'esistenza. Questa metodologia permise a Le Bel di concepire una spiegazione chiara e semplice dell'asimmetria molecolare definita da Pasteur nel 1848. Il suo articolo teorico sulla relazione tra l'asimmetria molecolare e il potere rotatorio fu pubblicato nel novembre 1874.

Due mesi prima Jacobus Henricus van 't Hoff aveva pubblicato un lavoro su quello che aveva definito carbonio asimmetrico e la sua relazione con il potere rotatorio. Ma i due chimici, colleghi presso il laboratorio di Wurtz nel 1874, affermarono sempre di non essersi confrontati su queste loro idee. Il contesto della scuola di Wurtz era dunque il grembo di una scoperta pronta a sbocciare.

Le Bel lavorò tutta la vita sulla stereochimica, in particolare sull'asimmetria dell'azoto e delle molecole del mondo vivente, confermando la fondatezza del principio enunciato nel 1874.

Parole Chiave: Joseph-Achille Le Bel, alcool amilico, carbonio asimmetrico, potere rotatorio, stereochimica

Introduction

Le Bel's article reporting the discovery of asymmetric carbon (an expression proposed by van 't Hoff, which Le Bel subsequently adopted) is a landmark. It marks, along with van 't Hoff's article, the beginning of stereochemistry, and it reads well today. It did not trigger a strong reaction in France, the only exception being Marcellin Berthelot's in March 1875. Such objections as were raised arose mainly from a conviction that such a geometric law could not be general. Le Bel devoted most of his laboratory life to studying the stereochemistry of carbon and then that of nitrogen. In this work, he supported his arguments with a wide range of indisputable experiments, with a view to confirming the generality of the proposition and its predictive power. The question I asked myself, after reading Le Bel's articles between 1871 and his publication of 1874, was the following.

How was he able to move from oil analysis to asymmetric carbon?

Information on this subject is scarce and vague. The experimental procedure improved as observations progressed. The detailed knowledge of Pasteur's work, on the one hand, and the mastery of the recently invented techniques of structural chemistry now used in Wurtz's laboratory, on the other, can also provide keys to understanding. Reading the later articles, where he refers to his early work, likewise provides some answers. Here, I will try to present a few points that can help us understand the pathway followed by Le Bel.

Fig. 1. Joseph-Achille Le Bel, as president of the Société chimique de Paris, 1892. By courtesy of the Société chimique de France. Public domain.

1. 1874: Near-simultaneous discoveries of asymmetric carbon

In 1874, without consulting each other, two chemists, students of Charles-Adolphe Wurtz at the Faculty of Medicine of Paris, published independently and almost simultaneously a definition of asymmetric carbon and the rules which govern its action on polarized light, characterized by rotatory power. The rules or principles are set out below. Although they were similar in the two cases, the approaches used were different.

J.-H. van 't Hoff's paper

In 1874, the word "stereochemistry" did not yet exist. Victor Meyer proposed it in 1888 [4]. The article by Jacobus van 't Hoff (1852-1911) appeared in a Dutch brochure in Utrecht, and in French in the *Archives néerlandaises* in September 1874. Finally, a concise version, taking account of Le Bel's article, was published in the *Bulletin de la Société chimique de Paris* (*BSCP*) in March 1875 [37]. From Kekulé's model for the methane molecule, van 't Hoff defined the asymmetry of its trisubstituted derivative, giving a non-superimposable shape to its image. Carbon was placed at the center of a regular tetrahedron with its binding affinities directed towards the vertices, the only configuration making it possible to explain the number of isomers of a polysubstituted methane. The discussion was supported by a representation of two tetrahedrons arranged facing each other. We know that van 't Hoff built such models in wood. In his words:

> «In the case where four affinities of a carbon atom are saturated by four different univalent groups, we can obtain two, and only two, different tetrahedra, which are the mirror image of each other (…); that is to say, we are dealing with two isomeric structure formulae in space » [4].

Introducing a new word, "asymmetrical", he then deduced:

> « I. Any carbon combination which, in solution, causes a deviation from the plane of polarization, has an asymmetric carbon atom. II. Derivatives of optically active combinations lose rotational power when the asymmetry of all carbon atoms disappears; otherwise, in certain cases, however, they do not lose it.» [4][1].

Van 't Hoff then moved on to the case of carbons doubly bonded by the image of two tetrahedra touching one edge, giving two isomers $R_1R_2C{=}CR_3R_4$, then triple bonded by three tetrahedra joined by one face. In the latter case, no asymmetry is observed.

Le Bel's paper

In November of the same year, in the *Bulletin* of the Société chimique de Paris (*BSCP*), a theoretical paper appeared entitled: *On the relationships which exist between the atomic formulas of organic bodies and the rotatory power of their dissolutions* [19].

This periodical, considered a leading one in Europe at the time, generally presented only reports of experiments and very few theoretical articles, certainly no wholly theoretical article like that of Le Bel. As the title indicates, Le Bel set out to find rules for predicting rotatory power by considering still undeveloped formulae and principles of symmetry.

He began by recalling the work of Pasteur defining molecular asymmetry in 1848. The correlation between asymmetry and rotational power is evident for crystals. If it is only due to the crystalline form, the solution will not be active, but if it is due to the molecule itself, the solution will retain its rotatory power [19]. Before 1874 there was no rule that would reliably predict whether a


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MÉMOIRES PRÉSENTÉS A LA SOCIÉTÉ CHIMIQUE.

Sur les relations qui existent entre les formules atomiques des corps organiques et le pouvoir rotatoire de leurs dissolutions; par J.-A. LE BEL.

Fig. 2. Title of Le Bel's 1874 paper, Bulletin de la Société chimique de Paris, t. 22, 337-347. Public domain, open access on Gallica-BnF.

body was endowed with rotatory power. Le Bel's paper presented a series of principles and rules, followed by examples taken from the author's experiments, or offered for verification in accordance with two principles.

The *first general principle* reads:

> «In general, if a body derives from our primitive type MA_4 by the substitution for A of three distinct atoms or radicals, its molecule will be asymmetrical and it will have rotatory power.» [19].

M can be any tetravalent element other than carbon. A can be a simple element or a group or radical. The MA_4 formula underlines the abstract character of the proposition at the same time as its generality.

Le Bel, however, added two exceptions:

> « 1° if the standard molecule has a plane of symmetry containing the four A atoms, the substitution of these by radicals (…) cannot in any way alter the symmetry in relation to this plane, and then the whole series of substituted bodies will be inactive. 2° the last radical substituted for A can be composed of the same atoms as all the rest of the group into which it enters, and the effect of these two equal groups on polarized light can compensate or reinforce: if this compensation occurs, the body will be inactive; but it is possible that this arrangement presents itself as a derivative of an active and asymmetrical body with a very little different constitution.» [19].

The *second general principle* states that:

> «If we substitute two radicals R and R' for the fundamental type MA_4, there can be symmetry [no rotatory power] or asymmetry depending on the constitution of the MA_4 molecule. If this molecule originally had a plane of symmetry passing through the two atoms A which were replaced by R and R', this plane will remain a plane of symmetry and the body obtained will be inactive.
>
> In particular (…), if two or even three substitutions provide only one and the same chemical isomer, it will be necessary to admit that the four atoms or radicals A occupy the vertices of a

[1] Translations of the French texts [3, 4, 19, 31, 35] are the work of the author.

regular tetrahedron whose planes of symmetry will be identical to those of the molecule MA_4, in this case, no bisubstituted body will possess rotary power.» [19].

Then follows a series of examples illustrating these propositions.

The immediate application to bodies of the fatty series showed the generality of the first principle. An example is CH_4, where various radicals can be substituted for hydrogens. Active bodies were then obtained by substituting three of the hydrogens with different radicals, provided that the four initial hydrogen atoms were not in the same plane[2].

«Thus, if in the structural formula of a substance we find a carbon combined with three monatomic [univalent] radicals different from each other and different from hydrogen, we must encounter an active body.» [19].

Le Bel then reviews the carbides of the unsaturated fatty series, and finally the aromatic series, to end with a theorem:

«If in a reaction an asymmetric body is formed in the presence of two active bodies themselves, there will be in the same proportion two isomers of inverse symmetry, therefore the result will be inactive. The typical example being tartaric acid obtained by synthesis which is always an inactive or racemic acid.» [19].

The publication appeared in the *Bulletin* of a young learned society, founded in 1857, and was not presented before the Academy. In fact, the article was the result of a long process of maturation that drew both on Le Bel's own experiments and by the contact he had within the circle of chemists close to Wurtz. If the primary aim of Le Bel's analyses was to better exploit the products extracted from petroleum, isolating them to understand their properties and see if an industrial application was possible, his true desire now drove him to pure research.

In Wurtz's laboratory, there reigned an intellectual context aware of the very latest discoveries [2]. This focussed, on the one hand, on the identification and properties of organic bodies extracted from coal, the establishment of series concerning alcohol, aldehyde, ketone and acids, and their mutual reactions. On the other hand, these substances were studied, supported by the concept of Kekulé's tetrahedral carbon, radicals assimilable to univalent elements, structural writing (graphic formulae) developed in the 1860s (introduction of hyphens in a developed formula) proposed by Abraham Couper in 1858 and which had evolved with Alexander Crum Brown (1838-1932), until the adoption in 1866 of the definitive form that we know by Edward Frankland (1825-1899) [10, 23]. The work of Wurtz and Friedel in this area had been decisive for the diffusion of new ideas in France. These modern ideas were present in the *Bulletin de la Société chimique de Paris* and in the *Annales de chimie et de physique* and discussed on Saturday afternoons at Wurtz's regular seminar.

2. Joseph-Achille Le Bel: a young Alsatian chemist

Let's come back to Le Bel the person [22, 36]. The family had left the south of France for Alsace in 1761, to operate a bitumen concession in Pechelbronn. The main product was a grease in high demand for vehicle axles. It was extracted from asphalt and bitumen and collected by buckets at the bottom of mine shafts. Joseph-Achille Le Bel, the fourth and last with this name, was born on January 21, 1847, the youngest child and only son of a family of four. His father, Achille, had also developed the agricultural estate thanks to his brother-in-law Jean-Baptiste Boussingault (1801-1887), who had made it a true experimental agronomy station run according to the methods pioneered by Lavoisier. Professor of chemistry at the Conservatoire national des arts et métiers, in Paris since 1841, Boussingault had shown the importance of the role of nitrogen in agronomy [12]. With Achille, Joseph-Achille's father, he carried out analyses of the asphalt produced on the property, and opened other wells from which he extracted anthracene and petrolen. There is no doubt that it was he who introduced Joseph-Achille to experiments from a very young age and encouraged him to embark on the study of chemistry.

In 1865, at just eighteen, Joseph-Achille, a gifted student, entered the École Polytechnique with a very honorable rank. He left two years later and joined the Service du Génie in 1867. He was first in his class but he preferred to resign to devote himself to chemistry [13]. At the École Polytechnique, he attended the lectures of Auguste Cahours (1813-1891), assistant professor of chemistry [8]. This internationally recognized chemist applied the principles of Charles Gerhardt to homologous series. Among other things, he discovered an amyl alcohol. An outstanding experimenter, his research on vapor densities and radicals provided decisive arguments for the adoption of Avogadro's law and the development of the theory of valency [1]. Le Bel was therefore a competent chemist both experimentally and theoretically when he

[2] At that time, different models were proposed for methane. Talking about arrangements in space was a very new way of considering molecules and remained the object of severe criticism.

became an assistant at the Faculty of Science in Strasbourg, under Professor Jean-Pierre Liès-Bodart (1811-1882), Gerhardt's successor in the chair of chemistry.

In December 1868, Le Bel joined the laboratory of Antoine Balard (1802-1876) at the Collège de France. There the emphasis was on traditional chemistry along with research on possible industrial applications. But in Paris, there was a laboratory in the Faculty of Medicine, that of the Alsatian Charles-Adolphe Wurtz (1817-1884), whose research offered exciting opportunities for the young polytechnician. From the end of 1869, Le Bel moved from the Collège de France to become an assistant to Wurtz.

In Wurtz's laboratory

Le Bel quickly preferred the bubbling, creative atmosphere of Wurtz's laboratory to the routine of Balard's. The laboratory was a real melting pot of new ideas. It was a unique place in France where research in organic chemistry was carried out in accordance with new theories, notably the representation of formulae according to the rules of so-called structural chemistry, allowing them to be written in semi-developed formulae (Today expression). This clearly highlighted the groups of atoms or radicals and made it possible to predict the possible isomers which could then be determined by experiment. The laboratory was frequented by many foreigners. It also welcomed women, and everyone paid their share of the products and materials necessary for the experiments [32]. Le Bel found there the intellectual breeding ground that suited him.

His first contributions, however, did not stray from the path set for him by the family operation, now under family co-management, as Le Bel et C[ie], following the death of his father in 1867. The primary aim of his analyses was to better exploit the products extracted from petroleum, isolating them so as to understand their properties and see if exploitation on the industrial scale was possible.

3. Analyses of Pechelbronn oils

A laboratory existed on the family estate, where the extracted crude oils were analysed. There, Le Bel repeated the analyses of the different deposits made twenty years earlier by his uncle Boussingault. His observations were published in the *BSCP*, and Wurtz also presented them to the Academy [14-16]. The distillation of Pechelbronn oils attracted particular attention. Le Bel observed that the pyrogenic products obtained were very rich in saturated carbides (paraffins) and fatty products (ethylenic in particular). He obtained liquids of two kinds, distilling in one case between 60° and 70°, and in the other between 30° and 40° [15, 16]. Each part was then separated and analysed.

Analysis of the fraction distilling between 30° and 40° leads to two amylene iodhydrates corresponding to «C^5H^{10}.HI» ($C_5H_{11}I$). Le Bel then thought that the starting product contained two isomeric amylenes which must therefore be separated.

He found the way of separating them by chance. A first treatment by the action of cold hydrochloric acid led to an amylene hydrochloride resembling the hydrochloride of fermentation amylene. By this procedure, Le Bel had therefore isolated one of the two amylenes [15]. A second treatment with hot hydrochloric acid led to Wurtz's ethylallyl, the alcohol of which is different from the fermentation amyl alcohol. This method, cold treatment then hot treatment, also made it possible to separate two hexylene hydrochlorides for the distillate collected between 60° and 70°. Preparing the iodhydrate in the same way – a method that Le Bel invented and used throughout his life – led to the same results for the hexylene.

We know that between 1869 and 1874, Le Bel was mainly in Paris. As listed in the directory of the Société chimique, he was resident at the Faculty of medicine. That, at least, was his professional address; it was given with no further details, though he could have been staying with his uncle Boussingault in Paris or even have been back in Pechelbronn. The question remains open[3]. He also spoke at meetings of the Société chimique. For example, on July 19, 1872, he reported the preparation of isohexyl alcohol from the pyrogenic essences of Pechelbronn oil [34]. On this occasion he described a first two-ball distillation apparatus in which a metal mesh allowed the condensed liquid to reflux into the ball, while maintaining distillation.

He had already undertaken in-depth research on a category of substances, alcohols, forming a series characterized by types of well-known reactions. Among the alcohols, those of the amyl series had already been well inventoried. Today, we know eight amyl alcohols, three of which are chiral[4].

[3] In fact, there is no accommodation at the Faculty of Medicine. Le Bel specified that large quantities of these volatile oils were obtained at the factory. The more delicate distillations had to be done in Paris.

[4] https://fr.wikipedia.org/wiki/Alcool_amylique (Seen on 31 January 2025).

4. 1873: On the trail of active amyl alcohol

So far, there was no indication that Le Bel was on his way to a fundamental discovery. But then, in 1873, he published an article, *Procédé pour préparer l'alcool amylique actif* [17, 18]. Active amyl alcohol derived from commercial amylene was well-known, but difficult to prepare. This time, Le Bel abandoned the industrial aspect and focussed his discussion entirely on fundamental research. Until now, he had not presented any formula or talked about rotatory power. But the title itself is suggestive of the fact that rotatory power was to have a major role to play in his research.

In the article, Le Bel begins by referring to Pasteur's work on commercial amyl alcohol [25]. Pasteur had removed an abundant inactive alcohol of known constitution and an active alcohol whose rotatory power was 20° for a column of 50 cm. This last alcohol was little studied, to the point of being considered as a state of physical isomerism of the inactive alcohol, especially since it lost its rotatory power by the action of potash. Amyl chloride was also known to be somewhat levorotatory, while the corresponding iodide and bromide were dextrorotatory. Le Bel decided to study this anomaly, thinking that it was due to the different method of preparation of these three halogenated bodies. This is the first time that Le Bel invokes the rotatory power of the substances he was examining. He used a purified commercial amyl alcohol. The bromide and iodide were prepared by the action of iodide and phosphorus bromide on amylene. Amyl chloride was prepared by the action of hydrochloric acid. However, Le Bel noted that this amyl chloride contained a residue of amyl alcohol which it was necessary to purify. As he discovered, after a new treatment with hydrochloric acid by the method developed a few months previously, the deviation became minimal. When then treated successively with sulfuric acid and phosphorus perchloride, any trace of residual amyl alcohol had disappeared.

The mixture formed by the two chlorides was more active than the original chloride, so that the chloride obtained from the residual alcohol (1/10 of the mixture was untransformed) during the first reaction was itself active. «It remained to isolate this untransformed amyl alcohol and directly measure its rotational power.» [17]. After a long series of purifications, he obtained a dextrorotatory chloride, then an active alcohol whose rotational power was 22.5° for 50 cm in sodium D radiation with a Cornu polarimeter, a higher figure than Pasteur's. The value of the rotatory power was now associated with the degree of purity of the solution studied.

Fig. 3. J.-A. Le Bel with his polarimeter, in his laboratory, 250 rue Saint-Jacques, Paris (France). By courtesy of the Société chimique de France.

The procedure for obtaining a pure active alcohol (cold treatment, then hot with hydrochloric acid), followed by purifications taken to the limit thanks to a suitable fractional distillation apparatus [11], and successive measurements of the rotatory power during the operations, was subsequently to become a standard method. These compounds had to be obtained as pure as possible, in order to track the location of the radicals in the chain formed, and to ensure the structure of the isomers obtained.

A research in a known world

Let's now return to the title of the article. This shows that Le Bel placed his research in a known world, that of amyl alcohols obtained by a series of reactions and distilled for purification. Indeed, several studies on alcohols and their derivatives had appeared in the *Annales de chimie et de physique*, and in the *BSCP*. For the period which concerns us, let us note some useful articles for the rest of our discussion.

In 1869, Isidore Pierre (1812-1881), dean of the Faculty of sciences in Caen, and his assistant Ed. Puchot, reported on their method of repeated fractional distillations to separate an alcoholic mixture. The first operation was to transform the mixture into iodides and then separate them. Each fraction was analysed and then retransformed into alcohol. In this way, they were able to determine the density and the boiling temperature, the two physical criteria of purity sought for each alcohol [26]. In 1870, they proposed a series of investigations of the oxidation products of normal amyl, butyl and propionic alcohols [27-29]. Each alcohol was to be studied in three distinct situations: 1. Dehydration and successive rectifications. 2. Action of an oxidizing mixture of potassium dichromate and extended sulfuric acid. 3. Etherification [esterification] then regeneration with a hydrated alkali. The properties to be determined were in order: boiling temperature, density at 0°, refractive index at 0°, and *action on polarized light*.

The authors provide a table of their results. In the three conditions described, each alcohol behaved as a single chemical species. This identity of fundamental physical properties can be considered as an index of purity. Only amyl alcohol has a significant effect on polarized light [29]. Only the raw formulae are given.

In the same year, the *BSCP* reported a process for separating the two amyl alcohols from potato oil by Ernest T. Chapman and Miles H. Smith, one of which is active on polarized light, the other inactive. The English chemists separated the two alcohols after saturating them with soda (or potash). The active alcohol was distilled first until the residue solidified. Water was then added and distilled again. They obtained amyl alcohol whose rotatory power was weaker than that of primitive alcohol. The operation was repeated until the limit of reduction in rotatory power was reached. «We thus obtain large quantities of pure inactive alcohol.» [3].

In 1871, at the SCP meeting, Joseph Riban (1838-1917), assistant to Balard, reported on the continuation of his research on the rotatory power in the amyl series, starting with amyl alcohols from various sources (rice, potatoes, beets), whose rotatory power was approximately the same (-2°8', for a length of 20 cm). A table of results was provided with a comment by Riban. Amyl alcohols and amyl chloride had a left deviation, wile derivates (aldehyde, acid, iodide, oxalate) had a right deviation. Riban concluded that the greatest number of derivatives therefore had a deviation contrary to the generating alcohol. Only chloride deviated in the same direction as the corresponding alcohol but Riban did not exploit this observation [33][5]. We are thus gradually seeing the rotatory power appear in the literature, but though not as an object of mainstream interest.

In 1873, the *Bulletin* offered a summary of the article by Pierre and Puchot on the action of the main derivatives of amyl alcohol on polarized light [30], published in the *Comptes Rendus de l'Académie des sciences (CRAS)* in June [31]. Pierre and Puchot confirmed Riban's observations of 1871 without naming the author, and concluded that the optical action seemed inherent to the amyl molecule, without being able to go further:

> «Although there do not appear to be simple, easily grasped relationships between the rotatory powers of the various substances that we have studied and their accepted molecular constitution, we thought that the observation of this property, as well as the measurement of its intensity for a certain number of them, could offer some interest, both from the point of view of their exact specification, and from other points of view of a more general or higher order» [31].

None of these three chemists proposes formulae or goes beyond this observation that the rotatory power is inherent to the molecule itself since it is preserved in its derivatives, although here inverted; an anomaly is noted but its study was not pursued. Pierre, Puchot and Riban clearly felt that the purity of the original product was a determining element for the observation. Le Bel was aware of this and had developed his own technique to approach it as closely as possible, wanting to respond to the anomaly of a levorotatory chloride, and the method of obtaining a pure substance. The two are linked. The article on the process for obtaining an active amyl alcohol responds to these two aspects of this known problem. So, when Le Bel's article on amyl alcohol appeared, it was a contribution to a broader body of research on the same subject.

5. The founding article of 1874: Some examples

In 1874, Le Bel moved from articles with a mainly industrial focus, to an experimental research article and then to one with a theoretical focus. The study of amyl alcohols gradually led him to reflect on the reason for their optical differences. For this, it was necessary to take developed or semi-developed formulae into account. Although Le Bel did not explain his thinking, he probably applied the rules of structural chemistry that had been used in the Wurtz laboratory for several years. Charles Friedel, a committed activist for the atomic theory as a heuristic tool, used structural chemistry to identify the isomers of organic compounds, and then to verify these predictions in the laboratory [9]. Whereas Friedel worked on three and four carbon carbides, Le Bel worked on the five and six carbon carbides present in the pyrogenic products from Pechelbronn. From the corresponding developed plane formulae, he would have made the connection between the heterogeneity of the substituents around a particular carbon with its corresponding rotatory power, which would explain the asymmetry of the solution.

[5] A few months later, at the SCP session on January 5, Le Bel presented his work on isohexyl alcohol obtained from Pechelbronn essences.

Generally speaking, atoms and monatomic radicals (with a single bond possibility) are assimilated to material points or spheres in space, the same if these atoms or radicals are identical, and different if these are different. This modeling, which on paper leads to a flat semi-developed structural formula, makes it possible to predict the possible isomers. The appearance of rotatory power can be predicted in the same way and as a result can lead to two optical isomers.

Le Bel's general principles that I presented at the beginning of this article were followed by examples numerous enough to illustrate all aspects of them. Here are some.

Saturated bodies derive from marsh gas, CH_4, by substitution of hydrogens by various radicals. One of its derivatives, lactic acid CH_3-C*HOH-CO_2H, is active by application of the first principle, while ethylenolactic acid is inactive: CH_2OH-CH_2-CO_2H. Malic acid is active: CO_2H-CH_2-C*(H,OH)-CO_2H, as is the asparagine which derives from it.

The most interesting case is that of tartaric acid, the subject of Pasteur's studies: the semi-structural formula is CO_2H-CHOH-CHOH-CO_2H, structurally deriving from formene (methane), but it can appear under two inverse symmetries (the molecular model attests to this). If the two groups are superimposable, the effects on polarized light will be reinforced. If, on the contrary, the two groups are not superimposable, the effects on polarized light are neutralized. In the latter case, the acid is inactive. This example illustrates the second principle. In fact, tartaric acid exists in three forms, two active and one inactive.

Then comes amyl alcohol and sugars. Here we return to our example, amyl alcohol, C_2H_5-C*H(CH_3)-CH_2OH. Many of its derivatives retain its rotatory power:

> «This body provides a very large series of derivatives in which we always encounter the rotatory power, as long as its characteristic is found in the formulae: ethers [esters] of amyl alcohol, conjugated acids including valeric acid, valerates and ethers [esters] valeric, amylamine, etc. But amyl hydrure (2-methylbutane, CH_3-CH(CH_3)-C_2H_5) is inactive, which is obvious from its structural formula (two identical radicals linked to the asymmetric carbon). This proves that the existence of the amyl radical is not related to the rotatory power of its combinations.» [19].

Consequently, it was not the amyl radical itself that was active, as some imagined. What gave it this property was the respective arrangement of the four substituents linked to the central carbon.

In the case of sugars, Le Bel added:

> «The general constitution of the bodies is known, but their exact formulae have not yet been determined; we must therefore limit ourselves to predicting the facts using general formulae.» [19].

He then detailed at length the case of a sugar whose normal hexatomic alcohol had several asymmetric carbons. All its forms were not yet known, but the reciprocal influence of asymmetric carbons could explain the dextrorotatory, or levorotatory, power, or its low or high value. It was not until 1890 that Emil Fischer clarified these different aspects [23].

Le Bel then addresses the case of fatty substances with double bonds (two atomicities, for example ethylene), which are more complex. The case of bodies of the aromatic series followed.

If we compare Le Bel's article with van 't Hoff's, the approach is similar. Like van 't Hoff, Le Bel relied on geometric considerations. In this, he was clearly following in the footsteps of Pasteur and his experimental approach. However, he chose a more abstract path to illustrate his propositions, using plane-developed formulae.

But 1874 was also a pivotal year on the family level. Under the pressure of German occupation in Alsace, Le Bel had to be away from Paris, so as to devote more time to the family business.

6. From the Paris laboratory to Alsatian oil deposits and back, 1874-1889

By now, Pechelbronn had been in annexed Alsace since 1871. Le Bel, like other Alsatian entrepreneurs, had to deal with the German administration. This led to his being officially recognized as the head of Le Bel et C^{ie}, a position that required him to reside permanently in Alsace after 1882. From 1874 to 1889, he improved the operating conditions, causing the company to grow by 40% per year [36]. At this time, in Pechelbronn, the materials he collected by drilling was no longer bituminous sands but Pennsylvania-type oil. In fact, a well had just yielded a significant quantity of low-density oil, from which lighting oil could easily be extracted. News of this discovery of this type of oil in Pechelbronn spread quickly, and several manufacturers set up on the margins of the concession, creating de facto competition.

Between 1885 and 1889 Le Bel published a number oil analyses including a comparative study of the oils of Pennsylvania, Baku and Crimea, though always as part of his personal research programme. By analysing the different oils, he showed that they were all composed of normal chain carbides *and* side chain carbides. Using his

Lactic series	
$CH^3-\underset{HO}{\overset{H}{C}}-CO.OH;$ le carbone central se trouvant dans le cas exigé pour l'application du premier principe général, ce corps doit être actif.	**Lactic acid** The central carbon fulfils the conditions for the first principle. Hence, this substance is necessarily *active*.
Tartaric series	
Groupe tartrique. — L'acide tartrique a pour formule: $\left[CO\text{-}OH-\underset{HO}{\overset{H}{C}}\right]——\underset{HO}{\overset{H}{C}}-CO\text{-}OH.$	**Tartaric acid** The first principle can be applied. But here, viewed in three dimensions, two symmetries are possible, *active* in one case, *inactive* in the other.
Amyl series	
Groupe amylique. — L'alcool amylique actif a pour formule: $CH^3-\underset{H}{\overset{C^2H^5}{C}}-CH^2.OH.$	*Active* amyl alcohol
le diamyle, etc. Il n'en est plus de même de l'hydrure d'amyle: $CH^3-\underset{H}{\overset{C^2H^5}{C}}-CH^3.$ On voit en effet qu'il contient deux méthyles unis au même carbone; ce corps est en effet inactif. Ce fait prouve que l'existence du radical amyle n'est pas corrélative du pouvoir rotatoire de ses combinaisons.	[2-methylbutane] *Inactive*. This shows that the amyl radical bears no relation to the rotatory power of its combinations.

Table I. Le Bel's formulae, from his 1874 article [19]. Public domain, open access on Gallica-BnF.

familiar technique of distillation, he extracted the amylenes (or the other unsaturated fatty carbides), which he treated using the method he had devised during his early work: first, the *cold treatment with saturated hydrochloric acid*, leading to a tertiary carbide (a test for branched chain carbides); this meant that the amylene had a branch chain, and hence that *the oil contained branched chain carbides*, and secondly, *hot treatment with hydrochloric acid* (a test for straight chain carbides) with which only normal chain amylenes reacted. It followed that *the oil also contained straight chain carbides* [20].

Although Le Bel devoted time to the company, he always found time for his own research too. In this, active amyl alcohol remained a key which, along with the measurement of rotatory power, was the most important guiding principle of his work. Throughout, knowledge of the stereochemistry of substances was his primary goal. This showed that his theory of asymmetric carbon remained valid, and that in fact it could be extended. After his original article, between 1874 and 1889, he published around thirty articles closely connected with the relationship between stereochemistry and rotatory power, including six on amyl alcohol. It was then, in 1889, that he began the study of the stereochemistry of nitrogen [5].

In 1889 also, in the broader international context of the formation of large oil companies, the question of the future of the family business presented itself. The company had an integrated structure (production, processing, marketing) though on a small scale compared with the large groups that were beginning to form in the field. What followed was intense competitive pressure from foreign firms wishing to buy the Le Bel company. In response, the family decided to sell to a specially created company, the Pechelbronner Ölbergwerke (PÖBW) AG, made up of 21 Alsatian entrepreneurial shareholders brought together by Alfred Herrenschmidt[6], the brother of the husband of Adèle Joseph-Achille's sister, to avoid a sale to German interests. In this way, the PÖBW, with its roots in the Alsatian upper bourgeoisie, acquired the concession and real estate of *Le Bel et C^ie^* in 1889. Le Bel's château, however, remained in the family, and Joseph became advisor to the PÖBW [36].

As Le Bel's publications show, his return to Paris allowed him to assume the role of a savant, rather than an industrialist. He again attended the chemistry laboratory at the Faculty of Medecine, now directed by Armand Gautier (1837-1920) following Wurtz's death in 1884, and Friedel's laboratory in the rue Michelet. He set up a personal laboratory in or near his successive homes. Finally, in 1904, he moved definitively to a private mansion built by him at 250 rue Saint-Jacques, behind the Pantheon. On the first floor, he installed a laboratory, where he resumed active research on the asymmetry of nitrogen derivatives. This was his main center of interest until the beginning of the 20th century. One notable result was an important article on the constitution of ammonium in 1904 [5]. This summarized his previous research on the subject, though it is a subject that I will not develop here.

7. A Life in Chemistry: Successes, Criticisms and Failures

Fruitfulness of the theory

Le Bel and van 't Hoff's proposals bore fruit several years later. Although van 't Hoff did not pursue research in stereochemistry in as much depth as Le Bel, he did seminal work in chemical kinetics and the osmotic pressure of solutions, for which he received the first Nobel Prize in Chemistry in 1901 (not, we should note, for asymmetric carbon). There was no jealousy between the two men. In a spirit of mutual respect, they always stated that they had discovered the property of asymmetry independently of each other. In the 1887 version of *Chimie dans l'espace, dix ans dans l'histoire d'une théorie*, van 't Hoff dedicated his work to Le Bel and referred to the memoir of November 1874 [38].

Methodically, Le Bel continued to plough his own furrow. He enlarged upon certain aspects of the theory in publications immediately after 1874, notably in the tests for the separation of asymmetric carbides and on the absence of rotatory power in aromatic carbides, and from 1888 on the asymmetry of nitrogen.

On the occasion of the celebration of the fiftieth anniversary of the asymmetric carbon theory in 1924, Marcel Delépine published a retrospective of the advances in chemistry made possible by the theory since 1874 [4]. As Delépine observed, many of Le Bel's predictions only took on meaning some years later, mainly from the 1890s. Concerning the stereochemistry of nitrogen, for example, the low volume of radicals was seen to constitute a reason for mobility, and consequently racemization. When the volume was increased, the stability increased. In this way, Le Bel was able to separate quaternary ammonium salts (1900), an achievement that William Pope and S. J. Peachey subsequently confirmed. The optical consequences of steric hindrance, discovered later, had therefore been anticipated by Le Bel. He also studied the equilibrium conditions linked to stereochemistry, the change of sign of the rotatory power, the influence of temperature, etc.

Critical appreciations

These future studies confirmed the fruitfulness of the asymmetric carbon theory. In 1924, a group of French personalities, ministers, academicians, and foreign chemists, including Ernst Cohen from Utrecht and William Pope from Cambridge, came specially to honor the solitary scientist in Paris, following the celebration of his Dutch contemporary a few weeks earlier in Amsterdam.

The old quarrels were undoubtedly forgotten. Who now remembered Berthelot's reaction when Henninger reported van 't Hoff's work at a meeting of the Société chimique on 19 March 1875? Berthelot, who was chairing the meeting, pointed out that the proposals of neither van't Hoff nor Le Bel adequately explained the activity of a body. As he insisted, both van 't Hoff and Le Bel should have taken account of the rotatory and vibratory movements determining the behaviour of any particular atom or group of atoms in a molecule. In his words:

> «This dynamical conception of compounds opens the way to simpler, more general explanations than the purely geomet-

[6] A tanner in Strasbourg, at the head of several diversified companies, Alfred Herrenschmidt became president of the Strasbourg Chamber of Commerce in 1892.

rical representation of atoms lying on a plane, or even distributed at the vortices of a polyhedron … The existence of rotatory power is clearly explained by the different orientation of their vibratory motions…» [35].

Still others in the 1890s had minimized the concepts resulting from stereochemistry, such as the crystallographer Grégoire Wyrouboff (1843-1913) and the chemist and polytechnician Albert Colson (1853-1933). Le Bel responded with papers in the *CRAS* and the *BSCP* that countered their arguments. By repeating their experimental analyses, he showed that the substances studied were not pure, and that tiny traces were sufficient to distort the result. That is to say that the distillations to obtain them had not been pushed far enough [5].

Relative failure

Although the theory had some success, it was not enough for its author to be admitted to the Academy. Le Bel had applied several times under pressure from his academic friends, but without success. Disinclined to solicit the support that academic success demanded, he had to wait until the age of 82, in 1929, a year before his death, to don the ceremonial green uniform. Even then, he was not elected in the chemistry section, but as a *free* member (membre libre), as successor to Maréchal Foch's chair. Financially independent, he was indebted to no one and had never sought an academic career, a situation that left him free to follow his own interests. Why then had he not been elected to the Academy at the time of his discoveries? For Gérard Emptoz, one reason was that he did not have a doctorate or an academic position [6]. While he had the support of a large number of renowned French chemists, his friends did not have enough clout to get him accepted.

Finally, in the eyes of many, stereochemistry was only of interest to a small group of specialists. Speaking at a council meeting of the SCF in 1924, the secretary general Ernest Fourneau, observed that «the very name of Mr. Le Bel (was) unknown to the general public»[7]. Even so, Le Bel had been elected a foreign member of the Royal Society in 1913.

[7] SCF Archives, Book of the Council minutes, n°8, meeting of 22 October 1924.

Towards other interests

This non-recognition by the Academy may have contributed to directing Le Bel's attention towards other interests. In his private laboratory, he carried out experiments on what he calls catathermy. The catathermic effect, as he wrote in his 1925 essay, *Cosmologie rationnelle*, consists in transmitting energy in the opposite direction to heat and light radiation [21]. The times for such speculation were promising, marked by the discovery of radioactivity, X-rays and electromagnetic waves, or the no less hypothetical N-rays. The beginning of the 20th century also saw Le Bel devote himself to prehistoric excavations in his domain of Laugerie-basse at Les Eyzies in Dordogne.

Although he moved away from the scientific world, he remained an active member of the Société Chimique de France, of which he had been president in 1892 and on several occasions a member of the Council. A frequent but discreet benefactor of the SCF, he bequeathed his fortune, including the hotel in rue Saint-Jacques, to the society, today its headquarters [7].

Conclusion

Le Bel therefore remains a scholar apart, even if, from the beginning, he was part of a network of atomists. Although he had no students, he did have collaborators, including Henninger and Alphonse Combes (1858-1896), with both of whom he published. He was insatiably curious, constantly questioning. As Pasteur said: « remember that in the fields of observation chance only favors prepared minds… » [24]. This was the case for Le Bel as well as van 't Hoff, in the experience they shared as assistants in Wurtz's laboratory in 1874; both men had a profound understanding of the optical activity of molecules, and the consequences that followed. At much at the same time, other chemists, working in contexts different from Le Bel and van 't Hoff's, had come close to the discovery, but were unable to achieve it.

Le Bel's industrial activities unquestioninably set him apart a little, compared with the other members of this atomist network, who, in France or elsewhere, had academic careers. But his discovery of asymmetric carbon at the same time as his colleague Jacobus van 't Hoff made him an essential link in the understanding of matter and life.

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