Joseph Achille Le Bel.
His Life and Works

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Reseñas Biográficas

Joseph Achille Le Bel es un ejemplo de científicos como Réaumur que investigaron muchos temas, pero solo son recordados por uno. Le Bel es un nombre bien conocido por los estudiantes de Química en general, y estereoquímica en particular. El nos dejó los principios básicos que determinan las condiciones geométricas que un compuesto de carbón debe satisfacer para que presente actividad óptica. Aparte de esto, desarrolló una teoría curiosa respecto al origen del Universo.

Resumen
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Introducción
Joseph Achille Le Bel es un ejemplo de científicos, como Réaumur, que did research in many subjects but is remembered by only one. Le Bel is a well-known name to students of Chemistry in general, and stereochemistry in particular. He left us with basic principles that determine the geometrical conditions that must be satisfied by a carbon compound in order to have optical activity. In addition, he developed an unusual theory regarding the origin of the Universe.

Biografías

Joseph Achille Le Bel was born on January 21, 1847, at Péchelbronn, Alsace, the youngest of the four children of Louis-Frédéric-Achille Le Bel. From the side of his father he was a nephew of Jean-Baptiste Dieudonné Boussgault (1802-1887) an experimental agricultural chemist who also managed the Lobbsann petroleum field. Le Bel came from a wealthy family that controlled a bituminous sand and asphalt processing plant at Péchelbronn and he personally managed it between 1882 and 1889. Le Bel started his high school studies at the Collège d’Hauenguau and completed them in Paris. In 1865, at the age of eighteen, he entered the École Polytechnique from where he graduated in 1867.

The same year his father passed away and his two sisters, Marie and Emma, took charge of the family industry and in this way allowed Le Bel to continue chemical studies. He was appointed préparateur (responsible for preparing the apparatus needed in lecture demonstrations) to the General Chemistry chair held by Liés Bodart at the University of Strasbourg but after a short time he left to take a similar position with Antoine-Jérôme Balard (1802-1876, the discoverer of bromine) at the Collège de France, with an annual remuneration of 1,500 francs. In 1873 he moved to Paris to work in the laboratory of Charles-Adolphe Wurtz (1817-1884), at the École de Médecine in Paris. After Wurtz death, his successor Armand Gautier (1837-1920) continued to employ Le Bel as an assistant.

Simultaneously to his work with Wurtz he took an active role in the management of the family business, doing research in the area of petroleum and its chemistry. His results led him to adopt Dimitri Mendeleev’s (1834-1907) view that petroleum deposits resulted from the action of steam on metallic carbides at volcanic temperatures. In 1879 he introduced in Péchelbronn the Fauvelle well-perforation method that led to the production of new subproducts and the discovery of fields of light oil and gas. In 1885 Le Bel installed vertical stills that allowed him to quadruplicate the production of the factory and to obtain head products of distillation lamp oil. In addition he installed dewaxing units for separating the liquid oil...
from the materials that solidified at room temperature. All these improvements should be considered against the background that at that time Alsace was under German domination and France had no petroleum sources of her own.

In 1889 the Le Bel family transferred the Péchelbronn factory to a group of Alsacien investors, and moved Paris. The Péchelbronn works were severely damaged during the Second World War; on August 4, 1944, a total of 1,350 bombs was dropped on it, destroying it almost completely.

Le Bel was appointed member of the Société Chimique in 1869. He became its Vice President in 1890 and President in 1892. Afterwards, he served in different committees of the same and made many cash contributions to it. In April 1890, he offered a money prize of 50,000 francs for the rediscovery of a microscopic green alga, found and lost by him, which had the power of converting atmospheric nitrogen into ammonia.

Le Bel, like most of the scientists of the time, was interested in research related to agriculture. He was a great friend of the pioneer agriculturist Émile Lefton, who recommended him for the presidency of the Société des Sciences Rurales. In 1892, he was elected President.

Le Bel was a complete autodidact, and hardly ever made any attempts to join the academy, being a stranger to any form of vanity. Even though he published little, it would be a mistake to suppose that after his significant success in stereochemistry – he was hardly 30 years old then – he stopped his scientific work. During ten years he tried to establish a connection between the crystal forms of chemical compounds, but he rejected all attempts of his friends to publish the results of his work, saying that his observations were of no significance and fell short of the goals he had envisioned for himself. He had a 45 m deep shaft constructed, so that he would be able to perform certain experiments under constant temperature.

He treated his plants and flowers with great love. These grew first in the garden of his laboratory in Rue Amyot, but as he moved to another house, they had to be brought to a terrace, which soon became reminiscent of a hanging botanical garden.

An interesting point is that on the occasion of Le Bel's 80th birthday, a medal was issued in his honor. In it, next to his great discoveries of marine asymmetry (1872), petroleum, stereochemistry, crystallography, fermentation, cosmogony and prehistory, will be discussed now, with particularly emphasis on his work on the asymmetry of carbon.

SCIENTIFIC ACTIVITIES

Some of Le Bel's most relevant contributions to the chemistry of petroleum, stereochemistry, crystallography, fermentation, cosmogony and prehistory, will be discussed now, with particularly emphasis on his work on the asymmetry of carbon.

1. Petroleum and hydrocarbons

The first scientific publication of Le Bel appeared in 1872, was done at Wurtz's laboratory and was devoted to discussing the properties of the bitumen present in the fields located in Schwabwiller, Péchelbronn, and...
and Lobsann (Lower Rhine). This work is historically interesting because it signals Le Bel’s first acquaintance with amyl alcohol, a substance he would investigate thoroughly.

In this publication Le Bel showed that the most volatile fraction of these bitumens contained pentane, hexane, and unsaturated components. The latter were easily converted into their chlorides and iodides, particularly amyl iodide, and then into an amyl alcohol mixture boiling in the range 118 to 121 °C. His amyl iodide had a boiling point similar to that of the ethyl allyl iodide, synthesized previously by Wurtz. Treatment of the amyl iodide with silver oxide produced a mixture of isomyl alcohol (today 3-methyl-1-butanol) and isoamyl ether, while treatment with silver acetate yielded pure isoamyl acetate.

In a following memory Le Bel gave full experimental details about his procedure for separating the volatile components of petroleum and the preparation of several derivatives, for example, isoamyl and isohexyl alcohols, and the identification of two isomers of the same. His considered his procedure so simple that he added the comment that if a commercial use was found for these compounds it would be very easy to prepare them in large amounts.

In his investigation about petroleum sources containing large percentages of volatile (olefinic) components, Le Bel found that the amount of volatiles decreased if the oil was kept for a long time in contact with water. He believed that these volatiles reacted with water and that the resulting derivatives were soluble in water and in the oil; olefins from heptene on produced hydrate crystals that were soluble in both phases and decomposed easily on heating. Le Bel used these findings to substantiate his explanation that petroleum deposits that were in contact with water (like the ones in American oil fields) contained only saturated hydrocarbons.

In a study related to the reaction between hydrochloric acid and olefins in general Le Bel developed a simple procedure for separating olefins. He found that olefins having the general structure $\text{CH}_2=\text{CRR'}$ and $\text{CHR}=\text{CR'CH}_2$ reacted with a cold aqueous solution of saturated HCl while those with general formula $\text{CH}_2=\text{CHR}$ and $\text{CHR}=\text{CHR'}$ did not. This procedure allowed him to separate isomeric olefins like isobutylene (2-methylpropene) and 2-butenes.

Le Bel with his collaborators studied the reaction of several alcohols, according to the method proposed by Etard, in which an alcohol, dripped slowly over molten zinc chloride, was reduced to an olefin. In this manner he prepared $t\text{HCH}=\text{CHCH}_2$ from butanol and propylene from propanol. An unusual result of this reaction was that methanol, Le Bel expected that the dehydration of the alcohol would give place to several olefins of the ethylene series, instead he found that the reaction yielded hexamethylenbenzene, a crystalline laminar solid that melted at 160 °C and boiled at 259 °C. The elemental analysis was the same as a sample of hexamethylenebenzene prepared by Le Bel with Charles Friedel (1832-1899, codiscoverer of the Friedel-Craft reaction).

A subject that interested Le Bel in particular was the origin of petroleum. In papers published in 1885 and 1928 he discussed the following three significant theories about the origin of petroleum: (a) fermentation of animal or vegetable matter, as illustrated by the gas produced in marshes, (b) decomposition of soft coal under the simultaneous action of the heat from the Earth’s core and the pressure of the surrounding layers, the resulting products being petroleum and asphaltene, and (c) reactions of water with the Earth molten core (theory maintained by Mendeleev). He rejected the first hypothesis because it assumed that the petroleum formed was capable of stopping the fermentation process and killing the microorganism responsible. The other two seemed both reasonable, Le Bel preferred the one postulated by Mendeleev, although it was at odds with the fact that optical rotatory power had been detected in some petroleums. According to Le Bel the second theory explained well the presence of optical isomers but was unable to justify the presence in petroleum of asphaltenes and metals like iron, silicon, manganese, copper, and silver. Mendeleev’s theory did not require the presence of natural fuels because it was based of the reaction between water and metals present in the ferrisphere.

2. Amyl alcohol

In 1873 Le Bel became interested on why different halo derivatives of amyl alcohol presented opposite optical activities; amyl chloride was slightly levorotatory while amyl bromide and iodide were strongly dextro. The three chemicals were prepared by substitution of the OH group in the alcohol, they contained the same number of molecules grouped in the same manner, but nevertheless light rotation had changed direction significantly. Le Bel reasoned that the only possible explanation was the different manner in which the three halides were prepared: amyl bromide and amyl iodide were obtained by the action of phosphorus iodide or bromine on the alcohol, while the chloride was prepared by distilling the alcohol in the presence of hydrogen chloride. He proved his hypothesis by preparing the chloride by two different procedures, one distilling the alcohol in the presence of aqueous HCl, and the other heating to 110 °C amyl alcohol saturated with gaseous hydrochloric acid, followed by treatment with phosphorus pentachloride. The second procedure yielded dextro amyl chloride.

In a following publication found that the optical activity of active amyl alcohol disappeared if two of its radicals were made identical or one of them was transformed into the unsaturated form. Thus, treating active amyl iodide with methyl iodide in the presence of sodium yielded $\text{C}_5\text{H}_5\text{CH(CH}_3)^2\text{C}_2\text{H}_5$ while treatment with potassium ethoxide yielded $\text{C}_5\text{H}_5\text{CH}^2\text{C}_2\text{H}_5$; in both cases the loss of carbon asymmetry meant the loss of optical activity. Similarly, active amyl alcohol becomes racemic after treatment with sodium amylate.

Le Bel used the results of his work on amyl alcohol to justify the main consequences of his theory about carbon asymmetry: racemization, resolution by yeasts, disappearance of the required asymmetry, etc. In particular, Le Bel showed that the resolution of inactive amyl alcohol demonstrated that its structure necessarily contained four different groups and that it should be considered a mixture of the dextro and levo forms.

3. Crystallography

Le Bel did extensive work on the study of the crystals formed by the chloroplatinates of a large number of amines with the purpose of learning the influence of their composition on the crystalline form. It was well known that the chloroplatinate of ammonium was isomorphic with that of potassium, which was regu-
lar, and that the regularity was also valid for three of its relatives that is, for $M_n$, $M_2$, and $E_1$ (where $M$ is methyl and $E$ is ethyl). Le Bel's results indicated that this was also true for the octahedral salts $M_3$, $M_4$, and $MP$ (where $P$ is propyl). Salts like $PE_2$, and $EP_2$ derived from the cubic structure while salts like $MP_2$, $EP_2$, and $EMP$ that presented the particular characteristic of having their optical axes almost superimposed. Salts like $P_2$ and $P_3$ were characterized by having their axes perpendicular one to the other. According to Le Bel, the crystal form of all these salts derived from an equilateral pyramid having the four hydrogen of the ammonium group at the four summits.

Le Bel also prepared a large number of double salts formed by the chloroplatinate of ammonium bases, some of them were unable to combine between them but pairs like the chloroplatinates of tripropyl and triethylamine, dimethyl and methylpropylamine, and dimethyl and dipropylamine, were able to do so on a one to one mole ratio. The chloroplatinate of dimethylamine was particularly interesting for the large number of double salts it formed. Its double salts with another amine having two identical radical groups (like, for example, dipropylamine) were remarkably crystallized. Dimethylamine presented also the phenomenon of dimorphism, the ordinary stable form was reddish in color, had a density of 2.27, and its crystalline axis were in the ratio $a:b:c = 0.993:1:0.997$; the unstable form crystallized as yellow needles that were stable at 100 °C, had a density of 2.12, and its crystalline axis were in the ratio $a:b:c = 0.621:1.0:0.890$. Both crystals had an orthorhombic structure.

4. Fermentation and microorganisms

Le Bel investigated the fermentation of several substances, gelatin among them, as part of his work on the production of alcohols and fatty acids. Of particular interest is his paper on the fermentation of gelatin where he discussed the origin of the alcohols and fatty acids produced. Le Bel obtained the ferment (bacteria) of gelatin by seeding a 2% aqueous solution of gelatin with fecal matter, at 38 to 40 °C and gentle agitation. The resulting liquor became very alkaline and took a brown color. It was then used to seed 50 L of the same gelatin solution, the fermentation process was fast as long as every day Le Bel would neutralize the alkalinity with sulfuric acid; in about a few weeks the gelatin was totally consumed. The fermentation process was finished when no more ammonia was produced and addition of a small amount of acid turned the liquid acid. The product of the fermentation had an important characteristic: addition of a cord of gut and a cord of hemp caused the total dissolution of the first while the second was left untouched. From these results Le Bel concluded that the bacillus thus cultivated was capable of attacking the walls of the intestine and should certainly be considered one of the causes of acute enteritis, which at the time was treated with *bacillus bifidus* or the lactic ferment.

Le Bel analyzed the products of the fermentation of gelatin and found them to contain ammonium carbonate and several low fatty acids up to and including valeric acid. On the other hand, the fermentation of a sugar produced higher alcohols up to $C_5$, their quantity was larger if the substrate contained nitrogenous components. From this he deduced that these alcohols were derived from the nitrogenous substance. Fermentation of the nitrogenous substance alone gave a series of low fatty acids up to and including valeric acid. Le Bel explained the apparent absence of hexyl alcohols by assuming that distillation was unable to separate them from the pertinent fatty acids. Another finding was that *bacillus lactis* and others resisted the action of the light of a mercury quartz lamp. According to Le Bel, the resistance to this light was simply another confirmation of Svante Arrhenius' (1859-1927; 1903 Nobel Prize in Chemistry) panspermia theory that the light pressure of solar radiation could transport very small germs. These germs had a long longevity, particularly in interstellar space, and thus could be easily transported by a comet or an meteorite from one planetary system to another. Again, the required energy had to come from the ether and could be explained by the catathermic radiation Le Bel claimed to have discovered (see below).

5. Cosmogony

Besides his interest in petroleum and chemistry, Le Bel became interested in many philosophical subjects, particularly those related to the creation of the Universe. In a lengthy memory published in the Journal de Chimie Physique Le Bel presented his theories regarding the origin of the Universe stating from the beginning that his was a rational approach in that it assumed that the forces present in the cosmos had been able to maintain its existence without the help of any creator, and would continue doing it in the future. He was not trying to justify the existence of the Universe during a given period of time, no matter how long. It was necessary to find the causes able to maintain an indefinite cycle. He indicated that his discussion did not include supernatural phenomena, without negating the existence of a superior intelligent force. As we will see, the arguments presented in this paper are circular and somewhat unclear. They can be debated on the same basis he rejected the theories opposing his tenets.

The idea that the Universe was turning along the same circle was very old and the ancient philosophers had characterized it by a snake eating its tail. In modern times, it had been supported by Georges Louis Leclerc Buffon (1707-1780) and Emmanuel Kant (1724-1804), but it had lost crediblity after geology had shown that life seemed to have appeared on Earth, after an incandescence period, in the form of lower species that had evolved in time.

Le Bel went on to describe the different theories about the origin of the Universe, in order to justify his ideas on the subject. He claimed the best explanation was to be the one that the required the fewer hypotheses.

According to Pierre-Simon Laplace (1749-1827), the Universe was originally composed of matter distributed everywhere. Eventually, this matter had begun to concentrate very slowly giving place to the stars and planets. The discovery of the conversion of kinetic energy into heat explained the thermal energy present in these bodies. It was assumed that life had appeared spontaneously and Jean-Baptiste Lamarck (1744-1829) and Charles Robert Darwin's (1809-1882) theories justified the further evolution of living entities. According to Le Bel, although this hypothesis was very attractive it was basically wrong because it did not provide an explanation for the indefinite existence of the Universe. Not only that, Gustave Adolph Hirn (1815-1890) and Johann Wilhelm Ritter (1776-1810) had cal-
culated that according to Laplace’s theory it would have taken less than twelve million years to create the Sun, a number well below the one-hundred million years that the glacial age had lasted. In addition, the matter that had formed the Sun could not have come from everywhere in the Universe, after a certain distance it would have gone into forming other stars. Hence Laplace’s theory could not explain the permanence of the solar system in the past and in the future and it was contrary to the idea of a cyclic system or of an equilibrium state.

It was possible to extend Marie Curie’s (1867-1934; 1903 Nobel Prize in Physics) discoveries to assume that part of the matter constituting the stars had the property of decomposing, as radium did, and thus had provided during the Azoic and Paleozoic era the energy lost by the stars. Nevertheless, this fact could not be used to justify a cyclic theory because the mass of every star was limited and if the mass regenerated over the same star it would require the same amount of energy that had been released previously. The same arguments were to be used to reject a theory based on radioactive materials since they constituted a very small fraction of the total mass.

According to Charles Joseph Tissot (1828-1884), stars recovered the heat they were losing by absorbing radiation emitted by the ether, which originated from the transformation of the heat and light emitted by the stars (Le Bel called this radiation cathathermic). Tissot’s hypothesis had been rejected because it seemed to contradict Carnot’s principle: If the ether was at temperature $T_e$ and the star at temperature $T_s$, then the efficiency of the heat recovery process should be less than $(T_s - T_e)/T_e$, in other words, the radiation proposed by Tissot was unable to provide all the thermal energy required. Le Bel rejected this argument saying that to assume that the ether followed the same laws as material bodies was to accept not only that it had a temperature, it must also have a specific heat. Or, if the temperature of the ether was defined on the basis of the energy content per unit volume, this energy would be zero resulting in a value of unity for Carnot’s efficiency. In other words, there was no contradiction between Tissot’s hypothesis and the thermodynamic principle regulating the behavior of material bodies. Simply, the celestial space behaved like a perfect mirror, with the difference that this mirror did not send the primitive ray but a radiation. Le Bel substantiated his arguments by saying that Gavriil Adrianovich Tikhov (1875-1960) and Charles Nordmann had already demonstrated that ether influenced light in a similar way as material bodies, that is, the velocity of light depended on the wavelength.

According to Le Bel, Tissot’s theory implied that the heat recovered by a star like the Sun, was composed of three elements: (a) the one that came from the star itself and was returned by the surrounding celestial space, (b) the heat that came directly or indirectly from other stars in the Milky Way, and (c) the one received from stars located outside the galaxy. The last contribution was probably negligible due to the enormous distance between the galaxies and was also independent of the position of the Sun in the Milky Way.

The immediate consequence was that the hottest stars should be located in the central part of the Milky Way. This consequence was substantiated by the known fact that stars close to the Sun also possessed a metallic spectrum, hotter stars had a protometallic spectrum, while gaseous stars had temperatures in the range of 20,000 to 25,000 °C.

Le Bel went on to say that the Sun was traveling from a region poor in stars towards a point called the solar apex, located near the Hercules constellation, rich in stars. That is, our system was leaving a cold region (period) and approaching a hotter one. This was not surprising since it was known that our world was leaving a glacial epoch. The Sun was not following a linear or regular trajectory because it was forced to travel through a network of stars, being rejected, every time, towards a farther away position farther way that would lead to a new period of cold. These periods would be extreme every time the Sun would locate itself in the external part of the ring forming our galaxy. Thus, the existence of ancient glacial periods on the Earth was simply a consequence of Tissot’s theory.

Le Bel indicated that two arguments had been given against the cyclic planetary theory: One indicating that CO2 would eventually become unavailable because it would be absorbed by the alkali generated from the decomposition of granite rock. These carbonates would eventually become part of magnesium and calcium salts that in the end would settle in the bottom of the seas and become unavailable for recirculation. The second argument claimed that in the heat period corresponding to lunar volcanoes, life should have disappeared completely but the fossil record had not contributed primitive rocks proving that they had existed. Spontaneous generation was unattainable but we had proofs of a creation followed by destruction. According to Le Bel, these arguments were easily discarded. First of all, he had proven that a warm period fitted better a cyclic theory than the one proposed by Laplace. Not only that, the passing of the Sun through the central parts of the galaxy implied an increase in temperature but this did not mean that the planets had become incandescent. It was possible that the high temperatures achieved in the equatorial area could have killed tall animals and plants, but inferior forms of life would have certainly survived in the poles and their spores would have been easily transported by the winds from one pole to the other. In addition, the high temperatures would have increased substantially volcanic action and the water’s temperature, resulting in the transformation of sedimentary rocks into crystalline forms, thus destroying the fossil record.

Le Bel pointed out that Arrhenius had already raised the possibility that germs could be transported from one planet to another and that this transport could have been effected by the action of the pressure of light upon the spores. The same spores could also have been carried within a meteorite and survived the conditions in space. These were rare phenomena but certainly possible when considering the infinite life of the Universe.

Le Bel concluded that there was an absolute need for a cycle and that the Universe had functioned and continued to function by its own means. The heat lost by the stars returned to them by means of a material substance or by the vibrational movement of the ether or other fluid. Both mechanisms had to originate in the celestial space in order to pick up the energy required. These two hypotheses had the same difference as the one between the matter and wave theories of light. The latter theory was the one we were used to and thus he was tempted to think that energy recovery was due more
to vibrational effects than to the fall of material particles upon the stars.

Along with to these philosophical speculations, Le Bel dedicated time to investigate what he called catathermic radiation, that is, a radiation that originated in the interior of a body heated nonuniformly and that reflected, in a smaller scale, the radiation that Tissot claimed was emitted by the ether (for example, references 16, 17).

A curious fact about Le Bel’s speculations about the Universe is that he made no mention of the Principle of Entropy Growth, although it was well known in his time. According to Le Bel ether did not have mass, nevertheless, his reasoning implied that it was able to create energy without leaving traces (perpetual motion engine of the first class). His catathermic radiation had the same characteristic. Another curious fact is that Lépine, in his book about the life and works of Le Bel, mentions his theories but does not say a word about how they were received and to what criticism they were subjected (Lépine wrote his book while he was President of the Société de Chimique).

6. Prehistory

In two communications to the Société de Chemie Le Bel reported that in Eyzies, Dordogne, he had found a cave where the stalactites presented some interesting mineralogical characteristics. They were covered by a calcareous vegetation going in every direction although directed upwards. The water did not seem to ascend by capillarity but by a small internal channel. When hit by a pickaxe they gave sparks, which Le Bel assumed to be due to silica crystals or flint inserted between the other crystals. He took a sample to his laboratory and to his surprise when digested with HCl it yielded only a very small amount of jelly silica. Le Bel found that this phenomenon was uncommon, it existed in only few caves, usually characterized by being very old. Analysis of samples that came from other caves that presented the same characteristic (Han-sur-Lesse, Belgium; La Cave, Rocamadour) yielded again a very small amount of silica. Le Bel attributed the phenomena to triboluminescence.

The stalactites in Eyzies had also the characteristic of being generally inclined and taking bush-like shapes called coral bushes. Anyhow, the most curious formation were the ones called stag horns, very slim with their branches forming perfect half-circles. According to Le Bel, these formations were extremely rare because the air in the caves was normally very dry.

7. Stereochimistry of carbon

First of all, some words about the concept of stereochimistry and isomerization. It has been known for more than 150 years that asymmetric crystals of certain minerals, such as tourmaline (a borosilicate mineral of complex and variable composition) and quartz, rotate the plane of polarized light and that the rotatory power of these minerals is lost if the crystals are melted or dissolved. In other words, the asymmetry of the mineral resides only in the crystalline form. Certain carbon compounds, however, rotate the plane of polarized light in solution (for example, cane sugar solutions) or even in the gaseous state (turpentine, for example). In these cases, optical activity is a property of the molecules themselves. The crystals of optically active minerals are asymmetric and it is equally certain that the molecules of active carbon compounds are also asymmetric. Solutions of compounds described as optically active rotate the plane of polarized light either to the right (dextrogyres) or to the left (levogyres).

Stereoisomers are molecules that contain the same functional groups and have the same structure but differ in the spatial arrangement of the component atoms. Stereoisomers may be configurational or conformational; configurational isomers are interconverted by the breakage and reformation of a bond while conformational are interconverted by rotation about a single bond. Diastereoisomers are stereoisomers that do not have a mirror image relationship between them and this definition includes isomerism owing to the presence of a double bond. Traditionally, the term geometrical isomerism has been used to describe this type of stereoisomerism.

The terms cis and trans are usually used to describe the diastereomeric forms of simple alkanes. However, their use is not always ambiguous and recently, to avoid ambiguities that may arise, the so-called sequence rules have been employed to assign the configuration of an alkene. When the two groups of higher priority from each end of the double bond are on the same side of the double bond then the configuration is defined as Z (from the German, zusammen, together) and when the two groups of the higher priority are on opposite sides of the double bond then the configuration is defined as E (from the German, entgegen, across).

Dextro and levo optical isomers are known as enantiomers or enantiomorphs (from the Greek, enantios, opposite, and morphē, form). They differ in the direction in which they rotate the plane of polarized light; the difference, however, is in direction only, for the specific rotations of the two isomers are numerically equal.

Enantiomorphs usually differ markedly in their optical activity, biological behavior, and their reactions with chiral reagents, but are very similar in ordinary physical and chemical properties; they have the same melting points, boiling points, solubilities, dipole moments, and other such physical properties. Optical antipodes show identical chemical behavior in most of their reactions. For example, the reactions of l-lactic acid are exactly those of d-lactic acid. Both acids form salts, esters, and other acid derivatives in the regular manner. Furthermore, there is no difference in the rate of such reactions. There is a difference, however, in the rates of reaction at which optically active compounds react with other optically active substances in the formation of diastereoisomers.

Unlike enantiomers, diastereoisomers differ in their physical and chemical properties, allowing their separation by fractional crystallization or chromatography.

Before discussing Le Bel’s contribution to this area, let us look first at the history of the knowledge on optical activity. In 1815 Jean-Baptiste Biot (1774-1862) discovered the presence of rotary power in certain natural organic substances such as sugar, gum, dextrin, camphor, and turpentine. These findings came after his research on the rotation of polarized light in quartz, following the discovery of the same by François Arago (1785-1853), in 1811. His discoveries were followed by the inferences of René Just Haüy (1743-1822) and John Herschel (1792-1891) about the sense of rotation in quartz and certain facets of the crystal. From the very beginning, Biot realized that the rotatory power of the organic substances depended on the constitution of the substance and could take place in the solid, liquid,
and gaseous phases. The property was lost only when the substances decomposed. In 1843 Apollinaire Bouchardat (1806-1886) reported that the same phenomena was present in alkaloids and glucosides.

The real cause of the optical phenomena remained unknown until Louis Pasteur’s (1822-1895) pioneering research. In 1848 Pasteur discovered that the crystals of the sodium ammonium salt of tartaric acid, a dextrorotatory optically active substance, exhibited hemihedral facets, that is, one half of all the faces developed unequally. Observation of many other crystal forms of tartaric acid led him to believe that the phenomena of hemihedry and optical rotation were interrelated.

Pasteur found further that the crystals of paratartarate (racemic tartaric acid) also exhibited hemihedral facets but that the hemihedry sometimes faced to the right, and sometimes to the left, that is, the racemate crystals were specimens of two asymmetric types, one the mirror image of the other. Pasteur summarized his findings in the three following rules:

(a) When the elementary atoms of organic products were arranged asymmetrically, then the crystalline form reflected this asymmetry by non-superimposable hemihedry.

(b) The existence of molecular dissymmetry was reflected by the existence of rotatory power.

(c) If the non-superimposable molecular asymmetry occurred in opposite directions (like it existed in levo and dextro tartaric acids, as well as in their derivatives) then these bodies had identical chemical properties.

Pasteur succeeded in obtaining two forms of tartaric acid, one of which one rotated the plane of polarized light to the right (dextro tartaric acid), the other to the left (levo tartaric acid). The question arose immediately about the arrangements of the atoms in the molecules of these substances. In 1860 Pasteur asked. “Are the atoms of the right acid grouped on the spirals of a dextrogyrate helix, or place at the summits of an irregular tetrahedron, or disposed according to some particular asymmetric grouping or other? We cannot answer these questions. But it cannot be a subject of doubt that there exists an arrangement of the atoms in an asymmetric order, having a non-superimposable image. Pasteur was interested chiefly in the separation of optical isomers and in the study of bacteria and other microorganisms, which often produced such substances and left the theoretical explanation of the molecular structure to others. Pasteur’s ideas were not extended to molecular structures even after Kekulé had explained the structures of organic compounds on the basis of the tetravalence of carbon.

The year 1874 signaled the initiation of stereochemistry as we know it today. Le Bel, starting from the views of Pasteur, and van’t Hoff, starting from the more rigid ideas of August Kekulé (1829-1896), arrived independently at the theory that when the four substituents around a carbon atom are different, that is, the carbon compound is asymmetric, molecular images must exist and they must show opposite optical activities. Both Le Bel and van’t Hoff used this idea to explain many cases in which such isomers did or did not occur.

Le Bel started from a different consideration than van’t Hoff; they were not based on graphs, the latter were more abstract but also more general. As indicated by the title of his paper Le Bel was intent in finding the rules that allowed prediction of the existence of rotatory power.

Le Bel started his paper by stating that there was no known method to predict if the solution of a substance had rotatory power. Although the derivatives of an active substance were generally active, nevertheless it would be found often that this property would disappear in the most near derivatives and would persist in very remote derivatives. He went on to state that based on geometrical considerations alone he had been able to derive some general rules that would allow answering the following question: Given a molecule having the formula MA₄, composed of a simple or complex radical M, how will it combine with four univalent atoms or radicals (A) and become optically active?

Pasteur had already found that molecular asymmetry and rotatory power were closely associated. If asymmetry existed only in the crystalline molecule, then the crystal would be active, but if the asymmetry belonged to the molecule, then its solution would also show rotatory power. The crystal may also show this property of its structure allowed perceiving it, like in the case of strychnine sulfate of amyl amine alum.

Le Bel stated then that his reasoning ignored the possible asymmetries, which might arrive from the spatial arrangement of the atoms and monatomic radicals, that is, he considered them to be spheres or material points, which would be identical if these elements were equal, or different if they were different. He justified these assumptions on the basis that all the cases of isomerism observed thus far could be accounted for without assuming a particular spatial arrangement. He then went on to state the following two principles:

First general principle. Replacement of three of the A’s by simple or complex univalent radicals, differing from one another and from M, will yield a dissymmetric molecule that will have rotatory power. If we assimilate the three radicals (R, R’, and R”) and A to material points, they will form a structure that is not superimposable on its image and the residue M will be unable to reestablish symmetry.

This principle had two clear exceptions: (a) if the original molecule had a symmetry plane containing the four atoms A then the substitution product would be unable to change the original symmetry and all the set of possible derivatives would be inactive; (b) if the last radical substituted for A had the same atomic composition as the rest of the group into which it entered, then the net optical effect would result in the canceling or strengthening the original one. In the first case the final effect would be zero optical activity. For example, if in MR₄R₄R₄, the last radical was substituted by the grouping MR₄R₄, the two groups would neutralize or synergize one another.

Le Bel illustrated this first exception with tartaric and erythric acids, which also represents one of the exceptions cited by van’t Hoff’s paper.

In his first principle Le Bel analyzed the case of three substitutions in compounds of structure MA₄, he then went on to discuss what happened when only two new radicals were introduced.

Second general principle. If, in our fundamental molecule only two radicals were substituted (R and R’), it was possible to have and not have symmetry according to the structure of the original molecule MA₄. If the original molecule had a symmetry plane passing through the two atoms A that were replaced by R and R’, then this plane would remain a plane of symmetry after the substitution.
and the resulting compound would be inactive.

Le Bel went on to state that if a single substitution furnished but one derivative, but also if two and three substitutions gave only one and the same chemical isomer, then we were forced to admit that the four atoms of A occupied the vertices of a regular tetrahedron. The symmetry planes of the latter were identical to those of the original MA₄ molecule. In this case no bisubstituted product would possess optical rotary power.

Although Le Bel did not give an example for the second exception, it is clear that it would be applicable to combinations of bivalent platinum such as [PtABCDX₂], [PtA₂X₄], etc.

From the above principles it can be seen that the concept of tetrahedral carbon was a result of symmetry arguments and no more. Actually, in a later publication Le Bel stated clearly that he was not the originator of the tetrahedron theory.22

Le Bel applied then his principles to saturated compounds of the fatty series, noting that all of them derived from methane by substitution of one or more hydrogen atoms by various radicals. Since optically active trisubstituted derivatives were available it was clear that the four hydrogens did not lie on the same plane and thus his first principle was applicable. Not only that, since methane gave only one derivative when two or three substitutions were performed, then the second principle was also applicable and hence, any member of the fatty acid that had a carbon atom united to a hydrogen, a hydroxyl, and two different radicals; these sugars would generally be active. Sugars derive from hexatomic alcohols, such as mannose and glucose. Inspection of normal hexanol (Fig. 1) indicated that each of its four central carbons had potential rotatory power. If the only cause for the dissymmetry of the above molecules related to the manner in which the radicals surrounded one of these four carbons, we would then have a levogyre or dextrogyre substance only, but since its four carbons had this property then a large number of isomers was possible. Nevertheless, since the four carbons had similar structures, it could be well that some were levo and others dextro, resulting in a molecule that had very little rotatory power, as was the case for mannitol, dulcitol, and their nitric and acetic derivatives.

Le Bel concluded his paper by stating the following theorem: When an asymmetric body is formed in a reaction where only asymmetric bodies are present, then the two isomers of inverse symmetry will be formed in the same amount. He based this conclusion by considering two independent events having equal probabilities m and m′; in this case the ratio m/m′ would tend to one if the sum (m + m′) approached infinity (that is, if the event was repeated an infinite number of times). The synthesis of tartaric acid was an excellent example of this situation: it always produced dextro and levo acids (racemic acid) in the same proportion.

As we have seen, Le Bel’s paper is largely concerned with the relationship between molecular dissymmetry and optical rotation and only once (in the case of the tetrahedral carbon atom). A curious fact is that van’t Hoff was also working with Wurtz and he and Le Bel announced the same theory almost simultaneously. van’t Hoff’s paper appeared in Dutch in September 1874, and Le Bel’s was published in French in November of the same year; however, there is no evidence that either was influenced by the other. Each arrived at his conclusion independently at this time probably because organic chemistry had reached a point at which such a theory had become essential to further progress. The structural theory, which had so well explained many types of isomerism, had failed to account for optical isomers.

Although both of the two are linked together in the development of the theory of the tetrahedral arrangement of the carbon valences, the question of the relative importance of their contribution to the development of stereochemistry remains unsettled. According to Snelders24 “it is evident that the 1874 ideas of van’t Hoff rather than those of Le Bel must be considered as the foundation of the stereochemistry of organic compounds”.

On the other hand, Grossman states26 that “it is van’t Hoff’s system that was adopted by chemists; the symmetry considerations of Le Bel, although often cited as being among the founding ideas of stereochemistry, were usually pushed into the background.” Grossman explains this attitude on the fact that van’t Hoff’s concepts were easier to assimilate than Le Bel’s abstract ones. In addition, van’t Hoff made significant contributions to other fields, such as kinetics and physical chemistry. Grossman speculates that had Le Bel had been a professor at a major German university his contribution to stereochemistry would have been given much more weight.

Fig. 1. Hexanol normal.
8. Stereochemistry of nitrogen

Le Bel’s brilliant work in the domain of carbon asymmetry led him to believe that pentavalent nitrogen could exhibit the same phenomenon. Before considering his results we must realize that at the time they were done nitrogen was assumed to be quadrivalent and that the ammonium radical had a substitution value of the same order as that of the four substituent radicals. For example, some chemists considered the chloride of ammonia to be ammonium chloride while others described it as nitrogen pentahydrichloride. In the latter the five atoms attached to hydrogen had an identical role (all five valences were active and the other inactive. The preferred form was the inactive one. In the same paper Le Bel prepared the methylpropylisobutyl ammonium and described how he obtained a solution exhibiting a small rotatory power from the corresponding chloride by the action of Penicillum glaucum. Le Bel attributed the optical activity to the asymmetry of pentavalent nitrogen. Later, other researchers were unable to confirm this result, for example, Pope and Read[22] prepared the same compound from ethylpropylisobutyl iodide and methyl iodide and found that its behavior was the same as claimed by others, but different from the compound prepared by Le Bel. Pope and Read[23] claimed that Le Bel had not obtained methyl-substituted ammonium iodide, that is, the optical activity his product could not be associated with the presence of an asymmetric quinquevalent nitrogen atom.

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