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Alexandre Édouard Baudrimont: Crystallography, colloids, aqua regia

Alexandre Édouard Baudrimont: Cristalografia, coloides, agua regia

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ABSTRACT:

Alexander Édouard Baudrimont (1806-1880) was a French physician and pharmacist that carried on fundamental research on a wide variety of subjects, among them, philosophy of science, linguistic, colloidal chemistry, cosmology, crystallography, mechanics of materials, etc. The same as Ampère, he proposed a new theory where only certain geometrical shapes were able to induce a chemical reaction. When atoms combined to form an integral molecule, they assumed an arrangement that if not regular, was at least symmetric. Chemical formulas did not represent the absolute number of atoms present; they represented only a number proportional to the real one. Crystalline particles were always small polyhedrons, which adapted one to the other without leaving empty spaces, a condition satisfied only by only cuboids, hexahedral prisms, and dodecahedrons. Baudrimont was one of the pioneers of colloid chemistry; many of the results of his experiments about colloids anticipated in many years those of Graham. He showed that the stability of an artificial emulsion depended on the relation of the amount of water added to that of the glue, and not that of the oil. Organic products enjoying a more or less complex organization, they were always solid or soft, forming spherical or spheroidal particles having diameters varying from 2/100 of a millimeter to about one millimeter. At higher levels the particles arranged themselves under the influence of definite forces, Baudrimont proposed that the gas chloronitric acid as the active compound of aqua regia. Its liquid boiled at -7.2°C. This gas attacked all the metals it came into contact and with pulverulent silver it exploded and disappeared instantly. Its composition, NO_3Cl_2 , was very similar to that of anhydrous nitric acid.

KEYWORDS: Aqua regia, atomic structure, colloids, crystallography, physics.**RESUMEN:**

Alexander Édouard Baudrimont (1806-1880) fue un médico y farmacéutico francés que realizó investigación básica en un amplio rango de temas, entre ellos, filosofía de la ciencia, lingüística, química coloidal, cosmología, cristalografía, mecánica de materiales, etc. Igual que Ampère, propuso una nueva teoría en la cual reacciones químicas ocurrían solo entre moléculas que tenían una forma geométrica particular. La combinación de los átomos para formar una molécula integral resultaba en un arreglo que, si no era regular, era por menos simétrico. Las fórmulas químicas no representaban un número absoluto de los átomos presentes, solo un número proporcional al verdadero. Las partículas cristalinas eran siempre poliedros pequeños que se adaptaban entre sí sin dejar espacios vacíos; solo los cuboides, prismas hexaédricos y dodecaedros satisfacían esta condición, Baudrimont fue uno de los pioneros de la química coloidal. Muchos de sus experimentos sobre coloides anticiparon por muchos años los de Graham. Demostró que la estabilidad de una emulsión artificial dependía de la razón entre las cantidades de agua y de cola, y no las del aceite. Los productos orgánicos que estaban organizados en forma más o menos compleja, eran siempre sólidos o blandos, formando partículas esféricas o esferoidales, con diámetro entre 0.02 y 1 milímetro. A un nivel más alto, las partículas se ordenaban de acuerdo a fuerzas específicas. Baudrimont propuso que el ácido cloronítrico era el componente activo del agua regia. En forma líquida hervía a -7.2°C. Este gas atacaba todos los metales y con plata pulverulenta explotaba y desaparecía en forma instantánea. Su composición, NO_3Cl_2 , era muy parecida a la del ácido nítrico anhidro.

PALABRAS CLAVE: Agua regia, coloides, cristalografía, estructura atómica, física.**AUTHOR NOTES**^a Department of Chemical Engineering, Ben-Gurion University of the Negev, Israel. wisniak@exchange.bgu.ac.il

LIFE AND CAREER (MICÉ, 1880; BARY, 2011; BRAM, 2015)

Alexander Édouard Baudrimont was born in Compiègne on May 7, 1806, the son of Marie- Victor Baudrimont, foreman of roads and bridges, and Adélaïde Sauvage. After finishing his basic education at the age of twelve, he began working as general help in a pharmacy, and then moved to another pharmacy where he met Théophile-Jules Pelouze (1807-1867) who was also employed there. Eventually his father allowed him to move to Paris to begin formal pharmacy studies and in 1823 he matriculated at the École de Pharmacie. In 1825 he enrolled in the Faculté de Médecine de Paris. In 1826 he obtained his baccalauréat ès lettres and the following year his baccalauréat ès sciences. In 1828 he was accepted as pharmacist intern at the central pharmacy, under the direction of the anatomist Antoine Serres (1786-1868), with whom he published his first paper about an encephalic tumor (Serres & Baudrimont, 1829). He financed his medical studies managing a glass manufacturing industry near Valenciennes and giving private classes of physics and chemistry. He received his medical degree in 1831 after successfully defending a thesis about the classification of medicines (Baudrimont, 1831). Afterwards he practiced medicine at Valenciennes, at the time of the cholera epidemics of 1832. The observations he made about this illness led him to develop a very particular and successful method for its treatment, which he also applied afterwards during the epidemics of 1849 and 1854 that decimated the city of Bordeaux (Baudrimont, 1866).

In 1866 the *Académie des Sciences* awarded him a reward of 1866, within the Bréant Prize, for his researches about epidemic cholera. After returning to Paris in 1832, he completed his studies of pharmacy and in 1834 he was awarded the diploma of pharmacien de 1re classe. The following year he passed the aggregation examination of the Faculté de Médecine. During these years he also worked at a sugar factory (Baudrimont, 1841) and collaborated in the publication of the *Dictionnaire de l'Industrie Commerciale et Agricole* (Baudrimont, 1833-1841). He also published his book *Introduction à l'Etude de la Chimie par la Théorie Atomique* (Baudrimont, 1833), a book opposing the prevalent theories, which earned him a position as préparateur at the laboratory of Louis-Jacques Thenard (1777-1857) in the Collège de France. In 1835 he quitted the Collège de France to open a preparatory school of chemistry for those interested in learning chemistry in preparation for the entrance examinations of the faculties of Chemistry and Medicine. In 1838 he tried, unsuccessfully, to become agrégé to the chemistry chair at the École de Pharmacie, with a thesis about the present state of chemistry and the use of microscopic techniques (Baudrimont, 1838). In 1839 he postulated to the chair of medical substances, with a thesis about the dosing of medicines from the viewpoint of their intensity and mode of action (Baudrimont, 1839). In 1846 he was awarded the *Grand-Prix des Sciences Physiques* by the *Académie des Sciences* for a memoir presented in collaboration with Gaspar Joseph Martin Saint-Ange (1803-1888) describing the embryonic evolution of birds and amphibians (Baudrimont & Saint-Auge, 1844b). In 1847 he received his degree of *docteur-ès-sciences* and was then appointed suppléant to the chair held by Auguste Laurent (1807-1853) at the Faculty of Bordeaux. In 1848 he was promoted to *chargé de cours* (responsible for the course) and in 1849 to titular of the chair. He tried and failed to obtain the chemistry chair at the *Institut Agronomique de Versailles* and at the *Collège de France* (Micé, 1880; Bary, 2011; Bram, 2015).

Baudrimont received many honors and awards for his scientific and public work. He was elected corresponding member of the academic societies of Nantes, Lille, and Zaragoza, *Société d'Agriculture, Sciences et Arts de Valenciennes and Laroche-sur-Yon*, *Société Industrielle de Saint-Quentin* (1849), *Conseil Central d'Hygiène et de Salubrité du Département de la Gironde*, *Société Philomatique de Bordeaux*, and *Académie de Médecine* (1874). He was also member of the *Conseil Municipal de Bordeaux* (1861-1870), *Institut des Provinces*, *Académie des Sciences, des Belles-Lettres et Arts de Bordeaux*, and *Académie des Sciences* (1875). In 1859 he was appointed *chevalier de l'Legion d'Honneur*. He also participated in the Karlsruhe International Chemistry Conference held in 1860 to try to reach an agreement on matters of chemical nomenclature, notation, and atomic weights. There he defended the ideas of Ascanio Sobrero (1812-1888), Amedeo

Avogadro (1776-1856), and André-Marie Ampère (1775-1831) (Micé, 1880; Bary, 2011; Bram, 2015). Baudrimont passed away in Bordeaux on January 24, 1880, after suffering a cold.

SCIENTIFIC CONTRIBUTION

Baudrimont published more than 170 papers, booklets, and books in his numerous areas of interest like anatomy, chemistry, colloidal chemistry, crystallography, cosmology and dynamic cosmology, geology, mathematics, mechanics, physics, science philosophy, structure of substances, etc. The eulogy of Leopold Micé (1832-1906) contains a detailed list and a short summary of Baudrimont's publications (Micé, 1880). As customary for candidates to the *Académie des Sciences and Académie de Médecine*, he also published a booklet describing his contributions in these areas (Baudrimont, 1849a, 1853, 1869). In addition to the aforementioned few subjects, he also studied, for example, the origin of ambergris and spermaceti (Baudrimont, 1832c); geology (Baudrimont, 1840, 1867c); animal physiology (Baudrimont, 1840, 1867c); animal physiology (Baudrimont & Martin-St. Ange, 1844a b, 1847; Baudrimont, 1843a, 1847b, 1850, 1857); physics of sunlight (Baudrimont, 1851, 1861-1863, 1862); guano and fertilizers (Baudrimont, 1861b, 1873); philosophy of science (Baudrimont, 1865a, 1867b); mathematics (Baudrimont, 1865b c); linguistics (Baudrimont, 1867a); cosmology (Baudrimont, 1867c); music (Baudrimont, 1868, 1870); phylloxera and vine disinfection (Baudrimont, 1874b, 1875a b); etc.

SHAPE OF THE ATOMS

In his first paper about the relation between crystallization and shape of the atoms, Baudrimont presented the experimental facts he had accumulated regarding crystallization in the shape of fern leaves (illustrated by bismuth), and hollow pyramids (tremies or hoppers) having a square base (illustrated by sodium chloride) or a triangular or hexagonal base (illustrated by lead nitrate) (Baudrimont, 1832b).

During the crystallization of bismuth Baudrimont noticed the appearance of an increasing number of lines, which assumed the form of fern leaves and were more regular but less pronounced than the ones observed during the crystallization of antimony. These lines were disposed in a parallel arrangement and joined others, similarly arrayed, forming together angles of about 120°. The vertexes of the angles were aligned in the same direction and forming lines more obvious than the previous ones. All the observed arrangements produced a multitude of circumscribed hexagons, crossed by three diagonals, of which the first half of each was completely different from the second half, as shown in figure 1.

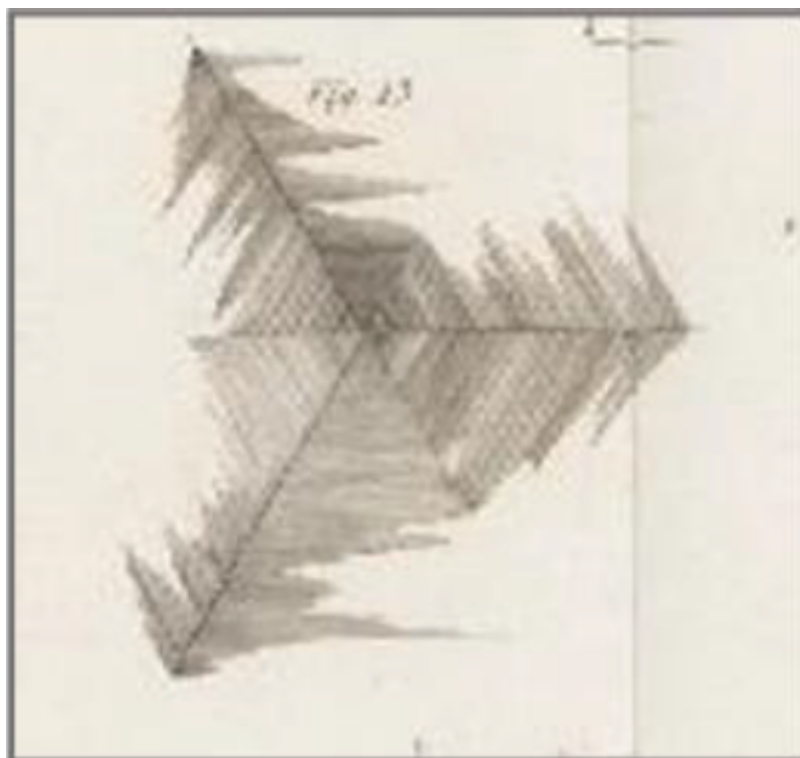


FIGURE 1
Fern leave crystallization of bismuth.

Initially, Baudrimont was surprised to find in bismuth, known to crystallize in a cubic shape, a geometrical figure, which seemed to be the base of a hexahedral prism belonging to a rhombohedra system. He soon realized that these hexagons were probably the horizontal projection of cubes having an axis perpendicular to the observed surface, an assumption, which he quickly verified: he collected the remaining liquid in the center of the mass and then, with the help of a saw, detached the upper part and noticed that it was plastered with cubic hoppers having an axis indeed perpendicular to the surface been examined (Baudrimont, 1832b).

Baudrimont believed that his observations proved that cubic crystals were susceptible of forming a hexagonal figure, although no one had seen bismuth adopting it. He did not consider that this possibility was impossible; if this prism were ever discovered it would be found that its axis was parallel to the cubes that constituted it, and the modifications it could experience would all be in relation to the cube. In all other shapes derived or generated by this prism, the cubic molecules would keep the form reported above. Baudrimont added that his assumption was correct: bismuth had been found crystallized as a rhombohedron, which could only be built from a regular octahedron having two tetrahedrons attached to two of its opposing faces. Baudrimont believed this *was the only rhombohedra that a simple body could possibly assume*: If a cube formed by a multitude of smaller cubes was truncated at the end of each of its four axes, it would originate an octahedron and the axis of the smaller cubes would also be perpendicular to the triangular faces of this octahedron. Similarly, a tetrahedron could be formed from a cube by truncating four of its solid angles, at only one extreme of each of the axis. All these facts demonstrated clearly that crystallization in the shape of fern leaves belonged to the cubic system (Baudrimont, 1832b). According to Baudrimont, the tremies of sodium chloride corresponded to an obtuse pyramid formed by steps of decreasing length (see Figure 2).

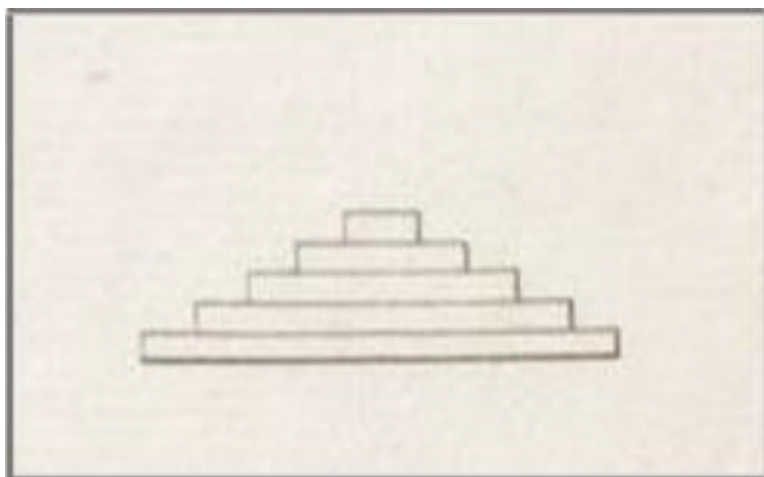


FIGURE 2
Graded crystals of sodium chloride

Six identical tremies, arranged by their ridges, formed a pyramidal cube having graded faces. Baudrimont wrote that it was easy to see that the shape of the tremie and that of the constituent molecules were related somehow. Thus tremies belonging to the cubic system possessed a square base parallel to two of the faces of cubic integrant or constituent molecules. Indeed, molecules having one face parallel to the base of the tremie could assemble only by application of the other faces, and consequently, at straight angles (Baudrimont, 1832b).

It was known that lead nitrate and barium nitrate crystallized as regular octahedrons; very often the crystals were also shaped as hollow triangular tremies. These facts proved that the axis of the integrating cubic molecules forming this octahedron had to be perpendicular to the triangular face; in any other position they would be unable to do it because they would not be able to form a regular triangular frame. Various chemical combinations, such as lead sulfide and iron pyrite, crystallized as a cube or an octahedron, proving that the integrating molecules were cubic; octahedral tremies were seen to have a hexagonal base. Cubic molecules always kept their position relative to this base; be it triangular or hexagonal. Baudrimont wrote that these facts represented a new law: In every case where the tremie possessed an equilateral triangular base or a regular or symmetric hexagonal one, the base had to be perpendicular to the axes of the constituent cubes (Baudrimont, 1832b).

In his book about chemistry and atomic theory, Baudrimont provided additional information about the relation between crystallography and molecular and atomic constitution (Baudrimont, 1833). Thus, for example, he wrote that *constituent molecules* were the atoms, which concurred to form a combination and *integrant molecules* were groups of these atoms, which could be formed without destroying the combination. When atoms combined to form an integrant molecule, they assumed an arrangement, if not regular, it was at least symmetric. Hence, integrant molecules must have a regular or symmetric shape, depending on how its atoms were arranged. When the integrant molecules were sufficiently separated so that they could move, they also presented a regular or symmetrical arrangement and formed solids ending in faces slanted according to certain angles. In crystals, only the angles were constant; the size of their faces varied substantially. Facets replaced the angles and ridges and angles and ridges frequently replaced the facets.

The primitive forms of crystals were not numerous, but the number of secondary forms was considerable. Independently of their nature, atoms *had the same volume and regular shape*. This property explained the phenomenon of *isomorphism* where certain bodies having the same atomic composition could mutually replace one another in certain combinations, without changing the crystalline form of the latter. Since atoms in their relative position were subjected only to the law of symmetry, it resulted that this condition could

be satisfied by numerous different arrangements, giving place to the phenomenon called *heteromorphism*. Accordingly, certain substances could be present in different crystalline arrangements, having the same composition and chemical properties, while bodies having the same composition would have different properties (isomers). Therefore, chemical formulas did not represent the *absolute* number of atoms present; they represented only a number *proportional* to the real one. As a result, the formula PbS of lead sulfide was not the real one because it was impossible to obtain a cube (the primitive form of lead sulfide) with two atoms assumed to have the same volume and shape and positioned one next to the other. To do so it was necessary to have *at least* four atoms of each of these substances, located symmetrically at the eight angles of the cube. Baudrimont gave an interesting example of this situation for sodium chloride, which at his time was assigned the wrong formula NaCl₂: 19 atoms of chlorine and 9 of sodium were required to properly form a cube (Baudrimont, 1833).

Baudrimont published several other papers describing the geometry of different crystals where he concluded that admitting that crystalline particles were always small polyhedrons, which could adapt one to the other without leaving empty spaces, meant that only *three classes of polyhedrons* satisfied this condition: (1) cuboids, (2) hexahedral prisms, and (3) dodecahedrons (Baudrimont, 1864, 1869).

Baudrimont tried unsuccessfully to introduce some other ideas regarding the intimate structure of bodies. For example, he indicated that the elements of these bodies were the atoms, molecules and particles. Molecules could successively divide into intermediates parts, among them, the atoms. Thus, a molecule subdivided into *merons*, the merons into merules, the *merules* into mericules, and finally, the mericules into atoms. Mechanical systems formed of 4, 6, and 8 parts were named tetrameron, hexameron, octameron, etc., respectively (Baudrimont, 1861a).

COLLOID CHEMISTRY

Baudrimont was one of the pioneers of colloid chemistry; interesting enough, he reported his findings mostly in his books and not in scientific publications (Baudrimont, 1830, 1833, 1844-1846). His first paper was a short note regarding the preparation of artificial emulsions (Baudrimont, 1830). In the opening remarks he mentioned that most pharmacy books recommended that emulsions be prepared by mixing mucilage with glue, syrup, or water, and then adding the oil drop wise. Baudrimont believed that this procedure rarely yielded a white emulsion; not only that, the latter after some time usually split into two phases, a lower transparent one and an upper opaque white. Another well-known unpublished procedure recommended putting the oil in a mortar, adding powdered glue and a certain amount of water, and mixing thoroughly. Unfortunately, this procedure required practice because improper mixing could result in the formation of lumps, the oil floating on top, etc. Baudrimont wrote that his experiments indicated that the best results were obtained when the amount of water to be added was determined in relation to that of the glue and not the oil. For example, three parts of water and one of mimosa glue gave very thick mucilage but when the glue was dissolved in the oil, the latter retarded the action of water and the resulting emulsion was defective and lumpy. The best proportions were two of water and one of glue, mixed with an arbitrary amount of oil not exceeding six parts (Baudrimont, 1830).

In a following paper Baudrimont discussed the circumstances that favored the total dispersion (Baudrimont called it *extinction*) of mercury in lard (Baudrimont, 1832a). He indicated that preparation of the corresponding mercurial unguent involved significant physical effort and many pharmacists had tried to find methods to make it easier; some had suggested using very viscous substances such as honey and turpentine essence, others, the use of rancid fat, although the pharmaceutical regulations prohibited the use of foreign substances in the preparation of medicinal preparations. Jean Baptiste Alphonse Chevallier (1793-1879) and Manuel Hernández de Gregorio (in his *Diccionario Elemental de Farmacia*, 1803) had proposed carrying the process with melted lard and Baudrimont himself had found that melted lard, agitated

rapidly during cooling to the solidification point, easily dispersed mercury. Lard was composed of two fatty materials: one liquid at ordinary temperatures (olein), and another solid under the same circumstances (stearin), and only partially soluble in olein. The properties of lard were strongly influenced by the possible states of the stearin present. During the slow cooling of melted lard, the stearin solidified as mamelonated (covered with rounded protuberances) crystals. In this state it seemed less solid, had an unpleasant taste, and was inadequate for preparing the mercurial unguent. Under sudden cooling it turned into a white substance, more homogeneous, having a pleasant taste, and very appropriate for preparing the unguent.

According to Baudrimont there was an easy explanation for the difference in behavior: under slow cooling stearin crystallized and became *suspended* in olein, while rapid agitation of melted lard during cooling avoided the formation of crystals and led to a fine dispersion of the matter forming the crystals. This characteristic was easily observed by pressing between paper sheets crystallized lard and solid lard prepared from melted and agitated lard. Lard composed of olein and crystallized stearin lacked the cohesion to disperse mercury; the density and solidity of the crystals prevented a large division of the metal occluded in the interstices of the crystals. This obstacle was not present in melted lard, which was agitated during cooling (Baudrimont, 1832a; 1833-1841).

Baudrimont expanded the above raw concepts in great detail in his treatise about chemistry and atomic theory, which eventually became the basis of colloidal physical chemistry (Baudrimont, 1833). Here we quote some of them:

- (1) "Organic chemistry is that special part of chemistry that deals with organic products and their derivatives (...) Some organic products have a very complicated organization (...) there is a very large number of organic compounds deprived of organization, which are uniquely characterized by their origin...they have a definite composition, they can crystallize or they are liquids having a precise boiling or decomposition temperature, or they are gases (...). They combine in definite proportions in the same manner as inorganic compounds. Organic products enjoying a more or less complex organization are always solid or soft; they are formed of spherical or spheroidal particles (...) having diameters varying from two hundredths of a millimeter to about one millimeter. This enormous variation in volume can be observed with a single kind of particle, for example starch...When in contact with certain liquids, they absorb it and swell considerably (starch, for example) or they yield part of the liquid they contain to the surrounding fluid and shrink (for example, Arabic gum dissolved in water and then contacted with alcohol). When these particles are free, they never crystallize but by their agglomeration they form lumpy masses or organic forms...They seem to have an undefined composition, varying according to the nature and age of the beings to which they belong. They are subject to special reactions, different from those of defined bodies. The combinations they form are of a particular order and are not completely defined" (Baudrimont named these complexes *particular organic compounds*);
- (2) In another section Baudrimont added that the particular compounds were formed of particles visible under the microscope and had no definite axes; left to themselves they became free and assumed the form of a liquid (like albumin), or they agglomerated and formed tubercular masses (like gums, resins, etc.). At a higher level, the particles arranged themselves under the influence of definite forces, originating organic tissues like the cellular tissues and the nerves, and eventually they assumed forms and methods of arrangement, which varied with the beings to which they belonged;
- (3) liquids held in a state of pseudo-combination with the particles were always very viscous; if the viscosity increased, that is, if the particles became more adherent, they united and formed a jelly like starch, paste, mucilaginous gums, pectin, gelatin, and chondrin. In the solid state they formed lumpy masses like gums, starch, fats, and cellular tissue;
- (4) solid bodies belonged to one of two clearly defined classes: amorphous or crystallizable. Amorphous bodies such as agate, glasses, cellulose, gelatin...were formed of joined spheroidal particles...An amorphous particular body should be considered a solidified liquid;
- (5) under the microscope, starch was seen to be formed of particles covered by a tegument; the soluble matter they contained could absorb water and swell, leading to a breakup of the structure that kept them together, although without rupturing the particles themselves;
- (6) under the microscope, blood was seen formed of a transparent liquid mixed with particles of different shapes; the red ones were the most abundant. Abandoned to itself, blood separated into a yellow green liquid in which clot was floating...The red globules were formed of solid albumin and colored matter; the white ones were probably formed of fatty matter. The serum was formed of dissolved albumin, several fatty materials, water, and salts;
- (7) the formation of particular combinations did not take place necessarily in the inside of the molecules...the particles were joined and maintained joined by a larger energy than the mechanical energy required for separating them; this force was quite analogous to the one that determined adhesion and capillary phenomena. An affinity of this nature caused animal charcoal to combine with coloring matter and retain them energetically. The action of the pertinent forces was different from that resulting of ordinary chemical combinations;
- (8) a large number of chemical reactions that took place in the dyeing of tissues

and textiles seemed to be controlled by the capillary spaces in which they were required to occur. The textile material did not seem to be destroyed because the only thing the dye did was to fix itself on its particles, producing a particular combination. For a dye to join and color a tissue in a permanent form, it had to be dissolved in a liquid able to impregnate the tissue, without dissolving it, etc.” (Baudrimont, 1833).

Baudrimont provided a detailed description of a number of colloidal substances, such as mucilage, bassorin, dextrin, pectin, cellulose, casein, albumin, fibrin, gelatin, and beer yeast (Baudrimont, 1833). An interesting fact is that Wilder Dwight Bancroft (1867-1953) claimed that Baudrimont and Francesco Selmi (1817-1881) published their experimental results and theoretical explanations about colloidal chemistry years before Thomas Graham (1805- 1869), and their results went unnoticed probably because Graham went further and discovered dialysis (Bancroft, 1924).

DECREPITATION

Baudrimont wrote that many bodies subjected to sudden high temperature increase, divided and let heard a crackling noise, known as decrepitation. Although many authors believed that decrepitation was caused by the sudden vaporization of water or by decomposition accompanied by formation of gases capable of producing a violent rain of particles, the largest number of decrepitating substances was anhydrous and heat stable (e.g., potassium sulfate, barium sulfate, sodium chloride, etc.) (Baudrimont, 1836).

In order to explain this anomaly, it was supposed that these particular substances contained water between their constituent parts; Baudrimont rejected this assumption: He dried several stable anhydrous bodies at a low temperature by several procedures and found they still decrepitated when heated rapidly. Some of them, like schist mixed with coal, decrepitated strongly when thrown into a hot furnace and mineral pieces having the largest surface decrepitated the loudest. Schist was known to have a well-developed laminar structure, a fact that led Baudrimont to test the behavior of well-crystallized anhydrous bodies, because in this state they could be cleaved easily into pieces having a large surface. His results indicated that this disposition always led to decrepitation and thus afforded an easy first explanation of the phenomenon: Decrepitating substances were known to be poor heat conductors; their external parts heated first and the resulting dilation and stress forced them to separate from the colder neighboring parts; a process facilitated by their property of cleaving (Baudrimont, 1836).

Baudrimont believed that his explanation was also valid for heat labile substances, capable of decomposing and yielding volatile products when heated. In this situation it was difficult to decide if the phenomenon was due to an unequal dilatation of their parts or to the repulsive action of the volatile products. However, most of them possessed a crystalline structure or a least one direction of easy cleavage; either factor was probably often the only cause because these substances (e.g. mercuric cyanide and emetic tartar) decrepitated without having suffered the least apparent decomposition. Substances, which did not have a crystalline structure, could decrepitate when they had not been perfectly dried (e.g. plastic clays and argillaceous schist) (Baudrimont, 1836).

According to Baudrimont, these observations allowed dividing decrepitating substances into two classes: (a) stable bodies (e.g. the sulfates of barium, strontium, and potassium, potassium chromate and dichromate, calcium fluoride, sodium and potassium chlorides and bromides, etc.), and (b) bodies yielding gaseous products; some of these were anhydrous (e.g. barium and lead nitrates, rhombic calcium carbonate, and mercuric cyanide), and others were hydrates, (e.g. tartar emetic, lamella calcium sulfate, cupric acetate potassium bitartrate, and potassium ferrocyanide). Baudrimont remarked that substances, which were combined with a large quantity of water, did not really decrepitate, unless they were susceptible of cleavage (e.g.: the hydrates of sodium carbonate, sodium sulfate, magnesium sulfate, etc.) (Baudrimont, 1836).

AQUA REGIA

In 1843 Baudrimont read to the Académie des Sciences a paper in which he claimed he had discovered the compound that gave reagent its properties (Baudrimont, 1843b, 1846). He mentioned that although aqua regia was known for over ten centuries and was frequently used, it had been the subject of very few researches. It had been accepted that aqua regia owed its property of dissolving gold to the presence of free chlorine until 1831, when Edmund Davy (1785-1851) published a memoir reporting his experiences about the mutual action of nitric acid and different chlorides, and also of nitric acid and HCl on each other (Davy, 1831). These experiments led him to discover a new gas, which Davy believed was an actual compound formed of equal volumes of chlorine and nitrous gas, and which he named *chloronitrous acid*. This new acid had a specific gravity of 1.759 relative to atmospheric air; bubbling it through water produced an acid which resembled very closely aqua regia. Davy believed his results indicated that the power of aqua regia of dissolving gold was not due to the liberation of chlorine; chlorine and chloronitrous gases were the gaseous products originating from the mutual action of concentrated nitric and HCl gases on each other. Aqua regia and chloronitrous acids reacted with platinum in the same manner but the action of chloronitrous was stronger (Davy, 1831).

Baudrimont commented that the presence of chlorine in the gas mixture had prevented Davy of making a more detailed study of chloronitrous acid, and for this reason he had decided to conduct additional experiments on the subject. For this purpose, he heated a mixture of two parts by weight of nitric and three of commercial HCl (specific gravity about 1.314) and noticed that a red gas began to disengage at about 86 °C. Passing the gas through a U-shaped tube, placed in powdered ice, separated the condensable portions. The first fractions of gas were mixed with HCl and only the latter was sufficiently pure. This gas did not redden dry litmus paper but decolorized it after some hours, and when moist it reddened the paper immediately. The condensed liquid was of a deep red color, much less than that of hypochlorous acid (HClO); it boiled at about -7.2 °C; and its specific gravity at 8 °C was 1.3677; the specific gravity of the gas was about 2.49. Chloronitrous acid was found to attack all the metals it came into contact; with pulverulent silver, derived from the reduction of silver chloride, it exploded, and disappeared immediately. Elemental analysis indicated that it contained, by weight, 12.6% of nitrogen, 22.4% of oxygen, and 65% of chlorine, corresponding to the formula NO_3Cl_2 , very similar to that of anhydrous nitric acid, NO_3O_2 . For this reason, Baudrimont proposed calling the gas chloronitric acid instead of the name proposed by Davy (Baudrimont, 1843b, 1846).

ACOUSTICAL TRANSPARENCY AND OPACITY OF THE ATMOSPHERE

On January 16, 1874, John Tyndall (1820-1893) delivered to the Royal Institution a lecture about the acoustical transparency and opacity of the atmosphere (Tyndall, 1874). He had carried his experiments during six months and had found that there was a significant variation in the distances at which the signals produced by guns and trumpets were heard. In apparently similar days the hearing distances changed not only for the same instrument, but also between them. Some days the sound of the trumpet would be heard before that of the gun, and in others the reverse results would be true, although the wind was not in favor or against the sound, but obliquely unfavorable and obliquely favorable. In one example given by Tyndall, "On another day, when a thick haze hid the land from view and limited the visible horizon to one and a half mile, the sounds were heard at twelve and three-quarter miles, while on some clear days the sounds were inaudible at very much shorter distances". The significance of these results was critical for navigation. Tyndall believed that these contradictory results could be explained on the basis of the homogeneity conditions of the atmosphere: Complete homogeneity allowed the easy and uninterrupted transmission of the sound waves; in the presence of an irregular mixture of light dense air, fog, snow, the sound waves would be reflected back from the limiting surfaces of the denser portions of the air. Thus "when a cloud hid the sun, and when the sun sank, the air became more homogeneous, and the sounds were able to penetrate to distances of

five, six, and seven miles, when they had been quite inaudible at three miles at mid-day." In particular, the extinction of sound could be caused by the imperfect mixing of air and water vapor, which produced in the atmosphere spaces of different degrees of saturation; the surfaces limiting these spaces, had to have the necessary conditions for generating partial echoes, and consequently, a reflection and partial loss of the sound (Tyndall, 1874).

Baudrimont believed that Tyndall's results were important because they suggested the possibility of replacing the light signals emitted by a light house by another system based on acoustic signals, to serve navigation in under conditions of heavy fog or vapors, impenetrable to light (Baudrimont, 1874a). Nevertheless, he disagreed with Tyndall's explanation of the phenomenon. He could not see how, in calm weather, sheets or simple vertical columns of air charged very differently with moisture would generate spontaneously. Actually, layers of different moisture should be expected to generate *horizontally* and not vertically. The air layer next to the water surface would probably be saturated with water and would transfer humidity to all the other horizontal layers above it. It was logical to expect that the existence of a horizontal layer was much more probable than a vertical one. It was also hard to understand how layers containing variable quantities of moisture should only be produced at a certain distance from the shore, forming a vertical wall, which would reflect sound and generate echo. Another explanation should be offered for the possible generation of vertical walls (Baudrimont, 1874a).

According to Baudrimont, the speed of sound in humid air should be larger than in dry air, because of the density difference; the Newton's simple equation for the speed of sound (c) in

elastic fluids, $c = \sqrt{e/d}$, predicted that the square of the sound speed varied inversely with the density (d) of the fluid. Hence, the speed of sound would be the faster in the layer next to the water surface and lower in the layers above it, and consequently, a sound-wave going out inclined from above downwards would *not move* in a straight line, but a curve, which at a certain distance from its origin would become horizontal. The sound waves would deform and soon extinguish or no more produce sound. Baudrimont wrote that his explanation was easily understood when considering that

"sound was not due merely to *evasive* waves going out from its origin, and owing their existence to propulsion, but required the concurrence of *invasive* waves produced by the opposite movement of the vibrating substance. When the evasive waves became horizontal, the invasive waves could coincide with them beyond that place, and the sound was consequently extinguished" (Baudrimont, 1874a, p. 1222).

Baudrimont believed that the vertical layers assumed to originate echo (as reported by Tyndall), were probably due to currents known to exist in the Straits of Dover, and which transported masses of air, which may differ greatly in temperature, moisture, and density from those they met in a particular locality. For example, at Bordeaux, when the temperature of the Continent differed noticeably from that of the ocean, it was possible to observe daily variations of temperature, which were caused by the masses of air carried along by the water of the Bordeaux river, which changed its course completely four times every day (Baudrimont, 1874a, p. 1223).

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