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Four brilliant students of Henri Sainte-Claire Deville
3. Paul Gabriel Hautefeuille

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ABSTRACT
Paul Gabriel Hautefeuille (1836-1902) carried on a large number of significant researches, alone or with Deville, Troost, Chappuis, and other colleagues, in the areas of mineralogy, crystallization, synthetic reproduction of natural crystals, allotropy, combination of hydrogen with sodium, potassium, and palladium, ozone, its properties and liquefaction, dissociation, conversion of cyanogens into paracyanogen and cyanic acid into cyanuric acid, and phosphoric acid, phosphorus, and phosphates.

KEYWORDS: allotropy, crystal reproduction, crystallography, dissociation, mineralogy, ozone, paracyanogen, phosphorus, phosphates

Resumen (Cuatro estudiantes brillantes de Henri Sainte-Claire Deville 3. Paul Gabriel Hautefeuille)
Paul Gabriel Hautefeuille (1836-1902) llevó a cabo un gran número de investigaciones importantes, solo o junto con Deville, Troost, Chappuis y otros colegas, en las áreas de mineralogía, cristalización, reproducción sintética de cristales naturales, alotropía, combinación del hidrógeno con el sodio, potasio y paladio, ozono, sus propiedades y licuefacción, disociación, conversión de cianógeno en paracianógeno y de acido ciánico en ácido cianúrico, y ácido fosfórico, fósforo, y fosfatos.

Palabras clave: alotropía, reproducción de cristales, cristalografía, disociación, mineralogía, ozono, paracianógeno, fósforo, fosfatos

Life and career (Gernez, 1902, 1904; Lemoine, 1904; Marquis, 1903)

Paul Gabriel Hautefeuille, born at Étampes on December 2, 1836, was the son of Louis-François-Napoleon Hautefeuille (1706-1882), a town notary from 1832 to 1845, who was afterwards invited to Paris to direct the legal department of the Railway Company of Paris, Lyon, and the Mediterranean. Paul made his first studies at the college of his town, continued them at the Lycée Condorcet in Paris, and afterwards took private lessons preparing for the entrance examination to the École Centrale des Arts et Manufactures, where he was admitted in 1855 at the age of 18. Paul was a very successful student and graduated in the third place of his class. Jean-Baptiste André Dumas (1800-1884), who was the president the administrative council of the school, recommended him to his friend Henry Sainte-Claire Deville (1818-1881), professor at the École Normale Supérieure. Deville admitted Paul to do research at his laboratory and pursue his doctoral studies. While doing so, Hautefeuille also found the time to study medicine and thus in 1865 he was awarded both the degree of *docteur ès sciences* (Sorbonne) with a thesis on mineral chemistry entitled *Étude sur la reproduction des métaux titanifères* (Hautefeuille, 1865cd) and *docteur en médecine,* after defending his thesis *Recherches sur les résines* (Hautefeuille, 1865e). After graduation, Hautefeuille remained in the École Normale for the next 23 years, becoming successively répétiteur de mécanique, répétiteur de chimie industrielle, maître de conférence de minéralogie (1876-1885) [replacing Charles Friedel (1832-1899)], adjunct director of the chemistry laboratory [replacing Nicolas Ferdinand Isambert (1836-1910)], and in 1895, member of the conseil de perfectionnement de l'École Centrale des Arts et Manufactures. In 1885 he replaced Friedel as professor of mineralogy at the Faculty of Sciences of the Sorbonne (a position he kept until his death), and after the creation of the École des Hautes Études, Deville appointed him adjunct director.

In 1882 the Académie des Sciences awarded him the prize La Caze for his work on the combination of hydrogen with alkaline metals, the reproduction of minerals, and ozone.

In 1895, after three failed attempts (1881, 1882, and 1890), Hautefeuille was elected member of the Académie des Sciences (mineralogy section), replacing François Ernest Mallard (1833-1894). Hautefeuille was elected Officier de la Légion d'Honneur and member of many scientific societies, particularly, the Société Minéralogique, the Société Chimique,

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and the Société Royale de Bruxelles. Hautefeuille played an active role in the participation of the Mineralogy Laboratory at the Universal Exposition of 1900, where he exhibited his synthetic crystals.

Hautefeuille died suddenly in Paris on December 8, 1902, and was buried at the Père-Lachaise cemetery. He requested that no military honors be offered.

Hautefeuille's research activities covered a wide range of subjects, although his main contributions were in mineralogy and thermodynamics. He used Deville's method of mineralizing agents to reproduce synthetically a large number of natural materials, among them: white and green corundum, ruby, sapphire, zirconia, chrysoberyl, emerald, and phenacite (Hautefeuille, 1865ab; Hautefeuille and Perrey, 1888abc), the different titanium dioxide allotropes (Hautefeuille, 1863, 1864, 1865ab), the allotropes of silica (Hautefeuille, 1877ab, 1878ab, 1880), crystalline phosphates (Hautefeuille and Margottet, 1883abcd, 1886, 1887, 1888), the allotropes of phosphorus pentoxide (Hautefeuille and Margottet, 1884a) and beryl silicates (Hautefeuille and Perrey, 1888c). With Louis Joseph Troost (1825-1911) he studied the allotropic transformations of phosphorus (Troost and Hautefeuille, 1873), the transformation of cyanogens into paracyanogen (Troost and Hautefeuille, 1868ab), the transformation of cyamelide and cyanuric acid (Troost and Hautefeuille, 1868cd) the absorption of hydrogen by sodium, potassium, and palladium (Troost and Hautefeuille, 1874abcd, 1875), with Louis Philibert James Chappuis (1854-) the liquefaction of ozone and properties of the liquid and vapor phases (Hautefeuille, 1913; Hautefeuille and Chappuis, 1880abcde, 1881, 1882ab, 1884), and with Louis Cailletet (1831-1913) phenomena near the critical point (Cailletet and Hautefeuille, 1881abc).

Scientific contribution

Hautefeuille published over one hundred papers, several of them in the form of booklets (Hautefeuille, 1865f, 1913). As customary of all candidates to a position in the Académie des Sciences, he published two brochures describing his scientific work and results (Hautefeuille, 1881, 1890). He is best known for his extensive researches in the area of metallurgy, crystallization, dissociation, ozone, behavior of gases nears their critical point, etc. His work with Troost about allotropy, hydrogen reaction with sodium, potassium, and palladium, has been presented in another publication and will not be repeated here (Wisniak, 2014).

Mineralogy

Hautefeuille most important contributions were in the area of mineralogical chemistry, and begun with the reproduction of the natural forms of titanium dioxide using Deville's concept of mineralizing agents (Deville, 1861). In 1858 Deville and Henri Caron reported that they had been able to prepare a series of metal oxides, spinels, and silicates in a crystalline state by treating oxygenated compounds, fixed or volatile, with volatile metallic fluorides, at high temperatures via a dry method. They illustrated their procedure by describing in detail the preparation of white and green corundum, ruby, iron sesquioxide, sapphire, zirconium oxide, cymophane (chrysoberyl), ghanite ($ZnAl_2O_4$), staurolite, rutile, etc. etc. (Deville and Caron, 1858). In a following memoir Deville elaborated the idea that his process simply reproduced what was taking place in nature: the atmosphere contained many components that without fixing themselves to certain natural solid bodies, transformed them into mineral substances absolutely similar to those existing naturally. These components, which he named *mineralizing agents* (today, catalysts), acted indefinitely by their sole presence and were completely compatible with water. Water did not cancel or diminish their action. As example of these substances, Deville mentioned hydrogen sulfide, SO_2, CO_2, silicon fluoride, and hydrogen (Deville, 1861).

Hautefeuille obtained crystalline rutile (TiO_2) by treating a mixture of potassium titanate and potassium chloride with HCl, in a platinum capsule or a porcelain tube heated to white red. The liberated titanium oxide crystallized as yellow transparent prisms mutually attached. These prisms had eight faces, with 135° angles, and were the same as those obtained by Deville by passing HCl over amorphous titanium dioxide, heated red. The density of the crystals was 4.3, which identified them as rutile. Acicular rutile was obtained by a similar procedure, this time treating a mixture of potassium titanate and fluotitanate with HCl. The resulting golden yellow crystals, of density 4.26, resembled the acicular rutile contained in the quartz crystals of Madagascar. Laminar rutile was obtained by treating a solution of titanium dioxide and potassium fluosilicate with HCl. The resulting crystals, slightly green, were the same as the laminar rutile found in New Jersey, USA. A mixture of titanium dioxide, silica, and potassium fluosilicate, heated red in a stream of HCl, gave place to a large number of needles inserted in a silica skeleton (sagenite) (Hautefeuille, 1863).

Hautefeuille memoir also described the preparation of brookite (another natural form of titanium dioxide) and its morphological variety, arkansite, the synthesis of TiF_2, and the preparation of acicular rutile colored by the latter.

A following paper (Hautefeuille, 1864) described an improved reproduction procedure based on reacting steam directly with gaseous titanium fluoride in a reducing or oxidizing atmosphere. For anatase, titanium fluoride was conducted along a platinum tube to the middle of a second platinum tube through which water vapor was passing, The tube was so heated that the fluoride and the steam met at a temperature slightly below that of the volatilization of cadmium. Octahedral crystals were formed, having the axes of natural anatase, a density between 3.7 and 3.9, and a variable coloration depending if the carrier gas was humid air, hydrogen, or wet hydrogen. In the presence of HF, the titanium dioxide acquired the form and angles of brookite when the temperature of operation was between the volatilization temperatures of cadmium and zinc. The resulting rhombic prism was identical as those of natural brookite, with density

4.1 to 4.2. Rutile resulted when titanium fluoride and steam were mixed at a bright red heat. The forms obtained were acicular square prisms with octahedral terminations and density 4.3. According to Hautefeuille, in these reactions HF acted as HCl in the method of crystallization adopted by Deville; it was a mineralizing agent, as an ephemeral solvent of titanic acid (Hautefeuille, 1864).

A year later, Hautefeuille published another long memoir, divided into three sections. In the first one he summarized all his findings about the reproduction of the different forms of titanium dioxide found in nature (Hautefeuille, 1865b). He stressed his finding that calcium fluoride, calcium chloride, water vapor, HCl, and HF, were the bodies that allowed him to mineralize amorphous titanium dioxide and transform the titanic minerals one into the other. All these transformations started and finished with rutile, the only form stable at high temperature in a humid and very acid atmosphere.

The second section dealt with the reproduction of sphene, a calcium titanium nesosilicate mineral of formula $CaSiTiO_5$, by fusing together a mixture of silica, titanium dioxide, and calcium chloride in a platinum crucible. After about one hour the fused mass was dissolved in hot water acidified with HCl. The resulting crystals had the same shape and density (3.4-3.6) of natural sphene (3.45) (Hautefeuille, 1865b).

The third section described the reproduction of perovskite (a calcium titanium oxide, titanate, mineral with the formula $CaTiO_3$). This substance was prepared by heating to red in a platinum capsule, a mixture of calcium chloride, silica, and titanium dioxide, and then passing over it a stream of CO_2 saturated with water, or of air loaded with steam and HCl. The resulting transparent cubic crystals had a density 4, compared with 4.02 for natural perovskite. Hautefeuille also reported the preparation of magnesium titanate by heating a mixture of titanium dioxide, ammonium chloride, and magnesium chloride. The resulting rhombic crystals had a density of 3.91 (Hautefeuille, 1865b).

Hautefeuille summarized his main findings as follows: (a) It was possible to use HCl as the mineralizing agent for preparing the different varieties of rutile, (b) HCl was able to crystallize titanium dioxide only as rutile, (c) HF could be used to mineralize rutile, brookite, anatase, and corundum, (d) titanium dioxide always becomes rutile in the presence of HCl, and of HF at high temperatures, (e) use of HCl and HF allowed to reproduce at will, for the same reaction, rutile, anatase, and brookite. Temperature was the only factor, which determined the crystallization form, (f) he had been the first one to reproduce brookite and anatase, two incompatible morphological forms of titanium dioxide, corundum, and sphene, and (g) he had shown that perovskite could originate from the decomposition of sphene (Hautefeuille, 1865b).

Hautefeuille next studied the crystallization of silica (Hautefeuille, 1877ab). Heating to dark red a mixture of titanium dioxide and a sodium silico-aluminate having the appropriate ratio of silica and alumina easily reproduced albite. An alternative process was to replace the silico-aluminate by a mixture of six equivalents of silica and one of alumina. The product of this reaction had a constant composition and was completely crystallized; the density of triclinic crystals was 2.61, against 2.59 to 2.66 for the natural variety (Hautefeuille, 1877a). Orthose was prepared by heating between 900°C to 100°C a mixture of titanium dioxide and a silico-aluminate of potassium containing one equivalent of alumina and six equivalents of silica; again, a suitable mixture of silica and alumina could replace the latter. Hautefeuille remarked that using a mixture of silica, alumina, and potassium tungstate produced tridymite, orthose, and triclinic feldspars. If the silica and the alumna were properly dosed, the tridymite and the triclinic feldspars promptly disappeared and their elements helped the growth of the crystals of orthose. Orthose crystals were monoclinic and had the same angles as the natural product. In summary, between 900° and 1000°C potassium tungstate generated orthose and sodium tungstate albite (Hautefeuille, 1877b).

In 1868 Gerhard vom Rath (1830-1858) discovered tridymite (another natural form of silica) in trachyte (vom Rath, 1868) and a year later, Gustav Rose (1798-1873) (Rose, 1869) reproduced it from silica using a phosphorus salt. Hautefeuille, found that replacing the phosphates by alkaline tungstates allowed crystallizing silica as tridymite or as quartz (Hautefeuille, 1878a). It was enough to maintain a mixture of amorphous silica and sodium tungstate for several hours at about the melting temperature of silver (961.9°C) to convert the silica to tridymite. Carrying the reaction at about 750°C converted the amorphous silica to quartz (Hautefeuille, 1878b). Hautefeuille also showed that using a mixture of alkaline phosphates and fluorides allowed the simultaneous conversion of amorphous silica to a mixture of orthose and quartz (Hautefeuille, 1880).

Hautefeuille also succeeded in preparing prismatic crystals of cadmium sulfide and hexagonal crystals of zinc sulfide, from their amorphous form (Hautefeuille, 1881).

All this work was the core of Hautefeuille's doctoral thesis.

Hautefeuille, together with Adolphe Jean Edme Perrey, carried on the reproduction of phenacite, green emerald, zirconia, and cymophane (Hautefeuille and Perrey, 1888abc). Phenacite, a nesosilicate consisting of beryllium orthosilicate (Be_2SiO_4), was obtained by heating at about 600-700°C and during 15 days, a mixture of silica, glucine, lithium carbonate, and lithium vanadate (as mineralizing agent). Addition of an excess of the vanadate favored the crystallization by triggering the formation of lithium feldspar. Phenacite crystals originated from the latter instead of from amorphous silica. Treating the cooled mixture with water and cold diluted HF was enough for separating phenacite as rhombohedral crystals. Emerald was obtained by heating at 800°C and during 15 days, a mixture of silica, alumina, glucine, and lithium bimolybdate (as mineralizing agent). Higher temperatures resulted in decomposition of the emerald into phenacite. The artificial emerald had the same composition and crystal characteristics of the natural mineral (Hautefeuille and Perrey, 1888b). Zirconia was obtained by heating to 800°C a mixture of amorphous zirconia, silica, and lithium bimolybdate (Hautefeuille and Perrey, 1888c).

Using melted alkaline sulfides as mineralizing agent, Hautefeuille and Perrey reproduced glucine and cymophane, and carried on the opposite reaction of separating alumina from glucine (Hautefeuille and Perrey, 1888a). Hautefeuille used similar procedures to reproduce leucite, nepheline, petalite, micas, willemite, vanadite, and beryl.

Phosphoric acid and phosphates

Hautefeuille in collaboration with Julien Margottet (1848-1903), a professor at the Faculty of Sciences of Dijon, investigated the properties of phosphoric acid and phosphates from many points of view. In one work they studied the use of metaphosphoric acid, silver tribasic phosphate, and mixtures of the two in different proportions, for the crystallization of these salts. Other phosphates crystallized from these solutions through a chemical reaction, because they dissolved easily in them. Since the degree of acidity of the molten mixture could be controlled at will, it was possible to keep the fusibility larger that those of the phosphates they wanted to prepare. Similarly, the number of possible chemical equilibria for a given base was also very large (Hautefeuille and Margottet, 1883a).

In their first work they studied in detail the phosphates prepared using molten metaphosphoric acid (HPO_3). Their results indicated that the sesquioxides of iron, chromium, and uranium, as well as the phosphates obtained by precipitating the salts of these bases, were rapidly attacked by molten metaphosphoric acid and transformed into phosphates containing three equivalents of acid per equivalent of sesquioxide. These phosphates were clearly crystallized, insoluble in water and in acids, so that they were easily separated from the solvent by the action of boiling water. The crystallization was extremely rapid; it was enough to contact the metaphosphoric acid with the oxide or the amorphous phosphate to obtain a new phosphate with a net crystalline form and constant composition (Hautefeuille and Margottet, 1883a).

Aluminum phosphate was obtained in a similar manner by treating alumina with molten metaphosphoric acid. Its crystals were colorless and transparent and did not affect polarized light; their predominant form was a combination of cubic and octahedral, or trioctahedral. The crystals of iron sesquioxide phosphate and of chromium sesquioxide were transparent and shaped like long orthorhombic prisms. Those of uranium phosphate had an emerald color and appeared as rectangular tables, derived from an orthorhombic prism. All these crystals had the general formula of a metaphosphate, (M_2O_3, $3PO_3$) (Hautefeuille and Margottet, 1883a).

A similar procedure was used to prepare silica metaphosphate (Hautefeuille and Margottet, 1883b), and then modifying it by using molten metaphosphoric acid mixed with increasing amounts of silver tribasic phosphate. With these mixtures it was possible to prepare crystalline pyrophosphates, orthophosphates, and intermediate phosphates (Hautefeuille and Margottet, 1883cd).

Hautefeuille and Margottet found that it was possible to dissolve hydrated silica in phosphoric by slowly heating their mixture to 260°C in a platinum vase. The solution was not stable, under the action of heat it deposited crystallized silica phosphate; the crystalline form and the properties of the phosphate depended essentially on the temperature at which it separated from the solution (Hautefeuille and Margottet, 1884b). Cooling to a temperature above 260°C, spontaneously deposited small crystals looking like flattened disks; keeping the solution at temperature slightly above that of boiling sulfuric acid, deposited crystals shaped as hexagonal prisms, which acted strongly on polarized light. These crystals were attacked by water but not by alcohol, a property that allowed eliminating the phosphoric acid they contained. Heating the silica solution to about 360°C resulted in the precipitation of thin hexagonal flakes, which did not act on polarized light. Treated with molten silver nitrate they precipitated red silver phosphate, a result, which proved that they were not tridymite. These two kinds of crystals were not deposited if the mixture was rapidly heated even up to 700°C; between 700°C and 800°C it deposited regular octahedral crystals; between 900°C and 1000°C the crystals were now clinorhombic and acted upon polarized light.

Additional experiments showed that all the different crystals had the same chemical composition, (PO_3, SiO_2). Inother words, the experimental results proved that silica phosphate crystallized spontaneously in four crystallographic forms, incompatible between them, and hence, constituted four chemical species crystallizing at different temperatures: hexagonal formed at temperatures below 300°C, pseudo hexagonal plates, similar to tridymite, towards 360°C, regular octahedral ones between 700°C and 800°C, and clinorhombic prisms between 800°C and 1000°C (Hautefeuille and Margottet, 1884b).

In a following paper Hautefeuille and Margottet proved that the oxides of titanium, zirconium, and tin reacted with phosphoric acid in a similar manner and that their phosphates had the same atomic composition of silica phosphate, that is, (PO_3, MO_2), but that they could obtained only as octahedral crystals (Hautefeuille and Margottet, 1886).

A further paper proved that silica phosphate could also exist as a hydrate having the composition ($2PO_3$, SiO_2, $4H_2O$) and solidifying as spherical globules. This compound decomposed rapidly in contact with humid air and water decomposed it into phosphoric acid and gelatinous silica (Hautefeuille and Margottet, 1887). Afterwards, Hautefeuille and Margottet showed that the sesquioxides of iron and aluminum also gave place to hydrated phosphates having the general composition (M_2O_3, $3PO_3$, $6H_2O$). Heating these hexahydrates to a temperature between 150° and 200°C resulted in water loss and transformation into tetrahydrates,

(M_2O_3, $3PO_3$, $4H_2O$). Further heating led to total dehydration (Hautefeuille and Margottet, 1888a).

Hautefeuille and Perrey demonstrated that phosphorus anhydride, P_2O_5, could exist in three different forms: crystalline, amorphous and pulverulent, and amorphous and vitreous. They burned phosphorus in a stream of dry air and observed that the anhydride accumulated as crystals in the cooler parts of apparatus, as amorphous and pulverulent material in the zone heated by the combustion, and as vitreous anhydride on the zone heated red. They considered the latter two forms as polymers of the first (Hautefeuille and Perrey, 1884).

Liquefaction of gases

In their first paper on the subject, Louis Paul Cailletet (1831-1913) and Hautefeuille recalled that Thomas Andrews (1813-1885) had introduced the concept of critical temperature and so given a very precise meaning to the concepts of gas and vapor (Cailletet and Hautefeuille, 1881a). A vapor heated above this temperature became a non-condensable gas and a gas cooled below that temperature behaved like a vapor; its pressure could not be increased above a certain value without condensation. In the vicinity of the critical point Andrews also observed certain phenomena that had led to him consider the gas and liquid state as separated states, which could be connected through a continuous series of changes (Andrews, 1869).

In practice, it was impossible to know in which state was present a substance that gave place to moving and rippling grooves, which moved above the mercury, when operating on the neighborhood of the critical point. These grooves were easily seen when adding blue oil of galbanum to the liquid. A slow decrease in pressure allowed often knowing if a tube was full with a mixture of gas or liquid, because in the first case the relaxation gave place to clouding and liquid drop formation. For these reasons, Cailletet and Hautefeuille decided to further study the phenomenon, using CO_2 and a colorless gas that liquefied into a colored liquid. Iodine and ozone seemed appropriate candidates but iodine rapidly attacked mercury and the properties of ozone did not facilitate the phenomena of change of state in the vicinity of the critical point. Cailletet had already shown that during the compression of a mixture of a gas and a partially liquefied vapor the separation surface between the two phases disappeared when increasing the pressure applied on the mixture (Cailletet, 1880). Hence it was hard to decide if the disappearance of the meniscus formed by a colorless liquid was caused by total liquefaction or total vaporization. Now, if the CO_2 was colored by a foreign material and the operation conducted in a capillary, then it was possible to establish that the liquefied gas had returned to the gas state, because when a mixture was compressed isothermally it abandoned the coloring matter present in the meniscus. Cailletet and Hautefeuille illustrated this point by compressing a mixture of CO_2 and air near the point of disappearance of a colorless meniscus. It was seen that the blue color formed a blue viscous layer that slowly descended on the mercury, while the liquid grooves appeared as a wave that chased up a slightly blue ring. Afterwards, the tube contained only a homogenous gas mixture showing the liquefaction signs by either lowering the temperature or the pressure. In other words, in either case, matter did not pass from the liquid to the gaseous state by insensitive degrees (Cailletet and Hautefeuille, 1881a).

Cailletet and Hautefeuille studied in more detail the liquefaction of a gas mixed with a permanent gas (Cailletet and Hautefeuille, 1881b). Previous experiences had shown that a mixture of CO_2 and air produced liquid layers of decreasing density, surmounted by a gas phase, and that under certain higher pressures the liquid meniscus ceased to be visible. Their experimental procedure consisted in compressing the mixture to high enough temperatures where no condensation could take place, and then lowering the temperature in a regular form until it reached the critical value. In this manner it was possible to convert the system from a homogeneous gas to a homogeneous liquid; the gas behaved as a pure component, presenting a critical temperature above which the mixture remained as a gas and below which it condensed. This procedure allowed obtained liquid CO_2 containing a large proportion of oxygen, hydrogen, or nitrogen. Cailletet and Hautefeuille illustrated their procedure using mixtures of CO_2 and cyanogen (components having very different critical temperatures). At 33°C the mixture remained in the liquid state, in spite of the fact that this temperature was above the critical temperature of pure CO_2 (31°C) (Cailletet and Hautefeuille, 1881b). In this paper, and in a following one (Cailletet and Hautefeuille, 1881c), Cailletet and Hautefeuille reported the liquid density of CO_2, oxygen, hydrogen, and nitrogen, at different values of the pressure and temperature, assuming that liquid CO_2 mixed with each of the other liquids with a negligible volume of mixing.

Ozone

Hautefeuille and Louis Philibert James Chappuis (1854-) carried on extensive work on ozone and its liquefaction. At very high temperatures, the transformation of oxygen into ozone and of ozone into oxygen probably followed the laws of dissociation of homogeneous system, as Troost and Hautefeuille had made it known to the Académie in a communication regarding compounds able to be produced at temperatures above the one that determined its complete decomposition (Troost and Hautefeuille, 1877). At intermediate temperatures, the decomposition of ozone was considered to be complete; it was slow at ordinary temperatures and rapid at about 250°C. Reversibility, the necessary and sufficient physical condition limiting the changes of state, was not observed in ozone at these temperatures. Accordingly, its instability was comparable to that of hypochlorous acid or of nitrogen chloride vapors. Although the heat necessary to form these explosive compounds could only be obtained from a simultaneous secondary reaction, the allotropic transformation of oxygen could be carried on by electric emanation alone. The electrifying act placed, momentarily, the oxygen in similar conditions to those of compounds able to combine directly or polymerize under the action of heat (Hautefeuille and Chappuis, 1880a).

It was accepted that the pressure and temperature affected the proportion of ozone formed in oxygen. No quantitative data were available on this matter; although it was possible to vary and measure the pressure at will, it was not the same situation for the temperature of the gas during the formation of ozone. This fact made difficult the research on the subject. In their experiments, Hautefeuille and Chappuis used the apparatus designed by Marcelin Berthelot (1827-1907) for submitting a given volume of a gas to the action of an electric emanation (Berthelot, 1877). They presented their results in table giving the partial pressure of ozone and the weight proportion of ozone in the mixture, for pressures varying between 760 and 180 mmHg and temperatures varying between −23° and 100°C. The table showed that the transformation pressure changed very rapidly as the temperature was lowered; for example, it was about double when going from 20° to −23°C. The results plainly showed that the transformation pressure was not function of the temperature alone; it noticeably depended upon the pressure. Interestingly enough, the results indicated that the volume fraction of ozone in the product was almost independent of the pressure within ample limits; a fact that pointed to the analogy between the allotropic transformation of oxygen under the action of electrical emanations to the thermal dissociation of gaseous compounds (e.g., hydrogen iodide and hydrogen selenide). At temperatures above 0°C, the ozone proportion was the maximum for 0.5 atm; increasing the temperature decreased the percentage of ozone (Hautefeuille and Chappuis, 1880a).

In another publication, Hautefeuille and Chappuis reported the liquefaction of ozone and its color in the gaseous state (Hautefeuille and Chappuis, 1880c). Ozone, as usually prepared, exerted a very low partial pressure in oxygen (53 mmHg), making it difficult to determine its properties. Therefore, to determine the properties of the compound, it was first necessary to prepare mixtures rich in ozone. Hautefeuille and Chappuis had already found that for a given temperature, the proportion of ozone changed little with pressure, while changing the temperature from 20° to −55°C it increased by five times. If the electric emanation was stopped, the mixture of oxygen and ozone ceased to be a homogenous system in equilibrium, nevertheless, it was not altered as long as the temperature was kept constant and below 0°C. This relative stability allowed compressing the mixture and increasing the partial pressure of ozone to several atmospheres.

Hence, Hautefeuille and Chappuis used the following experimental procedure: Oxygen was introduced into an apparatus of alternating current, where the thin concentric glass tubes were submerged in methyl chloride, and kept there for 15 minutes. Afterwards, it was transferred into the Cailletet apparatus, kept at −23°C and 200 atm with methyl chloride, and then compressed by mercury, activated by a hydraulic press. After the first strokes, the gas became sky blue, changed to blue indigo as the pressure was increased, and then liquefied when the pressure reached about 75 atm. Hautefeuille and Chappuis mentioned that the mixture of oxygen and ozone was explosive. The compression and cooling had to carried slowly, otherwise the ozone decomposed with release of heat and light, and detonated strongly (Hautefeuille and Chappuis, 1880c).

Two years later, Hautefeuille and Chappuis returned to the question of liquefaction of ozone, this time using the apparatus built by Cailletet for liquefying ethylene (Hautefeuille and Chappuis, 1882b). The liquefaction of a mixture of oxygen and ozone was now carried at about 125 atm and −100°C.

In a following work, Hautefeuille and Chappuis studied the conversion of oxygen into ozone in the presence of several foreign gases (chlorine, nitrogen, hydrogen, and silicon fluoride) (Hautefeuille and Chappuis, 1880d). Although free chlorine and free oxygen where considered not to react with ozone, their mixture could be assumed to provide ozone and would enrich more rapidly than a mixture of oxygen and nitrogen. Nevertheless, the experiments gave negative results and showed that a small quantity of chlorine was enough to oppose the isomeric transformation of oxygen. More than this, addition of a small amount of chlorine into ozonized oxygen resulted in the complete destruction of the ozone. It seemed that a chlorine compound was formed whose instability provided the clue to the decomposition. Electrification of a mixture of nitrogen and oxygen led to a higher transformation of the latter into ozone. With air at 760 mmHg the weight percent of ozone was 0.216 at −23° and 0.143 at 0°C. Addition of hydrogen to oxygen did not oppose the formation of ozone; a predictable result since Berthelot had already found that a mixture of two parts of hydrogen and one of oxygen did not combine under the influence of low-voltage electric emanations (Berthelot, 1879). At a given temperature and oxygen pressure, the proportion of the ozone formed was larger in the presence of hydrogen than in the presence of nitrogen. Addition of silicon fluoride to oxygen resulted in its partial conversion to ozone (about 0.40%) (Hautefeuille and Chappuis, 1880d).

An additional paper discussed in detail the effect of electrical emanation on a mixture of oxygen and nitrogen, in the presence of chlorine (Hautefeuille and Chappuis, 1884). A mixture of pure oxygen and pure chlorine passed through Berthelot's apparatus without any noticeable changes, but when it contained traces of nitrogen it left a light white deposit in the annular space. The deposit became thicker as the experiment was carried on for longer periods of time, and gave place to an arborization process similar to the one offered by ice crystals. Hautefeuille and Chappuis separated the white material, purified it by vacuum distillation, and found that it rapidly decomposed at about 105°C, without melting, releasing vapors of hypoazotic acid. It absorbed humidity quickly, transforming into highly acid liquid drops. Elemental analysis indicated that it contained 9.12%

nitrogen, 22.80% chlorine, and 68.08% oxygen, suggesting the formula $NClO_{12}$ (Hautefeuille and Chappuis, 1884).

Later on, Hautefeuille and Chappuis found that if Cailletet's apparatus was maintained at −88°C with liquid NO, the color of liquid ozone became more intense while it became imprisoned in a vase sealed by solid mercury. The meniscus of the latter remained brilliant and was not attacked by the liquid ozone. Hautefeuille and Chappuis decided to investigate the liquefaction of ozone in the presence of CO_2. A comparative study of mixtures of oxygen with ozone and with CO_2 showed that the liquefaction point of the latter was very similar to that of ozone. The experiments were carried again at −23°C (with methyl chloride); under a slow compression two phases appeared, separated by a meniscus. The liquid was not colorless, as when liquefying CO_2; it was blue and quite similar to that of the gas above it. In the same manner that the compression of a mixture of oxygen, CO_2, and NO produced a mixed liquid, composed of the two gases liquefied; a mixture of oxygen, CO_2, and ozone gave a mixed liquid containing liquefied ozone. It was the latter the one that colored blue the liquid. The blue color of ozone in the liquid and in the gas states confirmed that the products of the decomposition of CO_2 by electrical emanations contained a large percentage of ozone(Hautefeuille and Chappuis, 1880e).

In a following publication, Hautefeuille and Chappuis reported that they had found that the gas flowing out from Berthelot's apparatus could be usefully studied using a spectroscope because the latter was sensitive enough to detect traces of ozone when operating with a gas column sufficiently long. Hautefeuille and Chappuis used the spectroscope to study the destruction of ozone by heat and the products obtained by electrifying a mixture of nitrogen and oxygen (Hautefeuille and Chappuis, 1881). Their main findings were as follows: (a) the absorption bands of pure and dry ozone disappeared slowly at room temperature and rapidly at red heat. The spectrum eventually became continuous, except for a new black ray that ran through it at various times; (b) the same phenomenon was observed when a mixture of ozone and nitrogen was destroyed by heat, as long as the nitrogen had not flowed through the apparatus; (c) the spectroscope allowed following the isomeric transformation of ozone to oxygen, and confirmed that this destruction did not produce hypoazotic acid. The latter was stable at the temperature dark red; (d) the spectroscope allowed observing that electrification at room temperature of a well-dried mixture containing at least $\frac{1}{7}$ of nitrogen, generated a non identified body, characterized by a remarkable absorption spectrum; (e) use of a humid mixture caused the rapid disappearance of the spectrum superimposed to that of zone; hence the disappearing spectrum corresponded a anhydrous compound, capable of generating an acid; and (f) a mixture of hypoazotic acid and oxygen became colorless when subjected to the action of the electric emanation apparatus; the resulting gas presented all the bands of the unidentified body mentioned above. According to Hautefeuille and Chappuis, the latter results could be easily explained by admitting the formation of a pernitric anhydride N_2O_7, obtained under similar conditions to those which had allowed Berthelot to discover persulfuric anhydride, S_2O_7. Pernitric anhydride decomposed at all temperatures above 0°C; at 130°C its decomposition was instant, generating a mixture of oxygen and nitrogen peroxide (Hautefeuille and Chappuis, 1881).

Dissociation

According to Hautefeuille, hydrogen iodide dissociated easily at temperatures appropriate for accurate thermometric determinations. Unfortunately, this thermal decomposition was seriously affected by the action of the components of glass. Hautefeuille proved this point by passing a stream of HI over crushed glass heated below red; the production of hydrogen sulfide and water was seen while the glass became opaque by the dissolution of sodium iodide in the water. These results indicated that the sodium sulfate present in the glass was attacked by the HI, generating water, hydrogen sulfide, iodine, an alkaline iodide, and traces of water. Hydrogen sulfide, heated progressively, started to present an appreciable violet shade under a glass thickness of 10 cm, already at 180°C, a temperature which was probably below that where the dissociation of the acid started, because the tube became lined with a light coating of iodine. The coloration of the gas increased slowly up to 440°C and substantially between 440° and 700°C, as measured by the amount of hydrogen liberated. This dissociation was also affected by the extent of the glass surfaces; it also occurred when passing at atmospheric pressure a stream of HI through a tube filled with glass particles: the proportion of dissociated gas was 2.6% between 100° and 440°, and 34% between 100° and 700°C. Platinum sponge was able to effect the dissociation at a lower temperature, as well as increase its degree, for example, from 10.5% at 175° to 22.2% at 700°C. In 1851 Benjamin Corenwinder (1820-1884) had already observed that the sponge was able of causing the combination of iodine and hydrogen (Corenwinder, 1851). Passing an equimolar mixture of hydrogen and iodine resulted in a proportion of the free elements identical to that obtained by passing HI at the same temperature over the sponge. Hydrogen and iodine, which separately did not react with glass, when mixed, attacked it the same as HI. Below 440°C, a mixture of hydrogen and iodine flowing through a glass tube, furnished less than traces of HI; but kept for one or more hours in a sealed tube at the same temperature, gave place to proportions of HI much larger than those in a tube filled with hydrogen and iodide at atmospheric pressure. This proportion increased substantially the larger the ratio of iodine/hydrogen introduced in the tube. Thus, a variable equilibrium was established, depending on this proportion (Hautefeuille, 1867a).

In another paper Hautefeuille discussed the properties of inverse reactions, a term introduced by Deville for some reactions which were the reverse of those obtained under ordinary circumstances (Hautefeuille, 1867b). It was well known that chlorine displaced iodine in iodides and hydrogen iodide decomposed silver chloride generating HCl and silver iodide. Hautefeuille's experiments proved that under the action of HI, and other chlorides, such as those of phosphorus, arsenic, titanium, lead, ammonium, and potassium, also generated iodine. Hautefeuille now studied the circumstances under which the inverse reaction took place, that is, the decomposition of iodides by HCl. The reaction of HCl and silver iodide was very slow at the temperature of fusion of the salt and became very fast at 700°C. Several crystals of iodine deposited in coldest part of the tube and the exiting stream contained HI and hydrogen. Silver bromide and HCl under the same conditions exchanged their elements more completely. Although these two similar iodides, heated in HCl at high temperatures, yielded similar products, it was not possible to generalize. Mercuric chloride, heated red, in a slow or fast stream of HCl, remained undecomposed. In the same manner, ammonium iodide, vaporized at its boiling temperature in HCl, and afterwards distilled in hydrogen, showed no signs of decomposition. Measurable decomposition started at a much higher temperature: At 360°, 448°, and low red heat, it was 4-5%, 16 %, and 44%, respectively (Hautefeuille, 1867b).

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