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Victor-Auguste Jacquelain

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Abstract

Victor-Auguste Jacquelain (1804–1885) was a French pharmacist who studied the phenomenon of allotropry in carbon and demonstrated the transformation of the diamond into graphite, at the high temperature of a special sun lens. He developed a cheap process for preparing iodic acid by the reaction between powdered iodine and nitric acid, developed a new process for preparing platinum black and malleable platinum by heating a mixture of potassium chloroplatinate and potassium chloride to very high temperature, the utilization of charcoal for illumination purposes, the fabrication of highly pure sulfuric acid for analytical and forensic purposes, and determination the composition of all the hydrates of sulfuric acid.

Keywords

Allotropy, diamond, iodic acid, platinum, starch, sulfuric acid

Resumen

Victor-Auguste Jacquelain (1804–1885), un farmacéutico francés que estudio el fenómeno alotrópico en el carbón y demostró la conversión del diamante en grafito, a la temperatura de un poderoso espejo solar. Desarrolló un proceso económico para preparar ácido yódico mediante la reacción entre el yodo en polvo y el ácido nítrico y un proceso nuevo para fabricar negro de platino y platino maleable mediante el calentamiento de una mezcla de cloruro de potasio y cloroplatinato de potasio a alta temperatura, la fabricación de ácido sulfúrico de alta pureza para usar en procedimientos analíticos y forenses, y determinó la composición de todos los hidratos del ácido sulfúrico.

Palabras clave

Ácido yódico, ácido sulfúrico, alotropía, almidón, diamante, platino

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Life and career (Larousse, 1885; Leblanc, 1885; Anonymous, 2021)

Victor-Auguste Jacquelain was born in Goro, Italy, on May 29, 1802 the son of Jacques Jacquelain, an artillery captain, who had married an Italian lady during the Italian campaign. Jacquelain took his basic education at the Collège de Cluny and then worked for some time as an apprentice student at local pharmacies in Lyon and Macon. He then moved to Paris where he obtained his degrees of bachelier ès lettres et ès sciences while following some pharmaceutical courses at the Faculty of Medicine of Paris. After receiving his degree of bachelier ès sciences physiques, he was admitted as aide-préparateur of the chemistry course given by Joseph-Louis Gay-Lussac (1778-1850) at the École Polytechnique. In 1832, Jean Baptiste Dumas (1800-1884, who was then working as préparateur for Louis-Jacques Thenard (1777-1857) at the École Polytechnique and teaching three courses at the École Impériale et Centrale des Arts et Manufactures, obtained for him a position as préparateur at the same place. During his long stay at the École Centrale, 1832-1873, where he served as head of the laboratories, he published a large number of papers on industrial chemistry, general chemistry, and analytical chemistry in different scientific journals. In 1848 Jacquelain was elected adjunct member of the committee of chemical arts of the Council of the Société d'Encouragement pour l'Industrie National, where he remained until is retirement in 1874 and transfer to Romanèche-Thorins, where he continued his researches in the private laboratory he built there.

Jacquelain passed away in Romanèche-Thorins (Saône-et-Loire) on May 16, 1885.

Jacquelain was a member of the Société Philomatique and of Société Chimique de Paris; he taught several elementary chemistry courses at various preparatory institutions and at the Association Philotechnique. In 1881 the French Académie des Sciences awarded him the Gegnez prize (4,000 francs) for his work in chemistry, particularly on the transformation of diamond into graphite under the influence of high temperatures.

Scientific contribution

Jacquelain wrote near 50 papers and books (i.e., Jacquelain, 1852, 1853) in the areas of inorganic and organic chemistry, biochemistry, analytical chemistry, medicinal waters, fertilizers, etc. In addition to the few subjects described below, he demonstrated that using diastase it was possible to obtain a starch that dissolved at 70 °C and kept stable for a long time (Jacquelain, 1843b); he developed an economical process for preparing potassium and calcium dichromate, and lead chromate (Jacquelain, 1847c); he studied the preparation and properties of hyposulfuric acid (Jacquelain, 1847b) and of dulcin (Jacquelain, 1850f, 1851); the action of steam at different pressures and temperatures on the carbonates of potassium, sodium, barium, calcium, manganese, lead, and silver (Jacquelain, 1850c); etc. As customary for candidates to membership in an Académie, he wrote a booklet describing his research and achievements (Jacquelain, 1849).

Platinum

Jacquelain wrote that the preparation of platinum black by means of the double chloride of potassium and platinum and its subsequent transformation into crystalline platinum, were two operations so close to each other that after a thorough literature search of the literature he hesitated to believe that the second phenomenon could be presented as a new scientific fact. Nevertheless, there was still much to say about it (Jacquelain, 1840b).

Heating potassium chloroplatinate without melting it, resulted in the partial decomposition of the platinum chloride and the appearance of a black powdered mixture of potassium chloride and the double chloride of potassium and platinum. The two salts could be separated by continuous washings with boiling distilled water. If instead of stopping the reaction, the temperature was raised and kept above the melting temperature of the alkali chloride, turned all the the platinum black into small shiny and very thin platinum strips. Visual inspection of the course of the reaction showed in the molten mass an intense motion of very small crystals of platinum black, which became clean and joined one with the other, in a sort of hot weld. Eventually, the process led to the formation of a sort of platinum foam composed of small blades that continued to grow as long as the experiment was continued. This foam, of crystalline appearance, was easily purified with boiling distilled water (Jacquelain, 1840b).

According to Jacquelain, this observation could be used, with small modifications, to manufacture platinum, by an alternative process to the one developed from the original method proposed by William Hyde Wollaston (1766-1828) (Wollaston, 1829), taking care of certain precautions. For example, it was necessary to decompose the platinum salt completely and to keep the sponge friable. The finest parts were separated, washed thoroughly, and finally dissolved in aqua regia. The final stage was the molding of the so-called platinum mud. According to Jacquelain, the basic problem was preparing a platinum salt which left, after its calcination, a single mass of very fine grains (condition of malleability), porous enough to be washed quickly, completely free of platinum chloride, and flexible enough to be compressed dry in suitable vases. Jacquelain gave a detailed description of the appropriate tools for carrying this process and also of the best procedure for eliminating the moisture. He recommended that the double salt be prepared by mixing 25 parts of potassium chloride with 36 of ammonium chloride, per 100 parts of platinum, added, as usual, in the state of acid chloride. The dried triple chloride was then broken down into small portions in a platinum vase, and then heated strongly for 15 to 20 minutes. The resulting metal suggested that platinum, like gold, crystallized in an octahedron (Jacquelain, 1840b).

Carbon allotropy and other properties

Jacquelain wrote that of all the elements, pure natural and artificial carbons were the ones that presented the largest number of external visual characteristics. Many of the most famous scientists had contributed proofs that pure diamond, carbon, and graphite, were chemically identical, they burned in oxygen yielding CO_2 and were insoluble in all known solvents. Nevertheless, chemists and geologists were at odds on the factors that could transform a colorless and transparent diamond into a black diamond and vice-versa. Similarly, scientists had been unable to explain the thermal and electrical conductivity of opaque carbon and the lack of these properties in transparent carbon (Jacquelain, 1847d).

In the first part of his publication, Jacquelain gave a short summary of what was known about the action of heat on diamond and its combustion in oxygen. For example, Louis-Claude Cadet de Gassicourt (1731-1799), Mathurin Joseph Brisson (1723-1806), Pierre-Joseph Macquer (1718-1784), and Antoine-Laurent Lavoisier (1743-1794), had exposed diamonds suddenly to the violent heat of a Tschirnhaus lens and observed how they decrepitated and shined, while nothing similar occurred when heated to a lower temperature. Microscopic examination had shown them to become blunt, hollow, presenting, here and there, small cavities like pumice stone, and a few times a flaky structure. Placed in a closed vase and exposed to the focal power of the large lens of Turraine, had shown the presence of slight superficial bubbling. Diamonds enclosed in a closed vase with CO_2, in de absence of air, had become black and acquired the property of blackening the fingers and paper. To Lavoisier, these results indicated that carbon should not be considered absolutely fixed (Jacquelain, 1847d).

In spite of all the evidence accumulated, other scientists such as Louis Bernard Guyton de Morveau (1737-1816), believed that ordinary carbons were actually diamond oxides (Guyton, 1799ab). Benjamin a (1779-1864) had carried electrochemical experiments with graphite and carbon using a one-pair Bunsen cell with copper or zinc electrodes, with the hope of melting the carbon and obtaining products analog to diamond (Silliman, 1826) (assuming that he had taken the precaution of using carbon free of silica and metallic oxides). Jean-Baptiste Biot (1774-1862), François Arago (1785-1853), and Humphry Davy (1778-1829) had assumed that the difference between carbon and diamond was the presence of a small amount of hydrogen in the latter, and Dumas and Jean Servais Stas (1813-1891) had shown that this assumption was wrong (Dumas & Stas, 1841).

According to Jacquelain, the work by Dumas and Stas had put an end to discussion about the chemical properties of carbon, graphite, and diamond, and the only questions left referred to the physical properties of these substances. The answer to this question depended on their behavior at the maximum temperature achievable with a Bunsen pile, the hydrogen-oxygen torch, or a compressed mixture of carbon monoxide and oxygen (Jacquelain, 1847d).

The first series of experiences were carried with a Bunsen battery having 100 couples, which Jacquelain described in detail. The diamonds employed were spherical, of about 1.5 mm diameter. Although small, they were big enough for intercepting the electric current during contact with the piles and sometimes to simulate the deflection of the flame during the interruption of contact, and assure that it did not fall according the vertical axis of the diamond. Thus, the latter was not heated by the tract of the flame, it became luminous, softened, and passed into the state of true coke, which could then function as an excellent conductor of electricity.

To his satisfaction, Jacquelain found that the diamond, having density 3.336 before the experiments; turned into coke of density 2.6778. Thus modified, the diamond still scratched the glass, but its cohesion had diminished to the point that it broke between the fingers (Jacquelain, 1847d).

In the next series of experiences Jacquelain repeated the experiments of Silliman in order to verify if the heat produced by the hydrogen-oxygen (in the ratio of water) torch melted a diamond as Silliman had reported. He also tested the action of the torch on carbon obtained from essence of turpentine, purified for eighteen hours with hydrogen, and small prisms of hard coal, 8x10 mm, from retorts treated at white-red for thirty-six hours with a stream of chlorine, followed by washed with HCl and water. The raw carbon left 3.6% of its weight as cinder, and 2.7 after the chemical treatment. Jacquelain remarked that he had taken all the necessary precautions to avoid accidents, by keeping the reservoir of the explosive gas separated from the mouth of the torch by a 10-meter-long pipe. To avoid the action of the air of the red-hot carbon, he had located the latter in a vase full of CO_2 (Jacquelain, 1847d).

Under these conditions, the diamond became dazzling with light and disappeared within a few minutes without residue. Stopping the experiment at different intervals showed that the diamond was no longer rough but smooth and shiny at the point of incidence of the jet of flame, without the slightest appearance of a brown spot. The same results were obtained replacing the diamond with the purified with the carbon of turpentine, and also replacing the hydrogen-oxygen mixture by another of carbon monoxide and oxygen. The small prisms of hard coal showed a different behavior: the carbon disappeared along the experiment, while forming the molten globules mentioned by Silliman, except that these, tested with the blowtorch with sodium carbonate on a platinum wire, were found to produce a tar beautiful glass, and not molten carbon as claimed by Silliman. Nevertheless, Jacquelain speculated that this difference in behavior was probably due to the fact that the available gas mixture carbon monoxide-oxygen provided a temperature lower than that produced by the hydrogen-oxygen flame. The fact that a very high temperature was necessary for the dimorphism of converting transparent carbon into opaque carbon, suggested the opposite phenomenon at an appropriate temperature. Instead of assuming igneous origin to the diamond, it could also be admitted that the carbon slowly deposited, as a result of the action of a metal or any other body, on carbon sulfide or chloride, gave birth, over time, to a transparent and extremely hard material. This assumption was supported by the experiences of Jacques-Joseph Ebelmen (1814-1852) on the hardening and transformation of jelly silica into a hard and transparent body challenging the purest hyaline quartz (Ebelmen, 1844; Jacquelain, 1847d).

Several years later, Jacquelain published another paper discussing how the increasing knowledge about charcoal and its electrical properties had been used to produce a material appropriate for public lighting (Jacquelain, 1882). In the first part of his memoir, he gave a short summary of the development of this process. In 1823, Robert Hare (1781-1850) reported that when carbon, a good electrical conductor, was put between the two conducting wires of his special pile named *deflagrato*r, it assumed a pasty consistency and appeared as in a state of fusion (Hare, 1823). Shortly thereafter, Silliman confirmed Hare's results and reported that putting the charcoal points into contact and then withdrawing them a little, resulted in very intense ignition. As a result, the charcoal part of the positive pole enlarged and increased from 2.5 to 3 mm in length, while the charcoal of the negative pole showed the opposite behavior; it had diminished and a circle-shaped cavity appeared at its end (Silliman, 1823, 1826). Silliman believed that this phenomenon indicated that matter had been actually transferred by a current flowing from the negative to the positive pole. A microscopic examination of the positive pole exhibited clear signals of having gone through a real fusion. It had a mammillated appearance and appeared formed by an aggregation of small spheres. Its luster was metallic and had completely lost its fibrous appearance; its pores had disappeared and the matter had become harder and heavier (Silliman, 1823, 1826). William West (1792-1851) strongly criticized Silliman's conclusions, claiming that the deflagrator was not an indispensable part of the experiment. He had reproduced Silliman's results with an ordinary pile, obtaining the same crater on the negative pole, while the opposite cone was seen to end in a filament, which elongated during the separation of the two charcoals until it broke by its own weight (West, 1823).

Jacquelain added that Professor Chevreuse, of the École Royale d'Artillerie de Mézières, had found that the properties of carefully carbonized vegetable charcoal and of the same charcoal strongly calcined, were substantially different. Carbonized charcoals, well dried, were poor electrical conductors, less dense, more hygroscopic, and more combustible than the same charcoals submitted to a second calcination in open or closed vessels. According to Jacquelain, these properties, which were very important for the manufacture of gunpowder, were equally critical when these charcoals were intended for the operation of equipment destined to the production of continuous current (Jacquelain, 1882).

Since that time, this property had been highlighted every year in public courtyards, first using charcoal, cone-shaped and recently calcined, and then extinguished in a vacuum; then, very hard coals, and hence less combustible, were used to show the effect of electric light on vacuum. Extended use of this method of lightning showed that from the view point of electrical conductivity, the use of hard charcoal was preferable; to obtain similar effects with calcined charcoal required immersing it incandescent, in mercury. Unfortunately, under the influence of an electrical current, the treated charcoal generated substantial amounts of mercury vapors that fogged the glass bowl of the lamp. A similar effect was found when using retort charcoal; in this case, the terreous silicates it contained volatilized and fogged the glass. In addition, these silicates were found to affect the regularity and color intensity of the light Hence, two disadvantages were an obstacle for the advancement of the technology: calcined vegetable charcoal was less conductive and more combustible, while very hard retort charcoal was more conductive, but its silicate impurities diminished the quality of the light (Jacquelain, 1882).

According to Jacquelain, the next step required preparing a charcoal more conductive than calcined charcoal, and if not completely pure of hydrogen, at least free of mineral matter. Three were available for achieving this goal: (1) treating red hot carbon with dry chlorine; (2) treating the charcoal with molten KOH or NaOH; and (3) immersing the cold cones of charcoal in aqueous hydrogen fluoride; the length of the process determining the degree of hardness.

Jacquelain found that the use of chlorine was very appropriate for treating small amounts of finely divided charcoal. Carrying the process at high temperature converted the silica, alumina, magnesia, alkaline oxides, and metal oxides into volatile chlorides, and the hydrogen into HCl, which was carried away with the chlorides. This was not the case for large and compact masses of retort charcoal; the process slowed down and became highly complicated. In this situation, it was necessary to direct a stream of dry chlorine, for thirty hours at least, over the coal shaped as four-face prismatic pencils maintained at white red. As a result of this operation, the disappearance of the terreous oxides, the hydrogen, and part the carbon as chlorides, left numerous voids in the carbon which had be filled, in order to restore, as far as possible, the original compactness, conductivity and low combustibility. This was achieved by submitting the treated rods to the carbureting action of the vapors of a hydrogen carbide (heavy coal oil), circulating slowly over white-red heated pencils, for five to six hours, in a cylinder made of refractory earth. This operation had to be carried at the maximum possible temperature to avoid the pencils being covered with a layer of hard charcoal, thick enough to weld them in a single block (Jacquelain, 1882).

In the second process, the melted caustic soda converted the silica and alumina more rapidly into silicate and alkaline aluminate. These products were then washed away with distilled water, together with part of the remaining alkali. Any left alkali was eliminated with washes of oil or water acidulated with HCl, followed by more washes of distilled water (Jacquelain, 1882).

The purification with hydrogen fluoride was very simple; it was enough to immerse the pencils in aqueous hydrogen fluoride for twenty-four to forty-eight hours at a temperature of 15° to 25 °C, in a rectangular lead vase. The excess acid was then removed by water washes, followed by drying and carburation like in the previous treatment. Anyhow, this was a very dangerous process because of the possible physiological dangers of hydrogen fluoride. Proper handling conditions had to be provided accordingly (Jacquelain, 1882).

Jacquelain added that all the hydrocarbons obtained by the thermal decomposition in a closed vessel of coal, peat, schist, resins, vegetables, turpentine, naphthalene, tar, etc., were appropriate carburant materials. Those of high boiling point were particularly appropriate because they were cheaper and provided a higher percentage of hard charcoal (Jacquelain, 1882).

This paper included a detailed description of the pilot plant built at the École Centrale to carry all the experiences described, and a table providing the photometric tests carried on the different varieties of charcoals tested. Inspection of these results indicated that the luminous power and the fixity of the voltaic arc increased at the same time as the density of carbon, its hardness, and its purity. The natural graphitoid carbon of Siberia was particularly exceptional, it acquired by purification a luminous power twice the one it had in its natural state, a power that exceeded by a sixth that of artificial pure carbons (Jacquelain, 1882).

Starch

Jacquelain carried an extensive research about the structure of starch, its properties, the influence of temperature, and the properties of its blue complex with iodine (Jacquelain, 1839, 1840a). He reached the following conclusions:

(1) The starch was formed of two substances, the inside consisted of concentric layers containing little nitrogen and being the only one capable of making cold or hot pastes; the outside substance was membranous and very nitrogenous. They could be separated by heating a mixture of starch and pure water, to 150 °C in a Papin pot (pressure cooker), for two to three hours. Filtration of the resulting liquor left the nitrogenous membranes on the filter. Upon cooling, the filtrate deposited the dissolved starch in the form of granules of 2/1000 mm, which were always colored in blue by iodine. Jacquelain remarked that the disorganizing or dissolving action of water alone in a closed vase, allowed reproducing the well-known phenomena of fluidization of starch in acidulated water. Thus, what lacked energy in the water was compensated by the help of the pressure and a higher temperature.

(2) The constant appearance of granular elements, separated from their aqueous solvent by cooling or by their insolubility in alcohol, demonstrated that the granules, composed of both dextrin colorable in blue or purple, and another, which could not be colored, were always organized products.

(3) Both matters were found to have the same chemical composition and rotary power and direction, demonstrating the chemical identity of starchy matter in its different states of aggregation.

(4) The mucilaginous consistency assumed by the porphyrized starch when moistened with cold water, allowed establishing some ideas regarding the possibility that the starch grain was enveloped by an external layer. The experimental evidence indicated

that the external part of the starch, whatever its nature, was extensible, resisted the action of cold water, and did not enjoy any plastic property before being crushed.

(5) According to Jacquelain, this envelope accounted for about 3.6% of the total weight but he was not sure that his various treatments had not dissolved part of it, as suggested by the fact that the amount of nitrogen supplied by the granules at the time of chemical analysis exceeded that of the nitrogen residue.

(6) Finally, from an industrial point of view, it had been noticed that the starch granules, dextrin or sugar, were obtained at will in a state of concentration not far from that required by the consumption of these materials, therefore saving time and fuel. The use of carbon black was not necessary (Jacquelain, 1839, 1840a).

According to Jacquelain, if there was a question of successfully replacing commercial dextrin, a highly hygroscopic substance, with another starchy material, the best candidate would be an aqueous of starch granules, made at 70 °C. This product, dried promptly in sheets, was very white, transparent, remarkably flexible, neutral, preparable in a very short time, and left a very small saline residue after incineration (Jacquelain, 1839, 1840a).

Jacquelain added the following facts regarding the formation of the blue color of the iodine-starch complex (Jacquelain, 1839, 1840a):

(1) The blue or purple coloring of the starchy principle with iodine should not be regarded as a chemical phenomenon. It was more rational to consider it the result of a more or less dense iodine condensation by the elements of dissolved starchy matter, according to whether them intimate tissue had been more or less distended by temperature and water vapor. Hence, we should call the processing, a real dye of organized matter.

(2) The iodine in excess with a solution of granules maintained for a long time at 100 °C in a closed vase, led to the decomposition of the amylaceous principle, so as to produce hydrogen iodide and generate another organic acid, which Jacquelain intended to examine. The reactions between the iodine and starch solution, nonetheless, persisted when the iodine was not in excess in the mixture, and, in this case, only the liquors became discolored at 100 °C or a little below.

(3) Finally, the production of hydrogen cyanide, as a result of the curious alteration which the starch experienced (blued with iodine and dried), when it was heated between 170 ° and 175 °C in a tube of 3 mm in diameter, was proof of the presence of nitrogen in the starch (Jacquelain, 1839, 1840a).

Sulfuric acid hydrates

In 1842, Jacquelain proposed a new and very simple method for purifying sulfuric acid monohydrate to be used in precision analysis and in forensic medicine (Jacquelain, 1842, 1843a). This procedure consisted in distilling a mixture of sulfuric acid (previously purified with sulfur) with a small amount of an aqueous solution of chlorine and removing the excess of the latter, as well as any HCl produced, by boiling the residue for a few minutes. The resulting sulfuric acid was completely deprived of nitrogen, sulfurous and hydrochloric acids, as shown by standard procedures. For example: (1) no precipitate was formed when treating 100 g of sulfuric acid dissolved in 500 g of distilled water with silver nitrate; (2) 100 grams of distilled zinc were converted into zinc nitrate and added to a sufficiently diluted solution of the purified acid. This mixture showed no reaction with a solution of barium chloride, and (3) 70.96 of this same zinc were reacted with 200 g of purified sulfuric acid (passes to sulfur and chlorine); the resulting hydrogen gas was passed several washing flasks containing a gold salt. No reaction was observed.

It was well known that an aqueous solution of ferrous sulfate was a very sensitive reagent for testing the presence of traces of nitric acid. For those willing to use it, Jacquelain recommended the following procedure: To 50 g of sulfuric acid, pour 0.5 g of distilled water on the surface and then let le mixture cool down. Then add ten drops of ferrous, sulfate slowly, to avoid a rise in temperature capable of destroying the purple compound formed during the possible reaction with the nitrogen compound (Jacquelain, 1842, 1843a).

Jacquelain wrote that chemists, at one or another stage of their work, had to handle sulfuric acid of different degree of hydration. The literature presented conflicting evidence of the freezing point of the acids containing one and two equivalents of water; for the first hydrate the values varied between -2.5° to -3.8 °C, and for the second, between 0° and +9 °C. These divergences were probably due to using acids of different concentration and different experimental conditions. These disparities led Jacquelain to make his own measurements (Jacquelain, 1850bd).

His experimental procedure was the following: Sulfuric acid was boiled until its relative density was 1.84, corresponding, more or less, to the monohydrate. A known amount of this acid was mixed in a closed vessel with enough water to have a composition equivalent to the dihydrate. Forty cubic centimeters of each acid were put in a tube provided with a calibrated alcohol thermometer and closure, which were then submerged, with agitation, in a refrigerant mixture. Once the liquids were solidified, the tubes were taken out of the mixture, until the temperature was seen to stop, brusquely, a fixed point, during all the melting process. This experiment was repeated several times. The average melting points observed were 0 °C and +8 °C, for the mono and dihydrates, respectively (Jacquelain, 1850bd).

Jacquelain repeated these experiences using open tubes and tubes under slight vacuum, and the same refrigeration mixture. No change in the results were obtained with the open tubes but this was not the case with the sealed tubes. This time the acid did not freeze when maintained at -40 °C, during 15 minutes, and 30 minutes at -35 °C. It turned out that the precaution of sealing the tubed to avoid hydration of the acids, was an obstacle to the process. Jacquelain wrote that this same behavior was observed with an aqueous solution of sodium sulfate saturated at 100 °C. He repeated the process with acid solutions containing enough water to form a tri and tetra hydrate, without producing a freezing process. The explanation of this behavior came accidentally. Jacquelain mentioned that at one time, an acid was offered commercially, which froze at +4 °C, in prismatic voluminous crystals. Analysis of this acid showed that it contained two equivalents of water, that is, SO_3HO, HO (Jacquelain is using the old nomenclature), Nevertheless, these crystals did not seem at all different from those obtained with a fast-freezing process. This result pointed the possibility that a fast and a slow crystallization led to the formation of different hydrates, an assumption that was confirmed experimentally. Using this idea, eventually, Jacquelain was able to prepare five different hydrates, corresponding to the following compositions (Jacquelain, 1850bd): $[4(SO_3),3(HO)]$; $[SO_3(HO)]$; $[SO_3,4(HO)]$; $[SO_3,5(HO)]$; $[SO_3,6(HO)]$.

Iodic acid

In 1843 Eugène Millon (1812-1867) published a very detailed description of the preparation of iodic acid (actually I_2O_5), its hydration (to true iodic acid), and the preparation of a large number of iodates (Millon, 1843). According to Jacquelain, this publication was not commented further, giving the impression that the problem had been definitely solved (Jacquelain, 1850a). Millon had reported one process only, using iodine in his purest form, particularly free of iron. A mixture of 80 g of purified iodine, 75 g of potassium chlorate, 400 g of water, and 1 g of nitric acid was boiled until it began releasing chlorine; heating was then stopped, and the solution treated with 90 g of barium nitrate. The precipitated barium iodate was separated, washed with water, boiled with 40 g of sulfuric acid and 150 g water for half an hour, filtered, and evaporated to crystallization. Millon remarked that his procedure allowed preparing iodic acid (IO_5) in three different states: combined with one equivalent of water (HO), IO_5, HO; with one-third equivalent of water, IO^5, (1/3) HO; anhydrous, IO_5, originating from the previous two forms by heating to 170 °C or more (Millon, 1843).

In 1850 Jacquelain published a paper discussing in detail four methods available methods for producing iodic acid in quantity: (1) The reaction of chlorine with iodine in the presence of water; (2) the reaction of chloric acid or potassium chlorate with iodine, by a wet procedure; (3) the interaction between hypochloric acid and iodine; and (4) the reaction of nitric acid in several concentrations, with powdered iodine, The first two procedures were too meticulous to be conducted in an industrial scale, and the third, too expensive. The fourth process was rapid, cheap, and easy to carry on in large scale; its only disadvantage was the need of nitric acid, pure and fuming. Jacquelain then gave a short description of each of these procedures (Jacquelain, 1850ae).

Basically, the first process consisted in directing a stream of chlorine over 20 g of iodine suspended in 700 g water at 40 °C, which caused the immediate disappearance of the iodine, forming a solution of an iodine sub-chloride solution in water. The excess chlorine was then eliminated by means of a stream of CO_2 or by exposition to sunlight. Addition of enough barium hydroxide precipitated the iodine as barium iodide, which was then decomposed with diluted sulfuric acid, followed by evaporation to dryness of the filtrate. Jacquelain wrote that his experience indicated that the solid material was barium acid iodate. The dosage of the iodine was rather easy: the iodate was dissolved in a dilute solution of nitric acid and converted into hydrogen iodide by means of sulfur dioxide. The acid was then titrated with a calibrated solution of silver nitrate (Jacquelain, 1850ae).

The second procedure was the one described by Millon in his paper (Millon, 1843): A mixture of 80 g of purified iodine, 75 g of potassium chlorate, 400 g of water, and 1 g of nitric acid was boiled until it began releasing chlorine; heating was then stopped and the solution treated with 90 of barium nitrate. The precipitated barium iodate was separated, washed with water, boiled with 40 g of sulfuric acid and 150 g water for half an hour, filtered, and evaporated to crystallization.

According to Jacquelain, the process of Millon had two objections: (1) the small amount of nitric acid needed was actually unnecessary; the same products and in the same amount were obtained when the reaction was carried in the absence of nitric acid; and (2) the decomposition of the barium iodate was very difficult and resulted in serious losses; one of them because of the use of large amounts of sulfuric acid. The precipitate of barium sulfate occluded part of the iodate (Jacquelain, 1850ae).

Jacquelain reacted nitric acid of different concentrations with powdered iodine and obtained the same results reported in the literature, iodic acid and iodine perchloride. The iodic acid appeared as a very pure white pulverulent material, which decomposed completely upon heating and did not seem to contain chlorine or one of its compounds. One disadvantage of this process was that it converted part of iodine into iodic acid and another into iodine perchloride. These, and other minor problems, indicated the need for improvement, before applying it industrially. Jacquelain described the equipment and experimental technique he had developed to allow the easy production, safely and without vigilance, 30 to 40 liters of hypochloric acid. After much experimentation, Jacquelain concluded that the best procedure of manufacturing iodic acid was to react dry and pulverized iodine with nitric acid of relative density 1.5, in the weight ratio 1 to 40, for one hour at 60 ^{o}C. The product was solid iodic acid, anhydrous and crystalline, surmounted by two liquid layers, the superior formed by a mixture of nitric and hyponitric acids, and the other, very dense and red brown, composed of a solution of iodine dissolved in nitric acid (Jacquelain, 1850ae).

The numerical information obtained allowed Jacquelain to determine that the value of the equivalent of iodine was 1570 instead of 1579 and 1586, as claimed by others (Jacquelain, 1850ae).

References

Anonymous. France (2021). Archives Nationales. Base Léonore, dossiers nominatifs des personnes nominées ou promues dans l'Ordre de la Légion d'Honneur.

Dumas, J. and Stas, J. S. (1841). Recherches sur le Poids Atomique du Carbone. *Annales de Chimie et Physique* [2], *1*, 6-58.

Ebelmen. J. J. (1844). Sur les Éthers Siliciques. *Journal de Pharmacie, 6*, 262-264.

Guyton de Morveau, L. B. (1799a). Sur la Combustion du Diamant. *Annales de Chimie*, *31*, 72-112.

Guyton de Morveau, L. B. (1799b). Sur le Passage du Diamant à l'État de Charbon, et la Désoxygénation du Soufre par le Diamant. *Annales de Chimie*, *32*, 62-66.

Hare, R. (1823). On the Peculiar and Comparative Effects of the Calorimotor and Deflagrator with Account of an Improved Deflagrator and Experiments therewith. *Silliman Journal, 5*, 97-102, 105-108.

Jacquelain, V.-A. (1839). Étude des Phénomènes que Présente la Fécule Hydraté Soumise en Vases Clos à Températures Constantes. *Comptes Rendus, 8*, 916-918.

Jacquelain, V.-A. (1840a). Mémoire sur la Fécule. *Annales de Chimie et Physique* [2], *74*, 167-207.

Jacquelain, V.-A. (1840b). Observations Relatives à la Cristallisation du Platine. Modifications Apportés dans l'Art de Travailler de Métal. *Comptes Rendus, 11*, 204-207 ; *Annales de Chimie et Physique* [2], *74*, 213-221.

Jacquelain, V.-A. (1842). Purification de l'Acide Sulfurique à un Atome d'Eau, pour Analyse de Précision et Recherches de Médicine Légale. *Comptes Rendus, 14*, 642-645.

Jacquelain, V.-A. (1843a). Purification de l'Acide Sulfurique à un Atome d'Eau, et Rectification du Nombre Proportionnel du Zinc. *Annales de Chimie et Physique* [2], *7*, 189-207.

Jacquelain, V.-A. (1843b). Moyen de Communiquer à la Fécule, sans Secours de la Torréfaction ni des Acides la Propriété de se Dissoudre dans l'Eau de 70º Degrés et de Conserve cette Solubilité Pendant un An et Plus. *Annales de Chimie et Physique* [2], *8*, 255.

Jacquelain, V.-A. (1847b). Études sur les Acides du Soufre. *Annales de Chimie et Physique* [2], *21*, 110-111.

Jacquelain, V.-A. (1847c). Procédé de Fabrication Économique du Bichromate de Potasse, des Chromates de Plomb et de Bichromate de Chaux. *Annales de Chimie et Physique* [2], *21*, 484.

Jacquelain, V.-A. (1847d). De l'Action Calorifique de la Pile de Bunsen, de Chalumeau à Gaz Oxygène et Hydrogène sur le Carbone Pur, Artificiel et Naturel. *Comptes Rendus, 24*, 1050-1052 ; *Annales de Chimie et Physique* [3], *20,* 439-472.

Jacquelain, V.-A. (1849). *Titres Scientifiques et Programme du Cours de Chimie de M. V. Jacquelain*, Martinet, Paris.

Jacquelain, V.-A. (1850a). Sur les Diverses Procédés Connus pour la Préparation de l'Acide Iodique. *Annales de Chimie et Physique* [3], *30,* 332-343.

Jacquelain, V.-A. (1850b). Observations Diverses sur les Hydrates d'Acide Sulfurique. *Annales de Chimie et Physique* [3], *30,* 343-355.

Jacquelain, V.-A. (1850c). Action de la Vapeur d'Eau à des Températures et Pressions Variables sur les Carbonates de Potasse, de Soude, de Baryte, de Chaux, de Manganèse, de Plomb et d'Argent. *Comptes Rendus, 30,* 106-107.

Jacquelain, V.-A. (1840d). Mémoire sur les Hydrates d›Acide Sulfurique. *Comptes Rendus, 31,* 624.

Jacquelain, V.-A. (1840e). Mémoire sur l›Acide Iodique Anhydre et Cristallisé. *Comptes Rendus, 31,* 624-625.

Jacquelain, V.-A. (1840f). Mémoire sur la Dulcine. *Comptes Rendus, 31,* 625-626.

Jacquelain, V.-A. (1851). Sur un Nouvelle Matière Organique Sucrée (la Dulcine). *Revue Scientifique, 10*, 1-20.

Jacquelain, V.-A. (1852). *Considérations sur la Fabrication Économique de l'Hydrogène Pur Destiné aux Opérations Manufacturières de Chauffage et de l'Éclairage*. Vve Bouchard-Huzard, Paris.

Jacquelain, V.-A. (1863). Méthode Générale d›Analyse des Eaux Fluviales. *Les Mondes, 3*, 769-804. Published as booklet by Girard, Paris.

Jacquelain, V.-A. (1882). Purification des Carbones Graphitoïdes soit Naturelles, soir Artificielles et sur la Préparation Directe de Carbone Pur Graphitoïde, Destinés Principalement à l'Éclairage Électrique. *Comptes Rendus, 94*, 873-876; *Annales de Chimie et de Physique* [6], *27*, 537-554.

Larousse, P. (1890). Jacquelain (Victor-Auguste). In Larousse, P. *Grand Dictionnaire Universel du XIXe Siècle*. Tome 17, Deuxième Supplément, page 1450. Administration du Grand Dictionnaire Universel, Paris.

Millon, E. (1843). Mémoire sur l›Acide Iodique Libre et Combiné. *Annales de Chimie et de Physique* [3], *9*, 400-431.

Silliman, B. (1823). Fusion of Charcoal, Graphite, Diamond, Anthracite, etc., with the Deflagrator and the Compound Blowpipe. *Silliman Journal, 6*, 341-353.

Silliman, B. (1826). Notice of Some Recent Experiments on Charcoal. *Silliman Journal, 10*, 119-121.

West, W. (1823). On the Galvanic Ignition of Charcoal. *Annales de Philosophy, 5*, 314-315.

Wollaston, W. H. (1829). On a Method of Rendering Platina Malleable (Bakerian Lecture, 1828). *Philosophical Transactions*, *119*, 1-8.