Educación Química

Refexión

Léon Péan de Saint-Gilles

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Resumen

Léon Péan de Saint-Gilles (1832-1863) fue un químico francés, autodidacta, que estudió la alotropía del azufre y las propiedades y reacciones de las diferentes especies, las propiedades oxidantes del permanganato de potasio, la oxidación del cobre bajo la influencia simultánea del aire y el amoníaco, y la acción del cianógeno sobre el acetaldehído. Con Marcellin Berthelot determinaron las reglas básicas de la esterificación de un ácido por un alcohol en sus múltiples vías.

Palabras clave: afinidad; alotropía; amoníaco; azufre; cianógeno; esterificación; oxidación; permanganato de potasio.

Abstract

Léon Péan de Saint-Gilles (1832-1863) was a French chemist, without a formal education, who studied the allotropy of sulfur and the properties and reactions of the different species, the oxidizing properties of potassium permanganate, the oxidation of copper under the simultaneous influence of air and ammonia, and the action of cyanogen on acetaldehyde. With Marcellin Berthelot they determined the basic rules of the esterification of an acid by an alcohol in its many routes.

Keywords : affinity; allotropy; ammonia; cyanogen; esterification; oxidation; potassium permanganate; sulfur.

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Life and career (Berthelot, 1863; Boutron-Charlard, 1863)

Little information is available about the life and basic education of Léon Péan de Saint-Gilles. He was born in Paris, on January 4, 1832, the son of Armand Péan (1791-1860), a wealthy notary, and Eugénie Jars (1803-1888). He grew up as a very sick and weak child, unable to attend a regular school. For this reason, he received his basic education at home, and at the age of seventeen he earned his bachelor of letters degree. Unable to pursue a higher education, he joined the laboratory of Théophile-Jules Pelouze (1807-1867))a friend of the family) at the École Polytechnique where he acquired the necessary practical experience to open his own laboratory and carry research. In 1856 he married Pauline Thion de la Chaume (1838-1914); two children (Helen and Louis) were born of this union. In 1861 he became ill with tuberculosis, which forced him to move to Cannes, in search of a cure, which did not come. Péan de Saint-Gilles died of tuberculosis in Cannes on March 22, 1863, at the age of thirty-one, and was buried in the Père Lachaise cemetery in Paris.

Scientific contribution

Péan de Saint-Gilles carried most of his research on inorganic and organic chemistry and the laws regulating the formation of an ester from an acid and alcohol. This work led to the publication of near 20 scientific papers. In addition to the few subjects described below, Péan de Saint-Gilles, synthesized many new sulfites from mercuric and cupric oxides (Péan de Saint-Gilles, 1852-1853, 1853, 1854); studied the effect of heat upon iron hydrates and acetates (Péan de Saint-Gilles, 1855ab); the action of heat upon iron sesquioxide (Péan de Saint-Gilles, 1856); the oxidation of sulfur and arsenic compounds by means of iodine (Péan de Saint-Gilles, 1859b); the allotropic modifications of ferric oxide by the action of heat upon iron sesquioxide (Péan de Saint-Gilles, 1860); the synthesis of manganese oxichloride (Péan de Saint-Gilles, 1862); etc.

Care should be taken that in many of their equations, Berthelot and Péan de Sainte-Gilles used the old values of atomic masses, i.e., C = 6, and HO (equivalent) as the formula of water.

Sulfur and its derivatives

Berthelot published a detailed study about sulfur, its allotropic forms, and properties, and several of its derivatives (Berthelot, 1857). He mentioned that the study of sulfur had always been a popular experimental subject among chemists. Despite its simple nature and its chemical identity, sulfur occurred under very different forms, according to the conditions of its preparation and the influences on which it had been subjected. Sometimes it appeared as octahedral crystals derived from the right rhomboidal prism and others in the form of rhomboidal prisms obliques. It also appeared as a soft, more, or less liquid, and elastic state, often emulsifiable in water, sometimes colored with a reddish or greenish tint, and finally, it appeared in an organized form or as an amorphous matter, insoluble in carbon disulfide (Berthelot, 1857). Between all the states of sulfur there were two essential and stable limits to which all the others could be converted, namely, octahedral sulfur or electronegative sulfur, acting as an oxidizing element, and electropositive sulfur or combustible sulfur, generally amorphous and insoluble in solvents proper. Within octahedral sulfur, there were two states: a less stable prismatic sulfur and soft sulfur, and emulsifiable polysulfides. All these varieties were soluble in carbon disulfide (Berthelot, 1857).

Electropositive sulfur could be prepared by pouring sulfur heated above 170 °C into cold water and followed by purification with carbon disulfide. It was amorphous and insoluble in standard solvents (water, alcohol, ether, carbon disulfide, etc.) and could be transformed into soluble and crystallizable sulfur by the action of heat or by contact with certain bodies (i.e., cold hydrogen sulfide). The sulfur produced under the influence of fuming nitric acid presented the same characters as the previous one (Berthelot, 1857).

Péan de Saint-Gilles added that the various varieties of sulfur manifested different affinities with respect to oxidizing agents, and with respect to nitric acid (Péan de Saint-Gilles, 1858a). On the one hand, octahedral sulfur was hardly attacked by nitric acid at the temperature of boiling, while releasing nitrous vapors with slowness and difficulty. On the other hand, insoluble sulfur, purified by carbon disulfide, was violently attacked by nitric acid below 80 °C and disappeared rapidly while releasing abundant gleaming vapors. This reaction was usually incomplete because the accompanying rise in temperature was usually sufficient to transform a part of amorphous sulfur into crystallizable sulfur. The residual sulfur had also become crystallizable and soluble in carbon disulfide. Essentially, the same results were obtained with sulfur flowers (a mixture of crystallizable sulfur and insoluble amorphous sulfur) and on sulfides (although with less conversion). (Péan de Saint-Gilles, 1858a).

Péan de Saint-Gilles added that one could assume that the resistance of crystallizable sulfur to oxidation, opposed to the easy oxidizability of insoluble sulfur, was due to the difference, which existed between the cohesion of these two varieties of sulfur. This assumption could be easily rejected by first crushing mechanically both varieties of sulfur to a similar state of division, or by taking advantage of Marcellin Berthelot's (1827-1907) finding that amorphous sulfur became crystallizable by the mere contact with an aqueous solution of hydrogen sulfide. Péan de Saint-Gilles found that the resulting sulfur was an impalpable powder, easily wettable by water. Powdering by both procedures eliminated almost completely the unequal cohesion of both sulfurs (Péan de Saint-Gilles, 1858a).

This reasoning was completed by subjecting equal weights (1.000 g) of soluble amorphous sulfur and of insoluble amorphous sulfur to five successive washings with carbon disulfide, followed by mixing the purified materials with equal volumes of nitric acid, and heating the two mixtures in the same water bath, maintained below 80 °C, for half an hour. The insoluble sulfur was promptly seen releasing abundant nitrous vapors, while the crystallizable sulfur hardly showed this effect. The weights of the resulting residues were 0.009 g for the amorphous insoluble sulfur and 0.965 g for the amorphous soluble sulfur, showing that 99% of the insoluble amorphous sulfur oxidized, while the same sulfur made crystallizable lost only about 3% of its weight (Péan de Saint-Gilles, 1858a).

Péan de Saint-Gilles concluded that his results indicated that in contact with nitric acid, amorphous sulfur, insoluble in carbon disulfide, oxidized much more easily than crystallizable sulfur, and that this difference appeared to be due to a more pronounced affinity of insoluble sulfur for oxygen, and not to a more or less perfect state of cohesion of these two varieties of sulfur (Péan de Saint-Gilles, 1858a).

In a following paper, Péan de Saint-Gilles reported that he had discovered a new reaction of amorphous sulfur, based on Berthelot's findings that amorphous sulfur dissolved in sodium sulfite and in potassium bisulfite much more easily than crystallizable sulfur, while the latter exhibited a stronger tendency to combine with mercury (Berthelot, 1857; Péan de Saint-Gilles, 1858b). As written above, Péan de Saint-Gilles had found that the reaction of insoluble sulfur with boiling nitric acid was accompanied by the release of abundant nitrous vapors, while that with crystallizable sulfur hardly showed this effect. Hence, sulfur flowers, which contains 20 to 30% of amorphous sulfur, could be stripped of the latter in a few minutes. The residue, composed of crystallizable sulfur, sometimes pulverulent, sometimes molten, hardly reacted with nitric acid, and dissolved entirely, or nearly so in carbon disulfide. This experiment proved that the temperature of the reaction was not sufficient to completely transform the insoluble sulfur extracted from the sulfur flowers sulfur into crystallizable sulfur. Consequently, the insoluble sulfur that could be released from oxygenated sulfur compounds oxidized more readily than octahedral sulfur, which seemed to respond to combinations of sulfur with metals (Péan de Saint-Gilles, 1858b).

Péan de Saint-Gilles described the results of several experiments that proved his findings. For example, 10 g of sulfur flowers, containing 24 g of insoluble sulfur, heated for only two minutes with commercial nitric acid lost 14% of their weight, that is, about two-fifths of the primitive amorphous sulfur had been transformed into crystallizable sulfur, thanks to the temperature produced (Péan de Saint-Gilles, 1858b).

Péan de Saint-Gilles wrote that the combination of sulfur and mercury was a straightforward process that took place very rapidly by the simple contact between both substances, without the help of heat and favored by the liquid state of mercury. The resulting product, mercuric sulfide, was very stable and unalterable to the air (Péan de Saint-Gilles, 1859c). These facts led him to compare the reaction between mercury and insoluble sulfur and with crystallizable sulfur, to add more information about the previous question regarding if this process was activated by the unequal cohesion of both varieties of sulfur and/or by the chemical affinity between the reagents.

The basic experiment consisted in contacting one gram of each variety of sulfur, finely powdered, with 60 g of mercury in flasks of equal capacity and shaken simultaneously for several hours (Péan de Saint-Gilles, 1859c). During this process, the crystallizable sulfur began the blacken and turn like lampblack, while its volume increased significantly. During the same time, the insoluble sulfur hardly changed color and volume. Under microscopic examination, the crystallizable appeared as an amorphous and black powder, while the insoluble sulfur was seen composed of distinct spherical globules. Both products were then slightly heated with fuming hydrogen chloride and the hydrogen sulfide released collected in a flask containing a KOH solution of known composition. The results obtained clearly indicated that the sample of crystallizable sulfur contained about 10 times more mercuric sulfide than the sample with insoluble sulfur, implying that the main driving force for the reaction between mercury and crystallizable sulfur was the chemical affinity between the two reagents and not the mechanical cohesion (Péan de Saint-Gilles, 1859c).

Oxidizing properties or potassium permanganate

Péan de Saint-Gilles wrote that his study of the oxidizing reactions of potassium permanganate had taught him that to carry them to their end, required using an excess of permanganate and that the liquor being tested be alkaline or acid. Fulfillment of these conditions allowed him to transform instantaneously and at room temperature, hyposulfites, sulfites and sulfides into sulfates, free iodine and iodides into iodates, nitrites into nitrates, and arsenites in arsenates (Péan de Saint-Gilles, 1858c, 1859a). The determination of the various compounds was easily conducted using a modification of the process developed by Lous-Joseph Fréderic Margueritte for the analysis of iron by the humid via (Margueritte, 1846), which required the use of two solutions: (1) a titrated solution containing approximately 25 g crystallized potassium permanganate for 2 liters of water. This solution was very stable, if it was kept away from direct sunlight; and (2) a solution containing approximately 1 liter of water, 100 g crystals of ferrous sulfate, and 100 cm^3 of sulfuric acid free of nitrous compounds (to slow down the oxidation of the ferrous salt in contact with air. Basically, the experimental procedure consisted in making the liquor being tested basic or acid by addition of an alkaline carbonate or an acid, followed by addition of an excess of potassium permanganate enough to attain a deep red color. The excess permanganate was then titrated with the ferrous sulfate solution (Péan de Saint-Gilles, 1858c, 1859a).

Péan de Saint-Gilles described the procedure he followed to determine the oxidizing action of potassium permanganate on mineral acids (i.e., iodine and hydrogen iodide, hyposulfuric and dithionic acids, sulfur dioxide and hyposulfurous acid, hydrogen sulfide, hypophosphorous acid, nitrous acid, and arsenious acid) and organic acids (i.e., oxalic, formic, prussic, thiocyanic, tartaric, malic, and citric acid) (Péan de Saint-Gilles, 1858c, 1859a). Thus, hydrogen sulfide, soluble sulfides, or metallic sulfides, mixed with an alkaline carbonate and an excess of potassium permanganate, were found to absorb four equivalents of oxygen to be converted into sulfates. Formic acid in the presence of mineral acids did not discolor potassium permanganate, even when hot, but in an alkaline liquor the oxidation was instantaneous and complete, with all the carbon oxidizing to CO_2:

$$C_2H_2O4 + O_2 = 2CO_2 + 2HO$$

and potassium permanganate gave 5 equivalents of oxygen to free iodine and 6 equivalents to iodides to convert them to iodic acid, $IO5,HO$, which did not act upon diluted acid ferrous chloride (Péan de Saint-Gilles, 1858c, 1859a):

Affinity effect on the formation and decomposition of esters

Berthelot and Péan de Sainte-Gilles wrote that the reaction between acids and alcohols to yield an ester was characterized by its slow kinetics and incomplete consummation (Berthelot & Péan de Sainte-Gilles, 1861; 1862abc, 1863abc, 1862-1863). For these reasons, they decided to study it in detail to find how it was affected by the affinity between the components and the operating conditions (for example, molar ratio acid/alcohol, pressure, and temperature).

Execution of project took two years and involved the performance of more than three hundred experiments involving monoatomic and polyatomic alcohols, monobasic, dibasic, and tribasic acids, and their esters, in a wide range of molecular weights and molar ratio acid/alcohol, at temperatures from 66° up to 360 °C and above, pressures from a few millimeters up to 30 atmospheres and more, and duration of the reaction up to 460 consecutive hours at 200 °C. Special care was taken to thoroughly determine the purity of each chemical employed and to carry the reaction in the presence of a liquid phase. Also, various experiments were made related to the simultaneous action of several acids on the same alcohol, to that of several alcohols on the same acid, and to the reciprocal displacement of acids or alcohols in esters (Berthelot & Péan de Sainte-Gilles, 1861; 1862-1863).

Their main results were as follows (Berthelot & Péan de Sainte-Gilles, 1861; 1862-1863):

1) The reaction of equal equivalents of an alcohol and an acid (or of one equivalent of the pertinent ester) with two equivalents of water, ended up reaching an identical state of equilibrium, with incomplete conversion.

2) The reaction between equivalent amounts of an acid and an alcohol, carried in the presence of a water absorbing substance such as anhydrous barite, resulted in the complete combination of the reagents and neutralization of the acid.

3) The amount of ester formed by the reaction between one equivalent of acid and one equivalent of alcohol was substantially independent of the temperature at which one operated and of the pressure exerted in the apparatus (provided that a certain amount of the reactants retained the liquid state). The reaction slowed down as one operated at a lower temperature and the rate of the reaction varied with the nature of the acid and the alcohol.

4) The reaction of a series of mono-alcohols of molecular weight varying from 32 to 372, in equal equivalents with the same acid, resulted in almost the same conversion of the acid (about 68% of its weight) .The same results were obtained a triatomic alcohol.

5) The reaction of the same number of equivalents of a given alcohol with and equal number of equivalents of a series of acids whose equivalents varied from 60 to 284, changed very little the proportion of combined alcohol. The extreme limits were necessarily the same as above, but the numbers relating to the union of the *same alcohol* with the various acids were much closer than the numbers relating to the union of the *same acid* with the various alcohols. For example, the proportions of ethanol combined with ten different monobasic, bibasic, and tribasic acids varied from 66 to 70% at most.

6) The preceding facts proved that the equivalent proportions of acid and alcohol, which formed an ester, were almost independent of the particular nature of the acids and alcohols. This result was also observed whatever the equivalent proportions of alcohol, acid, and water reacted (series 2, 3, 4, 5, 6). The quantity of ester formed seemed to be independent of the individual nature of the acid and that of the alcohol. A possible exception could occur when polyatomic alcohols were reacted with several equivalents of acid.

7) The decomposition of an ester by a variable number of equivalents of water occurred in a continuous manner, which increased as the relative number of equivalents of water increased (Berthelot & Péan de Sainte-Gilles, 1861; 1862-1863).

In the following paper, Berthelot and Péan de Sainte-Gilles used the above results to broaden the rules that characterized the esterification of an acid by an alcohol (Berthelot and Péan de Sainte-Gilles, 1862a; 1862-1863). They now wrote that the reaction took place in a slow, progressive manner, with a rate that depended on the influences acting on the system; it was never immediate and complete, even in the cases of systems that remained totally liquid during the duration of the experiment. It always attained a fix limit, no matter how long the contact. The same features characterized the reverse equation, the hydrolysis of the ester (Berthelot and Péan de Sainte-Gilles, 1862a; 1862-1863).

The new results reported the effects of the temperature and length of the reaction, for the following systems:

1. Conversion achieved during the reaction of equal equivalents of acetic acid and ethanol, at temperatures between 6^o and 9 ^{o}C, for reaction times from 1 (0.9%) to 96 days (30.0%).
2. The same experiment, at about 25 ^{o}C, for reaction times from 15 (10.0%) to 368 days (55.0%).
3. The same experiment between valeric acid and ethanol, at about 25 ^{o}C, for reaction times from 22 (3.2%) to 277 days (31.4%).
4. The same experiment between acetic acid and ethanol, at 100 ^{o}C, for reaction times from 4 (25.8%) to 150 hours (65.0%).
5. The same experiment at different times and temperatures, 3 hours at 170 ^{o}C (64.1%); 42 hours at 170 ^{o}C (66.5%); and 22 hours at 200 ^{o}C (66.4%).

Additional experiments were performed for sulfuric acid and ethanol, acetic acid and amyl alcohol, and acetic acid and glycerin (Berthelot and Péan de Sainte-Gilles, 1862a; 1862-1863).

The pertinent results indicated (Berthelot and Péan de Sainte-Gilles, 1862a; 1862-1863) that (a) the affinities of alcohols and esters were already present at ambient temperature, but in general in a very slow manner. Increasing the temperature accelerated the rate of reaction of acids with alcohols, as well as that of water with esters (hydrolysis); (b) the rate of reaction slowed strongly as the reaction advanced towards its end, for example, 8 days were enough to combine 7.3% of the acid at the beginning, later it took 56 days to achieve the same result. Berthelot and Péan de Sainte-Gilles added that the slow initial rate of reaction accelerated very rapidly: the average amount combined in one day during the first 22 days was equal to 0.12% and from the 22nd to the 72nd day, it almost tripled itself. Also, 1200 hours between 6^o and 9 °C combined about the same proportion as 4 hours at 100 °C. The decomposition of esters by water obeyed laws analogous to those of their formation; but it was much slower, all other things being equal (Berthelot and Péan de Sainte-Gilles, 1862a; 1862-1863).

The next publication presented the features that characterized the esterification of various acids with the same alcohol and of various alcohols with the same acid (Berthelot & Péan de Sainte-Gilles, 1862b; 1862-1863).

The first experiments compared the conversion of the reaction of one equivalent of acetic, butyric, valeric, and stearic acids, with one equivalent of ordinary ethanol, at several lengths of time and temperatures. For example, at 100 °C and 5 hours, the conversion of acetic acid mixed with ethanol was 31.0% and of butyric acid with ethanol, 17.1%, indicating that the combination of ethanol with acetic acid was faster than the one with butyric acid. Mixtures of one equivalent of ethanol with one equivalent of acetic acid and with one of valeric acid, were maintained at room temperature for contact time increasing from 22 to 277 days. At the end of the experiment the conversions of acetic and valeric acid were 53.7% and 31.4%, respectively, indicating that alcohol reacted with butyric acid more than with valeric acid. Berthelot had already shown that the conversion of the reaction between stearic acid and ethanol was extremely small; these results suggested that the rate of combination of the acids of the same series, $C_{2n}H_{2n}O_4$, with ethanol decreased as their molecular mass and boiling point increased (Berthelot & Péan de Sainte-Gilles, 1862b; 1862-1863).

Additional experiments showed that the reaction of polybasic acids with alcohols of similar molecular mass was faster than that with monobasic acids (Berthelot & Péan de Saint-Gilles, 1862b).

The next series of experiments compared the results of the combination of various alcohols with the same acid. The main results were as follows (Berthelot & Péan de Saint-Gilles, 1862b; 1862-1863):

1) The formation of the metameric esters ethyl valeric and amyl acetic, took place with very dissimilar rates.

2) The alcohols of the same series, $C_{2n}H_{2n+2}O_2$, combined with the same acid with almost identical rates, independently of the temperature. This result was not true for alcohols belonging to different series, such as ethanol, cholesterol, and menthol.

3) At room temperature, the affinity of a polyalcohol such as glycerin for acetic acid was stronger than that with ethanol (Berthelot & Péan de Saint-Gilles, 1862b; 1862-1863).

This paper also included details about the decomposition of esters by water (Berthelot & Péan de Saint-Gilles, 1862b; 1862-1863). The pertinent experiments led to the following general conclusions:

1) The esters formed by monobasic acids were more resistant to hydrolysis than the esters formed by polybasic acids having comparable equivalents.

2) The greater or lesser resistance to hydrolysis depended on the nature of the acid component and not on that of the alcohol. For example, in the esters of the acid $C_{2n}H_{2n}O_4$, the resistance to hydrolysis increased in the order butyric ester > acetic ester > formic ester (Berthelot & Péan de Saint-Gilles, 1862b; 1862-1863).

The next paper reported the effect of pressure on the esterification reaction carried in sealed vessels (Berthelot & Péan de Sainte-Gilles, 1862c; 1862-1863). According to Berthelot and Péan de Sainte-Gilles, in this situation the conversion was influenced simultaneously by three factors: the pressure, the temperature, and the ratio weight of vapor/(weight of liquid + vapor) (the quality of the mixture) (Berthelot & Péan de Sainte-Gilles, 1862c). For these reasons, they carried the following experiments, using equal equivalent mixtures of acetic and ethanol, for equal or different time duration: (a) the mixture kept fully in the liquid phase, at 80 ^{o}C and 50 atmospheres, for 1 to 3 hours; (b) the mixture maintained fully in the vapor phase, at 200 ^{o}C and volumes 2.6 and 1351 cm^3, for

10 hours, (c) on a mixture of ethyl acetate mixed with two moles of water, fully in the vapor phase, at 200 °C and volumes 2 and 476 cm^3, for 0.5 to 140 hours, and (d) one mixture of high quality (a large amount of vapor in equilibrium with a small amount of liquid), and another mixture of low quality (a small amount of vapor in equilibrium with a large amount of liquid) Compared to the same reaction carried at atmospheric pressure, system (a) showed a negligible change in conversion, system (b) reacted slower that system (a), system (c) showed a decrease in the rate as the volume was increased and a conversion lower than the maximum, and system (d) showed that the conversion increased as the quality decreased (Berthelot & Péan de Sainte-Gilles, 1862c; 1862-1863).

Berthelot and Péan de Sainte-Gilles also carried experiments in which the volume was increased by addition of a solvent that did not participate in the reaction (i.e., benzene and ether). No definite conclusions were obtained but the results seemed to indicate that the rate of esterification decreased as the amount of solvent increased, although the conversion seemed to increase (Berthelot & Péan de Sainte-Gilles, 1862c).

As shown above, the combination, the esterification reaction of an acid by an alcohol was never complete, it always terminated in a mixture of alcohol, acid, neutral ester, and water, representing the equilibrium reached between the affinity of the acid for the alcohol, which tended to combine them, and the inverse affinity of the water for neutral ester, which tended to regenerate acid and alcohol. It was enough to eliminate the water to obtain a complete combination (Berthelot & Péan de Sainte-Gilles, 1863a; 1862-1863).

Berthelot and Péan de Sainte de Gilles carried numerous experiments to determine this limit of combination for several hundred systems formed by mixtures of various acids and alcohols (Berthelot & Péan de Sainte-Gilles, 1863a; 1862-1863). Their results indicated that the maximum conversion attained depended on the relative proportions of acid, alcohol, and water present. For the same system in the liquid state, the limit was essentially independent of temperature, pressure, and the presence of an inert solvent such acetone or dry ester. Monobasic acids and various alcohols of a variety of physical and chemical properties combined in an almost constant equivalent proportion; the slight differences observed between the limits should be attributed to the inevitable diversity of physical properties of the systems tested. An equivalent of polyatomic alcohols acted on an equivalent of acid in the same way as an equivalent of monoatomic alcohol (Berthelot & Péan de Sainte-Gilles, 1893a; 1862-1863).

The last paper described the variation of the conversion in systems containing an excess of one component, for example, monobasic and polybasic acids with an excess of alcohol; mono-alcohols and polyalcohols (i.e., glycerin) with an excess of acid; 1 equivalent of alcohol with 1 equivalent of acid, and *n* equivalents of the ester; one equivalent of ethyl benzoate with *n* equivalents of water; 1 equivalent of alcohol, 1 equivalent of acid, and *n* equivalents of water, etc. (Berthelot & Péan de Sainte-Gilles, 1863b; 1862-1863).

Miscellaneous

Berthelot wrote that after Péan de Sainte-Gilles premature death he had gone through his notes and found two entries, which he believed should be published: one related to the oxidation of copper under the simultaneous influence of air and ammonia; the second, to the action of cyanogen on the aldehyde (Berthelot & Péan de Sainte-Gilles, 1863c).

The first item was related to the fact that in many chemical reactions the active substance divided between two other bodies, which combined with it simultaneously. For example, it was known that spraying ammonia on copper turnings resulted in two concurring effects: oxygen was absorbed from the air and copper oxide was formed, while ammonia was oxidized into nitrous acid. Péan de Saint-Gilles had investigated these processes and found that if concentrated ammonia was used, the proportion of oxygen bound to copper was double that which bound to ammonia, according to the reactions (sic) (Berthelot & Péan de Sainte-Gilles, 1863c):

$$3O_2 + NH_3 = NO_3 + 3HO$$
$$6O2 + 12\ Cu = 12CuO$$

In 1860, Justus von Liebig (1803-1883) reported that he had found that water saturated with cyanide and mixed with a little of acetal aldehyde behaved quite differently from the aqueous cyanide solution alone. While the latter promptly turned brown, with the formation of oxalate of ammonium, urea, hydrogen cyanide, and a paracyanide compound, the solution mixed with aldehyde remained water-white and gradually deposited white crusts of oxamide, into which apparently had absorbed all the cyanide (Liebig, 1860).

Péan de Sainte-Gilles repeated this experiment in a slightly different manner and got a different result (Berthelot & Péan de Sainte-Gilles, 1863c). He passed cyanogen through a raw acetal aldehyde prepared by the direct condensation of the more volatile products of the action of potassium dichromate and sulfuric acid on ethanol. This resulted in an abundant white powdery precipitate, very similar to oxamide but having a very different composition: by weight: 36.3% of carbon, 5.1% of oxygen, 26.4% nitrogen, and 32.2% oxygen, corresponding to the formula $C_{12}H_{10}N_4O_8$, having the elements of cyanogen together with those of acetaldehyde and water, as per the equation (sic) (Berthelot & Péan de Sainte-Gilles, 1863c):

$$\underset{\text{cyanogen}}{2C_4N_2} + \underset{\text{acetaldehyde}}{C_4H_4O_2} + \underset{\text{water}}{3H_2O_2} = C_{12}H_{10}N_4O_8$$

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