

JEAN-LOUIS HENRI BUIGNET

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RESUMEN

Jean-Louis Henri Buignet (1815-1876), fue farmacéutico francés que estudió la sacarificación de frutas ácidas, la maduración de las frutas, los azúcares presentes en las frutas, la presión de vapor, el poder rotatorio y los cambios de entalpía y volumen de mezclas líquidas, la composición del ámbar y del maná, la síntesis y el análisis del ácido cianhídrico, etc.

ABSTRACT

Jean-Louis Henri Buignet (1815-1876) was a French pharmacist who studied the saccharification of acid fruits, the ripening of fruits, the sugars present in fruits, the vapor pressure, rotatory power, and changes of enthalpy and volume in liquid mixtures, the composition of amber and manna, the synthesis and analysis of hydrogen cyanide, etc.

Life and career¹⁻²



Fig. 1. Jean-Louis Henri Buignet (1815-1876)

Jean-Louis Henri Buignet (Fig. 1) was born in 1815 in Chelles (Seine-et-Marne), to a family of farmers. He received his primary education in Chelles and then enrolled in the Lycée Henri IV in Paris. After graduation he decided to study pharmacy and for this purpose he served as apprentice in the pharmacy of Boutron in Paris (1832-1835). He then matriculated in the Faculté des Sciences Physiques and in the École Supérieure de Pharmacie where he won five prizes between 1838 and 1839. In 1840, after graduating as pharmacist of 1st. class, he won by competition an internship in the Parisian Hospitals and in the following year he began to manage the pharmacy founded by Planche. (1841-1858). In 1842 he won by competition a position of agrégé at the École Supérieure de Pharmacie de Paris, working for Eugène Souberain (1797-1859), a position he kept for 5 years. He then entered the Collège de France to work under Antoine-Jérôme Balard (1802-1876) and Marcellin Berthelot (1827-1907) and in 1860 he was awarded his degree docteur es-sciences physiques from the Faculté des Sciences de Paris, after defending successfully a thesis about the sweet matters contained in acid fruits, their origin, nature and transformations.^{3,4} In this work he added new facts about the ripening of fruits, the influence of acids and ferments, grape sugar (dextrose) and glucose, and the ratio

between these two sugars. In 1861 he was promoted to adjunct professor of physics and in 1866 to full professor replacing Edmond Robiquet (1822-1860).

Henri Buignet passed away on May 9, 1876 after suffering from acute pneumonia. A year later, his widow Hally Dabot Buignet instituted at the Académie de Médecine an annual prize of 1,500 francs to the author of the best work about the application of physics and chemistry in medical sciences.

In addition to his academic and research activities Buignet was also active in several professional, public, and social areas. He was resident member of the Société de Pharmacie de Paris, its secretary in 1846, president in 1855, and general secretary between 1855 and 1876. In 1850 he joined the editorial board of the *Journal de Pharmacie et de Chimie* and afterwards he directed it for 12 years; he was also one of the collaborators of the *Nouveau Dictionnaire de Médecine et de Chirurgie Pratiques* (1864). He was a member of the Commission des Logements Insalubres (1860), of the Commission de Rédaction du Codex (1862), and of the Conseil d'Hygiène et de Salubrité of the department of the Seine (1871). In 1866 he was appointed Chevalier of the Légion d'Honneur and in 1868 he was elected member of the Académie de Médecine (Pharmacy section).

Scientific contribution

Buignet wrote over 30 paper, books, and booklets⁵⁻¹³ in the areas of analytical, inorganic, mineral, and organic chemistry, physics, wine chemistry, etc. As customary for all candidates to the Conseil d'Hygiène et de Salubrité, he published a booklet describing his researches and achievements.¹⁴

In addition to the research work detailed below Buignet also studied nitroprussic acid and nitroprussiates;¹⁵ the dosage of CO₂ in mineral waters;⁵ arsenious acid and the Fowler liquid;¹⁶ the use of the displacement method for preparing alcoholic tinctures;¹⁷ the action of potassium permanganate on sulfur dioxide;¹⁸ the reduction of ferric salts;¹⁹ the purification of arseniferous sulfuric acid;²⁰ the vapor pressure of petroleum;²¹ the plastering of wines;^{12,23} digitalin²⁴, etc.

One of his most important books was devoted to the physical techniques employed in medicine and pharmacy, for example, density of solids, liquids and its vapors, barometers, thermometers, fusion and boiling temperatures, refrigeration mixtures, ebullioscopy, calorimetry, saccharimetry, etc.¹⁰

Vegetable and vegetable principles

Strawberries

In 1859 Buignet examined several varieties of strawberry (*Fragaria* genre) in order to determine the amount of water, the nature and proportion of free acid, sugars, fatty matter, nitrogenous substance, and several different principles such as pectin, odorous components, coloring matter, and mineral components.⁶ His results indicated that the acid present in free form in the fruit was malic acid, in a proportion of 0.5 to 1.0%, depending on the species. The nature of the sugars was examined by fermentation, using the Fehling liquor, and optical means (rotatory power). His results indicated that the sugar matter was a mixture of sugar cane, grape sugar (dextrose) and levo-glucose in varying proportions, all in an average content of 6%. The cane-sugar was contained in cells distinct from those which contained the malic acid, and appeared to be the sugar first formed in the fruit, and to be more or less converted into the other kinds of sugar during the osmotic mixture of the several liquids contained in the cells. The percentage content of all the components was reported in two tables, one for 100 g of strawberries deprived of the calices, and another for 100 g of the same fruit dried at 100 °C.⁶

Camphor of yellow amber

According to Marcellin Berthelot (1827-1907) and Buignet, several researchers had reported the presence of camphor in yellow amber; some had isolated it treating the amber with nitric acid, others with potassium hydroxide. No exhaustive analysis had been made, probably because of its low amount; it was not known if this camphor was present as such or combined with other substances, or it corresponded to the product of its total destruction. In general, it was assumed to be identical with ordinary camphor.^{25,26}

Berthelot and Buignet decided to study this camphor in detail for its possible contribution to the subject of isomerism. Many substances were already known having the same appearance as camphors, but differing in their composition or physical properties. All of them were attached through their formula to the hydrocarbon C₂₀H₁₆, whose multiple isomeric states constituted most of the hydrocarbon essences. The hydrocarbon itself could appear as a solid, as its hydrochloride C₂₀H₁₆HCl, as camphor of Borneo (borneol), which differed from common camphor by the elements of water C₂₀H₁₆,H₂O₂ (at that time water was represented by OH); as the camphor of the Laurels, differing by the amount of oxygen, C₂₀H₁₆O₂, etc.^{25,26}

Berthelot and Buignet separated the camphor by steam distillation, at a moderate temperature, of a mixture composed of 1000 g of amber, 250 g of KOH and 2500 g of water. The entrained camphor, which condensed as a thin layer lighter than water, was separated by filtration, dried between two layers of paper, and purified by sublimation. This method allowed preparing about 3 g of very pure camphor per 1000 g of amber, having physical properties quite similar to those of ordinary camphor, but differing by its special odor, very penetrant and persistent. According to Berthelot and Buignet the camphor of amber was a crystalline solid, which upon heating melted and then boiled yielding vapors that condensed as a crystalline sublimate when cooled to room temperature. An elemental analysis

indicated that it contained, by weight, 77.5% carbon, 11.7% hydrogen, and 10.8% oxygen, corresponding exactly to the composition of camphor of Borneo, and to the formula $C_{20}H_{18}O_2$, that is, to camphol (today borneol, $C_{10}H_{18}O$) or campholic alcohol. Anyhow, the camphol of amber and borneol were not identical; they were isomeric, as shown by their different rotatory power, $+4.5^\circ$ and $+33.4^\circ$, respectively. The latter property allowed differentiating camphor of amber from artificial camphol and the camphor of *Rubiaceae*, having rotatory power $+44.9^\circ$ and -33.4° , respectively. The camphol of amber was an alcohol, as shown by its formation of the alkyl chloride $C_{20}H_{17}Cl$ and stearic ester $C_{36}H_{32}O_4$.^{25,26}

According to Berthelot and Buignet borneol was present in amber as an ester, because KOH liberated it without alteration and nitric acid oxidized it and changed it into a new substance, probably isomeric with ordinary camphor.^{25,26}

Manna in tears

Manna in tears is a sweet spontaneous exudation from the ash tree *Fraxinus ornus*, which grows in the Mediterranean shores. In a paper on the subject, Buignet wrote that the main two components of this manna were mannitol and sugar.⁹ Mannitol had been clearly identified, it constituted more than half of the material and it was crystallizable and extractable in a high degree of purity. Sugar was known to be present, although it had not been separated; its aqueous solutions fermented in contact with beer yeast, it reduced Fehling's liquor and deviated the plane of polarized light. Mannitol did not show any of these three properties. At some time Buignet had examined the aqueous solution and found that it deviated the plane of polarized light with an intensity similar to an equivalent solution of glucose, which to some could indicate that the sample had been adulterated with glucose.⁹

Buignet decided to carry a more detailed analysis of this type of manna and for this purpose he selected a sample originating from Palermo, which was found to contain 52% of mannitol. He subjected the sample to three tests: (a) fermentation, to determine the amount of sugar, (b) optical examination, and (c) reaction with the Fehling reagent.⁹

He first treated 10 cm³ of aqueous solutions containing 2 g of beer yeast, at 25 °C, and carefully measured the amount of gas released (55.90 cm³ of pure CO₂), which corresponded to 0.223 g of dry glucose (11.15% of the sample). The rotary power of a solution of manna containing 1 g per cm³ of solution was $+17.12^\circ$ (yellow light, 3 cm), which against pure manna gave $[a]_D = +28^\circ 40'$ and $+28^\circ 40' \times (100/11.5) = 257^\circ 6'$ for the pure sugar present. After fermentation these values decreased to $16^\circ 27'$ and $[a]_D = +27^\circ 25'$, respectively. These results indicated that on the one hand the sugar substance contained in manna exerted a very weak effect on the plane of polarized because its disappearance (by fermentation) changed very little the initial optical properties, and on the other hand, manna had to contain a second powerful dextrorotatory substance. The last hypothesis was tested using the known facts that dextrorotatory sugars became levorotatory under the action of acids, and that all non-crystallizable sugars of formula $C_{12}H_{22}O_{11}$ (e.g. glucose) reduced Fehling's reagent. The results of these tests indicated that 100 g of manna in tears contained 11.30 g of fermentable sugar, of which 4.25 were non-reducing sugar and 7.05 g of reducing sugar. The non-reducing sugar was cane sugar (glucose) and the reducing one, inverted sugar (fructose).⁹

A material balance indicated that the total weight of mannitol, sugar, and water was less than the weight of manna tested, indicating the presence of a large amount of a foreign substance. This substance was found to be dextrin, which after much experimenting was found to be easily isolated by treating crushed manna with alcohol of 70^o, separating the liquid by filtration, concentrating by evaporation, and adding alcohol of 90^o. This resulted in the formation of two liquid phases, the upper one containing the sugars and the lower one the dextrin. The lower phase was separated, washed several times with alcohol of 90^o, and then evaporated to dryness. The resulting material corresponded to about 20% of the original weight of manna. The solid residue presented all the properties of dextrin, for example, it was soluble in water and in diluted alcohol, its rotatory power was $+182^\circ 45'$, did ferment only after a long treatment with acids, was not acted by iodine, nitric acid converted it into oxalic acid, etc.⁹

Buignet summarized his results as follows: (a) Flake manna in its natural state possessed a very energetic dextrorotatory power, which did not depend on saccharine matter it contained because it remained the same after the destruction of all the sugar by fermentation; (b) the rotatory power was due to dextrin, which formed one of the principal elements of its composition; (c) the saccharine matter (besides the mannitol) consisted of a mixture of cane sugar and non-crystallizable sugar. These two sugars were found united in such proportion that they mutually neutralized their opposite optical properties; (d) The different species of manna found in commerce all contained sugar and dextrin in the constant ratio of two equivalents of dextrin per equivalent of sugar; and (e) the mixture of sugar and dextrin in manna resembled the ordinary product of the saccharification of starch, hence was probable that it was derived from starch by a natural process, simulating that used in the laboratory by diastase and gentle heating.⁹

The sweet matter contained in acid fruits

As mentioned before, Buignet's doctoral work was related to the nature, origin, and transformations of the sweet matter contained in acid fruits.^{3,4} According to Buignet, there was no question that constituted the most important component present in the soluble part of acid fruits; it was very abundant on the pulp and in the parenchyma of variable consistency that formed the tissue. Leaving apart the water, sugar constituted more than half of the solid materials present in the fruit. It was accepted that this sugar had the same flavor as sugar cane and although it could ferment under the appropriate conditions, it did not have the same characteristics and properties, particularly the

crystalline ones. Part of it was crystallizable, while the rest remained liquid. These two sugars had become identified as sugar cane, appearing as transparent crystals, and glucose, hardly crystallizable as crystals having a less fresh flavor than sugar cane. Several different glucoses had been identified, for example, one being dextrorotatory and another levorotatory.^{3,4}

Buignet indicated that his thesis was intent in identifying, as exactly as possible, the nature of the sugar present in most acid fruits, for example, grape, red currant, cherry, strawberry, raspberry, prune, pear, apricot, peach, fig, etc. The thesis was divided in three parts; (a) nature and proportion of the sugars present in 100 g of fruit in a ripe state; (b) isolation of these sugars; (c) their origin and changes they go through under the influence of the substances that accompany them in the fruit. The answer to the first question was found through three different experimental procedures: fermentation, action of the Fehling liquor, and optical properties. A table was provided describing the percentage of sugar cane and inverted sugar (glucose) present in the each of the acid fruits listed above. An interesting result was that the sugar contained in cherries, red currants, raisins, and figs was 100% inverted sugar (glucose and dextrose).

After a long series of experiments Buignet concluded as follows: (a) The sugar formed originally in acid fruits was cane sugar, $C_{12}H_{22}O_{11}$, having the same properties and rotatory power as that obtained from the cane or beetroot; (b) during the maturation of fruits this sugar was gradually converted into inverted sugar, $C_6H_{12}O_6$, having the same properties and rotatory power as that obtained by the action of acids on cane sugar. The degree of conversion depended on the nature of the fruit; the final product could be pure and simple inverted sugar or a mixture in various proportions, of cane sugar and inverted sugar; (c) the inversion of cane sugar was no caused by the acidity of the fruits; the experimental evidence showed that organic acids, by reason of their relative proportion, their diluted state, and the low temperature at which they acted, had little power to change the cane sugar with which they were associated; (d) the differences in the relative proportions of the two sugars seemed to be due to a nitrogenized matter, acting as a glucose ferment (enzyme), analogous to that extracted by Berthelot from brewers' yeast; (e) the relative influence of the acid and ferment was exemplified by two parallel experiments made on the juice of the same fruit, one in which the ferment was precipitated by alcohol; the other in which the acid was neutralized by calcium carbonate. In the first case, the sugar remained unchanged for a very long time, while in the second, on the contrary, it was completely transformed, even in twenty-four hours; (f) the very close affinity between cane and inverted sugar explained why they were separable with extreme difficulty. Thus, cane sugar lost its crystallizing property when associated with even a very small proportion of inverted sugar, and lead oxide, known to act so differently on the two sugars separately, exercised the same action on them when they were mixed together; (g) the best method for separating cane sugar from the fruits was the one described by Eugène Melchior Péligot (1811-1890) for the analysis of molasses (forming a calcium saccharate, separating it by boiling, and decomposing it by a current of CO_2); (h) the abundance of starch in the vegetable kingdom led to the supposition that this substance was the true source of the sweet matter of fruits: on the one hand, it was impossible to discover its presence in green fruits, either by the microscope or by iodized water. On the other hand, the sugar produced from by means of transformations was dextrorotatory glucose, $+53^\circ$; while Buignet's experiments showed that the sugar found in acid fruits was cane sugar, wholly or partially inverted; (i) green fruits contained a peculiar principle, capable of absorbing iodine with even more energy than starch does, and of forming with it a completely colorless compound. This principle was of an astringent nature and appeared to be allied to tannin in many of its properties. The proportion of this tannin diminished in fruits in the same ratio that the proportion of sugar increased; (j) the sugar extracted from the tannin of the gallnut by the action of sulfuric acid, was a right-handed glucose, having exactly the same rotatory power as starch glucose. The sugar furnished by the tannin of green fruits, under the same conditions, was also a right-handed glucose, identical with sugar of starch; and (k) green bananas contained a large amount of starch the two principles diminished progressively and simultaneously until they disappeared in the ripe fruit.^{3,4}

Ripening of fruits

According to Berthelot and Buignet "the changes, which fruits underwent during ripening constituted the most remarkable phenomenon of vegetable physiology. A common sight was to see how the fruit lost little by little its astringent and acid flavor and acquired the sweet and agreeable taste which rendered fit for food. This change was particularly worth of attention in the case of a fruit detached from the plant on which it had developed. In this case, the fruit constituted a complete medium, which derived nothing from the plant, which formed it. All the ulterior changes it underwent resulted from the reciprocal metamorphoses of its own materials".²⁷

Berthelot and Buignet chose this situation to make a detailed investigation of the process, which they carried during the two-year period between the winters of 1858 and 1859. As subject of their study they selected the common orange because it showed very distinctly the different stages of the ripening phenomenon and allowed a very simple analysis of its juice. This juice contained mainly citric acid, fermentable sugars, and nitrogenous principles, and practically no gelatinous substances. For their experiments they selected a number of green oranges susceptible of the ripening process, divided them in two groups according to their actual ripening state, and stored them for a few weeks in a dry place, maintained at constant temperature. At the beginning and end of the process they carried out the following determinations: (1) weight of each orange; (2) separation into four parts (rind, seeds, juice, and pulp) and determination of the weight, water content and residue at $100^\circ C$; (b) determination of the amount of nitrogenous and

mineral matter present in the rind, pulp and seeds; and (c) determination of the amount of water, citric acid, inverted sugar (dextrose), cane sugar (glucose), and nitrogenous and mineral matter present in the juice.²⁷

Berthelot and Buignet concluded as follows: (1) the orange, before or at maturity, contains simultaneously cane and inverted sugar; (2) the relative amount of these two sugars change during ripening; at the beginning of the process inverted sugar predominates and at the end cane sugar preponderates; (3) the weight of inverted sugar changes little during the process while that of cane sugar increases; the increase is the same when compared to the total weight of the juice or to the weight of the fixed matter contained in the juice; (4) the juice becomes sweeter during ripening; (5) the formation of cane sugar is striking because it takes place in an acid medium; (6) citric acid does not appear to act in inverting the sugar already formed and does not oppose the increase of cane sugar.²⁷

Applications of physics to chemistry problems

In 1861 Buignet published a series of papers describing the applications of physics to the solution of certain chemical and pharmaceutical problems. The problems in question were (a) the vapor pressure of mixtures, (b) the density of water in crystalline solids, and (c) the rotatory power and refractive index of a large number of substances employed in medicine.⁸ These publications are interesting because they describe the state of the art of some of the experimental techniques available in the second half of the nineteenth century.

Vapor pressure of mixtures

Buignet wrote that Victor Regnault (1810-1878) had reported that the vapor pressure of a mixture of two mutually insoluble volatile liquids was equal to the sum of the vapor pressures they exerted individually at the same temperature (e.g. water and carbon disulfide, and water and benzene). If the two substances were soluble in all proportions the vapor pressure of the mixture was usually less than that of the most volatile component. The difference in vapor pressure increased as the concentration of the less volatile liquid increased (e.g. ether and carbon disulfide, alcohol and benzene).^{8,28} Buignet believed that the latter difference was an expression of the affinity of the two components. Thus, considering mixtures of water and alcohol and ether and alcohol, we could ask which of the two liquids, water or ether, had a larger affinity for alcohol. This question seemed to have been solved by using the information available for mixtures of ether and water: Common practice for eliminating the alcohol present in ether was to wash it with water, a practice that was based on the affinity between water and alcohol; but it was enough to increase the relative concentration of ether to obtain the *opposite* result. A better explanation could be obtained by comparing the vapor pressure exerted at the same temperature by mixtures of water and alcohol and alcohol and ether, having the same weight composition. Assuming that one of the mixtures exerted a vapor pressure F , then, if the two components kept their vapor pressure in the pure state, the affinity of the solution would be null, but if the real vapor pressure was f , then the affinity of the solution would be measured by the ratio $(F - f)/F$. According to Buignet, the latter formula could also be used to describe the change in boiling point of a liquid caused by the presence of the dissolved substance. As an example, Buignet mentioned that for mixtures of equal weights of alcohol and water or alcohol and ether at 15 °C, the corresponding values were $30.74/56.72 = 0.5419$ and $151.43/388.81 = 0.3995$. These two figures represented the decrease in vapor pressure of the mixture caused by the relative affinity between their components at 15 °C, or that this temperature the relative affinities of water and ether with alcohol were in the ratio 54:39. Although this relative value would change with temperature and the relative concentration of the two components, it was possible to compare the affinities using as standard a given composition.⁸

Buignet wrote that a very interesting application of his formula was to aqueous solutions of hydrogen cyanide because of their use in important medicines, such as cyanic syrup (prussic syrup) and the waters of cherry laurel and bitter almonds (all of them used for pectoral potions). His experiments indicated that a medicinal solution of HCN containing one part of acid in 13 of water exerted a vapor pressure of 171.66 mmHg at 15 °C, corresponding to an affinity of $(508.57 - 171.66)/508.57 = 0.6624$ (the denominator represents the sum of the individual vapor pressures at 15 °C). If the concentration was decreased to one part of acid per 42 parts of water, or one part of acid per 1000 of water, the affinity increased to 0.8706 and 0.9744, respectively. The last result indicated that 1000 parts of water were enough to have HCN lose almost all the considerable vapor pressure it had at 15 °C. Similar results were obtained with the waters of cherry laurel and bitter almonds.⁸

Density of water in crystallized hydrated salts

In 1845 Regnault proposed a modified form of the apparatus designed by H. Say for determining the volume of a body by measuring the volume of air it displaced. According to Buignet, Regnault's apparatus was particularly useful for measuring the density of bodies, which altered easily in the presence of water or of fibrous materials that retained a large amount of air in their pores. Not only that, the apparatus allowed the successive determination, and on the same sample, of the density of a crystallized hydrated salt and in its anhydrous state.^{8,29}

Buignet's results indicated that when a hydrated salt was abandoned to it in air, it released part or all of its water of crystallization, and assumed, at the moment of efflorescence, the volume and the density it had *before* the combination. The ratio between the weight loss and the change in volume did not represent the density of the water in the crystallized salt; it described only a lower limit of the value of this property. Thus, for example, the results indicated that in hydrated sodium sulfate, the density of water could not be less than 1.101, while in magnesium

sulfate it had to be at least 1.238. The expansion that took place during the crystallization of a hydrated salt could be observed directly by measuring the volume occupied by its supersaturated solution before and after crystallization. This increase in volume did not discard the possibility of a chemical reaction between the salt and water. The experimental results indicated that sodium sulfate had a larger affinity for water than potassium nitrate, contrary to the prevailing idea. This was easily proven by dissolving the same weight of each salt in the same amount of water: the decrease in the boiling point of the solution of sodium sulfate and the volume contraction were larger than those of the solution of potassium nitrate.⁸

Rotatory power

Buignet reported the value of the rotatory power for 23 volatile oils of medical use; the results indicated that all of those belonging to the Auranti and the Apiaceae, were dextrorotatory, while those belonging to the Lamiaceae and Coniferae were levorotatory, indicating that there existed a certain relation between the rotatory power of the essence and the botanical characters of the plants that produced them. He also measured this property for 16 non-volatile oils; thirteen of them (e.g. bitter almonds, nuts, olives, hazel nut, poppies, beech, black peppers, fish, etc.) had no rotatory power, while fish liver oils were levorotatory, and castor oil, dextrorotatory.

Buignet also reported the rotatory power of several alkaloids: atropine (-), aconitine (-), emetine (none), veratrine (none), and cicutine (+).⁸

Refractive index

Buignet reported the value of the refractive index at 12 °C of 23 volatile oils (e.g. cinnamon, bitter almonds, sassafras, juniper, thyme, lemon, orange, clove, turpentine, lavender, and chamomile) and 13 non-volatile ones (e.g. copahu, shark liver, fish liver, castor, rape, sweet almonds, nuts, and olives). He stated that this parameter could be used to identify possibly falsifications of the same.⁸

In 1876 Buignet published a book giving a detailed explanation of the many standard physical operations used in pharmacy and medicine.¹⁰

Hydrogen cyanide and cyanides

Analysis of HCN

Buignet reported that the reaction between solutions containing one equivalent of cupric sulfate and one equivalent of potassium cyanide resulted in the formation of a yellow green precipitate of cupric cyanide and a colorless or slightly colored liquid containing potassium sulfate. This reaction was not so simple as it looked because a careful examination of the precipitate showed the presence of a small amount of potassium cyanide that did not disappear after many water washes. Analysis of the liquid phase showed the presence of a small quantity of cupric cyanide forming a non-decomposable combination with traces of potassium cyanide. These results showed the strong affinity between the two cyanides.⁷

Further study of this reaction showed that if the equivalent of cupric sulfate was added drop-wise to the equivalent of potassium cyanide the precipitate formed at the point of contact redissolved on agitation, without the solution showing any change in color. This phenomenon was clearly the result of a combination between the cupric cyanide formed on the spot and the large excess of potassium cyanide present at the site. The experiment showed that this process repeated itself up to addition of about 50% of the solution of cupric sulfate; afterwards, the precipitate ceased to disappear. These facts indicated that the first reaction took place between one equivalent of alkaline cyanide and one-half equivalent of cupric sulfate. Evaporation of the pertinent solution precipitates the double cyanide as white transparent rhombohedra crystals, non-hydrated and very soluble in water; its saturated solution boils at about 120 °C. The solution, which is colorless, did not change its color when treated with by NaOH, KOH and ammonia. The last fact indicated that the copper was completely masked in the double cyanide because aqueous solutions of cupric salts acquired a beautiful blue color (bleu celeste) when treated with ammonia. The latter solution became colorless upon addition of an excess of potassium cyanide. The same result was obtained by addition of HCN the acid became ammonium cyanide, which reacted as alkaline cyanide.⁷

The facts that the double salt of copper and ammonia is colorless while the sulfate of copper and ammonia possessed a deep blue color led Buignet to suggest the following volumetric procedure for the determination of HCN in its solutions: (a) the liquid containing HCN is first oversaturated with ammonia; (b) a solution of cupric sulfate of known concentration is titrated until the blue color becomes permanent; (c) at this point the cupric sulfate has been just enough for the reaction with ammonium cyanide, and thus indicates twice an equivalent quantity of HCN.⁷

Buignet recommended the use of a titrating solution containing 23.09 g of cupric sulfate to 1000 cm³ of water because each cubic centimeter of the test liquid used indicates one mg of free hydrocyanic acid.⁷

Preparation of HCN

In a first paper on the subject Bussy and Buignet wrote that although HCN was easy to prepare, it was very difficult to keep for a long time. The freshly prepared acid was limpid and colorless but after a short time it became turbid and colored. The reason for its decomposition was unknown although it occurred particularly under the action of sunlight. The purpose of this publication was to report the experimental results carried to determine the relative advantages of preparing HCN by the methods of Joseph-Louis Gay-Lussac (1778-1850) and Giuseppe Pessina.³⁰

Gay-Lussac's procedure was very simple and based on the reaction between mercurous cyanide and HCl at a moderate temperature; its theoretical yield was 21.4 g of anhydrous HCN per 100 g of mercurous cyanide.³¹ Pessina's procedure was also very simple and based on the decomposition of potassium ferrocyanide by diluted sulfuric acid.³² The French Codex of 1837 had adopted Gay-Lussac's procedure but afterwards the Pessina one had become more popular because it provided a higher yield (in theory, 21.9 of anhydrous HCN per 100 g of mercurous cyanide) and the resulting medicinal acid was easier to keep.

Bussy and Buignet conducted a series of experiments to verify the validity of these assumptions. The acid was prepared by reacting enough material to produce a theoretical yield of 10 g of dry liquid HCN; Gay-Lussac's method yielded 6.69 g and that of Pessina 8.75 g. These acids were diluted in enough distilled water to produce a 10% solution, then put inside identical tubes of the same kind of glass, and exposed to the direct light of the sun for an hour. Gay-Lussac's acid began to turn yellow in 5 minutes; at the end of the hour it was quite brown. Pessina's acid, on the other hand, remained colorless. The same experiment, conducted in the dark showed that the acid of Gay-Lussac quickly became turbid, while that of Pessina began to change at the end of a month, and after six months it became quite opaque. At the end of six month both liquids had become completely black; chemical analysis of their content showed that there was then no traces either of HCN or ammonium cyanide.³⁰

In a following paper Bussy and Buignet explained why Gay-Lussac's process did not yield the stoichiometric amount of HCN. For example, reacting 126 g of mercuric cyanide and 109.5 g of HCl containing 33% of real acid (the quantities which corresponded to an equivalent of each of the two substances) yielded only about 18 g of acid, that is, only two-thirds of the theoretical quantity (27 g). The difference could not be explained by the loss of a small quantity of acid, which would have escaped condensation and not by the production of a trace of ammonium formiate. The missing acid remained entirely in the residue, from where it could be extracted by prolonged distillation. According to Bussy and Buignet the affinity of the mercuric chloride (corrosive sublimate) present in the residue rendered it fixed at the temperature ordinarily employed. To overcome this difficulty, they had the brilliant idea of adding to the other reagents an equivalent of ammonium chloride, which was known to form with the corrosive sublimate the stable combination known as Sal alembroth. They assumed that that this combination would neutralize the influence of the corrosive sublimate on HCN allowing it to be disengaged at a much lower temperature, taking with only a very small quantity of water. The result fully confirmed their supposition and by this means they achieved 95% of the theoretical yield. This significant result led them to extend their study to include the influence of HCN on water and other compounds.³³

Their findings indicated that HCN and water were miscible in all proportions, without chemical combination. The strong affinity between the two compounds was reflected in the significant reduction in the vapor pressure of the solution. For example a mixture of equal weights of the acid and water exerted at 13.35 °C a vapor pressure of 354.3 mmHg, against the total vapor pressure of the two pure components at the same temperature (472.0 and 11.4 mmHg for dry HCN and water, respectively). In addition, the mixing process was endothermic for all compositions; the maximum lowering of the temperature (9.75 °C) occurred when mixing 6.00 g of HCN (one equivalent) with 6.00 g of water (3 equivalents). The mixing process was also accompanied by a contraction in the volume, 6.23% of the theoretical volume (zero excess volume). Other results indicated that anhydrous HCN and its aqueous solutions exhibited zero rotatory power and that the maximum increase of the theoretical index of refraction (weighed average) occurred again when mixing 1 equivalent of HCN with 3 of water.³³

The last part of the paper reported the action of HCN upon mercuric chloride, mercurous chloride, and a large number of other chlorides (for example, magnesium, strontium, manganese, etc.), sulfates (for example, manganese, magnesium, zinc, etc.), nitrates (for example, sodium, potassium, magnesium, ammonium, etc.), and other compounds such a citric acid, tartaric acid, and sugar.³³

Heat and volume of mixing

Bussy and Buignet wrote that scientists had paid little attention to the thermal effects that accompanied the mixing of two liquids, although it was generally accepted that the process was exothermic and that the intensity of this effect was a result of the strength of the affinity of one liquid for the other. Bussy and Buignet believed that this interpretation was not justified by the available information, which seemed to prove that independently of the chemical affinity there was a general cause that seemed to modify the effects of affinity. This additional effect operated in the opposition direction of affinity and the final result was a consequence of the net effect of both factors.^{11,34} As an example of this argument they mentioned their previous finding that the simple mixing of the two liquids HCN and water, took place with an increase in temperature without any accompanying increase in volume to justify it. On the contrary, the maximum observed change in temperature (9.75 °C) was accompanied by a 6% contraction in volume. Bussy and Buignet also mentioned that Charles Cléophas Person (1801-1884) had reported that the dissolution in water of salts such as potassium nitrate and sodium chloride was accompanied by an exothermic or endothermic effect, depending on the concentration. Person also suggested that the cold effect produced during the dissolution of a salt was not due to the simple passage of a solid state to the liquid one (fusion) but mostly to the subdivision of the salt molecules and their dilution in a larger amount of water; which he named *latent heat of dilution*.^{33,35}

Bussy and Buignet decided to make a more detailed study of the problem and for this purpose they selected volatile liquids that could be easily obtained in a high degree of purity and were completely soluble one in the other, without producing a too energetic heat effect. These liquids were water, ethanol, ether, acetic acid, chloroform, carbon disulfide, and turpentine. The experimental apparatus consisted of a separating funnel mounted on top of a flask, and able to discharge into the bottom of the latter. The receiving flask was immersed in an insulating material. The vapor space of both flasks was connected through a rubber tube and two very sensitive thermometers measured the temperature of each liquid phase. The valve of the separating funnel was opened when all the apparatus had achieved the thermal equilibrium with the surroundings. A slight agitation permitted the complete dissolution of both liquids. The temperature change was noted for the different mixing proportions, particularly for the case of mixing equal *volumes* of both liquids. Bussy and Buignet also measured the change in volume that took place for every concentration tested.³³

Bussy and Buignet concluded as follows: (1) The mixing of two completely soluble liquids was always accompanied by a change in temperature, which could be positive or negative; (2) this effect was always the consequence of two simultaneous and opposing causes: one the *affinity* between heterogeneous molecules which produced heat, the other, *diffusion*, which consisted in the movement of homogeneous molecules, in order to be distributed through the mass, and which produced cold; (3) when the two liquids mixed had but a weak affinity for each other the effects of diffusion predominated and produced a fall of temperature; (4) the rise or fall of temperature did not entirely depend on the nature of the liquids; it varied for the same mixture according to the relative proportions of the components; (5) The influence of the relative proportions could completely alter the thermal effect, producing either heating or cooling. For example, mixing 5 equivalents of alcohol with 1 of chloroform resulted in an increase in temperature of 4.5 °C; while mixing 5 equivalents of chloroform with 1 of alcohol reduced the temperature by 2.6 °C; (6) the initial temperature of the liquids when mixed had a sensible effect on thermal result; the fall was more marked when the initial temperature was high; (7) the change in temperature was always accompanied by a change in volume; for example, an expansion as with alcohol and carbon disulfide, and contraction, as with alcohol and ether; and (8) there was no apparent relation between the changes of temperature and volume; some mixtures, which contracted produced heat, while others, which also contracted produced cold.^{11,34}

In a following work Bussy and Buignet decided to take a further look into the possible connection between the thermal and volume changes taking place when mixing two liquids completely miscible. For this purpose, they repeated their experiences, adding the measurements of the volumes of mixing, the specific heat of the pure components, and the specific heat of their mixtures. Basically, the experimental equipment consisted of two glass tubes of volume 80 cm³ joined at their bottom by a thinner tube, and enclosed in a water calorimeter. One liquid was added to each branch in the appropriate amount. The liquids were pressed one into another and the change in temperature recorded.³⁶

The results of these experiments indicated that (1) in all the cases examined, with one sole exception of chloroform + carbon disulfide, the specific heat of the mixture was larger than the mean heat capacity of the elements; (2) by a singular opposition, the liquids exhibiting the largest increase in heat capacity were the ones developing the most heat at the moment of their mixture, such as ether + chloroform, alcohol + water, and sulfuric acid + water. The only mixture showing a decrease of the specific heat was that of *chloroform + carbon disulfide*, which showed a decrease of temperature taking place at the moment of the formation; and (3) of the nine mixtures examined six produced a decrease and three a rise in temperature. The latter also showed an increase in specific heat and a considerable contraction of volume. Of the six showing an increase in temperature, five exhibited also an increase of specific heat. Three of the latter exhibited a slight increase in volume; the other two (alcohol + water and HCN + water), showed a considerable contraction. These two examples showed that independently of the heat loss due to change in volume and that which may result from the causes still unknown, which produce changes in specific heat, there still exists a cause that produces an absorption of heat equal or larger than the heat given out by the combination of the liquids.³⁶

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