

# Claude-Louis Berthollet

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Key words: phlogiston theory, oxygen, combustion, Lavoisier, chlorine, acids, prussic and tartaric acids, natron (sodium carbonate), silver fulminant, chemical nomenclature, chemical affinity.

**RESUMEN.** Claude-Louis Berthollet (1748-1822) fue el primer científico francés destacado que descartó la teoría del flogisto y aceptó la del oxígeno en la combustión. Demostró experimentalmente que los ácidos prúsico y sulfhídrico no contienen oxígeno probando así que la teoría de Lavoisier de la acidez basada en el oxígeno estaba equivocada. Sus descubrimientos sobre el cloro y sus propiedades blanqueadoras fueron decisivos en el avance de la revolución industrial química en general y la textil en particular.

**ABSTRACT.** Claude-Louis Berthollet (1748-1822) was the first prominent chemist to reject the phlogiston theory and accept the oxygen theory of combustion. His experiments showed that prussic acid and hydrogen sulfide did not contain oxygen thus disproving the generality of Lavoisier's oxygen theory of acidity. His discoveries about chlorine and its bleaching properties were a decisive step in advancing the chemical industrial revolution in general and the textile industry in particular.

## LIFE AND CAREER<sup>1-9</sup>

Claude-Louis Berthollet (Fig. 1) was born at Talloire in Savoy on December 9th, 1748. He was an Italian by birth and education<sup>1</sup> who came from a French family that had immigrated into Upper Savoy from the Protestant region of *Collonges-sous-Salève*, a small city located near *Genève* in the Pyrenees, during the previous century and had become members of the noblesse de robe. Berthollet's ancestors were Catholics and were probably running away from the French religious wars, a series of intermittent conflicts between Catholics and Huguenots (Protestants) between the middle of the 16th century until the Edict of Nantes (1598). Berthollet's grandfather lived at Annecy at the end of the seventeenth century. His son Louis (1708-1784) married Philiberte Donier and then settled at Talloire, where he was appointed bourgeois d'Annecy and then *secrétaire* and *châtelain de la commune de Talloires*. They had many children: Joseph, born in 1738; Antoine-Philibert, born in 1741; Joseph-Melchior, born 1742; Benoite-Marguerite, born 1743; Nicolas, born 1746, Claude-Louis, born on December 9, 1748; Jeanne-Aimée, born 1749; César, born 1752; and Michel-Menoit, born 1753. Only Claude-Louis and Jeanette-Aimé reached maturity.<sup>9</sup>

Berthollet began his studies at the *Collège d'Annecy*, founded in 1549 and that today carries his name (Lycée Berthollet). After graduation he transferred to the *Collège de Chambéry* and then to the *Collège des Provinces*, in Turin. According to Sadon and *Le Grand*<sup>8,9</sup> the school had been founded in 1729 by Victor Amédée II "pour maintenir la jeunesse dans les études de théologie, droit, médecine et chirurgie" (to keep the young in reli-



**Fig. 1.** Claude-Louis Berthollet (1748-1822).

gious, law, medical, and surgery studies). It granted scholarships to poor young men and did not award any degree in particular. According to Sadon<sup>9</sup> the students admitted were fed, lodged, and judged for their behavior and working habits. Religious assiduousness, good manners, and study dedication, were stimulated and the students were required to take the courses given at the university. Medical studies at the university included theoretical and practical courses, as well as hospital practice. The new students were required to take a complete course of philosophy, followed by one year of classes at the *École de Physique*; the third year was spent at the *Institutes de Médecine* and at the *École de Anatomie*. Afterwards they studied botany and did practical work at the hospitals. Normal length of studies was five years; which Berthollet finished in four (1768). The complete exercise of medicine was allowed only to doctors who took a two-year practical course at a hospital, a town, or

a city.<sup>6,9</sup> Berthollet completed this requisite at the University of Turin receiving his degree in 1770. After practicing for two years he realized he needed more education and went to Paris, where he studied chemistry under Augustin Roux (1726-1776), Pierre-Joseph Macquer (1718-1784), and Jean-Baptiste Bucquet (1746-1780), while continuing to study medicine. Since Berthollet had practically no money and no letters of introduction he requested the help of Théodore Tronchin (1709-1781), the well-known Swiss physician, a former student of Herman Boerhaave (1668-1738), an associate of the *Académie des Sciences*, propagator of the vaccination in France, and the chief personal physician to the regent, Louis Philippe (1725-1785), Duke of Orleans (the future Philippe Egalité). As a result of the meeting Tronchin obtained for him an appointment as physician-in-ordinary in the household of the duke, as private physician to Mme. Charlotte De Montesson (1737-1806) (who the Duke had married secretly on April 23th, 1773), and also permission to carry out research on the private laboratory installed by the regent and his son in the Palais Royal.<sup>7</sup> The Dukes of Orleans for several generations had actively encouraged and sponsored scientists, especially chemists. Here Berthollet repeated the experiments done by Antoine-Laurent Lavoisier (1743-1794), Joseph Priestley (1733-1804), and Carl Wilhelm Scheele (1742-1786), on the behavior of gases, and met Lavoisier, who had just begun his publications on oxygen and the drive to discard the theory of the phlogiston. Berthollet was especially interested by Scheele's discovery of muriatic acid and in the first stages of his career was a firm supporter of the phlogiston theory. Experiments with this acid led Berthollet to become one of the first important chemists to abandon the phlogiston theory and to accept the new system of oxygen completely.

Sadon<sup>9</sup> describes as follows the series of obstacles that Berthollet had to surmount to continue his medical training: Practicing medicine in France was not an easy endeavor. To exert public medicine, with reasonable success possibilities, it was necessary to obtain the title of docteur régent of the *Faculté de Médecine* de Paris, a demanding and expensive pursuit, requiring the French nationality and several administrative and academic stages. The process of becoming a French national was greatly simplified for Berthollet, thanks to his position in the Duke's court. He received it by letter expresse on February 25th, 1778. In this letter of naturalization, the King, considering that Berthollet had arrived in France at the end of 1770 in order to improve his knowledge, that he had worked for seven years, and that desired to establish himself in the kingdom, named him *sujet regnicole* (a royal subject). Accordingly, he was allowed to take residence in any place he desired and to acquire a property. In addition he was granted "*une dispense de tems d'étude*" that allowed him to register at the cours de license of the *Faculté de Médecine de Paris*. The series of exams to be taken extended over a period of two years during which the candidate had to defend four theses (called quodlibetal questions) on subjects of his choice (Note 1). He was not required to do a personal and original research work; only to show his aptitude of reasoning by way of syllogism.

By virtue of his position, Berthollet was allowed to practice without meeting the usual requirement of securing a medical degree at Paris; however, he preferred not to take advantage of this exemption and in 1779 he defended his first thesis, called *thèse cardinale*, titled *De Variorum Liqueurum Vinosorum Diaeteticis Proprietatibus*,<sup>10</sup> dealing with hygiene. This was followed by a thesis on the subject of physiology, *De Lacte Animalium Medicamentoso*,<sup>11</sup> where he tried to prove, without much success, the passage of mercury into the milk. His third thesis was in the field of surgery (*Num Bubones Critici in Febribus Malignis Incidendi?*<sup>12</sup>), and the last one, defended on February 17th, 1780, *De Aquarium Hepatisatarum Naturâ, Compositione Artificiali & Virtutibus*,<sup>13</sup> was on pathology. With this achievement he became licensed officially and qualified as a doctor of medicine at the University of Paris. In the same year Berthollet married Marie-Marguerite Baur (-1828), daughter of a teacher of music. Their only son, Amédée-Barthélemy, was born in October 1780.<sup>9</sup>

To achieve the title of doctor, the candidate had now to defend two more theses, quite different from the previous ones and consisting of oral interrogations. The last stage was the granting of the degree of *docteur regent*, which had two requirements: being accepted by his senior colleagues and presiding over a *thèse cardinale*. Berthollet fulfilled these requirements in 1781, and thus, after three years of hard work and heavy expenses, he was finally rewarded with an honorific title, carrying the heavy social prestige that constituted the passing mark to perform in the medical field.<sup>9</sup>

Parallel to his academic studies, Berthollet carried experimental work at the Duke's laboratories and compiled some notes on tartaric, sulfurous, and nitrous acids, which he published in 1776 as a 59-page book entitled *Observations Sur l'Air*.<sup>14</sup> In this publication, which was written entirely from the phlogiston standpoint, he stated: "*It is probable that all vegetable acids are equally due to fixed air (carbonic acid) differently combined*" and, "*L'air fixe se trouve abondamment dans les trois règnes & il entre pour beaucoup dans la composition des crops*" (fixed air is abundantly found in the three kingdoms, and it enters to a great extent into the composition of materials).<sup>7</sup>

Between 1778 and 1800 Berthollet presented 17 memoirs to the *Académie des Sciences*; these led to his election as a member on April 15th, 1780, on the death of Bucquet. The other candidates were Fourcroy, Denis-Bernard Quatremère-Disjonval (1754-1841) and Pierre-Clément Grignon (1723-1784). In 1784 Macquer passed away and Berthollet replaced him as inspector of dye works and director of *Manufacture Nationale des Gobelins*. An interesting item of this nomination is the fact that the letter of appointment from Charles Alexander Calonne's (1732-1802), France's comptroller general, stipulated very clearly that it precluded his continuing to practice medicine. He was allowed to be available for attending the duke and a few chronic patients, but nothing else. Otherwise, he was to spend all his time on experiments that would clarify the chemical arts, and on the preparation of his treatise of dyeing. His stipend was 6 000 livres, of which he diverted 600 to pay for the services of an assistant.<sup>9</sup>

#### Note 1.

*Quodlibetal questions differ from regular disputation in that they were asked by the student instead of the teacher. These questions might reflect contemporary controversies or might be designed to put the teacher on the spot.*

His most important contribution as director of the Gobelins was the finding of the bleaching properties of chlorine. This element was discovered by Scheele in 1774 but its singular properties became known in 1796 principally by the works of Berthollet. He showed that fixed alkalis aided the bleaching action, which he attributed to the oxygen, which he supposed was contained in the gas. The alkaline solutions were easier to handle than the gas or its water solutions. Berthollet showed his results to James Watt (1736-1819), who immediately realized the commercial importance of the discovery and brought it into practice.<sup>1</sup>

Berthollet subsequently collaborated with Lavoisier, Antoine-François Fourcroy (1750-1809), and Louis-Bernard Guyton de Morveau (1737-1816) in their publication of *Méthode de Nomenclature Chimique*,<sup>15</sup> incorporating the principles of the new chemistry of Lavoisier. In 1789 he published two main works, one summarizing his work on the structure and preparation of steel<sup>16-20</sup> and the other summarizing his findings in the art of dyeing.<sup>21-23</sup> The second edition of the latter, greatly improved and enlarged, was published in 1814, in two volumes, and soon became a standard manual, containing the state of the art of dyeing as well as the practical realization of the same. This important piece of work was written in collaboration with his son Amédée-Barthélemy.<sup>1</sup>

Napoleon Bonaparte (1769-1821) showed a deep admiration and affection for Berthollet; in 1796 he appointed him and Gaspar Monge (1746-1818) to accompany the commission that was to bring back the great works of Italian art to France. Two years later, Berthollet and Monge were selected by Napoleon to accompany the expedition to Egypt and to recruit other scientists for the same campaign. In Egypt Berthollet founded the *Institut d'Égypte* at Cairo (modeled on that of Paris) and accompanied various exploratory expeditions including one to the region of the natron lakes.<sup>6</sup> It was at this time that he began his great work *Research on Affinities*.<sup>4,24,25</sup>

Berthollet received many honors from Napoleon. Upon their return to France, in 1799, he and Monge were both honored by the First Consul with the rank of members of the conservative senate. The senate was the highest French institution within the hierarchy of governmental assemblies and Bonaparte wanted its members to be the highest dignitaries of France, immediately after the three Consuls.<sup>9</sup> In 1804 Berthollet was elected Vice-President of the senate and in the same year he was made *Grand Officier de la Légion d'Honneur*. He was also awarded the *Grand Croix de l'Ordre de la Réunion*, appointed Chevalier of the *Couronne de Fer* (1813), and decorated with the *Cordon de Sainte-Michele*. He was made titular of the rich Senatory of Montpellier, and Peer of France with the title of Count.<sup>7</sup> After the fall of Napoleon and the return of the monarchy in 1814, Louis XVII appointed Berthollet a member of the Chamber of Peers.<sup>1</sup>

A short time his return from Egypt, Berthollet, moved to *Arcueil a village near Paris*, where he pursued his chemical researches. In 1806 he established the *Société de Arcueil*, which met in his own house where he installed a cabinet of physical instruments for the use of its members, among them, his son Amédée-Barthélemy, Alexander von Humboldt (1769-1859), Louis-Jacques Thenard (1777-1857), August Pyrame de Candolle (1778-1841), Hippolyte Victor Collet-Descostils (1773-1815), and Étienne Louis Malus (1775-1812). The society met every fifteen days, and then new and interesting experiments were repeated, and memoirs upon different subjects

were read by the members. The latter were published in three volumes of their *Memoirs (Mémoires de Physique et de Chimie de la Société de l'Arcueil)*, the first of which appeared in 1807, the second in 1809 and the third in 1817.<sup>1</sup>

Before the appearance of the third volume a heavy tragedy affected Berthollet's life. In 1811 his only son Amédée, who had published several papers on scientific subjects in the *Mémoires d'Arcueil*, committed suicide in Marseilles in a very deliberate and distressing manner. Having closed up every vent in his room he lit a brazier of charcoal, and then wrote a careful account of his feelings as the fumes gradually overcame him, until he could no longer control his pen. From this grief Berthollet never recovered.<sup>8</sup> Some claim, that the reason for the suicide was the failure of his business manufacturing sodium carbonate according to a new method developed by his father, although according to Sadon<sup>9</sup> the enterprise was actually prosperous and the real reason was "...une légère maladie qui sans doute attaqué son cerveau" (a slight illness that undoubtedly affected his brain).

Berthollet's research activities regarding chlorine, its compounds, and their applications<sup>26-29</sup> not only had a decisive impact on his position regarding the phlogiston theory and Lavoisier views regarding the nature of acids, but also represent a critical stage in the industrial chemical revolution. Chlorine gas was discovered by Scheele when treating hydrogen chloride with manganese dioxide. According to the phlogiston theory, this reaction, an oxidation, corresponded to a loss of phlogiston. Lavoisier<sup>30</sup> believed that oxygen was a principle common to all acids and the cause of their acidity: "*This property of a combustible substance to be converted into and acid by the addition of oxygen...belongs to a great number of bodies...All acids are formed by the combustion of certain substances...it may be clearly seen that oxygen is an element common to which constitutes their acidity, and that they differ one from each other by the nature of the oxygenated or acidified substance. We must therefore, in every acid, carefully distinguish between the acidifiable base, which M. de Morveau calls the radical, and the acidifying principle or oxygen*".<sup>31</sup>

Berthollet, in a very detailed memoir about the combinations of chlorine,<sup>26</sup> confirmed this opinion. He dissolved the gas in alkaline solutions and obtained first the hypochlorite and then the chlorate. He observed that under the influence of light, aqueous solutions of chlorine liberated oxygen and transformed it into hydrogen chloride. His results led him to abandon the phlogiston theory and adopt the new ideas of Lavoisier that assumed that all acids were necessarily oxygenated compounds. Thus he considered chlorine to be a compound of marine acid (HCl) and oxygen rather than marine acid deprived of phlogiston, and renamed Scheele's dephlogisticated acid, oxygenated muriatic acid (today chlorine) a name that Richard Kirwan (1733-1812) shortened to oxymuriatic acid. Berthollet attributed the bleaching action to the oxygen present in the acid. This dephlogisticated marine acid was considered by all chemists until 1809, as a body composed of an acid and oxygen. The experimental work of Joseph-Louis Gay-Lussac (1778-1850), Thénard led André-Marie Ampère (1775-1831) and Humphry Davy (1778-1819) led to conclude that<sup>2</sup> "*l'acide muriatique oxygéné ne donnant d'oxygène que quand il se trouvait en contact avec des corps oxygénés, il était logique de considérer l'oxygène*

*devenu libre dans cette circonstance comme émané de ces corps oxygénés, plutôt que de l'acide marin oxygéné; qu'en conséquence il fallait considérer ce dernier comme un corps simple auquel on donna le nom de chlore; et cette conclusion était le retour à l'hypothèse de Scheele car on considérait l'acide marin déphlogistiqué comme un corps simple qui devenait acide marin en s'unissant à l'air inflammable*" (oxygenated muriatic acid releases oxygen only when it is in contact with oxygenated bodies; it is logic to assume that the oxygen has been liberated by the oxygenated bodies more than from the oxygenated marine acid; hence it is necessary to consider the latter as a simple body to which the name chlorine is given; this conclusion is a return to Scheele's hypothesis where dephlogisticated marine acid is considered as a simple body that becomes marine acid when united to inflammable air).<sup>2,26</sup>

Another fundamental contribution by Berthollet was proving that volatile alkali (ammonia) is composed only of nitrogen and hydrogen.<sup>32-34</sup> His first experiments were devoted to study the gases released when ammonium nitrate is decomposed by heat. During the distillation process large amounts of a gas were released that dissolved in water without acidifying it and a candle immersed in it burned like in pure air vital (oxygen). Berthollet assumed the gas to be a nitrous one, mixed with little oxygen. He concluded that the flammable gas of water (hydrogen) had to be a constituent of volatile alkali. When the hydroxide of volatile alkali (ammonium hydroxide) was poured over chlorine it produced effervescence because of the nitrogen released. In order to determine the components of ammonia Berthollet subjected it to an electrical discharge and found it to contain nitrogen and hydrogen in the mass ratio  $121/29 = 4.17$  by weight (Actually  $14/3 = 4.67$ . In making this calculation Berthollet assumed that the molecular masses of nitrogen and hydrogen were in the ratio 11 to 1).

The main results of Berthollet's researches and practical work at the Gobelins were summarized in his books *Description de Blanchissement des Toiles* (1795),<sup>21</sup> *Recherches sur les Lois de l'Affinité* (1801)<sup>24</sup> and *Essai de Statique Chimique*,<sup>25</sup> the latter published in 1803 in two volumes.<sup>1</sup>

Berthollet's personality and scientific success allowed him to survive and flourish under several different political regimes, and serving in many public activities. He was a member of the *Bureau de Consultation des Arts et Métiers*, established by the *Académie des Sciences* in 1791 as an advisor body for awarding recompense to the artists; member of the commission for the reform of the monetary system (1792), and in 1793 the Committee of Public Safety made him an important member of the scientific commission concerned with war production, particularly that of munitions. In 1794 he was appointed to the *Commission d'Agriculture et des Arts*, where Berthollet was in charge of rural economy, drying, training of domestic animals, veterinary schools, mechanical arts, etc.; and was made a professor at the *École Normale*. Berthollet was also charged, with his lifelong friends Monge and Guyton de Morveau, with the organization of the *École Polytechnique*, where for a time he taught animal chemistry. In 1795 he was one of the first members elected to the *Institut de France*, which replaced the suppressed Academy in 1793. A majorat was created for him in Westphalia, accompanied of a monetary award of 10 000 francs (1808). He also served as head of the *Académie de Médecine* and was appointed member of the Royal Society of London (1785), of the *Société*

*Hollandaise des Sciences de Haarlem* (1786), and of the *Académie des Sciences de Turin* (1787).<sup>9</sup>

His first paper on tartarous acid<sup>35</sup> was published in 1776 and about the same time he began reading papers at the *Académie*.<sup>36-45</sup> His first memoir was on *L'Acide Sulfureux* (sulfur dioxide),<sup>46</sup> and his second was on hydrogen sulfide.<sup>47</sup> These papers seem to have been reviewed by Lavoisier, and as a result, their publication was deferred until 1782 and 1798, respectively.<sup>8</sup> Between 1785 and 1786 Berthollet read two important memoirs to the *Faculté de Médecine*, the first about the comparison between the composition of animal and vegetable matter<sup>48</sup> and the second on the influence of light.<sup>9,49</sup>

In 1822 Berthollet had an attack of fever, which left behind it a number of boils. These developed into a large gangrenous ulcer, which probably was cancerous. He died on November 6th, 1822 and was buried in the cemetery at Arcueil.<sup>7</sup> Berthollet was survived by his wife, who had devoted her life to ensure the happiness and tranquility of her husband.<sup>1</sup>

## SCIENTIFIC CONTRIBUTION

The discovery of chlorine, its use in bleaching and the manufacture of bleaching powders, potassium chlorate, and their influence in the industrial chemical revolution, have been described in detail in other publications<sup>50,51</sup> and will not be discussed further.

### The composition of acids

Berthollet's first publication on the subject was a booklet called *Observations Sur l'Air*,<sup>14</sup> having a title which today may be misleading because the word air was then used loosely to designate the different gases that were disengaged during the decomposition of many substances. The memoir is divided into two parts. The first one is concerned basically with l'air fixe (fixed air, today CO<sub>2</sub>) that is released during the thermal decomposition (distillation) of many organic substances (vegetable or animal). Here Berthollet studied the decomposition of tartarous acid (an acid formed by the mixture of tartaric acid and other vegetable acids such as oxalic) and recognized that the gas released was composed mainly of fixed air but gave an erroneous quantitative analysis of the same. He concluded that it contained fixed air united with a flammable gas; he also attributed the acidity of vinegar to fixed air. He gave an interesting description regarding the nature of l'air inflammable (flammable gas, today hydrogen): "*Cet air inflammable n'est pas une espèce d'air particulière, un premier principe...c'est probablement de l'air simple saturé de phlogistique avec excès, mais jusqu'à ce qu'on ait une idée bien claire de sa composition, il faut le regarder comme une être simple, et comme l'on ignore s'il contient de l'eau il faut abandonner l'opinion des Chymistes qui regardaient l'eau comme cause de l'expansion du feu dans la flamme. J'en dis autant de l'air fixe qui paraît cependant plus composé et beaucoup plus éloigné de l'air simple que l'air inflammable*" (This flammable air is not a especial kind of air, a first principle...it probably is simple air saturated with an excess of phlogiston...it must be considered a simple being and since we do not know if it contains water, it is necessary to abandon the opinion of chemists that consider water as the cause of expansion of fire within the flame...I would say as much that fixed air seems more composed and farther from simple air than flammable air). Berthollet then discussed wine sprit (ethanol), which for him seemed to be "*composed of flammable air, of phlegm*

(water), and a little of fixed air that serves as the joint between the two other principles." He believed that on forming ether "alcohol loses part of its water and part of its fixed air so that ether must be flammable air joined largely to a little phlegm, a little fixed air, and another acid..." Regarding the formation of alcohol from fruit juices, Berthollet seemed to believe that during fermentation "air joined with phlogiston and transformed into flammable gas that combined immediately with fixed air to give alcohol".<sup>9</sup>

Berthollet closed the first part of his book stating that "fixed air is found abundantly in the three kingdoms and is part of the composition of many substances, it seems to be the only acid of vegetables, we know of nothing that can destroy it. It is a substance of the class of vitriolic acid, of nitric acid, etc... a mixte (mixture) having properties quite different from those of common air...and I believe that it should be called universal acid..."<sup>9</sup>

The second part of the publication discusses dephlogisticated acid (oxygen). Berthollet first studied nitric acid and its salts (nitres), whose decomposition released large amounts of oxygen, and interpreted the action of this acid on metals through the intervention of both air and phlogiston. He considered atmospheric air to be nitric acid united to an earth and the atmosphere as a nitric salt mixed with phlogiston. He then expressed clearly his ideas about phlogiston: "this pure air, this dephlogisticated air, discovered by Priestley and forming part of nitric acid and most of the metal calces, confirms the absence of phlogiston in metal calces".<sup>9</sup>

A following publication was devoted to tartarous acid.<sup>35</sup> In the introduction to this paper Berthollet wrote that chemists believed that tartar was an oily acid although Andreas Sigmund Marggraff (1709-1782) and Hilaire-Marin Rouelle (1718-1779) had proved that tartarous acid contained a vegetable alkali, a finding that was further confirmed by Roux.

Berthollet then indicated that the appropriate procedure for separating the acid from cream of tartar was treating the latter with nitric acid under gentle heating. The resulting mixture was left to cool and crystallize and the process repeated five to six times until no more nitrate was produced. He then treated the acid with mineral alkali and noted that the resulting salt had the same appearance as the one prepared with vegetable alkali; they could only be distinguished by the appearance of their crystals; the mineral one was shaped like very fine and brilliant needles. Berthollet dissolved the mineral tartar in boiling water and then reacted it with vegetable alkali obtaining a mixed mineral-vegetable salt that also crystallized in small needles, very soluble and decomposable even by the weakest acids. Calcareous earth (calcium oxide) reacted with tartaric acid forming a salt almost insoluble in cold or boiling water, burning like tartar and giving the same odor. Berthollet roasted it in a crucible and found that it decomposed very easily, leaving a dark gray cinder that produced much effervescence when treated with acids, though it lost its fixed air that was made during its combination with tartaric acid. This earth (the same as the alkalis of the cinder) when burned, recaptured the released fixed air, a phenomenon that did not occur with metallic chalks, "a result which seems to confirm Priestley's opinion that air when saturated with phlogiston releases the fixed air it contains. The latter now joins other substances for which it has more affinity".

Berthollet prepared and determined the properties of salts of tartaric acid salts with a number of substances,

among them, iron, copper, cobalt, tin, antimony, arsenic, mercury, zinc, lead oxide, and spirit of wine. He then studied the decomposition of different vegetable acids.<sup>40</sup> At his time it was believed that most vegetables contain acids already formed or substances that would become spontaneously acids under the appropriate circumstances. Although mineral acids resisted the action of time, the vegetable ones were prone to its influence and suffered a rather rapid destruction.

Lavoisier's ideas that all acids must contain oxygen did not always agree with his definition of a simple body. On the one hand, the experimental evidence pointed clearly that oxygen was present in carbonic, phosphoric, and sulfuric acids, on the other hand, substances like hydrogen chloride, hydrogen fluoride and boric acid had never been decomposed and should therefore have been classed as simple bodies. But Lavoisier had insisted that each was a compound of an unknown radical and oxygen.<sup>6</sup> Berthollet's first memoir presented to the *Académie* dealt with sulfurous acid (sulfur dioxide) and in it he ignored the theory of Lavoisier regarding acidity and treated instead sulfurous acid within the traditional phlogiston framework.<sup>6,52</sup> As discussed below, Berthollet's experiments led him to believe that he acid was composed of phlogiston and an unknown base (instead of sulfuric acid). This compound contained less air than sulfuric acid and less phlogiston than sulfur.<sup>6</sup>

Berthollet's determination of the constituents of prussic acid<sup>53,54</sup> was another strong argument against the oxygen theory. In these memoirs he compared his results with those of Scheele and Torbern Olof Bergman (1735-1784) and concluded that prussic acid, or the coloring principle of iron prussiate, did not contain oxygen.<sup>6</sup>

Berthollet's experiences were as follows:<sup>53</sup> When potassium hydroxide or bicarbonate was digested with ferric prussiate, the latter lost its color; evaporation of the liquor deposited crystals of a product designated as saturated iron potassium prussiate (and afterwards, iron prussiate). However, although alkalis which were combined with CO<sub>2</sub> were able to decompose iron prussiate, they combined easily with prussic acid by simple and direct affinity instead of double affinity. The yellow residue of this operation was probably a kind of iron prussiate having an excess of iron oxide. Treatment with acid dissolved the fraction of iron oxide that made it yellow and changed the color to blue. Additional treatment with excess alkali and long boiling decomposed completely the iron prussiate.

According to Berthollet, these results indicated that iron oxide could be found combined with prussic acid in two different states, depending on their relative proportions, yielding either the yellow color or the blue one called Prussian blue. All acids were able to remove the portion of iron oxide that differentiated the yellow from the blue product. Simple boiling precipitated part of the oxide that was present in excess in common alkali prussiates. The precipitate was not iron oxide but iron prussiate with an excess of oxide. Treated with an acid, the latter yielded Prussian blue, unless heated or not exposed to light. Heat without light or light without heat was also able, in the presence of acids, to decompose solutions of alkali prussiates. In this case the iron oxide included in the combination of potassium prussiate, precipitated forming Prussian blue.

Scheele tried to determine the principles that constitute prussic acid and concluded that it was ammonia united to an elusive carbonaceous substance. He believed that when iron prussiate was distilled, the iron

oxide attracted a part of the phlogiston of the coloring matter. The carbon dioxide that was released left the apparatus together with the volatile alkali (ammonia) that was simultaneously liberated. Based on the same experiences, Bergman concluded that prussic acid was composed of carbon dioxide, volatile alkali, and phlogiston.

Berthollet believed that it was not logical to assume the presence of ammonia in prussic acid, as it is in animal matter. He found that when the acid was transformed into a green precipitate by the action of iron, it had the property of changing into ammonia when mixed with a fixed alkali or with calcium carbonate; abundant vapors were released. If an acid was now added it was not possible to detect the odor of prussic acid, which proved that it had been destroyed. If the experiment was repeated with an alcoholic solution of potassium hydroxide, free of carbon dioxide, a clear effervescence was observed, more obvious than during addition of an acid. Clearly carbon dioxide and ammonia had been produced but this production did not take place when the experience was repeated using the acid produced by Scheele's method. Berthollet concluded that hydrogen and nitrogen were present in prussic acid, combined with pure carbon. When oxygen was added, all the principles necessary for the formation ammonia carbonate were present, but in order for them to take the form of ammonia and carbon dioxide, it required the help of an alkali or calcium carbonate, which tended to combine with the carbon dioxide. This phenomenon was similar to the exposure of sulfur to vital air (oxygen). Sulfur combined more easily with oxygen with the help of alkali or iron.

Berthollet had not doubt then that prussic acid was composed of hydrogen, oxygen and carbon, in a proportion to be determined. Examination of this composition showed it to be less similar to those of acids and more to that of ammonia. Nevertheless, it had most of the properties of common acids so that it should be included in the same category. Berthollet brilliantly proved that prussic acid had affinity for and combining with alkalis; yielding crystallisable compounds, from which it was displaced by the more powerful acids.

Two years later<sup>54</sup> Berthollet made the categorical statement: *"Il me paroît donc qu'il ne reste rien de douteux sur la composition de l'acide prussique, si ce n'est la proportion de ses principes que je n'ai pas encore pu déterminer; c'est une combinaison d'azote, d'hydrogène et de carbone... Si l'on considère la composition de l'acide prussique, elle paroît bien moins voisine de celle des acides, que celle de l'ammoniaque; toutefois il a trop de propriétés communes avec les autres acides pour ne pas le placer dans la même classe..."* (It appears to me that there is no longer any doubt as to the composition of prussic acid except as to the proportion of its elements, which I have not yet been able to determine. It is a compound of nitrogen, hydrogen, and carbon... If the composition of prussic acid is considered, it seems to be not as close to that of the acids as it is to that of ammonia; however, it has too many properties in common with the other acids so as not to place it in the same class...).<sup>54</sup>

The studies of Jean François Clouet (1751-1801), who succeeded in synthesizing prussic acid, as well as those of François René Curandau, and of Gay-Lussac,<sup>55</sup> eventually proved Berthollet correct and confirmed the revolution that he had just brought about by his discovery of hydracids, which are oxygen-free. The latter were quite weak, and the Lavoisier theory that an acid must

contain oxygen was not seriously threatened by these exceptions to the rule. The dominant role of hydrogen in acids was not definitely established until Davy published his work on the hydracids in 1814.<sup>7,56</sup>

In a 1798 Berthollet added hydrogen sulphide<sup>47</sup> to the growing list of substances which acted as acids but did not contain oxygen. He showed that although this gas contained only hydrogen and sulfur it performed all the functions of an acid: It dissolved easily in water reddened the tincture of litmus, combined with the alkalis, barites, lime, and magnesia and it decomposed soap and displaced the oil from its combination with the alkali in soap. It precipitated most of sulfur from solutions of potassium sulfide or lime and tended to form a triple combination with other sulfides.<sup>6</sup>

### Natron

During his stay in Egypt Berthollet was told of the existence of the apparently inexhaustible source of sodium carbonate present on the shores of Lake Natron, at the entrance to the desert. This trona, or natron,  $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 3\text{H}_2\text{O}$ , had been in continuous exploitation by the natives since ancient times and used for various chemical purposes and in embalming. Old Egyptian documents from the 18th dynasty indicate that nitri was present in natural fields located in Wadi Natrun, next to Naukratis in the Delta, and near El-Kab, in Upper Egypt. The ancient Egyptians exported the salt to many countries and the believers used it to clean their mouth by chewing it wet, as a component of the incense fire, and also as a component of mummifying materials.

Aware of the dire needs of sodium carbonate by the French industry, particularly for manufacturing gunpowder, Berthollet decided to survey the area in order to study the possibilities of commercial exploitation. In his paper reporting the visit<sup>57</sup> he wrote that the valley of the Natron lakes constituted a vast laboratory where nature prepared an immense amount of soda. Chemical analyses indicated that the water from the lakes contained sodium nitrate, sodium carbonate, and a little of sodium sulfate, in a proportion that varied from one lake to the other. As an example, he remarked that lake #3 was divided into two sections with no communication between their waters. The waters of the oriental section contained only sodium chloride while those of the occidental section contained almost sodium carbonate alone. In this way, by natural evaporation, sodium chloride crystallized on one side of the lake and almost pure sodium carbonate on the other. When the waters contained both sodium chloride and sodium carbonate, the chloride crystallized first followed by the carbonate, forming alternate white layers of each salt, easy to remove. Elsewhere, part of these crystals was dissolved by rainwater, fact that explained the presence of natron in water in a closed section of the lake.

By clever reasoning, Berthollet deduced that sodium carbonate had been and was still being formed by a double decomposition reaction between the saturated brine and the limestone bed of the lake. The reaction had already been proposed as early as 1737 by Henri Louis Duhamel du Monceau (1700-1781) as a possible method of preparing sodium carbonate. Guyton de Morveau and Jean-Antoine Allouard Carny (1751-1830) erected a factory for making soda by a process based on Scheele's observation that when a mixture of common salt and lime was exposed to air, an efflorescence of soda gradually developed on the surface. According to Guyton

de Morveau their method duplicated that employed by nature in producing an efflorescence of soda on the surface of cement mortar in certain cellars and in the dried residue of saline lakes and springs. In this process quicklime was slaked in water and then mixed with a saturated brine solution. The mixture was concentrated to a paste and left exposed to the air in some closed and humid place, preferably a cellar. Sodium carbonate would then form on the surface of the mass. When it was removed another layer would form and the process would be repeated until the materials were exhausted. For this process Guyton de Morveau received a privilege dated June 3rd, 1783.<sup>58</sup>

In the Lake Natron area Berthollet found that the terrain covered by sodium carbonate layers did not contain sodium carbonate but were always impregnated with the salt, but the terrain ground where the decomposition of sodium chloride took place, always contained a considerable amount of calcium carbonate, and was always very humid. Sodium carbonate appeared only at the spots where the soil, formed of limestone rock, was soaked with salty water. To Berthollet it seemed quite clear that calcium carbonate was the substance that drove the decomposition of sodium nitrate with which it was in contact in a humid and hot environment. The calcium nitrate formed from the decomposition of sodium nitrate is very deliquescent and thus permeated deep inside the terrain. In the neighborhood where the terrain is particularly clayey, the formation of sodium carbonate was particularly favored by the stems of reed, which grew abundantly in the region. The stem favored the reaction by helping the efflorescence of the carbonate as it was formed. Interesting enough, nature was executing the opposite reaction observed in the laboratory. Berthollet attributed the inversion of the reaction direction to the change of experimental conditions between those used in the laboratory and the natural conditions prevalent in the particular area.<sup>9</sup>

Berthollet had already found that during the extraction of saltpeter from crude nitre rock by dissolution in water, the increasing concentration of saltpeter in solution made the remaining portions more difficult to dissolve, even though the water was never saturated with salt. Further quantities could be dissolved easily by using fresh water, but each successive washing yielded a smaller amount. With the new information gathered at the lakes, Berthollet explained the reaction by the great quantities of sodium chloride and calcium carbonate and the continuous removal of the products: the deliquescent calcium chloride by seepage below ground. The large quantities in solution of the original substances compared to those of the products maintained a reaction which would not take place by affinities alone. When a salt solution filtered slowly through the pores of the limestone, the relatively weak affinities between these two substances were enhanced by the combined effects of the temperature and the enormous mass of limestone. This led to decomposition of the salt, assuring a constant production of sodium carbonate and calcium chloride through double decomposition.<sup>59</sup>

These conclusions lent a renewed interest to Berthollet's earlier suggestion that physical conditions such as temperature, relative concentration, and quantities of reactants, affected the nature and direction of affinities in a chemical reaction (as stated by the laws of chemical action). Berthollet already read a paper on this subject at Cairo, *Recherches sur les Lois de l'Affinité*,<sup>60</sup> which was published in the *Mémoires de l'Institut* for

1801.<sup>61</sup> This was the starting point of his complete new system of chemistry, first briefly sketched in *Recherches sur les Lois de l'Affinité* (1801)<sup>24</sup> and later developed into the comprehensive two-volume *Essai de Statique Chimique*.<sup>25</sup> In this work Berthollet developed his main thesis that chemical action is due partly to affinity, which he thought of as similar to gravitational attraction, and partly to the masses of the reactants, but also led him to doubt the reality of constant composition of chemical compounds, and was the origin of a live discussion with Joseph-Louis Proust (1754-1826).<sup>8,62-64</sup>

### Fulminate

On 1788 Berthollet read at the Academy a paper in which he described his discovery of fulminant silver, a substance which proved to be one of the most erratic and dangerous of all explosives.<sup>65,66</sup> He first dissolved silver in nitric acid and then precipitated the solution with a suspension of calcium carbonate and left the precipitate to dry in air for three days. The dry precipitate, when treated with a solution of ammonia, turned into a black powder, which after drying in air yielded fulminant silver; which proved to be a much stronger explosive than cannon powder or gold fulminate. In Berthollet's words: "*Gunpowder, even fulminating gold, cannot be compared with this new product. Contact with fire is required to make powder explode; fulminating gold has to be heated to a sensible degree to fulminate it, whereas contact with even a cold object is enough to set off fulminating silver. In short, after this material has once been obtained, it may not be touched. No attempt should be made to put it into a bottle; it must be kept in the open vessel.*" A weight of one grain left in a glass capsule was enough to pulverize the capsule; the particles released went through many pages of paper. According to Berthollet the reason for the strong detonation was that the remaining oxygen in the silver, combined with the hydrogen (generator of water) from ammonia, and produced vapor water. This water, vaporizing instantly, with all its elastic and expansive power, was the main cause of the phenomenon, although nitrogen disengaged from ammonia also played also an important role amongst others.

In 1800 Edward Charles Howard (1774-1816) reported his discovery of the highly explosive mercury fulminate, by the reaction of mercury with alcohol and a mixture of concentrated nitric and sulfuric acids.<sup>67</sup> In his lengthy monograph he described its method of preparation, its chemical properties, and its remarkably violent detonating powers. Such was the universal interest in this new explosive that The Times of London reported about this finding (August 5th, 1800) and the Royal Society awarded him his highest distinction, the Copley Medal. Comparable fulminating compounds were not obtainable by Howard's procedure, except for silver fulminate. The latter was even more unstable than mercury fulminate, and could explode even under water.

Berthollet examined the results reported by Howard and disagreed with his conclusions.<sup>68</sup> According to Howard, mercury fulminate contained per weight 21.28 % oxalic acid, 64.72 % mercury, and 14.00 % nitric gas and excess oxygen. Berthollet prepared the compound following Howard's procedure but first separated and analyzed the supernatant liquid. Addition of powdered calcium carbonate produced a black precipitate similar to the one produced from solutions of mercury that contain ammonia, results that led him to believe that the precipitate also contained ammonia. For this



reason he treated fulminant ammonia with potassium hydroxide and noticed the release of ammonia. The alkali did not show presence of oxalic acid, the powder became brown and hardly melted when put on top of burning coal. He then subjected mercury fulminate to the action of hydrogen chloride and of sulfuric acid, the same as Howard had done. He did not try nitric acid because the alteration that it could produce could lead to confusing results.

The dissolution of mercury fulminate in hydrogen chloride was not always uniform and depended on the conditions under which it was prepared. The clear solution was treated first with a suspension of potassium sulfide to precipitate the metal, followed by addition of a solution of calcium chloride, whence precipitation occurred, as if oxalic acid was present. The same experience, repeated with mercury oxalate, produced now a precipitate with the calcium chloride proving that mercury fulminate did not contain oxalic acid.

A similar solution of mercury fulminate was distilled alone and brought to sublimation. The sublimate consisted of fine needles in which it was easy to identify the presence of ammonia, and were similar to those obtained when distilling a mixture of a little of ammonia chloride with a dissolution of mercury dichloride. This result confirmed the presence of ammonia in mercury fulminate and also proved that the metal was as oxidized as in mercuric chloride.

Berthollet verified Howard's claim that mercury fulminate is decomposed by dilute sulfuric acid, reducing it to a white non flammable powder that Howard had assumed to be mercury oxalate. Berthollet disagreed with this conclusion, believing that the powder was actually mercuric sulfate, (which he named sweet mercuric sulfate). When boiled in water it became yellow, the same as if left wet in contact with air or if it was oxidized even more. It did not burn over ardent coal, like with mercury oxalate if it was dissolved in nitric acid and treated with a solution of barite; it was not barium oxalate that is soluble in acids, but barium sulfate. The action of sulfuric acid was accompanied by the release of a considerable amount of gas. Howard had recognized this gas to be largely carbon dioxide, but he had also assumed that the part of the portion that is insoluble in water had the properties of what the Dutch chemists call *gaz nitreux éthéré* (ethylene dichloride), because it was changed by the action of sulfuric acid. This is the reason why Howard concluded that mercury contains *gaz nitreux éthéré*. Berthollet did not find anything that would lead to the assumption of the presence of this gas. The largest part of the gas he obtained was carbon dioxide and the rest, about 1/12 volume of the gas, was *gaz hydrogène oxicarboné* (a mixture of hydrogen, carbon dioxide, and carbon monoxide)

From these results Berthollet concluded that mercury fulminate is actually a combination of (a) well-oxidized mercury, like the one present in mercuric chloride, (b) ammonia, and (c) a substance still not identified, but which is not oxalic acid or a similar acid. This substance seemed somewhat different from an alcohol because it easily decomposed forming carbon dioxide at the same that it reduced mercury producing *gaz hydrogène oxicarboné*.

In 1989 Teles *et al.*<sup>69</sup> used modern spectroscopic techniques to elucidate the definite composition of fulminic acid and to prove that the acid assumes the formyl oxide configuration



## Nomenclature

During the eighteenth century there had been numerous attempts to construct a systematic chemical nomenclature. Guyton de Morveau was in the forefront of nomenclatural reform in France, suggesting numerous ways by which the names of substances could be made simpler and more precise. His most significant ideas were embodied in a memoir of 1782 in which he proposed that the names of compound substances should reflect their composition. For example, the name of a salt should indicate the acid and the base, which formed it.<sup>70</sup> Not the least of the services which chemistry owes to Lavoisier and his three contemporaries, Guyton the Morveau, Berthollet, and Fourcroy, which first accepted and helped promulgate his views, is their successful reform of the nomenclature, based upon the principle of making the name indicative the qualitative composition of the substance. Toward the end of 1786 Guyton the Morveau held a meeting with Lavoisier, Berthollet, and Fourcroy, as a result of which they agreed to collaborate in recasting the terminology of chemistry and the results of their efforts was a new method of nomenclature, which reflected Lavoisier's theories concerning oxygen and Guyton's concern for nomenclature based on composition.<sup>6,71</sup> Their suggestions, augmented by a scheme of chemical symbols proposed by Jean-Henri Hassenfrantz (1755-1827) and Pierre August Adet (1763-1832), were published in 1787 in the now famous "*Méthode de Nomenclature Chimique*".<sup>6,7,15</sup>

## Affinity<sup>6,72-76</sup>

The causes of chemical combinations had fascinated chemists for many years. The concept of chemical affinity was introduced for the first time by Albert Le Grand (1193?-1280) in the sense it is attached to today: "*Le soufre noircit et brûle en général les métaux à cause de l'affinité naturelle qu'il a pour eux*" (Sulfur blackens and burns metals in general because of the affinity it has for them). Herman Boerhaave (1668-1738) attributed the combination to an especial force, which was the greater the more the two bodies were dissimilar.

In the beginning, a certain number of affinities were distinguished: affinity of aggregation, of composition, of dissolution, of decomposition, of precipitation, simple, double, or complicated. Guyton de Morveau reduced them to five: aggregation, composition, prepared by co-operation (double), and affinity of excess. Initially Fourcroy distinguished only two types of affinity: by aggregation and by composition (chemical affinity) but in his *Système des Connaissances Chimiques*<sup>72,73</sup> he adopted that of Guyton de Morveau. Fourcroy, noting that nitric acid and mercury combined with violence and formed a compound that decomposed easily, while hydrogen chloride yielded with difficulty a compound, which was unaffected by heat, proposed to measure affinity more by the difficulty of separating a compound into its principles than by the vivacity of their union. His first book<sup>72</sup> already contains a tabular description of affinities. For example, the affinity of sulfuric acid towards alkali fixe végétal (potassium hydroxide) was 8 while towards alkali volatile (ammonium hydroxide) was 5. Since the sum of affinities between potassium nitrate and calcium sulfate was 13 and the sum of affinities between potassium sulfate and calcium nitrate was 12, then potassium sulfate was decomposed by calcium nitrate to yield potassium nitrate and calcium sulfate.

A systematic method of arranging both this compositional knowledge and the information concerning the



interaction of these salts was lacking until 1718 when Etienne François Geoffroy (1672-1731) summarized it in a convenient tabular form.<sup>73</sup> In this affinity table as it became known, the constituents of salts were arranged so that a chemist, by looking at this chart, would be reminded that if iron were added to a solution of silver nitrate, the iron would combine with the acid and silver would be precipitated.<sup>6</sup> Nevertheless, this viewpoint was not accepted by all. Lavoisier had shown, for example, that the nature of chemical combination varied with the temperature. Consequently, he pointed out, a separate table of affinity should be constructed for each degree of temperature. Bergman built a table showing how affinity varied with temperature.<sup>74</sup>

Newton suggested in Query 31 of his *Opticks*<sup>75</sup> that the particles of bodies were endowed with certain attractive forces by which they interacted to produce various chemical and physical phenomena: *"Have not the small Particles of Bodies certain Powers, Virtues or Forces, by which they act at a distance, not only upon the Rays of Light for reflecting, refracting, and inflecting them, but also upon one another for producing a great part of the Phaenomena of Nature?"* Newton's idea was used in the late eighteenth century to describe affinity as a manifestation of the inverse square law of gravitational attraction, but subject to the modifications that at very short distances the influence of the shape of the molecules became a decisive factor, negligible when considering astronomical interactions. According to Bergman *elective affinity* was an invariable force, and of such a nature that a body which expelled another from its combination could not possibly be separated from the same by the body which it had eliminated; if three substances were mixed, the two whose mutual affinity was strongest combined, to the exclusion of the third. If a compound of two substances was mixed with a third substance, no reaction took place when the affinity of the original compound was stronger than that of either of its constituents for the free substance. If the free substance possessed an affinity for one of the constituents stronger than the affinity of the compound, it combined completely with that substance, displacing an equivalent amount of the other constituent.

The most important reactions to which chemists applied the concept of elective affinities were those between acids, bases, and salts. Believing that a salt was the direct combination of an acid and a base, they considered the reaction between the salt and an acid to be a displacement of one acid by another in combination with the base. According to the theory of elective affinities, an acid would replace another if its affinity for the base was stronger than that of the previously combined acid for the base. Similarly a base would replace another base in a salt if its affinity for the acid was stronger. Reactions between two salts were considered to be double displacement reactions, resulting in an exchange of bases between the respective acids.<sup>56</sup>

In 1803 Berthollet published, under the title *Essai de Statique Chimique*,<sup>25</sup> a memoir that Michel Eugène Chevreul (1786-1889) claimed may be considered the first general work dedicated to chemical mechanics.<sup>2</sup> In it he intended to distinguish the forces that acted in chemical reactions, thus he studied not only affinity but also the forces that operated together with affinity, be it for producing combinations, be it for bringing about decompositions: *"Tous les phénomènes chimiques sont le résultat de l'action réciproque que les molécules des corps exercent en raison de leur nature, cette action dépend*

*des forces attractives qui tendent à les réunir et des forces répulsives qui tendent à les séparer"* (all chemical phenomena are the result of the reciprocal action that molecules exert one on another by reason of their nature; this action depends on attractive forces that tend to join them and repulsive forces that tend to separate them). Berthollet adopted the Newtonian idea that chemical affinity is a form of universal gravitation. He added: *"Toutes les combinaisons et compositions sont sollicitées par deux forces: par une attraction à distance dans laquelle la quantité fait varier les effets et une attraction de la surface dans laquelle les dimensions et les rapports de figure des lames qui la forment exercent leur influence..."* *Cette attraction ne doit pas être confondue avec l'attraction générale...cause de la pesanteur et des phénomènes célestes..."* (All combinations and compositions are acted by two forces: by an attraction acting at a distance in which the quantity affects the effects, and a surface attraction by which the dimensions and shape proportions of the salts which form it. Chemical attraction should not be confused with general attraction...the source of weight and celestial phenomena...).

Berthollet opened his book<sup>25</sup> with the statement that *"a theory of chemical affinities solidly established, and serving as the basis for the explanation of all chemical questions, ought to be a collection of, or contain, all the principles from which the causes of chemical phenomena can proceed, in every variety of circumstances; because observation has proved that all these phenomena are only the various effects of affinity, to which all the various chemical powers of bodies may be attributed... If I can prove that a weaker degree of affinity can be compensated by an increase of quantity, it will follow that the action of any body is proportionate to the quantity of it which is necessary to produce a certain degree of saturation. This quantity, which is a measure of the capacity of saturation of different bodies, I shall call mass...when a substance acts on a combination, the subject of the combination divides itself between the two others, not only in proportion to the energy of their respective affinities, but also in proportion to their quantities."*

*"The powers which produce chemical phenomena are all derived from the mutual attractions of the molecules of the bodies and have been given the name affinity, to distinguish them from astronomical attraction. It is probable that each is only the same property, but astronomical attraction is exerted only between masses placed at a distance, where the form of the molecules, their intervals, and their particular affections have no influence; its effects always proportional to the mass and the inverse of the square of the distance, can be rigorously submitted to calculation. The effect of chemical attraction or affinity are, on the contrary so altered by the particular conditions...that a general principle cannot be deduced... The immediate effect of activity which a substance exerts is always a combination, so that all the effects which are produced by chemical action are a consequence of the formation of some combination...All substances which tend to enter in combination act by reason of their affinity and their quantity...the chemical action of a substance depends not only on the affinity, which belongs to the parts which compose it and the quantity; it depends also on the state in which these parts are found, either by an actual combination which causes a greater or lesser part of their affinity to disappear, or by their dilation or condensation which causes their reciprocal distance to vary..."*

Berthollet affirmed that the force of affinity depended on the relative distance between the particles composing a substance, the more closely packed these were, the stronger their reciprocal affinity. Consequently, it was more difficult for substances to combine in the solid state than in the liquid; in the former case the particles of a given substance had to overcome their affinity for each other before combining with another whereas in a liquid these particles were further removed from each other and were more susceptible to attraction on them by those of a foreign body.<sup>76</sup>

According to Berthollet there were three types of affinities, which could be considered as different degrees of the same power: simple attraction, elective attraction, and complex attraction. Elective attraction was the property of a body of chasing away another body from a combination, to take its place. Complex affinities took place when there were more than two bodies present.<sup>76</sup> Simple affinity was the one which is exerted between two substances which, although composed of different principles, nevertheless acted with a collective force. Elective affinity was that involved in the competition between two substances for a third. As a result of this competition one substance combined with the third to the exclusion of the second. As an example of elective affinity Berthollet mentioned the reactions of carbon dioxide with potassium compounds: *"Bubbling carbon dioxide through an aqueous solution of potassium silicate precipitates silicic acid and the gas combines with potash. We say that the elective affinity of carbonic acid for potash is higher than that of silicic acid. But now, if a mixture of silicic acid and potassium bicarbonate is heated to red, the opposite phenomenon takes place. Carbon dioxide is liberated and potassium silicate is produced. We then say that by the dry via silicic acid has a stronger elective affinity for potash than carbon dioxide."*

Berthollet claimed that every reaction proceeds by reason of its affinity, its amount, and its constitution. By the last term he understood the state of combination under which the substance is present, its state of dilatation or condensation that varied with the reciprocal distance of its molecules.<sup>2</sup> This diversity of the nature or properties of compounds manifested itself mainly by the fact that between them they did not attract chemically with the same identity, when subjected to the same temperature, pressure, etc., and that this fact manifested itself in the most obvious manner on what was called elective attraction, by virtue of which a body expelled another from one of its combinations, to take its place. It was this inequality that allowed performing decompositions, analysis, without recourse of light, heat, and electricity, when they sufficed for reducing a compound into its elements without the resort of other forces.

Berthollet also tried to prove that the proportions in which two substances combined also varied according to the conditions, an argument opposed to Proust's hypothesis (1799)<sup>62,63</sup> that all combinations occurred in definite proportions: The weight composition of any compound was the same, independently of the method used for preparing it.

From Berthollet's concept of chemical mass it followed that the proportions in which one substance combined with another increased directly with its chemical mass, the active quantity in any given reaction. There were a maximum and a minimum proportion in which one substance would combine with another. Between these two limits the substances would combine in any proportions, depending on their respective quantities,

the difference in the proportions being continuous between one extreme and the other. From this it obviously followed that the proportions in which substances combined were not fixed, at least within limits. This was not borne out by experiment. Berthollet did not contest such evidence, although he continued to affirm that in the majority of cases, combinations occurred in conformity with his theory of variability of proportions, a claim which he repeated very boldly near the end of the first volume of his *Essai*: *"I have been led, through these various observations, to conclude that chemical affinity does not follow any special laws, but rather that all phenomena which depend on the reciprocal effects of the bodies are effects of the same qualities which physics seeks to encompass; that, therefore, in this respect one should not differentiate between physics and chemistry, and that the affinity of various substances which causes their combination is not selective but variable according to the effective quantity and the conditions which contribute to these operations... Thus we have three physical conditions on which the course of the chemical reactions depends: (a) elasticity, the endeavour of gases to fill up a large space; (b) cohesion, the firm clinging together of parts of some substances, which cause their insolubility; and (c) the mass of participants in a reaction which can be influenced when gases and insoluble substances leave the system."*<sup>4</sup>

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