

## Nicolas Théodore Saussure: Contributions to chemistry and physical chemistry

### *Nicolas Théodore Saussure: contribuciones a la química y a la fisicoquímica*

Jaime Wisniak<sup>a</sup>

<sup>a</sup>Department of Chemical Engineering, Ben-Gurion University of the Negev, Israel 84105. [wisniak@exchange.bgu.ac.il](mailto:wisniak@exchange.bgu.ac.il)

Received: 24 February 2018; Accepted: 2 April 2018

### ABSTRACT

Nicolas Théodore de Saussure (1767-1845) is well recognized for his pioneering work about plant physiology and the interaction between plants, soil, and atmosphere. Here we describe some of his findings in chemistry and physical chemistry, in particular the possible combination of alumina with carbon dioxide to generate aluminum carbonate and its different degrees of desiccation in its various states. He demonstrated that starch mixed with water alone was able to generate crystallizable sugar in larger amount than when acted on by sulfuric acid; his procedure yielded also amidine, a substance with properties intermediate between starch and gum. Saussure used a eudiometric procedure to determine the correct composition of ethanol, diethyl ether, and ethylene. He carried an extensive study of the absorption of pure gases and their mixtures by many solids and liquids and proved that all porous bodies were capable of absorbing gases and that this property depended on factors such as the number of pores and their dimension, the affinity between the gas and the solid body, and the compressibility of the gas. In the case of mixtures, two gases absorbed in charcoal often experienced a greater condensation than each would in a separate state. The absorption of a gas by a liquid was little affected by its viscosity, although it affected the time required for achieving saturation. His electrical experiments showed that hydrogen appeared to combine with part of the oxygen of carbon dioxide to form water, while the dioxide was reduced to he monoxide.

**Keywords:** Absorption; alcohol; alumina; CO<sub>2</sub> decomposition; eudiometry; sugar.

### RESUMEN

Nicolas Théodore de Saussure (1767-1845) es altamente reconocido por su trabajo pionero en fisiología vegetal y sobre las interacciones entre plantas, suelo y atmósfera. En este trabajo se describen algunas de sus contribuciones a la química y la fisicoquímica, en particular la posible combinación del óxido de aluminio con el dióxido de carbono para generar carbonato de aluminio y sus diferentes grados de secado en sus varios estados. Demostró que el almidón mezclado solamente con agua era capaz de generar azúcar cristalizante en mayor cantidad que la por medio del ácido sulfúrico; su método producía también amidina, una sustancia con propiedades intermedias entre azúcar y goma. Saussure usó un método eudiométrico para determinar la composición correcta del etanol, el éter etílico y el etileno. El realizó un estudio extenso del fenómeno de la absorción de gases, puros y mezclados, por un gran número de sólidos y líquidos y demostró que todos los cuerpos porosos eran capaces de absorber gases, y que esta propiedad dependía de factores tales como el número de poros y sus dimensiones, la afinidad entre el gas y el sólido, y la compresibilidad del gas. En el caso de mezclas de dos gases por el carbón activo, los dos componentes experimentaban en

muchos casos una mayor condensación de la que ocurría en forma individual. La viscosidad del líquido afectaba muy poco la absorción de un gas, pero influenciaba el tiempo requerido para alcanzar la saturación. Los experimentos eléctricos de Saussure demostraron que el hidrógeno podía combinarse con parte del oxígeno del dióxido de carbón para generar agua, al mismo tiempo que reducía el dióxido a monóxido.

**Palabras clave:** absorción; alcohol; alúmina; azúcar; descomposición del CO<sub>2</sub>; eudiometría.

### *Life and career*

Most of the available information regarding the life and career of Nicolas Théodore de Saussure comes from a long biography written by Isaac François Macaire-Prinsep (1796-1869) (Macaire, 1845), (also known as Jean François Macaire-Prinsep), professor of medicinal chemistry at the Académie de Genève, and so does the following material.

Nicolas Théodore de Saussure was born in Geneva on October 14, 1767, the son of Horace Benedict de Saussure (1740-1799) and Albertine Amelie Boissier. His father was a well-known scientist who had made important contributions in the areas of hygrometry, geology, and mineralogy, and was one of the first and most successful Alpine travelers. Théodore's initial education was different from the Geneva youth of his time. Geneva's primary schools had been reorganized according to the ideas of the pastor and reformer Jean Calvin (1509-1564), who believed in disciplined behavior, cleanliness, and promptness. Education was to be based in humanism, have a strong training in the liberal arts, with little or no training in science, geography, history, and the live languages. It was supposed to be almost free for students from all social classes. Horace de Saussure, a graduate of this structure, and a teacher, was deeply unsatisfied with the system and had published two booklets criticizing it and suggesting ways for its reform (Saussure, 1774ab). Therefore, he decided to carry the education of his children at home, a decision, which would affect the future personality and social behavior of his son. Théodore spent most of his youth at the home of his maternal grandmother, hardly in the company of children of his age, and continually under the authority of his father, an eminent scientist, of strong and severe personality (Macaire, 1845).

His father trained him in physics, meteorology, natural history, and experimental chemistry, and helped preparing him for entrance to the Académie de Genève. There he acquired a strong interest in the natural sciences, and became eventually his father's assistant and companion during his many trips into the Alps. The most famous of these were the ascent of Mont Blanc (1787), the expedition to the Col du Géant (1788) and the climbing of Monte Rosa (1789). During these expeditions, Théodore made a large number of measurements and analysis of the composition of the atmosphere, the density of the air, etc. etc., which eventually would reflect in his publications (Macaire, 1845).

The French Revolution created turmoil in Geneva and led many of young people to abandon the country for some time. Théodore moved to England and remained there until the commotion had cooled down. While in England he continued his pioneering research on plant physiology and the interaction between plant, soil, and atmosphere, which he had begun during his expeditions to the Alps. Eventually, the results of these researches would lead to his master publication, *Recherches Chimiques Sur la Végétation*<sup>4</sup> and fame, and put him at the peak of the scientific community. During a short stay at Geneva he married Renée Fabri in 1796. In 1802 he returned to Geneva in 1802 and was

appointed honorary professor of mineralogy and geology at the Académie de Genève, a title he held until 1835. Saussure passed on April 18, 1845, in full health and intellect (Macaire, 1845).

Théodore Saussure received many honors for his contributions to science and public life. He was honorary, correspondent, or associate member of the most important European scientific societies, among them, Section d'Agriculture de la Société des Arts (1790), Institut de France (1805), Société Helvétique des Sciences Naturelles (1815), Académies Royales of Naples, Turin, and Munich, Institut des Beaux-Arts et des Sciences of Amsterdam, Sociétés Philomathiques et Linnéenne of Paris, the Wernerian Society of Edinburgh, and the Royal Society of London (1820). He was elected member of the Conseil Représentatif de Genève (1814) and president of the Congrès Scientifique de Lyon (1804) (Macaire, 1845).

His research activities about plant physiology included the influence of carbon dioxide and the sun on vegetation (Saussure, 1797, 1800), phosphorus content of seeds (Saussure, 1808), conversion of starch into sugar (Saussure, 1814, 1819), carbon dioxide in the atmosphere (Saussure, 1816ab, 1828), maturation of fruits and flowers (Saussure, 1821, 1822), influence of desiccation on several food grains (Saussure, 1826), formation of sugar during the germination of wheat (Saussure, 1833), germination and fermentation (Saussure, 1833), plant nutrition (Saussure, 1841b), and germination of oil seeds (Saussure, 1841c).

His publications in chemistry and physical chemistry included the carbonation of alumina (Saussure, 1801), the action of electrical sparks on CO<sub>2</sub> (Saussure, 1802), the composition of alcohol and ether (Saussure, 1807, 1813), the combustion of coals (Saussure 1809), the composition of olefiant gas (ethylene) (Saussure, 1811), absorption of gases by solids and liquids (Saussure, 1812), analysis of inflammable bodies such as the naphtha found in Amiano, and the fractions of the petroleum of Travers (Saussure, 1827ab), the action of HCl and oxygen on several essences and vegetable oils (Saussure, 1820, 1832), eudiometry (Saussure, 1836), the action of fermentation on the oxygen and hydrogen of air (Saussure, 1839), and alcoholic fermentation (Saussure, 1841a).

### *Scientific contribution*

Saussure published near forty papers about his researches in a wide variety of subjects. His findings related to plant physiology have been reported in detail in many sources (i.e. Browne, 1944; Morton, 1981) and will not be discussed here. The following material presents some of his important findings in chemistry and physical chemistry.

### *Carbonation of alumina*

In 1801 Saussure published a paper regarding the possible combination of alumina with CO<sub>2</sub> and the different degrees of its desiccation (Saussure, 1801). In the opening statements he mentioned that although most combinations of alumina with acids were well known, there were some doubts regarding its union with CO<sub>2</sub>. For example, Torbern Olof Bergman (1735-1784), Antoine-François Fourcroy (1750-1809), and Jean-Henri Hassenfratz (1755-1827) believed that it was possible to prepare an artificial carbonate, while Friedrich Albrecht Carl Gren (1760-1798) had the opposite opinion. In order to try to clarify the problem Saussure carried on a series of experiments in which he treated a cold solution of aluminum sulfate (Roman alum) with a saturated solution of potassium

carbonate. Little effervescence occurred when the original solution was diluted enough. The precipitated alumina was washed several times with water and then dried at atmospheric temperature. The solid residue, weighing 29% of the original aluminum sulfate, dissolved in nitric acid with a strong effervescence and lost about 7% of its weight as  $\text{CO}_2$ . Similar results were obtained when using sodium carbonate or ammonia carbonate (Saussure, 1801).

Saussure divided the alumina thus prepared into two portions, one, which was pulverized, and the other left in its natural state, and then exposed them to the open air for a period of 18 months. After this period of time he found that the pulverized portion produced no effervescence while the non-pulverized portion produced a sensible one. Saussure thought that the effervescence of the alumina, which he believed to be in the carbonate state, actually arose from the ammonium carbonate present in it. The pulverization procedure had allowed ammonia to evaporate with ease, while in the second case, it was prevented of doing so because it had no access to free air (Saussure, 1801).

After many experiments with ammonia, reaction with nitric acid, treatment with water saturated with  $\text{CO}_2$ , etc., and inspection of natural carbonates of alumina such as clay of Cologne and clay of Hales (so called because it was found the first time in the garden of the college of Hales), Saussure concluded as follows: (a) alumina did not form with  $\text{CO}_2$  a solid aluminum carbonate, or at least no one had been unable so far of doing so, (b) the substance considered as an artificial solid aluminum carbonate was actually the product of the combination of alumina with alkali and  $\text{CO}_2$ , (c) alumina seemed unable to combine with  $\text{CO}_2$ , except in the case that the latter was dissolved in water. When this earth was precipitated from the solution by evaporation of the  $\text{CO}_2$ , it was not in the state of carbonate, (d) natural clays, assumed by some to be aluminum carbonate, did not seem to be in that state, and (e) precipitation of a solution of Hales' clay in nitric acid, with an excess of ammonium carbonate, left in solution with ammonium carbonate, a substance or combination that deserved further examination (Saussure, 1801).

The second part of the paper was devoted to an examination of the different degrees of desiccation of pure alumina in its different states. Saussure mentioned again his finding that alumina precipitated by ammonia or ammonium carbonate, appeared in two different forms, according to the quantity of water used to dissolve it, although the dried precipitates had the same weight. When the amount of water used did not exceed what was necessary for dissolving the aluminum salt (alum), the dried precipitate was a light white earth, friable, extremely spongy, and sticking to the tongue, which Saussure named *spongy alumina*. If the alum was dissolved in a very large quantity of water, the dry precipitate was transparent, yellow, brittle, cracking in the heat of the hand like rolls of sulfur, with a smooth conchoidal fracture, without appearing like an earth, not adhering to the tongue, and not again miscible with water. Its volume was about 10 to 12% of that of the same weight of spongy alumina and resembled gum Arabic or dried jelly (Saussure named it *gelatinous alumina*). Although both precipitates had the same weight and contained the same amount of water, spongy alumina released all its water (58% of the total weight) when heated to incandescence (a temperature lower than that of melting silver), while gelatinous alumina required a degree of heat larger than the one that could be achieved with the available furnaces. It lost 43% of its weight at incandescence and 48.42% when reaching  $130^\circ$  of the Wedgwood pyrometer (a temperature high enough to melt iron; Josiah Wedgwood (1730-1795) invented this pyrometer in 1782 and used it to measure the temperature in his kilns. It is based on the contraction of a block of dry clay when

heated to high temperatures caused by changes that take place in the chemical nature of its component) (Saussure is assuming that the weight loss is caused only by water evaporation) (Saussure, 1801). Saussure used this phenomenon to suggest using the loss of weight of gelatinous alumina to determine the temperature inside a furnace, and provided the following correlating table:

**Table 1: Reading of the Wedgwood pyrometer against water evaporated**

Temp/°F	Wedgwood pyrometer	% Water evaporated
		12.2
144	...	19
157	...	23.7
369	...	27.2
482	...	42.3
		45
		46
		47.5
		48.25
		48.25

Saussure clarified that although the contraction of clay at the lower temperatures was probably due to the loss of water, at higher temperatures it was probably caused by new combinations or modifications experienced by the earthy elements of the clay. This assumption was supported by the fact that the decrease in weight from 13 degrees of Wedgwood to the highest value was very small, while the contraction in the bulk of the clay, was more than 25% of its bulk (Saussure, 1801).

### *Starch and sugar*

In his first paper on the subject (Saussure, 1814), (Kirchhoff, 1811) Saussure stated that Gottlieb Sigismund Kirchhoff's (1770-1833) process for converting starch into sugar by boiling in dilute sulfuric acid had been frequently repeated by chemists, but no one had elucidated the changes in composition that starch underwent during the reaction. For this reason, he decided to investigate first the weight of the sugar formed from a given weight of starch. His results indicated that 100 parts of starch formed 110.4 parts of sugar. Since in this process the starch increased its weight without combining with any sulfuric acid or gas, or without releasing any gas, it was necessary to accept that the change in weight was due only and only to the fixation of water, that is, starch sugar was nothing else than a combination of starch with water in the solid state. Consequently, the acid role was only to promote the fluidity of the aqueous solution of the starch, and thereby facilitate its combination with water (Saussure, 1801).

In order to justify his assumptions, Saussure went on to determine the ultimate analysis of starch and starch sugar, by burning the dried products with oxygen. His results indicated that starch contained (ash-free basis) 45.39% weight of carbon, 48.31% of oxygen, and 5.90 of hydrogen (or 50.48% water and 3.76% oxygen in excess), while starch sugar contained 37.29% carbon, 55.87% oxygen, and 6.84% hydrogen (or 58.44%

water and 4.26% oxygen in excess). Comparison of both compositions showed clearly that the only difference between sugar and starch was that the former contained a larger proportion of water (Saussure, 1801).

The change of farinaceous substances into sugar, by making seeds grow to a certain extent, (as in the process of malting barley), and by the fermentation of these substances, especially if mixed with saccharine matter (in the process for obtaining ardent spirit or brandy from grain) had been known for some centuries past, but several new modes of producing sugar had been discovered within the last twenty years; and some improvements of these new modes were the subject of Saussure's next paper (Saussure, 1819).

Kirchhoff's experiments on producing sugar from a mixture of starch and gluten with sulfuric acid were well known (Kirchhoff, 1811), but Saussure proved now that starch mixed with water *alone* was able to generate crystallizable sugar in a larger amount than when acted on by sulfuric acid. In addition to sugar, his procedure yielded gum and a material intermediate between gum and starch. He mixed twenty parts of wheat starch powder with twelve times its weight in boiling water, and left the paste to digest in an open vessel during two years, in a place where the temperature in summer was not higher than 22.5°C. In this space of time, the mixture became a grey liquid odorless paste, covered by humidity, and no longer fit for the purposes of starch jelly. It remained so even after dilution filtration, without becoming acid or alkaline. The pasty matter was then digested for twenty-four hours with about an equal weight of cold water (equivalent to twenty times the weight of the starch used in its dry powdery state), and afterwards filtrated and washed with fresh water. The filtrated liquid, transparent and of a pale yellow color, was evaporated to dryness, leaving an extract weighing about 47% of the original dry starch. This extract was first mixed with an equal weight of water, and then with ten times its weight of spirit of wine of 35° Baumé (density 0.848). The sugar dissolved leaving a gummy residue, which was washed several times with alcohol. The washed residue was dried and found to weigh 1/10th of the initial dry starch. The recovered crystallized sugar amounted to about 37/100 or one-third of the dry starch-powder employed, and had the same properties as the sugar produced from starch by sulfuric acid, according to Kirchhoff's method (Saussure, 1819).

The residue remaining after separation of the sugar and the gummy matter was washed repeatedly with boiling water. After cooling and filtration, the liquid phase was evaporated to dryness leaving a substance with intermediate properties between starch and gum, which Saussure named *amidine*. Amidine was soluble in water and found to retain the power of coloring blue the solution of iodine. The solid retained in the filter paper corresponded to 1/6th of the original starch. It contained a brown coloring material, soluble in alcohol, and amounting to about 3/1000 of the original starch. A ligneous matter was also obtained from the residue of the dissolution of starch in sulfuric acid diluted, which Saussure named *ligneux amilacé* (starchy lignin). Repetition of the above experiments using potato starch or a vessel sealed with mercury indicated that atmospheric oxygen had little effect on the reaction, for the products were the same. The volume of the air was unchanged; an equal volume of CO<sub>2</sub> had replaced the oxygen consumed (Saussure, 1819).

A material balance of the reaction carried on in the presence or absence of air gave the following results: (a) 100 parts of wheat starch, dried at 22.5°C and left to spontaneous

fermentation in water during thirty-eight days excluded from air, yielded 47.4% sugar, 23% gummy matter, 8.9% amidine, 10.3% starchy lignin, 4% un-decomposed starch, and a negligible amount of lignin and charcoal (for a total of 93.6%); (b) one hundred parts of dried wheat-starch, fermented with water and exposed to the atmosphere, furnished: 49.7% sugar, 9.7% gum, 5.2% amidine, 9.2% starchy lignin, 0.3% lignin and charcoal, and 3.8% undecomposed starch (for a total of 77.9%) (Saussure, 1819).

Saussure concluded that starch left to decompose spontaneously at a temperature between 20° to 25°C, in the presence or absence of oxygen, (a) produced sugar very similar to the one obtained by the action of diluted sulfuric acid at a higher temperature, gum, amidine, and starchy lignin; (b) air had no influence in the formation of sugar, and (c) that in contact with air the starch produced more water from oxygen and hydrogen than the starch when excluded from the air; in this circumstance, so far from producing water, it appeared that a small quantity of water was appropriated from the elements of the mixture (Saussure, 1819).

Saussure ended his paper with a description of the properties of the gum, amidine, and starchy lignin. The gum was completely soluble in water and insoluble in alcohol. The aqueous solution was not precipitated by lead acetates, an infusion of nutgalls, or of iodine. Amidine appeared to be a modified starch; insoluble in alcohol and slightly soluble in cold water, the solution was coagulated into a white paste by lead sub-acetate, but not by lead acetate. It was copiously precipitated by barytes water; but not by limewater, or an infusion of nutgalls. It dissolved in an aqueous solution of potash, and acids and alcohol precipitated it from this solution. The starchy lignin had the luster of jet, was highly combustible, and gave a blue color to the aqueous solution of iodine. This last property, together with its solubility in weak alkaline lye, distinguished it from common lignin (Saussure, 1819).

#### *Composition of ethanol and diethyl ether*

According to Saussure, the proper method for determining the proportions of the ultimate elements of vegetables was yet very uncertain. The theory of fermentation could be developed only by an analysis of its products and among this alcohol would certainly have a central place. The change experienced by alcohol during its transformation into ether was the subject of contradicting opinions; some believed that ether contained more oxygen and less carbon than alcohol, other embraced the opposite opinion. Some had analyzed the residue left by the alcohol and sulfuric acid after the separation of the ether, others had analyzed both the alcohol and the ether and deduced from their differences the changes they had undergone (Saussure, 1807).

Saussure decided to use the second procedure to try to answer the question. He decided to oxidize each of the two components with oxygen into CO<sub>2</sub> and water, and estimate from the known composition of the latter, the quantities of carbon, oxygen, and hydrogen present in each. Thus, he measured the volume of oxygen caused to disappear by burning a given weight of alcohol and of ether, and measured the volume of CO<sub>2</sub> produced at the same time. He based his calculations assuming that (a) 100 parts of water contained 88 parts of oxygen and 12 of hydrogen, (b) two parts of hydrogen saturated one of oxygen to form water, (c) 1000 cm<sup>3</sup> of dry hydrogen at 28 inHg and 54.5°F weighed 34.303 g, (d) at the same conditions, 100 cm<sup>3</sup> of oxygen saturated with water, weighed 512.37 g, (e) under the same conditions, 1000 cm<sup>3</sup> of CO<sub>2</sub> weighed 693.71 g, (f) CO<sub>2</sub> contained its own bulk of oxygen (that is, one mole per mole), and (g) at the same

conditions, 100 parts by weight of CO<sub>2</sub> contained 26 parts of oxygen, neglecting fractions (Saussure, 1807).

The alcohol was oxidized by three procedures: burning it by means of a lamp under a receiver filled with a mixture of oxygen and common air, by detonation of alcohol vapor mixed with oxygen, in a Volta eudiometer; and by decomposing the alcohol in a red-hot tube of porcelain. After proper calculations, the average results of three runs made using the first procedure gave as the elemental composition of alcohol, 36.89% carbon, 15.814% oxygen, and 47.296% hydrogen, which compared very well with those reported by Lavoisier (36.97% carbon, 15.87% oxygen, and 47.16% carbon). Saussure remarked that alcohol, burning in a lamp under a closed receiver, diffused a vapor that smells like alcohol, suggesting that the combustion was incomplete. For this reason, he repeated the process, this time detonating a mixture of alcohol vapor and oxygen by means an electric spark produced in a Volta eudiometer. The results indicated that the elemental composition of alcohol was 48.82% carbon, 15.82% hydrogen, and 41.36% oxygen. Saussure believed that the latter analysis was more accurate than the previous one, based on a slow combustion (Saussure, 1807).

The following section of the memoir was devoted to the decomposition of alcohol in a red-hot porcelain tube. Although several scientists had already reported that the product consisted of a mixture of water, carbon, oxycarburated hydrogen gas (a mixture of CO, CO<sub>2</sub>, and H<sub>2</sub>), and a crystallized volatile oil, none had reported the number and proportion of the elements of alcohol. Saussure carried the process in a red-hot porcelain tube, eight inches long; connected first with a glass worm surrounded by cold water, and thence a small globular receiver, which retained the liquid products and allowed the gaseous products to pass into a pneumatic trough. The alcohol vapor was generated in a retort maintained at 50° to 62 °C and the process maintained for about twenty hours, to assure the total decomposition of the alcohol. An initial charge of 2183 grains of pure alcohol, yielded 4.25 grains of charcoal deposited in the porcelain tube, 4 grains of a paste formed of a crystallized oil and a very thick brown oil, deposited in the glass worm, 193.50 grains of colorless mixture of alcohol and water, collected in the receiver, and 1786.61 grains of oxycarburated gas, for a total of 1988.36 grains. The remaining 192.14 grains corresponded to fumes released, consisting mainly of water. The crystalline deposit appeared as thin and transparent white scales, very soluble in alcohol, and having a strong smell of benzoin (Saussure, 1807).

An overall analysis of the materials indicated that the original alcohol contained 43.65% carbon, 37.85% oxygen, 14.94% hydrogen, 3.52 nitrogen, and 0.04% ashes. According to Saussure, these results were very similar to the ones he obtained by detonation of alcohol vapor in the eudiometer, setting aside the nitrogen, which he could not calculate in that process, and which remained mixed with the water as ammonia. Subtracting this nitrogen from the table gave an even better agreement between the two analyses (Saussure, 1807).

The next section of the memoir described the preparation of ether by reacting sulfuric acid with alcohol, and its analysis by detonation in a eudiometer and by decomposition in a red-hot porcelain tube. Detonation of the ether and analysis of the products indicated that it was composed of 58.2% carbon, 22.14% hydrogen, and 19.66% oxygen. Although this experiments showed correctly that ether contained much more carbon and hydrogen, but much less oxygen than alcohol, Saussure indicated that his results were

mere approximations and contained only the rudiments of further experimentation (Saussure, 1807).

Six years later, Saussure published another paper where he described the results of additional experimentation to determine the elemental composition of alcohol and ether, this time using an improved eudiometric method and some corrections in the data from which his analysis were calculated. He now took the standard density of dry air and dry CO<sub>2</sub> as 1.293 and 0.5378 g/dm<sup>3</sup>, respectively (at 0°C and 29.992 inHg), that 100 parts by weight of CO<sub>2</sub> contained 72.63 of oxygen and 27.37 of carbon, and 100 parts of water contained 88.3 of oxygen and 11.7 of hydrogen. He carried on, once again, the analysis of alcohol by decomposing it in a red-hot porcelain tube. This time, an initial charge of 81.37 g (1256.7 grains) of alcohol, containing 70.14 g of alcohol and 11.23 g of water, yielded 0.05 g of charcoal deposited in the porcelain tube, 0.41 g of a mixture of volatile crystals and an essential brown oil smelling like benzoin, deposited in the glass worm, 17.24 g of colorless mixture of alcohol and water, collected in the receiver, and 60.25 g of moisture saturated oxycarburated hydrogen (59.069 g dry gas). Considering the analysis of each portion, 81.37 g of aqueous alcohol yielded 59.069 g of oxycarburated hydrogen, 17.771 g of water, 0.410 g of oil, 0.050 g of charcoal, 0.650 g of undecomposed alcohol, and 3.42 g of loss. Considering the loss as aqueous alcohol not decomposed, the original alcohol contained by weight, 51.98% carbon, 34.32% oxygen, and 13.70% oxygen; this composition represented a combination of the elements water and olefiant gas (ethylene) in the ratio 1:1. Saussure's results are in excellent agreement with the actual composition of ethanol: 52.14% carbon, 13.13% hydrogen, and 34.74% of oxygen. In addition, although Saussure did not give the formula of ethanol, one mole of ethylene (C<sub>2</sub>H<sub>4</sub>) + one mole of water (H<sub>2</sub>O) gives C<sub>2</sub>H<sub>6</sub>O (Saussure, 1813).

Analysis of ether by the same procedure indicated that it was composed of 67.98% carbon, 17.62% oxygen, and 14.40% hydrogen, by weight, so that ether could be represented by the elements of 100 parts in weight of olefiant gas and 25 parts of water. Here Saussure's results deviate from the actual composition of ether: 64.81% carbon, 13.60% hydrogen, and 21.59% oxygen. According to Saussure, the results indicated that the action of sulfuric acid on alcohol to produce ether, was simple to abstract water from the alcohol, a correct nominal conclusion since  $2C_2H_6O - H_2O = C_4H_{10}O$ .

It should be noted that in a previous paper, Saussure had reported his analysis of olefiant gas (ethylene), using a Volta eudiometer and an excess of oxygen (Saussure, 1811). The gas was prepared by distillation of one part by weight of pure alcohol and four parts of sulfuric acid, and the process stopped when SO<sub>2</sub> vapors started appearing. Analysis of the combustion gases indicated that olefiant gas was composed only of carbon (86% weight) and hydrogen (14% weight), with no traces of oxygen, and that it was slightly lighter than air. For these reasons, Saussure believed that instead of olefiant the gas should be called *carburated hydrogen*. Saussure's ethylene analysis was very close to the actual one: 85.63% carbon and 14.37% hydrogen (Saussure, 1811).

### *Absorption of gases*

Saussure carried on an extensive inquiry about the amount of gas absorbed by a large number of solids and liquids (Saussure, 1812). In the introduction to his memoir he reported that there were no accurate experiments on the question whether a gas when it penetrated a porous solid, contracted or not as a consequence of this entrance, even when

no chemical reaction took place between the gas and the solid. If the answer was positive, it was not known how the size of the pores and the density of the gas influenced the phenomenon, if a given body was capable of condensing all gases, what happened with a mixture of gases, and if the component gases reacted inside the pore (Saussure, 1812).

Saussure divided his experiments into three sections: (a) absorption of pure gases by a solid, (b) absorption of mixed gases by the same agents, and (c) absorption of gases by liquids.

*(a) Absorption of pure gases by solid bodies*

Previous investigators, such as Felice Fontana (1730-1805), Carlo Lodovico Morozzo (1743-1804), Rouppe and van Norden, had shown that red hot charcoal, cooled by any method that avoided contact with air, had the remarkable property of absorbing more than its own volume of various gases, that this absorption was different according to each gas and the kind of coal used, and a possible reaction occurred inside the pores (Saussure, 1812).

The experimental procedure consisted in submerging the incandescent coal under mercury and, after it became cool, introducing it into the gas to be absorbed, without ever coming into contact with atmospheric air. The experiments were normally made at 52° to 56°F and 724 mmHg, using as solid materials charcoal, Spanish Meerschaum from Valecas, adhesive slate of Melimontant (rock wood), asbestos from Tyrol, Saxon hydrophane (a variety of opal that turns translucent or transparent when immersed in water), rock cork, quartz, calcium sulfate, calcium carbonate, several woods (hazel, mulberry, fir), linen thread, silk, and wool, and up to twelve different gases (NH<sub>3</sub>, HCl, SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>2</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>). The results were expressed as volume of gas absorbed per volume of solid. The process was terminated after 24 or 36 hours, except for the case of oxygen with charcoal where the absorption process seemed to continue for several years with formation of CO<sub>2</sub>. Charcoal was able to absorb a larger amount of CO<sub>2</sub> than it did of oxygen, but at much slower rate (Saussure, 1812).

For each solid a table of numerical results was provided, in the order of decreasing absorption. The following important results were noted. Among the solids, charcoal had the highest absorption capacity; it absorbed 90 volumes of ammonia, compared to 64 for hydrophane, 15 for Meerschaum, and 10 for quartz. The respective amounts of CO<sub>2</sub> were 35, 2, 1, and 0.6. The absorption capacity and rate of absorption of dry coal were substantially different from those of moistened charcoal. For example, in a dry state it absorbed 35 volumes of CO<sub>2</sub> in 24 hours while when wet it took it 14 days to absorb 15 volumes. The absorption process was sufficiently exothermic to cause a clear increase in temperature. The thermal effect increased with the absorbability of the gas; charcoal became hotter in ammonia than in CO<sub>2</sub>, and hotter in CO<sub>2</sub> than in oxygen. A similar effect was absorbed when increasing the pressure of the gas at constant temperature. Pumping the air out of the charcoal by means of a vacuum pump and then putting the solid in contact with CO<sub>2</sub> at 53.25°F, resulted in the absorption of 31.5 volumes of the gas, compared to absorption of 35 volumes for red-hot charcoal (Saussure, 1812).

The results of these experiments proved that all porous bodies were capable of absorbing gases. In addition to the nature of the gas, this property depended on factors such as the number of pores and their dimension, the affinity between the gas and the solid body,

and the compressibility of the gas. Saussure found that, in general, the absorption capacity increased with the number of pores and smaller dimensions of the same. His results indicated that a given weight of charcoal from boxwood absorbed 7.5 times its volume when whole, and only 3 times its volume when in a pulverized state. Destruction, opening, and widening of the internal cells resulted in a clear diminution of the absorption capacity. The absorption capacity of the different kinds of charcoal appeared to increase with increasing density because it was accompanied by a decrease in the diameter of the pores. Thus, charcoal from cork, specific gravity 0.1, did not seem to absorb air, charcoal from fir, specific gravity 0.4, absorbed 4.5 times its volume of air; and boxwood charcoal, specific gravity 0.6, absorbed 7.5 times its volume of air. Obviously this phenomenon ceased when the pores became too small to allow gases to enter. Saussure remarked that this rule should be considered accidental because the absorbability also changed with the internal structure of the material (Saussure, 1812).

#### *(b) Absorption of mixed gases by solid bodies*

In the second section of his work, Saussure examined the characteristics presented by the absorption by porous bodies of a binary mixture of the gases O<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>. These experiments were carried in two different ways: (1) The solid freed from air was put in contact with a binary gas mixture, and (2) the solid was first put in contact with one gas and after saturation, in contact with a second gas. A eudiometric technique was used to follow the results (Saussure, 1812).

The following are some of the important results noted. When a piece of charcoal saturated with one of the gases was put in contact with another gas, a portion of the first gas was released, and a portion of the second gas was absorbed. Depending on whether the condensation of the first gas absorbed was greater or smaller than that of the second gas, the process was exothermic or endothermic. For example, the previous results indicated that charcoal absorbed more CO<sub>2</sub> than hydrogen, hence, if a piece of charcoal saturated with CO<sub>2</sub> was put in contact with hydrogen, the bulk of the gas increased remarkably and the charcoal became colder. The opposite results were observed if the charcoal was first saturated with hydrogen and then put in a CO<sub>2</sub> atmosphere. Two gases absorbed in charcoal often experienced a greater condensation than each would in a separate state. For example, the presence of oxygen in charcoal facilitated the condensation of hydrogen, and the presence of CO<sub>2</sub> or nitrogen, facilitated the condensation of oxygen. Significantly, the absorption of two gases on a solid did not necessarily lead to their chemical combination, contrary to the claims of Rouppe and Norden. Finally, in general, all porous bodies exhibited the same behavior as charcoal, regarding the mutual expulsion and condensation of the gases coming in contact with them (Saussure, 1812).

#### *(c) Absorption of gases by liquids*

It was well known that liquids absorbed all gases and that they could be released by either heating the solution or decreasing the external pressure, William Henry (1774-1836) had conducted a series of careful experiments describing this phenomenon<sup>37</sup> and John Dalton (1766-1844) had elaborated a theory, which explained the absorption of gases by water and other liquids. According to Dalton, the gases were held in solution by mechanical forces and not by a chemical combination. In the particular case of water, the volume of gas absorbed by one volume of water was represented by the series (1/1)<sup>3</sup>, (1/2)<sup>3</sup>, (1/3)<sup>3</sup>, and (1/4)<sup>3</sup>, depending on the nature of the gas. The first term corresponded

to CO<sub>2</sub>, H<sub>2</sub>S, and NO<sub>2</sub>, the second to ethylene, the third to O<sub>2</sub> and NO, and the last, to N<sub>2</sub>, H<sub>2</sub>, and CO.<sup>38</sup> Saussure claimed that Dalton's theory was in opposition to most of his experimental results on the subject (Saussure, 1812).

A first table, exhibiting the values of the number of volumes of ten gases (i.e. SO<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, etc.) absorbed by 100 volumes of water or alcohol of specific gravity 0.84, showed clearly that this absorption was far from being similar; with alcohol, in general, absorbing about twice the amount of gas absorbed by water. If, as claimed by Dalton, absorption was a mechanical phenomenon, then the phenomenon would not be influenced by chemical affinity, and all liquids would absorb the gases in the *same order*. To prove the fallacy of this hypothesis, Saussure measured the volumes of C<sub>2</sub>H<sub>4</sub>, NO, CO, and CO<sub>2</sub> absorbed by either 100 volumes of water, alcohol specific gravity 0.84, naphtha specific gravity 0.784, oil of lavender specific gravity 0.88, olive oil, or a saturated solution of KCl.

The results proved very clearly that in liquids, as in solids, there were great differences in the relative order and amount of absorption. Ethylene was the most soluble gas in naphtha, nitrous oxide in oil of lavender, and CO<sub>2</sub> in olive oil and a saturated solution of KCl (Saussure, 1812). Additional experiments showed that viscosity of the liquid influenced very little the solubility of a gas, although it affected the time required for achieving saturation. Specific gravity was an important factor; the lightest liquids had a greater power of absorbing gases than those of greater density. External pressure had a proportional effect on the solubility, as Henry had previously demonstrated. Saussure also carried on a few experiments on the absorption of a mixture of gases by water and found that the presence of one gas facilitated the absorption of the other, that is, the solubility was larger in comparison to the individual solubility (Saussure, 1812).

### *Decomposition of CO<sub>2</sub>*

Joseph Priestley (1733-1804) and Martinus van Marum (1750-1837) had studied the effect of electrical sparks on fixed air (CO<sub>2</sub>). Priestley was the first who found a change to take place in CO<sub>2</sub> when treated with an electrical spark repeatedly and for a considerable time. For example, when a small amount of CO<sub>2</sub> was enclosed in a glass tube sealed with mercury and sparked; the whole tube filled with a cloud of black matter while a yellow sulfur-like substance deposited at the bottom. Each of these substances was found to contain part of the mercury, which confined the gas. The volume of the air had increased somehow, but now, instead of being all absorbed by water (as CO<sub>2</sub> is), about a fifth of it was insoluble in this liquid. Gaspard Monge (1746-1818) repeated the experience in order to determine the nature of the gas present in the final elastic fluid, and if possible, the change that had taken place as the result of the electrical discharge. In his experiments the gas was enclosed in an inverted bowl, sealed at the bottom by mercury, and having two iron electrodes to produce the electrical sparks (Monge, 1788). Monge found that the electrical sparking not only produced the increase in volume observed by others, but also that the increase continued during a considerable time after the electrical excitation had been stopped (even for several days). In addition, the surface of the mercury became covered with a black powder that adhered to the walls, and was accompanied by corrosion of the electrodes. The resulting gas was found to be a mixture of two gases, one soluble in water and in caustic alkali, the other not. According to Monge, the insoluble fraction was highly inflammable air because it could be made to explode with dephlogisticated air (oxygen) by means of the electric spark produced with a gold exciter.

In addition, no reaction was observed when this gas was contacted with sulfur liver (potassium carbonate heated with sulfur), proving that it did not contain dephlogisticated air (oxygen). In other words, the calcination (corrosion) of the metal produced two opposing effects. On the one hand, it deprived the  $\text{CO}_2$  of the water it contained (reduction in volume) and on the other it restituted the inflammable gas (capable of a substantial expansion), increasing the total volume of the gas (Monge, 1788).

Saussure decided to carry on further experimentation in order to clarify the results of Priestley and Monge (Saussure, 1802). To a glass flask, enclosed by mercury, he added 13 in<sup>3</sup> of pure and dry  $\text{CO}_2$  and then submitted it for 18 hours, to the action of an electric spark generated by two copper electrodes. At the end, he found a substantial amount of the black oxide of mercury described by Priestley, that the electrodes were not sensibly oxidized, and that the initial volume had increased by no more than 0.1 in<sup>3</sup>. Treatment of the gas with KOH resulted in the absorption of 1 in<sup>3</sup>, obviously  $\text{CO}_2$ . The residue was found to be CO and not hydrogen because burning 100 volumes of it with about 1/3 its volume of oxygen yielded a gas containing 77 parts of  $\text{CO}_2$  and no water. Saussure explained the initial expansion by the difference in density of  $\text{CO}_2$  and CO, and concluded that the change provoked by the electrical spark did not arise from the decomposition of the water but from the decomposition of the  $\text{CO}_2$  into CO, caused by reaction between  $\text{CO}_2$  and the metal (Saussure, 1802).

It was long assumed that  $\text{CO}_2$  could be decomposed by hydrogen, but no one had succeeding in proving it. Saussure noticed that an equal mixture of the two gases, contained by mercury, and left to itself for one year, showed a very small decrease in volume. In order to accelerate the possible reaction, he repeated the above experiment using a mixture of 4 parts of  $\text{CO}_2$  and 3 of hydrogen, this time sparking it for 12 hours between two iron electrodes. A condensation took place, very rapid at first and very slight towards the end. As a result, very fine drops of water were deposited on the upper part of the tube. The resulting gas was treated with KOH to remove the undecomposed  $\text{CO}_2$ , and the remainder proven to be almost pure CO. The metallic conductors were not oxidized, and the mercury non-altered. According to Saussure, these results indicated that the hydrogen appeared to combine with part of the oxygen of the  $\text{CO}_2$  to form the water that was condensed, while the  $\text{CO}_2$  passed to the state of CO (Saussure, 1802). Further experiments by Charles-Bernard Desormes (1777-1862) and Nicolas Clément (1779-1842) showed that hydrogen was able to effect the complete deoxygenation of  $\text{CO}_2$  without sensibly passing into the intermediate state of CO (Desormes & Clément, 1802).

### *Eudiometry*

One common method used for the analysis of gases was Volta's eudiometer. In it, the gas or mixture of the gases to be examined was put in contact with a certain solid, gas, or fluid substance and the whole ignited by an electrical spark. The substance combined with the oxygen and left the other gases unchanged. Some the substances used were hydrogen, spongy platinum, a mixture of sulfur and iron filings, a solution of potassium sulfide, a piece of phosphorus, a solution of iron sulfate impregnated with nitric oxide, etc.

According to Saussure, it was known that leaden shot, moistened with water and agitated with common air, absorbed oxygen from the latter, at room temperature. This property, which had not before used for any practical purpose, suggested a new method by which the amount of oxygen in the air could be determined within 1/1000, while offering many

advantages over the eudiometers in common use. The process required about three hours agitation for its completion (Saussure, 1802).

The basic equipment consisted of a round glass flask of capacity 150 to 250 cm<sup>3</sup>, provided with a stopcock at its entrance. A known quantity of air was introduced into the flask together with moist very small shot (88 pieces per gram); the stopcock was closed and the whole setup shaken during three hours. The quantity of water added to the dry shot should be about 1/17th of its weight; a larger amount produced foam, which complicated the determination of the residual gas. The end of the process was signaled by the grayish tint assumed by the mixture of shots with the yellow oxide of lead, an indication that all the oxygen had disappeared. The flask was now weighed using a balance sensible to 1/100th the weight of flask, and the residual gas measured under water. With careful operation this process was highly precise because it determined the proportion of the oxygen in the gas analyzed, not by the diminution of the volume of the gases, but by the increase of weight in the small shot (Saussure, 1802).

Saussure remarked that using the Volta eudiometer to determine the amount of oxygen by the combustion of hydrogen led to uncertain results because of impurities present in the latter, as well as reaction of part of the nitrogen. This disadvantage was shown by the disparity of the results reported by several scientists about the amount of oxygen in the atmosphere. For example, Alexander von Humboldt (1769-1859) and Joseph-Louis Gay-Lussac (1778-1850) believed it was 21%; Dalton 20.7% or 20.8%, Henry 20% or 21%, while Thomas Thompson (1773-1852) thought it was 20%. The chief difference between these results appeared to depend on the different doses of hydrogen used to detonate with the atmospheric air; some had used a 1:1 ratio, others 1:0.5. Saussure believed that using a mixture of two parts of air with one part of hydrogen had the advantage of extending significantly the use of Volta's eudiometer, particularly for the analysis of impure airs such as those present in experiments on respiration and fermentation. On the one hand, 100 parts of vitiated air, containing 88 parts of nitrogen and 12 of oxygen, could be analyzed by a single detonation with 50 parts of hydrogen; on the other hand, 100 parts of air containing 84 parts of nitrogen and 16 oxygen, could not be inflamed by the electric spark, even when adding 100 parts of hydrogen. Addition of air, previous to its analysis, only complicated the operations because it required a separate analysis of the latter to ascertain its purity, thus decreasing the overall accuracy. The method by oxidizing lead introduced no new gaseous ingredient into the air inspected (Saussure, 1802).

Use of the phosphorus eudiometer had the disadvantage of leaving a residue contaminated by the vapors of phosphorus, by phosphine, and pure hydrogen, which accompanied the latter. These gases were produced, not by the phosphorus, but by the continued contact of water with oxide of phosphorus. Although these defects could be corrected by washing the residual gas with a solution of KOH, still they did not allow obtaining any greater degree of certainty than to fix the proportion of oxygen in common air between 20 and 21%. The lead eudiometric determination was certainly more accurate because instead of measuring the absorption of oxygen by its volume, it did it by determining the increase in weight of the metal caused by its oxidation (Saussure, 1802).

Saussure understood that lead in contact with air and water, also absorbed CO<sub>2</sub>. The lead eudiometric method indicated that atmospheric air contained 21.05%; since the mean CO<sub>2</sub> content of air was 4/10,000, deducting this value indicated that the oxygen content

was 21.01. Similar calculations yielded 20.903 parts of oxygen in air at an elevation of 10,000 feet above sea level, while air collected in a crowded ballroom at the theatre in Geneva, was found to contain 20.81% of oxygen, and 24/100 of one per cent of CO<sub>2</sub> (Saussure, 1802).

## REFERENCES

- Browne, C. A. (1944). A Source Book of Agricultural Chemistry. *Botan.*, 8, 192-204.
- Dalton, J. (1803). On the Absorption of Gases by Water and other Liquids. *Manchester Phil. Soc. Mem.*, 1, 271-287.
- Desormes, C. B. & Clément, N. (1802). D'Expériences faits au Laboratoire du C.<sup>en</sup> Guyton à l'École Polytechnique sur l'Oxide de Carbone Gazeux. *J. Écol. Polytech.* (Cahier 11<sup>e</sup>).
- Henry, W. (1803). Experiments on the Quantity of Gases Absorbed by Water, at Different Temperatures, and Under Different Pressures, *Phil. Trans.*, 93, 29-42.
- Kirchhoff, G. S. (1811). Über Zucker und Syrop ans Kartoffelmehle Getreide und Andere. *Bull. Neu. Wissen. Natur.*, 10, 88-92.
- Macaire, J. F. (1845). Notice sur la Vie et les Ecrits de Théodore de Saussure, *Bib. Univ. Genève*, 57, 102-139.
- Monge, G. (1788). Action des Étincelles Électriques sur l'Air Fixe. *Hist. Acad. Roy. Sci.*, 430-439 (published 1788). An extract appeared in *Obs. Phys.*, 28, 275-280.
- Morton, A. G. (1981). *History of Botanical Science*. Academic Press, London.
- Saussure, H. B. (1774a). *Projet de Réforme pour le Collège de Genève*, Genève.
- Saussure, H. B. (1774b). *Eclaircissements sur le Projet de Réforme pour le Collège de Genève*, Pellet, Genève.
- Saussure, N. T. (1797). Essai sur Cette Question: La Formation de l'Acide Carbonique est-elle Essentielle a la Végétation? *Ann. Chim.*, 24, 135-149, 227-228, 336-337.
- Saussure, N. T. (1800). De l'Influence du Sol sur quelques Parties Constituanes des Végétaux. *J Phys.*, 51, 9-40.
- Saussure, N. T. (1801). Recherches sur l'Alumine, *J. Phys.*, 52, 280-296.
- Saussure, N. T. (1802). Observations sur le Changement qu'Éprouve le Gaz Carbonique par l'Étincelle et sur la Décomposition du Même Gaz par le Gaz Hydrogène. *J. Mines*, 12, 103-109.
- Saussure, N. T. (1804). *Recherches Chimiques Sur la Végétation*, Nyon, Paris, 1804; *Ann. Chim.* [2], 1, 225-244.

Saussure, N. T. (1807). Mémoire sur la Composition de l'Alcool et de l'Éther Sulfurique. *J. Phys.*, 61, 316-354.

Saussure, N. T. (1808). Sur le Phosphore que les Graines Fournissent par la Distillation et sur la Décomposition des Phosphates Alcalins par le Carbone. *Ann. Chim.*, 65, 189-201.

Saussure, N. T. (1809). Sur la Combustion de Plusieurs Espèces de Charbon et sur le Gaz Hydrogène. *Ann. Chim.*, 71, 254-324.

Saussure, N. T. (1811). Analyse du Gaz Olefiant. *Ann. Chim.* [1], 8, 57-68.

Saussure, N. T. (1812). Observations sur l'Absorption des Gaz par Différents Corps. *Bib. Brit.*, 49, 299-340.

Saussure, N. T. (1813). Nouvelles Observations sur la Composition de l'Alcool et de l'Éther Sulfurique. *Bib. Brit.*, 54, 321-351.

Saussure, N. T. (1814). Sur la Conversion de l'Amidon en Matière Sucrée. *Bib. Brit.*, 36, 333-353.

Saussure, N. T. (1816a). Notes sur les Variations du Gaz Acide Carbonique dans l'Atmosphère en Hiver et en Été, *Bib. Univ.*, 1, 124-134, 1816a; *Ann. Chim.* [2], 2, 199-206.

Saussure, N. T. (1816b). Réponse aux Objections Faites à mes "Observations sur les Variations du Gaz Acide Carbonique dans l'Air". *Ann. Chim.* [2], 3, 170-176.

Saussure, N. T. (1817a). Recherches sur la Composition et les Propriétés de Naphte d'Amiano, *Bib. Univ.*, 4, 116-132.

Saussure, N. T. (1817b). Procède pour Dépouillé le Pétrole de Travers et quelques autres Huiles Minérales de leur Mauvaise Odeur. *Bib. Univ.*, 4, 116-132.

Saussure, N. T. (1819). Observations sur la Décomposition de l'Amidon a la Température Atmosphérique par l'Action de l'Air et de l'Eau. *Ann. Chim.* [2], 11, 379-408.

Saussure, N. T. (1820). Observations sur la Combinaison de l'Essence de Citron avec l'Acide Muriatique et sur quelques Substances Huileuses. *Ann. Chim.* [2], 13, 259-264, 337-362.

Saussure, N. T. (1821). De l'Influence des Fruits Verts sur l'Air avant leur Maturité, *Mém. Soc. Phys. Hist. Nat. Genève*, 1, 245-287.

Saussure, N. T. (1822). De l'Action des Fleurs sur l'Air, et de leur Chaleur Propre. *Ann. Chim.*, 21, 279-304.

Saussure, N. T. (1826). De l'Influence du Dessèchement sur la Germination de Plusieurs Graines Alimentaires. *Mém. Soc. Phys. Hist. Nat. Genève*, 3; 1- 28.

Saussure, N. T. (1828). Sur les Variations de l'Acide Carbonique Atmosphérique. *Mém. Soc. Phys. Hist. Nat. Genève*, 4, 407-478.

Saussure, N. T. (1832). Sur l'Action des Huiles sur le Gaz Oxygène à la Température Atmosphérique. *Mém. Soc. Phys. Hist. Nat. Genève*, 5, 303-320.

Saussure, N. T. (1833a). De la Formation du Sucre dans la Germination du Froment. *Mém. Soc. Phys. Hist. Nat. Genève*, 6; 237-256.

Saussure, N. T. (1833b). De l'Altération de l'Air par la Germination et par la Fermentation. *Mém. Soc. Phys. Hist. Nat. Genève*, 6, 545-582.

Saussure, N. T. (1836). Emploi du Plomb pour l'Eudiométrie. *Ann. Chim.*, 62, 219-221.

Saussure, N. T. (1839). De l'Action de la Fermentation sur le Mélange des Gaz Oxygène et Hydrogène. *Mém. Soc. Phys. Hist. Nat. Genève*, 8, 163-190.

Saussure, N. T. (1841a). Faits Relatifs a la Fermentation Vineuses. *Bib. Univ.*, 32, 180-184.

Saussure, N. T. (1841b). Sur la Nutrition des Végétaux. *Bib. Univ.*, 36; 340- 355.

Saussure, N. T. (1841c). Sur la Germination des Graines Oléagineuses. *Bib. Univ.*, 40, 368-371.