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REVIEW ARTICLE

Samuel Baup: Contributions about iodine, alkaloids, and vegetable substances

Samuel Baup: contribuciones sobre yodo, alcaloides y sustancias vegetales

Jaime Wisniak[a]

[a] Department of Chemical Engineering, Ben-Gurion University of the Negev, Israel. wisniak@exchange.bgu.ac.il

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Abstract

Samuel Baup (1791-1862), a Swiss pharmacist, understood the medical importance of iodine and its derivatives and prepared, for the first time, iodized potassium iodide starting from the reaction of iodine with iron. The resulting iodized iodine was then reacted with potassium carbonate or bicarbonate. His work on alkaloids led to the description of the properties of quinine supersulfate, the synthesis and properties of cinchona supersulfate, quinic acid, and a large number of new quinates and aconitates. Baup separated and identified the acids produced by the pyrolysis of citric acid and those present in rosin, and demonstrated the existence of several sulfates of cinchona and quinine. The pyrolysis of citric acid led to the synthesis of the new acid, citricic acid. He also extracted a variety of new substances from plants, for example, abietic and pinic acids from rosin, breine from the resin of Parkinsonia praecox, solanine from potatoes, and elemin from the resin of Amyris elemifera. He also carried extensive work on the determination of better values of the atomic mass of a variety of elements, particularly carbon, calcium and gold, and the molecular mass of important compounds such as water, carbon monoxide, and carbon dioxide.

Keywords: abietic acid, alkaloids; atomic mass; cinchona; citric acid; iodine

Resumen

Samuel Baup (1791-1862) fue un farmacéutico suizo que comprendió la importancia médica del yodo y sus derivados, y preparó por primera el yoduro de potasio yodurado, mediante la reacción entre el yodo y el hierro. El producto, yodo yodurado, fue tratado con carbonato o bicarbonato de potasio. Su trabajo con alcaloides lo llevó a determinar las propiedades del super sulfato de quinina, la síntesis y propiedades del super sulfato de cinchona, el ácido quínico, y un gran número de nuevos quinatos y aconitatos. Baup separó e identificó los ácidos producidos por la pirolisis del ácido cítrico y los presentes en la colofonia. La pirolisis del ácido cítrico condujo a la síntesis de un nuevo ácido, el ácido cítrico. También extrajo de las plantas un número de substancias nuevas, por ejemplo, los ácidos abiético y pínico de la colofonia, la breína de la resina de *Parkinsonia praecox*, la solanina de las papas y la elemina de la resina de *Amyris elemifera*. Baup trabajó activamente en la determinación de valores más exactos de la masa atómica de varios elementos, en particular, el carbón, calcio y oro, así como la masa molecular de compuestos importantes como agua, dióxido de carbón, y monóxido de carbón.

Palabras clave: ácido abiético, ácido cítrico; alcaloides; cinchona; masa atómica; yodo

Life and career (Roux, 1862; Robert, 1893)

Samuel Baup (Figure 1) was born in Vevey (canton of Vaud, Switzerland) on May 15, 1791, the son of Peter Andreas Ludwig Baup (1758-1824) and Johanna Henriette Dorothea Paschoud (1768-1812). His father, a pharmacist, belonged to one of the many French protestant families forced to leave France after the revocation of the Edict of Nantes in 1685. Samuel took his first basic studies at the college of Vevey but in 1804 his father moved him to the prestigious Snell boarding school in Nyon. In 1805, at the age of 15, Samuel transferred to Berne to begin a three-year pharmacy apprenticeship under Karl Friedrich Morell, a pharmacist well known for his analysis of minerals. At the end of this period he moved to Strasbourg to continue his preparation under Nestler, a pharmacist and professor of botany. His education was completed with additional stays at several other pharmacies, mainly in Strasbourg and Frankfort. In 1812 he was awarded the degree of maître en pharmacie, after passing with flying colors the final examination given by the Conseil de Santé of Lausanne. A year later he went to Paris where he took the courses of Antoine Louis Brongniart (1742-1804) (mineralogy), Louis-Jacques Thenard (1777-1857 (chemistry), Joseph-Louis Gay-Lussac (1778-1850) (physics), and René Just Haüy (1743-1822) (crystallography). At the end of 1813 he returned to Vevey to take over the pharmacy of his father. In spite of his heavy work at the pharmacy he found the time to visit Paris and London were he took additional courses. In 1823 he transferred the pharmacy to his younger brother in order to dedicate all his time to chemical research and public work. In 1836 the Conseil d'Etat requested from him to take over the management of the salt works of Bex, a position he kept until 1845. In this position he carried up significant improvements in the extraction process and the yield of the same. While in Bex he married Maria Sophia Schauffelberger (1801-1870). In 1861 was he appointed head of the gunpowder factory of Le Vaux. Baup passed away on February 9, 1862, victim of an attack of apoplexy (Roux, 1862; Robert, 1893).

Baup was corresponding member of several scientific and professional organizations, among them: Société Ducale de Minéralogie de Jena (1811), Société de Wettéravie de Hanau (1812), Société de Pharmacie de Paris (1814), Société Helvétique des Sciences Naturelles (1816) (one of it's four founders), Société Helvétique d'Utilité Publique (1830), and Cercle Pharmaceutique du Haut-Rhin (1842) (Roux, 1862; Robert, 1893).

Scientific contribution

Baup wrote about 45 papers on the subjects of inorganic, industrial, and organic chemistry, natural products, alkaloids, and atomic masses. In addition to the subjects described below he also designed a compression engine to substitute the Newmann blowtorch (1817a); he studied the manufacture of acetic acid (Baup, 1817b); discovered the presence of two new dyes (albomirine and commorine) in the bark of old fustic (*Morus tinctoria*) (Baup, 1830); carried on the analysis of mineral waters (Baup, 1835); demonstrated the presence of boric acid in the mother liquor of the Bex salt springs (Baup, 1853); studied the alterations of wine (Baup, 1855) and the preparation and properties of the cyanides of silver and alkaline metals (Baup, 1858); etc.

Iodine and derivatives

Baup wrote that the medical use of iodides (particularly potassium iodide) had become very frequent as a consequence of the many accidents caused by an excessive or wrong use of the alcoholic solution of iodine (Baup, 1821a), a tincture introduced in 1820 by the Swiss physician Jean-François Coindet (1774-1834) for the treatment of goiter (Coindet, 1820). This preparation contained 1/40 parts of iodine for one of alcohol. According to Pierre Jean Robiquet (1780-1840), only two procedures were available for the preparation of potassium iodide: saturation of KOH with HI, and dissolution of iodine in KOH (Robiquet, 1822). The first procedure was expensive and little practical: an aqueous solution of iodine was treated with a stream of hydrogen sulfide to convert the iodine into HI and the resulting liquid was neutralized with KOH. The second method always produced a mixture of potassium iodide and iodate, a byproduct easily separated because of its low solubility, or by heating to convert it into iodide. Unfortunately, heat transformed part of the iodate into iodine (Robiquet, 1822).

Robiquet's paper prompted Baup to publish in a French journal the new procedure he had proposed a year before for manufacturing of potassium iodide and its derivatives. This method was based on the action of iodine upon iron (Baup, 1823): A mixture of one part of iodine and three to four parts of water was put in a matrass and then one-third part of pure iron fillings were added in small portions, shaking the vessel each time. An immediate and highly exothermic reaction followed, the iodine disappeared and the liquid turned dark red. An iodized iodide was formed, which upon slight heating turned into iron iodide. The heating was continued until the liquid became colorless. The liquid was filtered, diluted with water, heated to boiling over a sand bath, and then mixed with a solution of potassium bicarbonate or carbonate until all the iron was precipitated as its oxide. The last operation was done carefully to avoid adding an excess of the carbonate. The latter could be eliminated by successive crystallizations or by addition of a little of HI. The precipitate was eliminated by filtration and thoroughly washed. The whole liquid was then evaporated in a sand bath at a low heat until all the solute had crystallized. The crystals formed were purified by successive recrystallization and finally dried. Potassium iodide appeared as cubic opaque or milky crystals, soluble in cold water or cold alcohol and more in hot water or hot alcohol. According to Baup, a supersaturated solution containing 100 parts of water and 221 of potassium iodide boiled at 120 °C (710 mmHg). Pure potassium iodide was not deliquescent even when heated in the presence of air. Anhydrous potassium iodide dissolved in water with a significant decrease in temperature (more than 24 °C) (Baup, 1823).

Baup reported that an aqueous solution of potassium iodide was able to combine with an amount of iodine equal to the amount of iodine present in the KI, forming an *iodized potassium iodide*. The heat released by this reaction was inversely proportional to the amount of water employed (Baup, 1821b, 1823). The iodides of sodium, ammonia, and other bases could be prepared by the same procedure. Baup found that zinc iodide was also able to combine with iodine in the amount of the iodide contained by the salt. From this result he concluded that that iodized iodides contained two atoms of iodine per atom of the base (Baup, 1821b, 1823). Baup also proposed that a solution made of two parts of potassium iodide, one of iodine, and 27 of water, be used for medical uses (Baup, 1821b).

In 1822 Amédée Cailliot (1805-1844) published a memoir describing the preparation of potassium iodide by a slight modification of Baup's method, without mentioning Baup's name, a curious fact considering that Baup's paper had been published in French. In Cailliot's words "potassium iodide was easily prepared by mixing four parts of iodine, two of iron filings, and 20 of water until the solution, initially having a strong brown color, became colorless. The liquor was then put in a glass or porcelain vessel and heated to boiling. At this point a solution of pure potassium bicarbonate was slowly added until no precipitate was formed, or mixed with a slight excess of potassium carbonate saturated with HI. The resulting solution was filtered and the precipitate washed with water until the wash showed no reaction with mercuric chloride. The filtrate was combined with all the washes and slowly evaporated to dryness. The same procedure could be used to prepare the iodides of sodium, magnesium, calcium, barium, and strontium. The iodides of mercury could be prepared by reacting mercurous nitrate (or mercuric chloride) with the solution of ferric iodide (Cailliot, 1822, 1823)".

Alkaloids and derivatives

Baup found that quinine was able to combine with sulfuric acid in two different proportions, one yielding the neutral salt described by Pierre-Joseph Pelletier (1788-1842) and Joseph Bienaimé Caventou (1795-1877) (Pelletier and Caventou, 1820), and the other, containing an excess of acid. Since quinine sulfate was a valuable medicine, it was important to determine its properties and composition (Baup, 1821a). Pelletier and Caventou had given a detailed description of the neutral sulfate; Baup added that at 12.5 °C one part of this sulfate dissolved in 740 parts of water and at 100 °C the solubility increased to one part in 30 of water. In addition, this salt effloresced in air at room temperature and stayed in that state until the water of crystallization had decreased to 2 to 3% of its original value.

When highly pure, the supersulfate appeared as white quadrangular prismatic crystals, soluble in cold water (12.5 °C) in the ratio 11 parts per part of water. The crystals melted at 100 °C in their water of crystallization, and were very soluble in diluted alcohol and a little less in absolute alcohol. The salt remained stable in air at room temperature but effloresced in contact with dry air, losing about 20% of its water content. Chemical analysis of the supersulfate showed that it contained double the amount of acid and quadruple the amount of water present in the neutral sulfate (Baup, 1821a).

In a following paper Baup extended the results to cinchona (Baup, 1824), mentioning that Pelletier and Caventou had reported that sulfuric acid did not seem to form a supersulfate with cinchona; the crystals obtained from a solution of cinchona in an excess or sulfuric acid were not substantially different from those precipitated from a neutral solution and they could be deprived of their excess of sulfuric acid by successive crystallizations (Pelletier and Caventou, 1820). Baup's experiences showed that this statement was wrong; the supersulfate was a physical reality. This derivative converted into the neutral sulfate when exposed to ammonia vapors or if dissolved in water containing earthy carbonates. According to Baup, the supersulfate could be prepared by adding sulfuric acid to the neutral sulfate, followed by evaporation of the solution until a pellicle formed, and then letting the solution to crystallize. The crystallization was very slow when the sulfuric acid was not sufficiently pure or when it was added in great excess. In this situation the resulting crystals were very small and fragile and should be recrystallized; if they did dissolve in their weight of cold water, was a proof that neutral sulfate was present. More sulfuric acid should be added to complete the conversion to supersulfate (Baup, 1824).

Cinchona supersulfate crystallized as colorless rhomboidal octahedral crystals, always imperfect and readily cleaving perpendicularly to the larger axis. They were unaltered at common temperatures in the air but readily efflorescing if the temperature was slightly raised; at 14 °C they were soluble in 0.46 parts of water, 0.9 parts of alcohol of relative density 0.85, or one part of absolute alcohol. Ether did not dissolve it (Baup, 1824). The neutral sulfate of cinchona crystallized as short rhomboidal prisms of 83° and 97°, cleaving parallel to the planes of the prism; they were soluble in 6.5 parts of alcohol of relative density 0.85, 11.5 parts of absolute alcohol, or in 54 parts of water (all at 13 °C). Baup reported that 100 part of cinchona combined with 13.201 parts of sulfuric acid, indicating that its molecular mass was 38.488 (assuming oxygen = 1) (cinchona is actually a mixture of alkaloids, including cinchotannic, quinic, and quinovic acids) (Baup, 1824).

Baup determined the amount of water of crystallization present in cinchona sulfate by heating it in a stove at 120 °C until no further diminution of weight took place (4.67% of the neutral crystalline sulfate). The content of sulfuric acid was determined by precipitation with barium chloride from a solution of the sulfate in diluted acetic acid (added to facilitate dissolution), and the cinchona by the deficiency. These results indicated that the "atomic mass" of cinchona was 38.689 (again assuming oxygen =1), not so different from the value 38.488 reported by Pelletier and Caventou, and corresponding to the compositions (Baup, 1824):

Table 1. Molecular mass of cinchona

Molecular mass of cinchona according to its physical state			
Neutral sulfate			
		Physical state	Physical state
Number of atoms		Crystallized, %	Dry , %
1 cinchona =	59	84.324	88.636
1 sulfuric acid =	5	10.811	11.364
2 water =	2.25	4.865	
Supersulfate			
Number of atoms			
1 cinchona =	39	67.241	79.592
2 sulfuric acid =	10	17.241	20.408
8 water =	9	15.518	

Baup confirmed the result of Robique (Robiquet, 1821) that quinine formed with sulfuric acid a neutral sulfate and a supersulfate (Baup, 1824). The neutral salt readily effloresced in the air, three-fourths of the water passing off and one-fourth remaining; it was soluble in 740 parts of water at 13 °C and in 30 parts at 100 °C. Alcohol of specific gravity 0.85 dissolved 1/60 part at room temperature and in much greater proportion at the boiling heat. The pure supersulfate was colorless and unaltered in the air at room temperatures. It crystallized in rectangular prisms, cleaving parallel to the planes of the prism. The crystals obtained at lower temperatures were small and acicular, but spontaneous evaporation yielded them of a large size. It was soluble in 11 parts of water at 13 °C and in 8 parts at 22 °C. It melted in its water of crystallization at 100 °C and was soluble in absolute and in aqueous alcohol. The solution in absolute alcohol precipitated the salt in a powdery state on exposure to air. Baup put some of the crystals still wet upon filtering paper and noted that they effloresced of 20 °C until they lost three-fourths of its water; the other fourth was eliminated when dried in a stove. The dry sulfate exposed to the air resumed the fourth it had lost in the stove.

Pelletier and Caventou had reported that the atomic mass of quinine was 45.906 (Pelletier and Caventou, 1820). The experiments of Baup led him to adopt the value 45 for quinine, corresponding to the following compositions (Baup, 1824):

Table 2. Molecular mass of quinine.

Supersulfate		**Physical state** **Crystallized, %**	**Physical state** **Dry, %**
Number of atoms			
1 quinine =	45	61.644	81.819
2 sulfuric acid =	10	13.698	18.181
16 water =	18	24.658	
Neutral sulfate			
1 quinine =	45	76.272	90
1 sulfuric acid =	10	8.474	10
8 water =	9	15,254	
Neutral sulfate effloresced			
1 quinine =	45	86.12	
1 sulfuric acid =	10	9.57	
8 water =	9	4.31	

The above tables showed that the amount of acid contained in the supersulfate of cinchona and quinine was twice that of their neutral salts.

Baup also remarked that in medicine the same doses of neutral quinine sulfate, which after having been merely dried in a cool damp place was preserved in a well-closed bottle, or of the same sulfate kept in a badly closed bottle or in the air, should in no case be employed indifferently. In the first case the salt would contain only 76% quinine, while in the latter it could rise as high as 86%. He considered that constancy would be most readily ensured by the use of the effloresced salt, as it was always of definite and invariable composition (Baup, 1824). According to Baup quinic acid was known for some time as a particular acid (Baup, 1832). Étienne Ossian Henry (1798-1873) and August Arthur Plisson (?-1832) had been the first to report its composition, by weight, as 34.4320% carbon, 5.5602% hydrogen, and 60.0078%, represented by 2 atoms of carbon, 4 of hydrogen, and 3 of oxygen, according to carbon = 6, hydrogen = 1, and oxygen = 8 (Henry and Plisson, 1829). Afterwards, Justus von Liebig (1803-1883) had reported a corrected analysis: 49.193% carbon, 6.101% hydrogen, and 47.706% oxygen, corresponding to 15 atoms of carbon, 24 of hydrogen, and 12 of oxygen (Liebig, 1831).

Baup prepared quinic acid by decomposing highly pure calcium quinate with sulfuric acid (6.2 parts of quinic acid per one part of sulfuric acid, and enough water) followed by evaporation to syrup and completing the process by evaporation in a stove or in air. He remarked the importance of avoiding the use of alcohol for separating the last portions of calcium sulfate because it formed with quinic acid an almost non-crystallizable combination. The resulting material was purified by repeated crystallizations. Chemical analysis of the final purified acid indicated that it contained, by weight, 50.000% carbon, 5.556% hydrogen, and 44.444% oxygen, corresponding to 15 atoms of carbon, 20 of hydrogen, and 10 of oxygen, or 50 of carbon and 50 of water, and atomic mass 180 (the actual composition is 43.75% carbon, 6.30% hydrogen, and 49.95% oxygen, corresponding to the formula $C_7H_{12}O_6$). Baup remarked that quinic acid was equivalent to a compound of equal weights of carbon and water, agreeing exactly with Joseph-Louis Proust's (1754-1826) analysis of lignin; therefore, quinic acid and lignin should be considered isomeric bodies, though their properties were singularly different. Crystallized quinic acid was not anhydrous; it contained one "atom" of water, which did not enter into the composition of the dried quinate (Baup, 1832).

Baup described the preparation and properties of a series of quinates: *sodium quinate* could be easily prepared by saturating sodium carbonate with quinic acid, pure or crystallized, and exposing the solution to spontaneous evaporation. This salt was not bitter when pure; it dissolved in half its weight of water at 15 °C and it contained four molecules of water. Baup was unable to obtain in crystallized form the quinate of potassium or ammonium, either neutral or acid; *calcium quinat*e was a natural salt present in several species of quinquinas; it was unalterable by exposure to the air and crystallized in rhombic laminae of about 78° and 112°. It contained, by weight, 60.403% of acid, 9.396% of lime, and 30.201% of water. Calcium quinate dissolved in 6 parts of water at 16 °C and its solubility was greatly dependent upon temperature; *strontium quinate* seemed to be isomorphous with calcium quinate. This salt contained, by weight, 55.911% of acid, 16.140% of strontium oxide, and 27.950% of water. It effloresced quickly by exposure to the air and was soluble in two parts of water at 12 °C; *barium quin*ate could be prepared by reacting barium carbonate with the acid; it crystallized in acute triangular dodecahedrons, which did not effloresce by exposure to the air. Chemical analysis indicated it contained, by weight, 58.064% of acid, 24.516% of barium oxide, and 17.420% of water; and *copper quinate* was actually present as two distinct salts, a biquinate and a sub-quinate. The former was prepared by reacting a solution of quinic acid with cupric carbonate or oxide, taking care that the acid be present in excess. A cold aqueous solution of the biquinate was unstable; this effect was accelerated by heat. Copper biquinate appeared as pale blue acicular crystals; it effloresced in the air and lost 2/5ths of its water of crystallization. It dissolved in about 3 parts of water at ordinary temperatures. Chemical analysis indicated that it contained, by weight, 67.925% of acid, 15.094% of cupric oxide, and 16.981% of water. The sub-quinate could be prepared by heating a weak solution of quinic acid with an excess of cupric carbonate or oxide, or by the double decomposition of a quinate with the acetate, but not with cupric sulfate or nitrate. This salt appeared as very small fine green brilliant crystals, which did not alter in the air. It was soluble in from 1,150 to 1,200 parts of water at 15 °C. Boiling water dissolved a larger quantity, which crystallized on and after cooling. Chemical analysis indicated that it contained, by weight, 57.931% acid, 27.586% of cupric oxide, and 14.483% of water (Baup, 1832).

In the same manner, *lead quinate* crystallized only when the solution was so concentrated that it was difficult to detach the precipitated acicular crystals. Chemical analysis indicated that it contained, by weight, 58.065% of acid, 36.128% of oxide, and 5.807% of water. The sub-quinate could be prepared by mixing a solution of sodium or ammonium quinate with lead sub-acetate. This salt had a great tendency to combine with CO_2 by mere exposure to the air; a solution of *silver quinate*, evaporated in the dark with a very gentle heat, or at common temperatures under the receiver of the air pump, gave in both cases a very white anhydrous salt, of a spherical or mammillated form. Upon heating it soon fused, swelled, and left (after giving abundant white vapors) silver in the metallic state. Chemical analysis indicated that it contained, by weight, 60.811% of acid and 39.189% of silver oxide, obviously an atom of each; *cinchona quinate* was soluble in half its weight of water at about 15 °C. It contained four "atoms" of water of crystallization and was partially decomposed by alcohol; and *quinine quinate* also contained four atoms of water of crystallization. It was soluble in 3.4 parts of water at 11 °C, and in 8.88 parts of alcohol at the same temperature (Baup, 1832).

Citric acid derivatives

Baup reported that the pyrolysis of citric acid was not as simple as reported in the literature (i.e. Lassaigne, 1822). In addition to pyrocitric acid, spirituous liquid, and bituminous liquid, the final product also contained a small amount of a new acid having properties quite different from those of pyrocitric acid (Baup, 1836). This acid could be prepared by evaporating at moderate heat the liquid resulting from the pyrolysis of citric acid. Upon cooling cool, the crystals of pyrocitric acid deposited were removed and the process continued until small needle-form crystals begin to make their appearance. All the crystals deposited were set apart, dissolved in water, and purified by repeated recrystallization. The separation was very easy on account of the great difference in the solubility of the two acids. Baup suggested naming *citribic acid* the pyrocitric acid of Lassaigne, and *citricic* acid the new acid he had discovered (Baup, 1836).

Citricic acid was odorless, had a strong acid taste, and crystallized from water as octahedrons consisting of two four-sided pyramids, with a rhomboidal base. The primary form was a right rhombic prism. The adjacent faces of the two pyramids of the octahedron met at angles of 136°20', while the pyramidal faces make with each other angles of 124° and 73° 15'. These crystals cleaved easily into brilliant plates, parallel to the plane passing through the obtuse pyramidal faces of the octahedron (Baup, 1836).

At 10 °C citricic acid dissolved in 17 times its weight of water, and at 20 °C, in 12 times its weight of water. The solubility increased substantially with the temperature and as a result a concentrated hot solution crystallized on cooling. At 15 °C it dissolved in 4 times its weight of alcohol of specific gravity 0.827. It was also soluble in ether. Heated up to 120 °C it did not lose its water of crystallization. At 161 °C it fused into a colorless liquid, which crystallized in plates on cooling. Just before it melted it began to release white irritating vapors having a peculiar smell and condensing into white needle-form crystals. At higher temperatures it volatized completely, without leaving a carbonaceous residue. Chemical analysis indicated that anhydrous citricic acid contained, by weight, 53.572% carbon, 3.571% hydrogen, and 42.857% of oxygen, corresponding to an atomic (molecular) mass of 7 (with C = 37.50 and oxygen = 1). The crystallized acid was a hydrate containing one equivalent of water. These results indicated that citricic acid was an isomer of pyrocitric acid. Citricic acid precipitated the acetate and sub-acetate of lead; it gave a white precipitate with the nitrates of lead, silver and mercury and a red one with ferric salts (Baup, 1836).

Baup described the preparation and properties of potassium, sodium, ammonia, barium, strontium, calcium, magnesium, lead nickel, silver, and copper citricates. For example, the neutral ammonium citricate did not crystallize; when exposed to heat or to air it gradually lost ammonia and converted into bicitricate, capable of crystallizing. There were two bicitricates differing from one another on their water of crystallization; the first was obtained when the salt was crystallized at about 20 °C or a little below, from a very concentrated solution, or that a crystal of the salt was put on the bottom of the vessel to speed the crystallization. This bicitricate crystallized as transparent tables or prisms, not altered by exposure to the air. The other ammonium bicitricate crystallized at a low temperature as long prisms, which effloresced rapidly when exposed to the air. The neutral potassium citricate did not crystallize and when evaporated to dryness, it rapidly deliquesced into a liquid if it was left exposed to the atmosphere. It was insoluble in alcohol (Baup, 1836).

Baup remarked that the present nomenclature of pyroacids was too complicated and vague. For this reason, he suggested another, which kept the index of their origin and indicated with consonants the modifications that the substance went through. These consonants were arranged alphabetically with the chronological order of the discovery of the derivatives. Thus the letter *b* indicated the first modification observed, *c*, the second, and so on (some of the additional letters were not used). For example, the first pyrotartaric acid (pyrotartrique) discovered would be named *tartribiqu*e, the second *tartricique*, and so on. The different pyrocitric acids would be named successively citribic acid, citricic acid, citridic acid, etc. (Baup, 1836). Crasso changed the names of these acids to the ones used today: citribicic acid to *citraconic acid*, citricic acid to *itaconic acid*, and citridic acid to *aconitic acid* (Crasso, 1840, 1841).

In 1851 Johann Gottlieb (1815-1875) published a first memoir about isomeric acids in which he described a new acid formed by the reaction between diluted nitric acid and citraconic acid. Gottlieb named this acid *mesaconic*. He also mentioned that concentrated nitric acid produced numerous products, which he intended to describe later (Gottlieb, 1851). Baup, who had been engaged in the study of the same reaction, reported that the reaction of citraconic acid with an aqueous solution of nitric acid (20% weight) transformed it into a new isomeric acid, and that concentrated nitric acid produced a more energetic reaction, yielding an oily liquid, which could be separated into two new substances (Baup, 1851a).

According to Gottlieb, his new acid crystallized as fine needles, which were slightly soluble in cold water and more in hot water, soluble in alcohol, and having the composition of citraconic acid. It fused at 208 °C into a colorless liquid and sublimed at a slightly higher temperature without decomposition. Its vapor was piquant and provoked coughing. Baup added the following properties: The new acid was soluble in 38 part of water at 14 °C and 29 parts at 22 °C. At the latter temperature it dissolved in 2.6 parts of alcohol of specific gravity 0.88. It was also soluble in ether. Heated over a platinum spoon it burned with a blue flame, without leaving a carbonaceous residue. Baup suggested naming the acid *citracartic acid.* This acid gave white precipitates with basic lead acetate and mercurous nitrate, and a brown flaky one with ferric chloride; neutral lead acetate furnished with it a crystalline salt. The aqueous solution of a mesaconate was precipitated by silver nitrate, cupric sulfate, and mercuric chloride. Baup reported the properties of the mesoconates of potassium, sodium ammonia, barium, calcium, and lead. Thus, for example, the neutral potassium mesaconate was deliquescent; the acid salt crystallized in micaceous laminae and was readily soluble in water and sparingly soluble in alcohol. The neutral lead mesaconate was prepared by precipitating a neutral mesaconate with lead acetate; the precipitate was at first cheesy and then became crystalline. From very dilute solutions it separated in small, short, transparent, flattened prisms. The acid lead mesaconate was deposited from the solution of the free acid when this was mixed with lead acetate. It formed prismatic crystals, which swelled when heated. The basic lead mesaconate was precipitated from a solution of the neutral salt by the addition of tribasic lead acetate of lead; the precipitate was first flocculent and then pulverulent (Baup, 1851a).

Baup also reported some of his results on the reaction of citraconic acid with concentrated nitric acid. The resulting oily substance turned, on cooling, into a yellow mass, which boiled with water released an aromatic odor resembling that of mint and communicating a sweet taste to water. Baup boiled the resulting crystalline mass with a new portion of water and afterwards extracted it with boiling alcohol of specific gravity 0.88. This simple procedure resolved the substance into two fractions of different solubility, which Baup named *eulyte* (easily soluble) and *dyslyte* (hardly soluble). Eulyte was the most soluble product; it crystallized from alcohol in white striated prisms of a silky luster; from its ethereal solution it separated in transparent shining crystals, very soluble in warm alcohol of specific gravity 0.838. The substance melted under hot water and afterwards it solidified into a laminar mass. At a higher temperature it entirely volatilized and diffused the odor of amyrin. Heated in a closed tube it gave off red fumes, which burned with a flame. It dissolved in hot concentrated sulfuric acid and a greater portion crystallized out on cooling. Dyslyle was the least soluble substance; it crystallized from the alcoholic solution in transparent, shining, small, and very fragile four-sided prisms. From ether it separated in acicular crystals. It was sparingly insoluble in water, one part requiring about 24,000 parts of water at 10 °C; it did not melt in water but in hot water it appeared to become partially crystalline. When melted, it solidified on cooling into prismatic crystals and at higher temperatures it volatilized at in acicular crystals, diffusing the odor of mint or cumin. It also dissolved in concentrated sulfuric acid (Baup, 1851a).

Atomic masses

Baup wrote that many famous chemists (among them, Dalton, Gay-Lussac, Berzelius, Richter, and Prout) had devoted much time to the determination of the atomic mass of the elements and the molecular mass of a large number of chemical compounds (Baup, 1842). In some of the original tables of atomic masses, oxygen had been taken as the relative unit, with a mass of 100 followed by three decimal points, which allowed writing atomic masses with six or seven figures. The increase in the reliability of chemical analysis had led to many modifications of the reported values. Several scientists had looked into the possibility of assigning a definite and final value to this property, assuming that the atomic masses followed simple ratios. The most famous of these had been the hypothesis of William Prout (1785-1850) where it was assumed that the atomic mass of an element was an integer multiple of the atomic mass of hydrogen (Prout's hypothesis), a hypothesis which had then been shown to be incorrect. The present state of the art showed that the values adopted for the atomic masses were not definite and fixed, they were subject to continuous modification, as the experimental techniques and methods became better and better (Baup, 1842).

Baup decided not to occupy himself with the atomic theory but with the number of *equivalents* or *proportional weights* by which the bodies combined between them. His basic assumption was that in the neutral salt of the simplest electropositive and electronegative elements, these were combined in the ratio of one equivalent, *barodose* (or *dose*), which was definitely and irrevocable fixed. In his first application, he considered the barodose of oxygen, hydrogen, and water. The proper calculations will be shown in detail to illustrate the procedure followed by Baup (Baup, 1842):

Table 3. Composition of water.

According to:	**Ratio in 100 parts**		**Ratio assuming**	
	Oxygen	**Hydrogen**	**H = 1**	**O = 1**
Lavoisier and Meunier (1875)	85	15	5.68	0.176
Fourcroy, Séguin and Vauquelin (1790)	85.66	14.34	5.98	0.167
Corrected by Gay-Lussac, Humboldt	87.41	12.59	6.94	0.155
Corrected by Biot and Arago	88.297	11.713	7.577	0.132
Berzelius (1810)	88.246	11.754	7.5077	0.1331
Berzelius and Dulong (1819)	88.941	11.059	8.0618	0.12435
Berzelius and Dulong (1820)	88.9	11	8.0076	0.12488
Recent tables			8.013	0.124796
Baradose	88.889	11.111	8	0.125

Consequently, Baup affirmed that water was constituted by (Table 4):

Table 4: Composition of water according to the reference element (oxygen or hydrogen).

	O = 1	**H = 1**	**100 parts**
Oxygen, 1 equivalent (=1 vol)	1	8	88.889
Hydrogen, 1 equivalent (= 2 vol)	0.125	1	11.111
Hence 1 dose of water was	1.125	9	100

[Baup remarked that according to the latest tables of Berzelius the double atom of hydrogen was 12.4796 and hence water was composed of 1 atom (1 vol) of oxygen and 2 of hydrogen (2 vol), so that on the basis of oxygen = 100 it contained 88.900 parts of oxygen and 11.100 of hydrogen]. Baup concluded that since the volume ratio between oxygen and hydrogen was 1:2, the ratio of specific gravities was hydrogen: oxygen = 1: 16 = 0.0615 (based on oxygen = 1.0000) (Baup, 1842). Baup went on to calculate the barodoses of carbon and carbon dioxide. He wrote that his analysis of different carbonates had shown that the value of the atomic mass of carbon reported by Berzelius (76.437) was in error and that the correct value was 75.000, as proposed by Prout and other chemists. The experiences of Jean-Baptiste André Dumas (1800-1884) and Jean Servais Stas (1813-1891) on the direct combustion of graphite and diamond in oxygen had shown that carbon joined with oxygen in ratio of 800: 300, that is, 2: 0.75 75 (Dumas and Stas, 1840). Hence carbon dioxide and carbon monoxide had the following compositions:

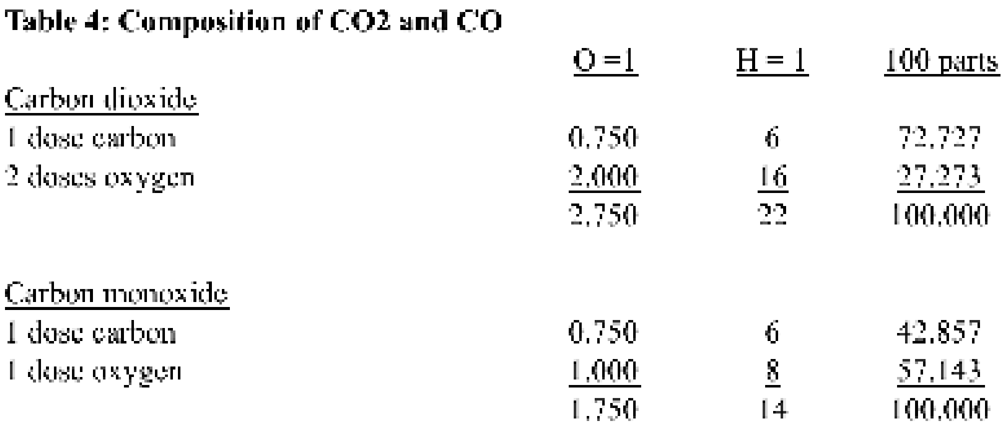

Table 4: Composition of CO2 and CO

	O =1	H = 1	100 parts
Carbon dioxide			
1 dose carbon	0.750	6	72.727
2 doses oxygen	2.000	16	27.273
	2.750	22	100.000
Carbon monoxide			
1 dose carbon	0.750	6	42.857
1 dose oxygen	1.000	8	57.143
	1.750	14	100.000

Cont. of table 4

	O =1	H = 1	100 parts
Carbon dioxide			
1 dose carbon	0.750	6	72.727
2 doses oxygen	2.000	16	27.273
	2.750	22	100.000
Carbon monoxide			
1 dose carbon	0.750	6	42.857
1 dose oxygen	1.000	8	57.143
	1.750	14	100.000

The specific gravity of CO_2 was to that of oxygen as 1.3750: 1.0000, and that of CO 0.8750: 1.0000 (Baup, 1842).

Baup added the surprising remark that he had never accepted the supposition that atmospheric air had a definite composition. Baup reported also the composition of silver citraconate, silver itaconate, silver quinate, calcium quinate, calcium bi-equisetate, calcium fumarate, calcium citraconate, calcium itaconate, and calcium aconitate. From the calcium salt he determined that the barodose of calcium was 350 on the basis of oxygen =100, and 20 for hydrogen =1. On the basis of the latter, the atomic mass of calcium was 40 (Baup, 1842). A posthumous paper by Baup reported the determination of the atomic mass of gold by the calcination of gold cyanide, a compound very easy to prepare in a very pure state. The value reported, 98.96 (base H = 1), is very close to the actual one (196.9665) (Baup, 1861).

Natural products from plants

In a letter to the editor of Annales de Chimie et Physique, Baup communicated the discovery of a series of new substances extracted from the juice of plants (Baup, 1826): (a) In the resin of the *Pinus abies* L. he found a new substance crystallizing in square plates, soluble in 7.5 parts of alcohol of density 0.880 at 14 °C, and insoluble in water. In the rosin of France, collected from *Pinus maritima* or *pinaster*, he recovered another substance, crystallizable in triangular plates, soluble in 4 parts of alcohol and insoluble in water. These two new substances reacted as acids; they combined as well with the alkalis as with the acids and formed real salts, some of which were soluble in water and alcohol, others only in ether. He named the first *abietic acid* and the second, *pinic acid*; (b) In examining the properties of potatoes Baup found they contained solanine, a peculiar alkaloid that Desfosses had discovered in 1821 in the berries of bitter sweet

(*Solanum dulcamara*) and of black nights shade (*Solanum nigrum*) (Desfosses, 1821). The tubercles contained much less than the germs, which also had a very acrid taste (Baup, 1826); (c) Baup also gave a short description of a new a new substance, *breine*, separated from the resin of the arbol-a-brea (today *Parkinsonia praecox*), a tree, not well determined, of the Island of Manila. This resin crystallized in very brilliant rhomboidal prisms, terminated on each side by a basil, soluble in about 70 parts of water and completely insoluble in water; and (d) Baup reported that the resin of the *Amyris elemifera*, L., a flowering plant of the citrus family, contained another new substance, *elemin*, similar to the one present in arbol-a-brea but differing in its greater solubility in alcohol, by its crystalline form, etc. (Baup, 1826).

In 1851 Baup reported a more detailed study of the resin extracted from the arbol-a-brea (Baup, 1851bc). The Société Vaudoise de Sciences Naturelles received a sample of the resin of arbol-a-brea that George Samuel Perrottet (1793-1870), a Swiss-born French botanist working for the Jardin de Plantes in Paris, had brought from the Philippines, and asked Baup to carry a preliminary analysis of it. In 1821 Jean-François Bonastre (1783-1856) had examined this resin and reported that it contained a soluble resin (61.3% by weight), a crystallizable sub-resin (25.0%), a volatile oil smelling like lemon (6.3%), a small amount of a bitter extract (0.5%), as well as acid material and ligneous and earthy impurities (6,4%). According to Bonastre, the resin was phosphorescent when pounded in a porcelain mortar with a glass pestle and also when treated with dilute sulfuric acid. It was more luminous than sugar and even emitted light by friction in water (Bonastre, 1824). Baup believed that the arbol-a-brea appeared to be the *Canarium album,* Raeusch. (Chinese olive tree) a source of wood and resin used for caulking ships. The resin looked like elemi resin; it was not homogeneous but consisted of translucent, gray or yellow masses, which in appearance and fracture resembled flint. Other parts had a smoky-gray or blackish color, which originated from the fact that in Manila the tree was surrounded by burning torches to accelerate the outflowing of the resin from the incisions. The resin smelled like lemon or turpentine.

Baup subjected the resin to several separation techniques (e.g. distillation, extraction with cold alcohol, pressing over paper, etc.) and obtained the following products: essential oil, *amyrin*, amorphous resin, *brein*, *bryodin*, *breidin*, and several impurities (Baup, 1851bc). The volatile oil was obtained by distillation and constituted about 7.5% by weight, of the raw material; it was lighter than water and had an agreeable odor. Extraction with cold alcohol of density 0.848 left a sub-resin almost completely soluble in boiling alcohol of density 0.815-0.833. On cooling, the sub-resin precipitated as very thin white filaments, forming magma with the alcohol. Pressing over paper separated the resin. According to Baup, this product was identical with the semi-resin of elemi and for this reason he named it *amyrin*. Amyrin melted at 174 °C into a colorless fluid, which solidified into a transparent mass; it was very soluble in ether from where it separated as brilliant silky fibers. It was completely insoluble in water and soluble in hot turpentine and almond oil and was not attacked by cold nitric acid. Upon heating with nitric acid, it swelled and released sparkling vapors; upon cooling it deposited a yellow resinous acid matter.

The material extracted with cold alcohol of density 0.848 yielded three new materials, which Baup named brein, bryodin, and breidin. The extract was steam distilled to eliminate the volatile oil and the residue remaining in the retort was further heated to eliminate the alcohol. *Brein* crystallized slowly from an alcoholic solution as rhomboidal transparent prisms exhibiting angles of 70° and 110°, completely insoluble in water, one part soluble in 70 of alcohol of density 0.850 at 20 °C, more soluble in absolute alcohol, and totally soluble in ether. It melted at 187 °C into a transparent colorless fluid and behaved like an indifferent resinous substance.

Bryodin crystallized from water as silky white crystals, having a slight bitter acid taste. On heating it released a vapor of particular odor, which on inhalation produced coughing. It melted at 135 °C into a colorless liquid. Bryodin was slightly soluble in cold water, one part in 350 of water at 10 °C, and more soluble in hot water. It was readily soluble in alcohol, ether, turpentine, and fatty oils; it dissolved in concentrated sulfuric acid yielding a red solution. Lead acetate and lead basic acetate precipitated the aqueous solutions but not so the salts of copper, silver, mercury, iron, and the gallnut tincture. *Breidin* crystallized in prisms, exhibiting angles of 102° and 78° and terminating in four-sided pyramids; one part of it dissolved in 260 parts of water at 10 °C, and more in hot water; the aqueous solution was readily precipitated by lead basic acetate. Breidin was readily soluble in alcohol and sparingly in ether. The crystals melted at a little over 100 °C and were volatile, inducing coughing like those of bryoidin (Baup, 1851bc).

The apparent great similarity between the resins from arbol-a-brea and elemi lead Baup to perform some comparative experiments between both materials. These led him to discover in elemi a new crystalline substance, which he named *elimin*. Elimin separated as small, transparent, colorless, hexahedral prisms, melting at about 200 °C and dissolving in 20 parts of alcohol of density 0.88 at room temperature. It was very soluble in alcohol and ether, and insoluble in water (Baup, 1851b,c).

In 1828 Henri Braconnot (1780-1855) reported that water horsetail (*Equisetum fluviatile*) contained a new acid, which he named *equisetic acid* (Braconnot, 1828). In 1836 Victor Regnault (1810-1878) found the same acid in water horsetail and a close variety (*Equisetum limosum*) and assumed initially that they were an isomer of maleic acid. After a detailed comparison of both acids he concluded that they were actually identical (Regnault, 1836). As mentioned above, in 1835 Baup reported the discovery of a new acid, citricic acid (itaconic acid), and in 1842 the analysis of calcium diequisetate (Baud, 1835, 1842). In 1843 Liebig stated that equisetic acid was identical with aconitic acid, isolated from *Aconicum napellus* (Liebig, 1843).

In 1850 Baup decided to study again these three acids to determine their probable relation (Baud, 1850). He precipitated the juice of *Equisetum fluviatile* (from which the chlorophyll had separated spontaneously) with lead acetate, and decomposed the greyish precipitate by means of sulfuric acid. From the resulting liquid he separated an astringent substance with gelatin and the malic acid by means of calcium carbonate. Further treatment with lead acetate and sulfuric acid, evaporation until precipitation, treatment with charcoal, and purification with ether, yielded equisetic acid in a very pure state. The acid was white and completely soluble in ether; at 12 °C it dissolved in twice its weight of alcohol of 88%. At 15 °C it dissolved in three times its weight of water and much more in boiling water. Upon cooling it separated in the form of white crusts. When slowly crystallized, it separated as transparent square tables. When heated, the acid became brown, released acid vapors and left a copious carbonaceous residue. The aqueous solution of the acid was precipitated by lead acetate and mercurous nitrate but not by silver nitrate and lead nitrate. Ferric salts produced a red color with the solution of the free acid and precipitated the solutions of its salts in red, gelatinous flakes (Baud, 1850).

Baup observed the same properties in the acid extracted from the juice of *Aconitum napellu* and in the acid (citridic acid) formed at the beginning of the decomposition of citric acid by heat, as well as on the properties of their salts. These results led him to conclude that the aconitic, equisetic, and citridic acids were one and the same acid and that they ought to be called exclusively *aconitic acid*, whatever the source from which they were separated. He believed that this decision was justified by Crasso's proposal of changing the names of citribic and citricic acids to citraconic and itaconic acids (Baup, 1850; Crasso, 1840). Baup added that aconitic acid was not identical with maleic acid: Maleic acid was volatile and aconitic acid not; they had different degrees of solubility and crystalline form, and maleic aid yielded with KOH a bi- and a quadri- salt, while aconitic acid yielded only a quadri-salt (Baup, 1850).

Baup also reported the preparation and properties of the aconitates of potassium, sodium, ammonium, calcium, and manganese. For example, sodium aconitate was a hygroscopic, non-crystalline mass. The sodium diaconitate separated from a concentrated aqueous solution on addition of alcohol in the form of micaceous tables, and dissolved at 15 °C in twice its weight of water; it effloresced in dry air losing one-half its water of crystallization. When dried at 100 °C it lost four equivalents of water, which could not be driven off without decomposition. The salt thus dried attracted again 1.5 equivalents of water when exposed to the air. Diaconitate of ammonia exhibited a behavior similar to that of the corresponding potassium salt, as regards to preparation and decomposition by water. The triaconitate crystallized in three-sided tables and dissolved in 6.5 times its weight of water of 15 °C. The calcium salt did not lose all its water of crystallization at 100 °C; it dissolved in from 98 to 99 times its weight of water at 15 °C. During these researches on the *Equisetum fluviatile,* Baup discovered in it a peculiar yellow crystalline matter, which he named *flavequisetin*. Flavequisetin imparted to mordanted cotton a yellow tint not inferior to weld (a natural yellow dyestuff) (Baup, 1850).

Glacier movement

In a memory read to the Royal Society of London, Henry Moseley (1801-1872) compared the progression of the descent of a glacier to that of a mass over an inclined plate, caused by changes in temperature (Moseley, 1854-1855). James David Forbes (1809-1868) hotly contested this view, quoting the former explanation he had given of the phenomenon, were the descent was described on the basis of the plasticity or viscosity of the glaciers (Forbes, 1844, Baup, 1856).

Baup wrote that although these explanation were widely adopted, they did not explain the facts observed, for the following reasons: (1) A state of plasticity of the glacier would generate a very slow motion of a glacier resting over terrains of little inclination, instead over planes more inclined, a fact not observed; (2) the faculty of glaciers of molding the terrain or the windings of the course of the valleys was not an specific propriety of elastic state, it was also a result of the compression exerted by the freezing of the internal water. The slower march of the borders of the glacier compared to that of the central part, illustrated by all the researches done on the Aar glaciers, had the natural explanation, in all the hypotheses, of being caused by the friction or the strong resistance that they met during their march, due to the asperities or uneven ground that enclosed them; (3) if the glaciers were not propelled by an almost irresistible force but only by a consequence of a plastic state, or their own weight, they would stop, in the same manner as the landslides of wet inclined terrains; (4) it was well known that glaciers moved also during winter when they were not lubricated or softened by liquid water, that is, when they formed an enormous mass of dry ice mass. How could a plasticity effect explain this course effect? (5) If the march of a glacier could be explained by a viscous or plastic state, how could we justify, for example, the march of the grand glacier of Rhone over the Leman basin, strangled initially by the St, Maurice narrow pass and then displaying erratic blocks, as far as the faces of Jura, with an estimated slope of only one-half degree? (6) Finally, we could also ask how it was possible to explain by means of the plasticity or viscosity of the glacier, why the erratic blocks; some of them of considerable dimensions (well over 3,000 cubic meters), remained *always* on top of the glacier and were transported without ever sinking (Baup, 1856)?

Baup believed that the reason for the march of the glaciers had to be looked in another factor, which was not original, except for a slight modification: The glacier movement was caused by the power of the expansion of the ice of the glacier, by the condensation of the water in their interior. This was one old explanation, which had been found insufficient. Another old explanation was that the march of the glacier was due to its own weight, perhaps combined by the fusion of the water at its bottom, o by the freezing of the water during the night and the following diurnal melting. Proper calculations had shown that these effects were too small to propel the glacier. Baup believed that the actual cause was the irresistible force of the expansion of the ice, *which led to an inside tension provoked by an unbalanced elasticity*. This tension could be compared to a spring extended by the expansion of the ice, generating little by little and step by step the irresistible march of the glacier, and strong enough to overcome all obstacles. A similar effect was observed with a dry wood wedge, which upon wetting was powerful enough to break rocks. This effect was not instantaneous, but slow like in glaciers. The expansion was not caused by the freezing of the water but by the capillary attraction of the water by the fibrous lignin (Baup, 1856).

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Figure 1: Samuel Baup (1791-1862) (Robert, 1893)