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Review article

ROBERT JOHN KANE: Inorganic chemistry and plant chemicals

ROBERT JOHN KANE: Química Inorgánica y productos químicos de planta

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ABSTRACT

Robert John Kane (1801-1891) was an English physician and chemist to whom we owe a new and very efficient process for the synthesis of iodine chlorides, the study of the nature and behavior of ammonia and its derivatives, and the existence of compounds containing nitrogen in the form of NH_2 (amidogene), which were not amides and resulted from the action of ammonia and the base of an oxide. The action of ammonia upon mercuric oxide resulted in an ammoniuret, a highly fulminating compound. Kane isolated, identified, and determined the properties of a series of plant chemicals, among them, thebaine, dumasine (cyclopentanone), the active component of a number of essential oils (rosemary, marjoram, peppermint, pennyroyal, spearmint, lavender, and sassafras), the coloring matter of Persian berries, and several lichens of the Rocella and Lecanora species. From Rocella tinctoria he isolated the new compounds erythrin, roccellin, erythrin, and telerythrin, and from archil alpha and beta orcein, erythroleic acid, azoerythrin, azolitmin, etc. Kane separated the components of litmus and proposed an explanation of the discoloration of the bodies present in archil and litmus: the reddening of litmus paper was produced by HCl, etc., generating the pertinent alkali chloride and setting free the red coloring.

Keywords: ammonia salts; archil; iodine chlorides; litmus; mercury

RESUMEN

Robert John Kane (1801-1891), fue un médico y químico inglés al que le debemos un nuevo y eficiente proceso para la síntesis de los cloruros de yodo, el estudio de la naturaleza y comportamiento del amoníaco y sus derivados, y la existencia de compuestos que contienen nitrógeno en la forma de NH_2 (amidógeno), que no son amidas y resultaban de la acción del amoníaco sobe la base de un óxido. La acción del amoníaco sobre el óxido mercúrico resultaba en un amoniuro, un compuesto altamente fulminante. Kane aisló, identificó y determinó la propiedades de una serie de productos derivados de plantas, entre ellos la tebaína, la dumasina (ciclopentanona), el compuesto activo de una variedad de aceites esenciales (romero, mejorana, menta, poleo, menta verde, lavanda y sasafrás), el material colorante de las bayas de Persia, y varios líquenes de las especies Rocella y Lecanora. De la Rocella tinctoria aisló los nuevos compuestos eritrina, roccellina, y teleritrina, y la archila, alfa y beta orceina, ácido eritroleico, azoeritrina, azolitmina, etc. Kane separó los componentes del papel tornasol y propuso una explicación de la descoloración de los cuerpos presentes en la archila y el tornasol: el enrojecimiento de éste último era causado por ácidos como HCl, que generaba el cloruro pertinente y liberaba la tintura roja.

Palabras clave: cloruros de yodo; litmus; mercurio; sales de amoníaco:

Life and career (Wheeler, 1844; Reilly, 1955; Brady, 1855; Geoghegan, 2009; Gilbert, 2012)

Robert John Kane (Figure 1) was born in Dublin on September 24, 1809, the son of John Kean, a chemical manufacturer, and Eleanor Troy. His father participated in the failed 1798 Irish rebellion, which intended ending British monarchical rule over Ireland and establishing an independent Irish state. To avoid arrest he flew to France, where he studied chemistry. Once the situation calmed down (1804) he returned to Dublin and continued his industrial activities. During his childhood Robert studied chemistry at his father's factory and afterwards entered Trinity College in Dublin (1828-1835) where he studied medicine and practical science. During this period he published his first two papers, one of them discussing the possible existence of chlorine in manganese dioxide (Kane, 1828) and the other reporting the analysis of a sample of manganese arsenide originating from Saxony (Kane, 1829). Between 1828 and 1829 Kane worked as clinical clerk to the Irish physician William Stokes, (1804-1878) in the Meath Hospital. In 1829 he became a Licentiate of Apothecaries' Hall (a qualifying medical diploma awarded externally in Dublin), and in 1831 he was appointed to the chair of chemistry in the Apothecaries' Company (manufacturing and selling medicinal and pharmaceutical products), a position he retained until 1845. In 1834 he graduated from Trinity and a year later he became a Licentiate of the King and Queen's College of Physicians in Ireland and a fellow in 1841.

During 1836 Kane travelled to Europe and visited the most important scientific institutions in France and Germany and stayed some time in Justus von Liebig's (1803-1883) laboratory at Giessen. During his stay in Giessen he isolated acetone (pyroxylic acid) and methanol from wood spirit, and prepared mesitylene by reacting acetone with sulfuric acid (Kane, 1836d, 1837a). Between 1841 and 1847 Kane was professor of natural philosophy at the Royal Dublin Society. In 1838 he married Katherine Sophia Baily (1811–1886), with whom he had seven surviving children.[1-5]

Kane died in Dublin, on 16 February 1890.

Kane was a member of several important public and scientific institutions. He was a founding member of the *Dublin Journal of Medical and Chemical Science* (now the *Irish Journal of Medical Science*) (1832); editor of the journal *Philosophical Magazine* (1840); member of the Royal Irish Academy (1832), secretary of its council and President of the same (1877-1890); member of several commissions to enquire into the Great Irish Famine of 1845-1852; director of the Museum of Economic Geology in Dublin (1845); fellow of the Royal Society of London (1849); National Commissioner for Education (1873); President of Queen's College Cork (now University College Cork) (1846-1873); and first chancellor of the newly created Royal University of Ireland (1880). He was knighted in 1846 and in 1868 he received an honorary degree of LL.D. by the University of Dublin, In 1841 the Royal Society of London awarded Kane a royal medal for his elucidation of the chemical nature of archil and litmus, the natural dyes extracted from lichens (Kane, 1840b), and in 1843 the Royal Irish Academy awarded him the Cunningham gold prize medal for his work on the nature and constitution of the compounds of ammonia (Kane, 1843).

Scientific contribution

Kane wrote more than 70 papers and books (e.g. Kane, 1831, 1842a, 1844a) on the subjects of inorganic, industrial, and organic chemistry, physiological fluids, vegetable, principles, agriculture, fertilizers, rural economy, etc. His most important books were *The Elements of Chemistry* (Kane, 1842a) (in 3 volumes; this book went through many editions) and *Industrial Resources of Ireland* (Kane, 1844a).

In addition to the subjects described below, he proved that the native manganese dioxide did not contain chlorine (Kane, 1828); he studied the composition of a new native arseniuret of manganese (afterwards named kaneite in his honor) (Kane, 1829) and of the urine and blood in diabetes mellitus (Kane, 1832a); the structure of acids, showing that hydrogen was electropositive (Kane, 1832b); the composition of blood in jaundice (Kane, 1833c); he synthesized a variety of new platinum derivatives (Kane, 1832c, 1833ad, 1834, 1842c); he studied pyroxylic acid (acetone) and its combinations (Kane, 1835, 1836d, 1837a); the chemical constitution of flax and hemp (Kane, 1844b); the composition of the ashes of flax (Kane, 1847b); etc.

Attention must be paid to the fact that in all his equations and formulas Kane assumed the atomic masses C = 6, H = 1, O = 8, and N = 14.1.

Iodine chlorides

Shortly after Bernard Courtois (1777-1838) announced the discovery of iodine (Clément, 1813) Joseph-Louis Gay-Lussac (1778-1850) and Humphry Davy (1778-1829) published the first memoirs describing the properties of this new element and the preparation and properties of a large number of its derivatives (Gay Lussac, 1813, 1814; Davy 1813). Gay-Lussac tried to decompose KIO_3 using acids and found that with HCl it formed oxygenated muriatic acid (HCl) and a combination of iodine and chlorine (iodine monochloride, ICl). Davy reported that iodine did not contain chlorine, hydrogen chloride, or oxygen, and that the new element combined rapidly with chlorine or HCl forming a crystalline yellow solid (iodine pentachloride, ICl_5) that crystallized in yellow needles. This solid was very volatile and very soluble in water and its aqueous solution reddened instantly the vegetable blues and destroyed them immediately. This action was similar to that of chlorine and super oxygenated muriatic acid ($HClO_3$). Little was afterwards published about the possible combinations of iodine with chlorine. This fact led Kane to carry on further experiments of the subject (Kane, 1833b).

The preparation of iodine monochloride was well known: Dry chlorine was passed over finely divided iodine until the gas ceased to be absorbed. The resulting product was a white mass containing one atom iodine and five of chlorine (ICl_5), soluble in a small amount of water without decomposition and decomposing in a large amount of water into iodic acid and HCl. Treatment with a metallic oxide yielded the iodate and the chloride of the metal. Stopping the absorption of chlorine before saturation yielded a solid, colored brown or red-brown, and of uncertain composition. Kane developed the following alternative process: A current of chlorine was passed through a water solution of iodine. The resulting liquor became of a deep brownish red, releasing iodine and having an odor intermediate those of its constituents. It first reddened and then bleached litmus paper; cooled considerably it precipitated a reddish yellow substance, which redissolved upon heating. Chemical analysis of the product indicated that it contained, by weight, 23.06% chlorine and 76.94% iodine, corresponding to one atom of chlorine (atomic mass 35.4) and one of iodine (atomic mass 126.5), that is, ICl (Kane, 1833b). Kane reported that this monochloride existed in solution, forming a reddish yellow solution, highly irritating the nose, and precipitating iodine when heated. With blue vegetable colors it reacted strongly acid, reddening the paper and then bleaching it. According to Kane, iodine monochloride presented some interesting reactions. As mentioned before, it reacted with an alkali precipitating iodine and forming a chloride and an iodate of the metal. Addition of an excess of alkali resulted in dissolution of the iodine and formation of an iodide and iodate. In the case of excess ammonia, the final products were ammonium iodide and fulminating nitrogen iodide. Contacted with red oxide of mercury resulted in the release of abundant oxygen, release of some iodine, and formation of both chlorides and iodides of mercury. A similar reaction took place with the red or brown oxides of lead: considerable gas was freed, some iodine released and lead chloride formed. Kane prepared a table giving the results of the reaction between iodine monochloride and 19 metallic chlorides (Kane, 1833b).

Kane synthesized what he believed was iodine trichloride by reacting iodine monochloride with mercuric chloride, separating the precipitated iodine, and distilling the remaining liquor [In 1837 Eugène Souberain confirmed the existence of iodine trichloride (Souberain, 1837)]. He also concluded that the probable compounds of iodine and chlorine corresponded to the series of compounds that oxygen formed with chlorine, iodine, and bromine, viz., 1, 3, and 5 (mono, tri, and pentachloride) (Kane, 1833b).

Ammonia and its derivatives

Kane dedicated much time to the study of the nature and behavior of ammonia and its derivatives (Kane, 1836ab, 1837b-d, 1838a-c, 1839a, 1840a, 1843). In his first work he studied the action of ammonia upon various metallic compounds and concluded that a large number of compounds believed to contain the nitrogen in the form of ammonia, actually contained it in the form of the group NH_2, which he named *amidogene*, because he considered it to be different of the amide group (Kane, 1836a). According to Kane the remarkable action of ammonia upon mercuric chloride (corrosive sublimate) had long attracted the attention of chemists and produced discordant results (Kane, 1836b, 1837d). Henry Hennell (1797-1842)[*] had given one of the popular explanations: The white precipitate "was composed of one atom of red oxide of mercury united to one of sal ammoniac (ammonium chloride) and produced by the reaction of (2Cl + Hg) with $2NH_3$ to give $[Hg + (ClNH_4)] + ClNH_4$, so that 273.6 g of mercuric chloride gave 272.34 g of white precipitate (Hennell, 1825). There were two procedures for carrying out this reaction: passing the gas over dry mercuric chloride, or mixing a solution of ammonia with another of mercuric chloride. The latter procedure produced a milk white bulky precipitate insoluble in water; the precipitate turned yellow if the original water was very hot, or if it was washed many times. Boiling the precipitate in water decomposed it completely and turned it into a yellow heavy granular powder. Heated in a closed glass tube it fully decomposed releasing a mixture of ammonia, nitrogen, and water. The white precipitate was readily soluble in nitric acid or HCl; mixed with the hydroxides of sodium, potassium, calcium, or barium resulted in the release of ammonia and formation of a yellow residue. Reaction with a solution of potassium iodide precipitated a red powder of mercuric iodide, accompanied by gaseous ammonia (Kane, 1836b, 1837d).

Kane carefully prepared the white precipitate and proceeded to determine its composition by different methods. His first results indicated that the supernatant liquid contained no mercury but much chlorine; all the original mercury was present in the white precipitate and part of the chlorine had been removed and appeared in the liquid as ammonium chloride. These facts were

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[*]. Hennell was killed by an explosion that occurred while preparing mercury(II) fulminate.

used to determine the amount of mercury and chlorine present in 100 g of washed and dry precipitate: 79.57 and 13.87 g respectively. In another procedure Kane heated carefully 15 to 25 grains (0.972 to 1.620 g) of white precipitate until all the ammonia and the water vapor had been expelled and the calomel completely sublimed white. From 100 g of white precipitate, corresponding to 97.98 g of calomel, he obtained 79.14 g of mercury and 13.84 g of chlorine. A third procedure consisted in dissolving the white precipitate in HCl and precipitating the mercury by means of tin dichloride; from 100 g of white precipitate he obtained 77.7 g of mercury (average of four experiments). In a fourth experiment the white precipitate was dissolved in HCl and the liquor decomposed by a stream of hydrogen sulfide. The precipitated mercuric sulfide was separated from the supernatant solution of ammonium chloride. Analysis of the different streams indicated the 100 g of white precipitate contained 77.96 g of mercury and 7.16 g of ammonia. After carrying additional procedures, Kane concluded that the white precipitate contained, by weight, 78.60% of mercury, 13.85% of chlorine, 6.77% of ammonia, 0.58% of water, with 0.20% of loss. This result contradicted those obtained by other researches, including Hennell. Kane believed that the results of his analysis indicated that in the white precipitate the chlorine was united with half its weight of mercury into calomel, and the "remaining mercury was present as its peroxide united with ammonia, giving the formula (2Cl + Hg) + 6H +2NH_3), and composition 2Hg (77.00%), 2Cl (13.45%), 2O (3.04%), and 2NH_3 (6.51%) (Kane, 1836b, 1837d)."

Kane added that from the researches of amides, such as oxamide and benzamide, it followed that the action of ammonia on an oxide "resulted in the formation of water and a compound of the body NH_2 with the base of the oxide" (Kane, 1836b, 1837d).

Kane did further work on the effect of boiling water on the white precipitate (Kane, 1837bd). He repeated his previous finding that boiling the white precipitate in water turned it into a heavy canary-yellow powder, easily dried and little soluble in water. He conducted several experiment trying to determine the composition of the yellow powder. The powder was separated by filtration, washed repeatedly, dried and weighed. The filtrate and the washings were acidulated with nitric acid and precipitated with silver nitrate, to determine the amount of chlorine present. Repeated tests indicated that they contained 18.89% of chlorine, a result showing that the yellow powder contained 88.381% mercury and 8.374% chlorine. Boiling the white precipitate with water yielded liquor containing only ammonium chloride. The above analytical procedure showed that the liquor contained 6.29% of chlorine indicating that the yellow powder contained 87.95% mercury of 8.44% chlorine. In a third experiment 100 g of yellow powder were boiled with water until completely decomposed. The resulting liquor was evaporated to dryness and found to weight

10.23 g of ammonium chloride. This result indicated that the yellow powder contained, by weight, 86.23% of mercury, 7.77% of chlorine, and 3.83% of ammonia. Additional analytical procedures led Kane to propose that the yellow powder contained, by weight, 85.72% of mercury, 7.48% of chlorine, 3.42% of amidogene, and 3.38% of oxygen. He concluded that the yellow powder was generated by the reaction of water with white precipitate resulting in the conversion of one-half of the chlorine and ammonia into ammonium chloride and oxidation of a corresponding portion of mercury (Kane, 1837bd).

Kane also studied the action of ammonia upon mercury(1) chloride (calomel) (Kane 1837cd). He remarked that this reaction did not seem to have attracted the attention of chemists; Hennell had mentioned that the reaction of calomel with an excess of ammonia yielded a black powder containing, by weight, 96% mercury and 4% of oxygen (Hennell, 1825). Kane repeated this experiment and obtained a compound having remarkable properties. The resulting wet powder was almost black and upon drying it became dark gray. The dry powder was not affected by air or moderate heat, even when heated in a platinum crucible for several hours at 180°F. When heated in a tube closed at one end, it released water, nitrogen, and ammonia, and then sublimed mixed with metallic mercury. Kane analyzed the black powder by processes similar to the ones used to analyze the white precipitate and found that it contained, on the average, 88.33% mercury, 7.95% chlorine, and 3.36% ammonia, with a loss of 0.36%. Hence, the black powder was the same as the white precipitate, except it was in a state of *proto-combination*; water acted on calomel abstracting half the chlorine and replacing it by the corresponding amount of ammonia in some form of combination (Kane, 1837cd).

Kane also studied the action of ammonia upon mercury(II) oxide. He believed this reaction was particularly important because the resulting mercury *ammoniuret* was a fulminating compound containing ammonia (Kane, 1837cd). Antoine-François Fourcroy (1750-1809) had prepared this compound by digesting aqueous ammonia with red oxide of mercury, HgO, during several days; during this time the oxide gradually covered itself with a yellowish-white powder, which eventually turned fine white (Fourcroy, 1789). Kane prepared it by precipitating a solution of mercury(II) chloride with KOH, filtrating the precipitate and washing it repeatedly with water to eliminate the excess of alkali, followed by mixing with aqueous ammonia and leaving the mixture alone for several days. Upon heating, his ammoniuret (amidogene) released a large quantity of ammonia, nitrogen, and water, leaving unaltered ammoniuret. This compound was dark red when hot and whitish when cold. When suddenly thrown on ignited coal it exploded very feebly. Analysis of the dry ammoniuret indicated that it contained, by weight, 88.67% mercury, 6.99%

oxygen, and 4.34% ammonia, corresponding to the formula $[2\ddot{H} + (2NH_2 + Hg) + 6\dot{H})]$, showing that nitrogen was combined as amidogene and not as ammonia (Kane, 1837cd).

The following publications described the basic salts formed by the reaction of ammonia with the sulfates and nitrates of mercury; their purpose was to identify the function of the ammoniacal element of the oxygen salts of that metal (Kane, 1838a, 1843). Kane mentioned that in his previous papers he had presumed the atomic mass of mercury to be 202.8, assuming that corrosive sublimate was a dichloride. He now took that the atomic mass to be 101.4, as suggested by Berzelius, were calomel was taken to be a sub-chloride (monochloride), and the sublimate as containing one equivalent of each component. On this basis the neutral mercuric sulfate and the turpeth mineral contained, by weight, 26.72% sulfuric acid and 72.98% mercuric oxide (total 99.70), and 10.97% sulfuric acid and 89.24% mercuric oxide, respectively (Kane, 1838a, 1843).

Kane wrote that the reaction of mercuric sulfate with aqueous ammonia produced a white powder, sparingly soluble in water and soluble in nitric acid and HCl. On the first addition of the ammonia, some turpeth mineral was formed, which gradually disappeared. Upon heating, the precipitate turned brown and released traces of ammonia mixed with large amounts of water and nitrogen and leaving the sulfate of the black oxide of mercury (Hg_2O). Chemical analysis of this compound by several methods showed that it contained one atom of sulfuric acid, one of ammonia, and four of mercury. Kane added that if one assumed that in this ammonia turpeth the nitrogen and the hydrogen existed as amidogene, then this turpeth contained, by weight, 83.47% Hg, 8.27% SO_3, 3.32% NH_2, and 4.94% O, corresponding to the formula $(SO_3 + 2HgO + HgNH_2)$ (Kane, 1838a, 1843).

Kane studied also the action of ammonia on the sulfate of the black oxide of mercury (Kane, 1838a, 1843). He noticed that this sulfate did not react with cold or boiling water, a result that seemed to indicate the existence of only one sulfate of the oxide. Treatment of the sulfate of the black oxide with aqueous ammonia produced a dark gray powder, which upon heating decomposed into water, ammonia, SO_2, oxygen, and mercury. This result indicated that this compound was a basic salt containing ammonia. Chemical analysis of the gray powder suggested that its composition corresponded to the formula $(HgO.SO_3 + 2HgO + HgNH_2)$ (Kane, 1838a, 1843).

Kane found that the composition of the crystallizable nitrate of the red oxide of mercury corresponded to the formula $(NO_5 + 2HgO + 2HO)$ (At that time it was not known that hydrogen contained two atoms and thus the formula of water was assumed to be HO). This salt crystallized as small deliquescent prisms, having a metallic taste. He also reported that there were two basic dinitrates of the oxide, one yellow and the other brick red (Kane, 1838a, 1843).

A similar work reported the ammonia and other basic compounds of the copper and silver families (Kane, 1838b, 1843).

All the work done by Kane on the different derivatives of ammonia confirmed his conviction that ammonia should not be considered an independent base capable of neutralizing acids and forming the corresponding salts. He believed that ammonia should be looked upon as a compound of the body NH_2 and of hydrogen. In his language, "ammonia as a gas was the amiduret of hydrogen. The hydrogen outside the radical could be replaced by the various metals, or by radicals of organic origin, and hence the amide of potassium, of benzoyl, etc." According to this hypothesis, ammonium chloride should be considered a compound of HCl and the amide of hydrogen (Kane, 1838c, 1840a, 1843). In a lengthy paper of the subject he summarized his ideas as follows: (a) the amidogene may combine with salts, and the metallic *amidides* have the particular tendency to combine with the chlorides or oxides of the same metals; (b) the hydrogen amidide can perform the same function in combinations as oxide of hydrogen, whether as basic water or as water of crystallization; (d) the so called ammonium oxide, NH_4O, is oxyamidide of hydrogen, and ammonium chloride is chloramidide of hydrogen; (e) the ordinary salts of ammonium ally themselves to the salts of the copper and zinc class, which contain two equivalents of oxide; and (f) if chlorine could be separated from ammonium chloride, the residual NH_4 should be regarded as (NH_2 + 2H), sub-amidide of hydrogen, as when by removing the chlorine from white precipitate, the sub-amidide of mercury, NH_2 + 2Hg, formed by the action of aqueous ammonia on calomel, should remain (Kane, 1838c, 1840a, 1843).

As mentioned before, this work on ammonia earned Kane the 1843 Cunningham Gold Metal of the Royal Irish Society.

Plant chemicals

Thebaine

This vegetable alkaloid was discovered by Pierre Joseph Pelletier (1788-1842) in opium and named *paramorphine*, and afterward separated by J. P. Couerbe (1805-1867) from an opium originating from Egypt, and named thebaine (Pelletier, 1835, 1836; Couerbe, 1836). The differences in the chemical analysis of this compound reported by both scientists led Kane to try to clarify the problem, analyzing a specimen prepared by the pharmacist Heinrich Emanuel Merck (1794-1855). Kane reported that thebaine contained, by weight, 74.57% carbon, 6.83% hydrogen, 6.89% nitrogen, and 11.71% oxygen, corresponding to the formula $C_{25}H_{28}N_2O_3$ (the actual composition and formula are 73.29% carbon, 6.80% hydrogen, 4.50% nitrogen, and 15.42% oxygen; and $C_{19}H_{21}NO_3$, respectively). Kane could not determine the atomic mass of thebaine because its salts with mineral acids were non-crystallizable (Kane, 1836c).

Dumasine (cyclopentanone)

According to Kane dumasine was a fluid obtained in very small quantity on the distillation of calcium acetate to obtain mesitic alcohol (acetone) (Kane, 1837e). Dumasine was a colorless liquid boiling at 120 ^{o}C and having a strong resinous smell. Elemental analysis indicated that it contained, by weight, 78.82% carbon, 10.46% hydrogen, and 10.72% oxygen, corresponding to the formula $C_{10}H_8O$, isomeric with camphor (Kane, 1837e).

Essential oils

Kane analyzed a number of essential oils (rosemary, marjoram, peppermint, pennyroyal, spearmint, and lavender) in order to find if there was a law connecting the composition of the oils derived from the same genus or natural family of plants, and if their composition signaled the chemical nature of their class (Kane, 1837f, 1838d). For example, he found that the composition of oil of peppermint (*Mentha pulegium*) was C_5H_4, the same as for turpentine oil or lemon oil. The composition of rosemary oil corresponded to the formula $C_{45}H_{38}O_2 = (9C_5H_4 + 2HO)$, that is, this oil could be considered to be a hydrate of numerous oils, for example, turpentine oil. Similarly, the composition of marjoram oil (*Origanum vulgare*) was $C_{50}H_{40}O = (10C_5H_4 + O)$. Similar results were found for the other oils (Kane, 1837f, 1838d).

Coloring matters of Persian berries

Kane wrote that the Persian berries were the fruit of the dyer's buckthorn (*Rhamnus tinctoria*), which were imported from the Levant and from the south of France to be used as source of a brilliant red coloring matter (Kane, 1842b). The appearance of the berries was not uniform, a fact that reflected on its ability to dye. Kane believed that the difference originated from the berries being collected at different stages of their development. The unripe berries gave little color to water and when extracted with ether, they provided a rich golden yellow substance, which Kane named *chrysorhamnine*. The dark colored berries were little extracted with ether but strongly by boiling water, yielding an olive yellow material which Kane named *xanthorhamnine*. Kane found that xanthorhamnine was produced only by decomposition of chrysorhamnine by means of air and hot water (Kane, 1842b).

Kane described chrysorhamnine as substance of rich yellow color, present as brilliant stellated tufts of short silky needles. It was sparingly soluble in cold water, soluble in alcohol and ether. It had no acid reaction but dissolved in alkaline solutions; treating an alcoholic solution with lead acetate gave place to a rich yellow precipitate. Chemical analysis of the dry material indicated that it approximately contained, by weight, 58.23% carbon, 4.77% hydrogen, and 37.00% oxygen, corresponding to the formula $C_{23}H_{11}O_{11}$. Xanthorhamnine was soluble in water giving an olive yellow solution. Chemical analysis of a vacuum dried sample indicated that its composition corresponded to the formula $C_{23}H_{27}O_{29}$ (Kane, 1842b).

Sassafras tree

Kane also determined the properties, composition, and derivatives of the essential oil extracted from *Laurus sassafras*, a tree growing on eastern Asia and in North America (Kane, 1847a). This oil had a specific gravity of 1.087, boiled at 226 ^{o}C, and its composition corresponded to the formula $C_{20}H_{10}O_4$, the same as reported by Edouard Saint-Evre (1791-1858) for its stearoptene (the oxygenated solid part of an essential oil) (Saint-Evre, 1844). The oil reacted with chlorine releasing an abundant amount of HCl and giving a thick oil of composition $C_{20}H_8O_4Cl_4$, which exploded violently at 177 ^{o}C. The reaction with bromine was highly exothermic; much HBr was released, leaving a solid product, which melted at about 149 ^{o}C and then decomposed giving off HBr and depositing charcoal. The solid product was moderately soluble in ether; from the ethereal solution it crystallized as brilliant oblique prisms, of composition $C_{20}H_7O_4Br_5$. Sassafras oil reacted violently with nitric acid forming a large amount of oxalic acid. The reaction with diluted acid produced a yellow resinous substance, soluble in alcohol, ether, and alkalis, and sparingly soluble in boiling water. The formula of this nitro-sassafras was $C_{16}H_6NO_8$. The reaction with sulfuric acid produced an intense and beautiful scarlet color, which Kane believed could be used to recognize this oil. This sulfo-sassafras was soluble in alcohol, ether, and in alkalis, and slightly soluble in water (Kane, 1847a).

Archil and litmus

Archil is the generic name of several lichens of the *Rocella* and *Lecanora* genres, which after fermentation and treatment with aqueous diluted ammonia yield a red-violet coloring matter. Litmus is a water-soluble mixture of different coloring materials obtained from the same lichens. Kane wrote that one of the most challenging questions in organic chemistry was the study of the nature and mode of origin of the remarkable dyeing materials forming the basis of commercial archil and litmus, which were obtained from raw materials totally devoid of color. Many famous chemists had been involved in isolating, examining, and identifying the different chemicals present in these lichens, among them Antoine-François Fourcroy (1750-1809), Louis Nicolas Vauquelin (1763-1829), Smithson Tennant (1761-1815), Pierre Jean Robiquet (1780-1840), Friedrich Heeren (1803-1885), Michel Eugène Chevreul (1786-1889), and Jöns Jacob Berzelius (1779-1848) (Kane, 1840b). Heeren, in particular, ha reported that the lichens *Parmelia Roccella* and *Lecanora Tartarea* contained an active substance, which he named *erythrin*, which was the basis of the red dyes (Heeren, 1825). Upon boiling in alcohol, erythrin transformed into another compound (*pseudo erythrin*) and by exposure to air, it became a water-soluble material (*erythrin bitter*). In contact with ammonia and air, erythrin and erythrin bitter yielded three differently colored pigments, one yellow, another red (which Heeren named *lichen red*), and a third one colored wine-red. Heeren wrote that lichen red was the coloring mater of cudbear and archil. Kane remarked that it was very unfortunate that Heeren had not reported the composition of the new materials he had discovered (Heeren, 1825; Kane, 1840b). Pierre Jean Robiquet (1780-1840) analyzed the lichen *Variolaria dealbata* and discovered it contained a substance incapable of producing color, which he named *variolarin,* and another sweet matter, which he named *orcin*. Orcin was the substance for producing the red color of archil (*orcein*) (Robiquet, 1829, 1835). Kane concluded that except for the composition of orcin, nothing fundamental had been published. For example, the composition of the colorless substance discovered by Heeren was unknown; nothing was known about the possible relation between the orcein of Robiquet and the lichen red of Heeren; it was not known if the various lichens contained the same colorless substances; if they produced the same final dyes, etc. Kane established three objectives for his research program: (1) To ascertain the primitive form of the color-making substance in a given species of lichen, and trace the stages through which it passed before the coloring substance was developed; (2) to determine the nature of the various coloring substances which existed in the archil of commerce; and (3) to examine the coloring materials of ordinary litmus. His final report was a lengthy (90 pages) memoir describing the results of hundreds of experiments and chemical analyses he had conducted to answer these questions. The archil and litmus he used came from a variety of commercial sources (Kane, 1840b).

1. Chemical examination of *Roccella tinctoria*

The lichen, cut into very small pieces, was repeatedly extracted with refluxing alcohol kept at a temperature slightly below boiling (60 °C). The alcoholic extract was then evaporated to dryness in a water bath and the yellow residue repeatedly boiled with water for a few minutes and filtered while hot until no more material seemed to dissolve. The residue was dissolved in diluted KOH at 38 °C and then acidified with HCl. The greenish precipitate was dissolved in weak aqueous ammonia and then treated with calcium chloride. The filtrate was treated again in the same manner. The precipitate was carefully washed with water and dried. This material that Kane considered to be the origin of the colored series was named *erythrilin*. The small amount of material separated by means of calcium chloride was the *roccellic* acid discovered by Heeren, which Kane proposed naming *roccellin*. The clear solution produced during the treatment of erythrilin yielded a crystallized body, which Kane found to be identical with the pseudo-erythrin discovered by Heeren and proposed changing the name to *erythrin*. Similarly, the watery solution obtained during the crystallization of erythrin was found to contain another bitter substance, very soluble in water, and found to be identical with Heeren's *erythrin-bitter*. Kane found that exposition of a strong solution of erythrin-bitter to air for a considerable time, converted it into a mass of soft white crystals, which he named *telerythrin*. Kane indicated that his erythrilin, erythrin, erythrin-bitter, telerythrin, ad roccellin, where identical with the corresponding substances discovered by Heeren in *Parmelia roccella* and *Lecanora tartarea*, and different from the ones found by Robiquet in *Variolaria dealbata* (Kane, 1840b).

The next stage was a description of the properties of these substances and the determination of their constitution: (a) Erythrilin was a white powder, insoluble in water but converted by ebullition into erythrilin bitter. It was soluble in alcohol, ether, and alkaline liquids, from which it was precipitated by an acid. It combined with metallic oxides yielding salts or lakes of a greenish color. Erythrilin fused a little above 100 °C and then decomposed without volatilization. Chemical analysis indicated that it contained, by weight, 68.06% carbon, 7.60% hydrogen, and 24.34% oxygen, corresponding to the formula $C_{22}H_{16}O_6$; (b) erythrin, (the pseudo-erythrin of Heeren) was sparingly soluble in cold water but very soluble in boiling water, and separating on cooling in brilliant, micaceous, snow-white scales. The aqueous solution was colorless, but in air, particularly hot, it rapidly became brown and was decomposed. Erythrin was very soluble in alcohol, ether and alkaline solutions, from which it was precipitated unaltered by an acid. It fused at 104 °C without losing water and decomposed at a higher temperature without volatilizing. It did not precipitate any neutral metallic solution but in ammonia solution it produced a copious white precipitate with lead nitrate or acetate. It formed a wine-red solution when exposed to the simultaneous action of ammonia and air. Chemical analysis indicated that it contained, by weight, 61.19% carbon, 6.20% hydrogen, and 32.71% oxygen, corresponding to the formula $C_{22}H_{13}O_9$; (c) erythrin bitter or *amarythrin* was formed when a solution of erythrin in hot water was exposed some days to the action of air. It had very peculiar bittersweet taste and smelled like burned sugar. It was very soluble in water, much less in alcohol, and insoluble in ether. It was precipitated, like the preceding compounds, by a lead salt. Its composition was determined from its salt with lead: 27.805% carbon, 2.69% hydrogen, 23.225% oxygen, and 46.28% lead oxide, corresponding to the formula $C_{22}H_{13}O_{14}$; and (d) telerythrin, formed when amarythrin, in a semi-fluid state, was exposed for several months to air, changing gradually into a mass of very minute granular crystals, of a brownish yellow color, but becoming white when purified by crystallization from alcohol. The crystals were very soluble in water, less soluble in alcohol, insoluble in ether, and having a sweet taste. Telerythrin was neutral to test paper. It combined with metallic oxides, forming a nearly white precipitate; with ammonia it yielded a deep-wine red solution. Its chemical analysis indicated that it contained, by weight, 44.79% carbon, 3.78% hydrogen, and 51.43% oxygen, corresponding to the formula $C_{22}H_9O_{18}$ (Kane, 1840b).

According to Kane, his results indicated the following changes in the production of the above compounds: erythrilin $C_{22}H_{16}O_6 - H_3 + O_3 =$ erythrin $C_{22}H_{13}O_9 + O_5 =$ amarythrin $C_{22}H_{13}O_{14} - H_4 + O_4 =$ telerythrin $C_{22}H_9O_{18}$. In other words, the change in the constitution of the substances primitively existing in Roccella tinctoria took place when exposed simply to the oxidizing action of the air (Kane, 1840d).

2. Chemical examination of the archil (orseille) of commerce

The ordinary *archil* (orseille) of commerce was prepared from the *Parmelia* or *Roccella.* The lichens were reduced to a pulp and treated with impure ammoniacal liquors. The complete production of archil required a considerable time and during which the coloring matter was in a constant state of transition (Kane, 1840b). For this reason Kane followed a different procedure for a better separation of the active components: A quantity of archil was slightly acidified with nitric acid and then evaporated to dryness. The dry mass was repeatedly extracted with alcohol until the extract was almost colorless. The accumulated extracts were evaporated to dryness yielding a crimson residue. The residue was extracted with warm ether and dried again to a fine crimson powder comprising the coloring substance According to Kane; this material contained two different modifications of orcin, which he distinguished by the names *alpha-orcein* and *beta-orcein*. The ethereal solution was found to contain another new substance, which Kane named *erythroleic acid*, and similarly, the alcoholic residue contained another new substance, which Kane named *azoerythrin*. Kane believed that the latter was identical with Heeren's wine-red pigment (Kane, 1840b).

The next step was the determination of the properties and composition of these new substances. *Azoerythrin* was insoluble in water, alcohol, and ether; it dissolved in alkaline solutions yielding the characteristic port wine color. This solution was not precipitated by acids but with lead acetate and other metallic salts yielded brown red precipitates. Kane found that sometimes it was mixed in very small amounts with another substance, which he named *azolitmin*. Chemical analysis of azoerythrin indicated that it contained, by weight, 38.80% carbon, 5.70% hydrogen, and 55.50% of mixture of oxygen (mainly) and nitrogen, corresponding to the formula $C_{22}H_{19}NO_{22}$. *Orcein* was of a fine red color; sparingly soluble in water but coloring it strongly a beautiful pink, and from which it was wholly precipitated by the addition of any neutral salt. It was very soluble in alcohol, which it colored scarlet, and from which water precipitated it. It was scarcely soluble in ether and dissolved easily in aqueous KOH or ammonia, coloring it a superb purple color (the color of ordinary archil). The coloring matter could be separated from this solution by the addition of an excess of common salt. An alkaline orceinate gave with metallic salts, lakes of a fine purple of different shades, which, however, lost much of their luster in drying. As mentioned above, Kane found that the orcein of archil was often a mixture of two substances, *alpha-orcein* ($C_{18}H_{10}NO_5$), and *beta-orcein* ($C_{18}H_{10}NO_8$) differing in their proportion with the age of the archil. Beta-orcein was produced by the oxidation of alpha- orcein. The two orceins were identical in all their essential chemical properties and had the same solubility in water, alcohol, and ether. As seen above both compounds differed in the amount of nitrogen they contained. *Erythroleic acid* was the purple substance, distinguished for its semi-fluid consistence at ordinary temperature. It was sparingly soluble in water, totally insoluble in turpentine, and very soluble in ether and alcohol. Chemical analysis indicated that it contained, by weight, 64.70% carbon, 9.33% hydrogen, and 25.97% oxygen, corresponding to the formula $C_{26}H_{22}O_8$ (Kane, 1840b).

3. *Litmus*. The following section was devoted to the components of litmus. For this purpose powdered commercial litmus was treated with boiling water until the solution ceased to give a deep-blue color. The insoluble matter was mixed with enough water to form a thin cream and then reddened with HCl until it ceased to effervesce. The whole was then filtered; the red insoluble substance was washed with water to eliminate the remaining HCl, and then carefully dried. The dry mass was boiled in successive portions of alcohol until leaving a totally insoluble residue. The deep-red alcoholic extracts were evaporated to dryness in a water-bath and the dry solid digested in warm ether until it latter no longer became colored. The ethereal solutions yielded on distillation a fine crimson oily material, *erythrolein*. Erythrolein was semi-fluid at room temperature and completely liquid at 38 ^{o}C. Its ethereal and alcoholic solutions were red; it was

sparingly soluble in water producing a pink color solution. It was insoluble in turpentine and dissolved in aqueous ammonia producing a purple color solution. With metallic salts it generated fine purple lakes by double decomposition (Kane, 1840b).

Chemical analysis indicated that it contained, by weight, 74.27% carbon, 10.68% hydrogen, and 15.05% oxygen, corresponding to the formula $C_{26}H_{22}O_4$. According to Kane the substance from which the erythrolein had been removed, and which was distinguished by its solubility, was a new compound, which he named *erythrolitmin.* Erythrolitmin was of a bright red color, sparingly soluble in water, which it colored red, and very soluble in alcohol, forming fine deep red liquor. It dissolved of a blue color in potash, and combined with ammonia forming a blue substance completely insoluble in water. Chemical analysis indicated that it contained, by weight, 55.78% carbon, 8.69% hydrogen, and 35.43% oxygen, corresponding to the formula $C_{26}H_{22}O_{12} + HO$. The brownish-red mass, which resisted the action of alcohol, contained a coloring matter sparingly soluble in water and soluble in a large quantity of boiling water. Upon evaporation it produced a deep blood-red mass, totally devoid of crystalline texture, and consisting of pure coloring material, which Kane named *azolitmin.* Azolitmin had the distinguishing feature of being colored blue by the alkalis. Chemical analysis indicated that it contained, by weight, 49.50% carbon, 5.35% hydrogen, and 44.3% of a mixture of oxygen and nitrogen, corresponding to the formula $C_{18}H_{10}NO_{10}$. This result indicated that azolitmin differed only from alpha-orcein ($C_{18}H_{10}NO_5$) and beta-orcein ($C_{18}H_{10}NO_8$). Kane reported that another substance was occasionally present in litmus and named it *spaniolitmin*. Spaniolitmin was of a bright red color, insoluble in alcohol and in ether, and very sparingly soluble in water, which it tinged bright red. Chemical analysis indicated that it contained, by weight, 44.54% carbon, 3.11% hydrogen, and 52.35% oxygen, corresponding to the formula $C_{18}H_7O_{16}$. Kane also mentioned that orcein reacted with chlorine to yield *chlororcein*, $C_{18}H_{10}NO_8Cl$, which possessed a yellowish-brown color. With azolitmin a similar compound of chlorine was produced, $C_{18}H_{10}NO_{10}Cl$ (Kane, 1840b).

The concluding section of the paper discussed the possible explanations of the discoloration of the bodies present in archil and in litmus. According to Kane, "litmus was reddened by acids because the acids removed the loosely combined ammonia by which the blue color was produced; the so called hydracids liberated the coloring matter by their combining with the alkali to form bodies (chloride or iodides), with which the coloring matter has no tendency to combine...Thus the reddening of litmus paper...was merely produced by hydrogen chloride, etc. forming with KOH potassium chloride, and with ammonia, ammonium chloride, and the proper red coloring becoming free." Hence it appeared that the reddening of litmus was no proof that hydrogen chloride was an acid, and that the double decomposition that occurred was the same, in principle, whether hydrogen or a fixed metal came to play (Kane, 1840b).

These arguments were also expressed in a letter that Kane sent to Jean-Baptiste André Dumas (1800-1884), the permanent secretary of the Académie des Sciences (Kane, 1839b).

As mentioned before, this work on archil and litmus earned Kane the 1842 Gold Metal of the Royal Society.

Figure 1: Robert John Kane (1801-1891)

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