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James Mason Crafts

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ABSTRACT

James Mason Crafts (1865-1927), an American mining engineer, is best know for his co-discovery of the Friedel-Crafts reaction, a powerful organic synthesis tool. He did basic work on the synthesis of organo-silicon compounds, determined the atomic weight of silicon, and published extensively on thermometry, on the calibration of thermometers, and proposed naphthalene and benzophenone as new fixed points for the thermometric scale in the range 100° to 400°C.

KEYWORDS: Friedel-Crafts reaction, organic synthesis, organo-silicon compounds, thermometry, hydrogen thermometer, vapor pressure, naphthalene, benzophenone, fixed points

Resumen

James Mason Crafts (1865-1927), un ingeniero de minas norteamericano, es famoso por el co-descubrimiento de la reacción de Friedel-Crafts, una herramienta poderosa para la síntesis de compuestos orgánicos. Realizó trabajos básicos en la síntesis de compuestos orgánicos del silicio y determinó la masa molecular de este elemento. Publicó extensamente en el área de termometría, en la calibración de termómetros, y propuso usar el naftaleno y la benzofenona como nuevos puntos fijos para la escala termométrica en el rango 100° a 400°C.

Life and career

There are only two papers giving information about the life and career of James Craft and the following material is taken from them (Cross, 1918; Richards, 1918).

James Mason Crafts was born at Boston, March 8, 1839, the son of Royal Altemont Crafts, a merchant and manufacturer of woolens, and Marianne Mason, the daughter of Jeremiah Mason (1768-1848), a lawyer and statesman of Portsmouth, New Hampshire. He married Clemence Haggerly (1841-1912) in June 13, 1868.

Crafts attended Boston Latin School and then, in 1856, entered the recently founded Lawrence Scientific School of Harvard University, receiving the Bachelor of Science degree in 1858. During part of 1859 he continued his studies under Eben Norton Horsford (1818-1893), professor of chemistry. He then went to Europe and studied with Karl Friedrich Plattner (1800-1858) at the Freiberg School of Mining (Bergakademie), Saxony, with Robert Wilhelm Bunsen (1811-1899) at the University of Heidelberg, and with Charles-Adolph Würtz (1817-1884) at the École des Mines in Paris. While in Paris Crafts published a large number of scientific papers, most of them with Charles Friedel (1832-1899). Friedel and Crafts became close personal friends and co-workers in many scientific researches in later years (Cross, 1918). In 1865 he returned to United States and worked for one year (1866-1867) as inspector of mines in Mexico. He was the first Professor of Chemistry (1867-1870) at the newly established Cornell University, and in 1870 succeeded Francis Humphreys Storer (1832-1914) as Professor of General and Analytical Chemistry at the Massachusetts Institute of Technology. In 1874 he took a leave of absence and returned to Paris and remained there until 1891, doing most of his research with Friedel and other coworkers. The most important result of his researches is the co-discovery of the Friedel and Crafts reaction, a powerful two for organic chemical synthesis. During these years he also began an important series of researches relating to the chemistry of organo metal compounds, high-temperature thermometry, and the measurement of the density of gases (Cross, 1918).

After his return to the United States he was elected a member of the corporation of the Massachusetts Institute of Technology and was also invited by President Francis Amasa Walker (1840-1897) to join the instructing staff. He became Professor of Organic Chemistry in 1892. After the death of Walker, Crafts was elected as his successor in 1898, which office he held for two years (1890) (Cross, 1918).

In the summer of 1911 he suffered a severe attack of neuritis, which prevented continuing to work in the laboratory. Crafts passed away on June 20, 191; he was survived by four daughters.

Crafts's investigations were largely in the field of organic chemistry, particularly in the development of new methods of synthesis and preparation of organometallic derivatives (silicon and arsenic). He was also very active in area of thermometry, he invented a new hydrogen thermometer; measured the density of halogens at very high temperatures; the vapor pressure of possible candidates for fixed points, hysteresis phenomena in glass, displacement of the zero point, etc.

Honors and awards

Crafts received many honors for his contributions to science and public life. He was honorary, correspondent, or associate

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member of the most important American and European scientific societies, among them the National Academy (1872), the American Academy of Arts and Sciences, the American Association for the Advancement of Science, the American Chemical Society, and the Washington Academy of Sciences. He was corresponding member of the British Association and honorary member of the Royal Institution of Great Britain and of the New York University and Technology Clubs. In 1880 the Académie des Sciences awarded him a Jecker Prize of 2,000 francs «for his researches relative to organic chemistry» and in 1911 the American Academy of Arts and Sciences awarded him the Rumford medal "for his research in high temperature thermometry and the exact determination of new fixed point on the thermometric scale". In 1885 he was made a Chevalier of the Legion d'Honneur. Soon after his accession to the presidency of MIT he received the degree of LL.D. from Harvard University. The Crafts entry at MIT's Senior House dormitory is named in his honor (Cross, 1918).

Scientific achievements

Crafts published more than 130 scientific papers, mostly in French journals. About 75 of his papers were in collaboration with Friedel. His main research activities were in the area of organic chemistry, synthesis, sulfoconjugated sulfonic acids, organometallic compounds (particularly silicon and arsenium); he also was active in thermometry and related subjects (displacement of the zero point, calibration, gas thermometers). The most famous contribution of Crafts to organic chemistry is the well-known Friedel-Crafts reaction. This reaction has been described in another paper and will not detailed here (Wisniak, 2009).

He also published a short book on qualitative analysis, which he dedicated to Würtz "as a token of affectionate regard, to a friend and teacher and as a tribute of respect and admiration to the master of a school in modern chemistry" (Crafts, 1869). In the introduction to his book Crafts writes: "This little work was written for the use of a class of students in the Cornell University... A considerable portion of the introductory part of this book is devoted to an explanation of the theory of chemical reactions and nomenclature... Chemistry certainly becomes a more attractive study when the practical and the theoretical present themselves side by side, so that while the theory explains the experiment, the experiment awakens an interest in the theory; and no course of study is more apt to interest the beginner in chemistry than that of the admirably simple and delicate tests of qualitative analysis; tests which illustrate the general laws of the science, while they have a very direct bearing upon some of the problems of every-day life... The importance of laboratory experiments is awakening every day increased attention, and the time is fast passing by when chemistry is taught to persons, who suppose that they have a vocation for a scientific profession, only by lectures and recitations."

These thoughts, written almost 150 years ago, continue to be valid today as then.

Density of pure compounds

In 1878 Victor Meyer described a new apparatus for determining the density of vapors in a very simple and precise manner (Meyer, 1878), which was rapidly adopted by many laboratories. A series of following papers of Victor Meyer and Carol Meyer reported the determination of the density of many compounds at various temperature levels. The Meyer method consisted in heating a cylindrical tall vase, made of glass, porcelain, or platinum, to a temperature such that when a liquid was introduced into it, it vaporized immediately. This vapor displaced from the vase an equivalent volume of air (both volumes were measured at the same temperature), which was measured and its weight compared to that of the added substance. The relative densities are in inverse proportion with the two volumes measured before and after the displacement. One important advantage of the method was the short time it took to make a measurement (2 to 4 minutes) (Crafts, 1880a).

Crafts believed that Meyer's method was subject to many experimental and calculation errors hence he improved the original apparatus to reduce the errors to a minimum. His modification consisted in connecting the vase with two U tubes, calibrated in tenths of cubic centimeters. To one of the branches was connected a mobile vase to allow a change in pressure. The other branch ended in a reservoir of about 9 cm^3 capacity and communicating with the vase through a capillary tube. One of the tubes led the gas through a tube of short dimensions to the bottom of the vase; the gas emerging from the top of the vase penetrated into the second U tube in order to be measured. The tubes were filled with mercury, water, or concentrated sulfuric acid, as appropriate. Crafts modifications assured that the results were accurate to within 0.02 cm^3. For gases such as chlorine, it was necessary to use concentrated sulfuric acid and avoid an excessive contact of the gas with the joints (made of natural rubber) (Crafts, 1880af).

Henry Sainte-Claire Deville (1818-1881) and Louis Joseph Troost (1825-1911) had determined that the density of iodine between 860 and 1040°C was normal, that is, the gas did not dissociate (Sainte-Claire Deville and Troost, 1860). Years later, Victor Meyer reported that the density of iodine was already abnormal at 590ºC (it had become 0.99 of the normal value); towards 1000ºC the density had decreased to 0.66 of the normal value and from there on remained constant up to 1570°C (Meyer, 1880). From these results Meyer concluded that iodine decomposed in the same manner as chlorine. The discrepancy between the results of Deville and Troost, and Meyer, led Crafts and Meier to make additional measurements to explain the divergency. Their results indicated that between 830 and 880°C the density of iodine was 0.92 of the normal value, between 1020 and 1050°C, 0.80, decreasing to 0.60 at 1390°C. From these results Crafts and Meier concluded that at a higher temperature the density would decrease to 50% of the normal density, that is, the iodine molecule decomposed into two atoms (Crafts and Meier, 1880b, 1881).

Meier and Crafts believed that the discrepancy between the results of Victor Meyer and Deville and Troost was partly due to the fact that the latter had taken the temperature of boiling zinc and cadmium as 1040 and 860°C instead of 940 and 746.3°C respectively (Meier and Crafts, 1880).

In a summarizing paper (Crafts, 1880f) Crafts provided a very detailed description of his equipment and operating technique. Experiments done with chlorine indicated that at the highest temperature of the furnace, 10 cm^3 of chlorine occupied the same volume as 10.37 cm^3 and 10.24 cm^3 of air at the same temperature. When the apparatus was filled with dry chlorine and heated as before, 10 cm^3 of air displaced 9.98 cm^3 and 10 cm^3 of chlorine. At the highest temperature of Perrot's furnace iodine diminished in density to increase in volume in the proportion of 1:1.5, and bromine in the proportion of 1:1.2; in the case of chlorine the increase in volume was 0, or at most only a few hundredths, and therefore nothing like an augmentation of 50%, as originally obtained by Meyer. According to Crafts the determination of the density could serve as a measure of the degree of dissociation of those gases that combined with a decrease in volume, and thus were decomposed with increase in volume, e.g. steam, CO_2, and NH_3 (Crafts, 1880f).

An important application of the use of the density of a gas was in elucidating the true formula of aluminum chloride, the catalyst in the Friedel-Crafts reaction (Friedel and Crafts, 1888b). In looking for the mechanism of their organic synthesis method, Friedel and Crafts assumed that the formula of aluminum chloride was Al_2O_6 but in 1887 Lars Frederik Nilson (1840-1899) and Sven Otto Pettersson (1848-1941) (Nilson and Pettersson, 1887) had reported that according to Meyer's method the molecular mass of the salt pointed to the formula $AlCl_3$, that is, aluminum was tervalent. Given the theoretical importance of the subject, Friedel and Crafts decided to perform their own measurements claiming that Meyer's method was unsuitable because it required operation at a temperature (440°C) well above that of the normal boiling point of the compound (183°C). Friedel and Crafts determined the vapor pressure of aluminum chloride at different temperatures (252 to 2277 mmHg) and measured very precisely its melting and fusion points. The vapor density of aluminum chloride was determined using Jean-Baptiste André Dumas' (1800-1884) method, modified for different tensions, with special care being taken to obtain the chloride in a perfectly anhydrous condition and to protect it from moisture during the subsequent operations. The vapor density was calculated at ten different temperatures, from 218 to 433°C and found to correspond with the molecular formula Al_2Cl_6. They speculated that at higher temperature aluminum chloride decomposed into two gases, which would explain the results of Nilson and Pettersson (Friedel and Crafts, 1888b).

Organic chemistry

In 1861 Crafts joined Würtz's laboratory and at his suggestion begun to study the action of halogens on ethylene sulfide and its derivatives. Ethylene sulfide was prepared by reacting ethylene bromide with potassium hydrosulfide. Bromine was immediately replaced by sulfur, in a highly exothermic reaction. A large part of the bromide transformed into a white compound, highly soluble in alcohol, ether, or carbon disulfide. The product was distilled at about 200°C, the first fraction condensing as white crystals was followed by another fraction consisting of an oily substance, which decomposed partly by heat, leaving a carbon residue. The white crystals were washed with ether and their elemental analysis corresponded to the formula C_2H_4S. The sulfide solidified at 112°C becoming crystalline and distilled without decomposition between 199 and 200°C. It was soluble in ether, alcohol, and particularly, in carbon disulfide. From the latter it crystallized in oblique rhomboidal prisms of 69.44°C. Crafts reported the crystalline geometrical characteristics, as measured by Friedel (Crafts, 1862a).

Ethylene sulfide did not react with aqueous or gaseous ammonia but was attacked by chlorine releasing HCl. Crafts was unable to identify the products of the reaction. Ethylene sulfide combined directly with bromine, without release of HBr. In the presence of an excess of bromine or ethylene sulfide, it always produced the compound $C_2H_4SBr_2$. This bromide was a yellow substance quite insoluble in ether or carbon disulfide. It absorbed avidly humidity from the air, yielding white crystals. The same result was obtained if heated in the presence of a small amount of water; the water was then found to be concentrated in HBr. The resulting crystals contained less bromine than the bromide and were completely soluble in water; their analysis indicated the formula C_2H_4SO, that is, the bromine had simply been replaced by oxygen (Crafts, 1862a).

In a following paper (Crafts, 1862b) Crafts reported that C_2H_4SO could also be obtained by the direction oxidation of ethylene sulfide with nitric acid, with the advantage that C_2H_4SO, was the only product of the reaction if conducted above 100°C. Operating under pressure at higher temperatures led the formation of another product containing two oxygen atoms, $C_2H_4SO_2$. To obtain C_2H_4SO pure it was enough to add fuming nitric acid in small portions to ethylene sulfide followed by evaporation of the acid and washing of the residue. Addition of a small amount of water to the latter deposited crystalline C_2H_4SO, which was purified by washing with alcohol until no acid reaction was detected with litmus. The dioxide was obtained by heating in sealed tubes C_2H_4SO to 150°C with fuming nitric acid. This was also a neat reaction like the first one. The dioxide deposited as small crystals and the remaining liquid was found to contain large amounts of hyponitric acid. The dioxide of ethylene sulfide was completely insoluble in cold or boiling water but very soluble in ordinary nitric acid (Crafts, 1862b).

Ethylene bromide reacted with an alcoholic solution of potassium hydrosulfide more energetically than the chloride of the same radical. The purified white solid was slightly soluble in water; treating the filtered liquid with lead nitrate yielded the yellow precipitate that characterizes slightly soluble organic sulfides, but after drying it became insoluble. Analysis of the product showed that it was a mixture of ethylene monosulfide and a higher sulfide of the same radical. Dissolved in ether or boiling alcohol it released a small amount of C_2H_4S that remained in crystalline form after evaporation of the solvent. Heated in a sealed tube with ether at 180°C it yielded a larger amount of crystals accompanied by a yellow orange oil very soluble in ether, which Crafts assumed to be ethylene disulfide, $C_2H_4S_2$ (Crafts, 1862c).

Bromine and ethylene sulfide combined directly when put in contact, but the combination was easily destroyed by a slight increase in temperature. A better preparation method was to mix bromine with ethylene sulfide dissolved in carbon disulfide. Ethylene sulfide bromide precipitated as a yellow body, which could be easily purified by washing with carbon disulfide. An elemental analysis of this compound yielded the formula $C_2H_4SBr_2$. This dibromide decomposed at temperatures below 100°C releasing HBr and leaving a resinous residue. It was insoluble in alcohol and ether but decomposed when left for some time in contact with alcohol. It dissolved in water with decomposition and the aqueous phase was found to contain an oxygenated compound (Crafts, 1862d).

Ordinary or fuming nitric acid attacked ethylene sulfide quite vigorously, and yielded a product very soluble in an excess of acid. The purified material was a white crystalline solid having the composition C_2H_4SO, corresponding exactly to that of the compound produced by decomposition of the bromide by water (Crafts, 1862d).

Ethylene sulfide oxide crystallized in small rhomboidal crystals, insoluble in alcohol and soluble in water, and destroyed by heating to about 200°C. Additional oxidation converted it to $C_2H_4SO_2$, stable to temperatures above 200°C (Crafts, 1862d).

According to Crafts, a number of products resulting from the action of chlorine upon ethyl acetate were known, but the first term of the series, $C_4H_7ClO_2$, had never been isolated. Würtz thought that it was possible that bromine acted in the same manner, although less energetically. For this reason he requested from Crafts to prepare the compound $C_4H_7ClO_2$ by reacting ethyl acetate with two equivalents of bromine. It was desired to find if bromine replaced part of the hydrogen in the acetyl radical or in the ethyl one. Crafts could not answer the question because the reaction occurred in a different manner from the one assumed. Bromine dissolved in the ether exothermally but without release of HBr, even if the mixture was left alone for several weeks at room temperature, in the presence of light. Subsequent treatment with aqueous alkali removed the bromine from the solution leaving the ethyl acetate unaltered. If the mixture was heated in a sealed tube to 150°C, the bromine color disappeared instantly; at 106°C this phenomenon took place after 12 to 20 hours. The reaction was not accompanied by the formation of a substantial amount of HBr. Distillation of the mixture produced two distillates, the first boiling at about 40°C and the second near 200°C. On cooling, the latter crystallized in the form of rhomboidal crystals, having a composition corresponding to bromoacetic acid. Continuous washing of the first distillate with an aqueous solution of KOH left a liquid having the properties of ethyl bromide, C_2H_5Br (Crafts, 1863).

Crafts and Silva were interested in studying the effect of chlorine and bromine and triethylphosphine oxide, $OP(C_2H_5)_3$ (Crafts and Silva,1871). They first tested the two-step preparation method proposed by Georg Ludwig Carius (1829-1875) (Carius, 1866) in which ethyl iodide was first heated in a closed glass tube with phosphorus at 160°C and the reaction product was then reacted with anhydrous ethanol in a new sealed tube at 160°C. According to Carius, the reaction mechanism was as follows:

$$2P + 4C_2H_5I = P(C_2H_5)_4I + PI_3$$

$$P(C_2H_5)_4I + C_2H_5OH = P(C_2H_5)_3O + C_2H_5I + C_2H_6$$

$$PI_3 + 3C_2H_5OH = P(OH)_3 + 3C_2H_5I$$

Crafts and Silva's experimental results indicated that this mechanism was mistaken, the first reaction yielded a white crystalline body, which did not decompose even at 100°C and was hardly soluble in water; tetraethylphosphonium iodide was known to be soluble in water and to decompose rapidly in the presence of phosphorus triiodide. In addition, the amounts of the different products were not consistent with the above mechanism. Hence Crafts and Silva believed that the first step went further than what Carius had assumed, all the phosphorus was actually converted into compounds capable of yielding triethylphosphine oxide by reactions such as

$$PI_3 + 3C_2H_5I = P(C_2H_5)_3I_2 + 4I$$

$$PI_3 + 3P(C_2H_5)_4I + I_2 = 4P(C_2H_5)_3I_2$$

$$P(C_2H_5)_3I_2 + C_2H_5I = P(C_2H_5)_4I + I_2$$

The absence of gaseous pressure allowed the preparation to be carried in large and thin tubes. According to Crafts and Silva the overall conversion of the phosphorus was about 80% and the absence of phosphorus iodides was proven by the fact that boiling and shaking the reaction product with water gave no indication of HI being present (Crafts and Silva, 1871).

Crafts and Silva studied in detail the properties of triethylphosphine oxide. The compound boiled at 242.8-243°C and melted at 51.9°C; it was highly hygroscopic, a small amount of water in the product lowered substantially the melting and the boiling points. An aqueous solution of the oxide, saturated with chlorine, retained its greenish color during many days of exposure to diffuse daylight, without formation of HCl. The dry oxide may be saturated with chlorine at 100°C without any reaction taking place but addition of a small amount of water resulted in the release of a considerable amount of chlorine (salting out). Similarly, bubbling chlorine through melted product resulted in the production of HCl. The oxide dissolved in bromine with a slight elevation of temperature. Evaporation of the bromine left crystals of the oxide. Crafts and Silva believed that HCl and HBr combined with the oxide in the same manner as these acids combine with water and that only under exceptional conditions they resulted in a product having a simple formula (Crafts and Silva, 1871).

Organo-metal chemistry

In previous communications about the esters of silicic acid, Friedel and Crafts had found that acids could displace silicic acid from its combinations (Friedel and Crafts, 1863ab, 1865, 1866). Thus heating anhydrous boric acid with silicic ester yielded the corresponding boric ester quite pure. Based on this observation, Crafts speculated that the same reaction could be used to prepare other ethers, particularly those of arsenic acid. Thus well-dried arsenic acid was mixed with ethyl silicate in a sealed tube. No reaction was observed below 220°C but a much higher temperature produced enough gas to shatter the tube. Between 220 and 230°C the reaction products filled the tube with silica gel. When the tube was opened a substantial amount of a gas resembling ethylene was released. Distillation of the product yielded a first distillate of ordinary ester, followed by a liquid passing between 150 and 200°C (Crafts, 1867).

The above reaction did not produce arsenic ester, for this reason Crafts tested the reaction between silver arsenate and ethyl iodide and found that in the presence of an excess of arsenate the reaction proceeded neatly producing the ester in stoichiometric ratio, having the elementary formula $As(C_2H_5)_3O_4$, a density of 1.3264 at 0°C and 1.3161 at 8.8°C. Similar results were obtained when heating arsenious acid with the silicic ester. The product was ethyl arsenite, having the formula $As(C_2H_5)_3O_3$, a liquid boiling at 166-168°C, without decomposition. In contact with water it immediately decomposed precipitating arsenious acid. Crafts also reported that tungstic acid and antimonious acid did not react at all with ethyl silicate (Crafts, 1867).

A later paper on the subject (Crafts, 1870) gave more details about the preparation of arsenic esters. Ethyl arsenate could be prepared by heating a mixture of dry silver arsenate with ethyl iodide in a sealed tube at 100°C; the temperature should not exceed this value by much and ethyl iodide should not be in excess because it led to the mutual decomposition of ethyl arsenate and ethyl iodide at high temperature. The ethyl arsenate was separated from the silver salt by washing the product of the reaction with ether, followed by distillation at 60 mmHg. At this pressure, ethyl arsenate distilled between 148 and 150°C; its density was 1.3264 at 4° and 1.3161 at 8.8°C, and the elementary analysis corresponded to the formula $As(C_2H_5)_3O_4$. Distilled in the presence of air caused partial decomposition but most of the arsenate passed without decomposition between 235 and 238°C. Mixed with water it decomposed immediately into alcohol and arsenic acid. A similar decomposition occurred in the presence of humid air or in contact with aqueous alcohol. Ammonia gas reacted easily with ethyl arsenate yielding alcohol and a crystalline substance insoluble in ether and very soluble in alcohol (Crafts, 1870).

Methyl arsenate was prepared reacting methyl iodide with silver arsenate. Its properties were very similar to those of the ethyl ester; elemental analysis indicated the formula $As(CH_3)_3O_4$; and density 1.5591 at 14.5°C; it decomposed when distilled at atmospheric pressure and at 60 mmHg it distilled between 128-130°C. Crafts also prepared an impure form of amyl arsenate by a similar procedure (Crafts, 1870).

Ethyl arsenite was prepared by three different procedures: (a) Heating at 200°C a mixture of ethyl silicic and arsenious acid, (b) heating at 120°C a mixture of ethyl iodide with silver arsenite, and (c) heating sodium alcoholate with arsenium chloride or bromide dissolved in alcohol. The latter method was complicated by a secondary reaction that decomposed the arsenious ester because the alcoholate reacted equally well with the arsenious ester to yield sodium arsenite and ethyl ether. The amount of arsenious ester present at any moment in the reacting mixture depended on the relative velocity of both reactions. Elemental analysis of the ester corresponded with $(C_2H_5)_3AsO_3$; it had a density of 1.224 at 0°C; at atmospheric pressure it boiled between 165-166°C, without decomposition. It decomposed immediately in contact with water, with humid air, or aqueous alcohol, giving alcohol and a precipitate of arsenious acid (Crafts, 1870).

Methyl arsenite was prepared using the same conditions as for the ethyl ester. The elementary analysis corresponded with $(CH_3)_3AsO_3$. Amyl arsenite was obtained by reacting sodium amylate with arsenic bromide. The elementary analysis corresponded to $(C_5H_{11})_3AsO_3$.

In his memorial lecture about Friedel (Crafts, 1900) Crafts resumed their work on organosilicon compounds as follows: They expected that the norma1 ester, $Si(OEt)_4$, would form a series of condensed esters of which the simplest should be $Si(OEt)_3{\cdot}O{\cdot}Si(OEt)_3$. Their results indicated that a trace of water produced the later compound mixed with many others having a more complicated structure, for example, $Si(OEt)_3{\cdot}O{\cdot}Si(OEt)_2{\cdot}O{\cdot}Si(OEt)$. All the additional compounds boiled at temperatures at which glass softens, undergoing polymeric transformations. Among other organosilicon compounds prepared by Crafts we can mention silicopentane and silicononane, silicononyl alcohol, triethylsilicon oxide, silicochloroform, silicoiodoform, silicopropionic acid, etc. (Friedel and Crafts, 1863ab, 1865, 1866).

Sulfoconjugated acids

The traditional method of regenerating an aromatic hydrocarbon from its sulfoconjugated combination consisted in heating it in a closed vase in the presence of HCl (Friedel and Crafts, 1884). This method was very inconvenient because acids attacked the tubes at the working temperature and shattered them frequently. In addition, it was restricted to very small amounts of material. Henry Edward Armstrong (1848-1937) and Alexander Kenneth Miller (1856-1945) (Armstrong and Miller, 1884) had proposed a better method in which the acid was decomposed by mixing it with an excess of diluted sulfuric acid, followed by bubbling steam through the mixture heated to about 170°C. Friedel and Crafts found that this method did not release the total of the hydrocarbon because of secondary reactions taking place. Sulfuric acid in the presence of water transformed part of the monosulfonic acids into disulfonic acids, which resisted the action of heat and water vapor even up to 250°C, and the yield of hydrocarbon was low. At higher temperatures the sulfonates oxidized releasing sulfur dioxide. Friedel and Crafts found that these shortcomings disappeared when the sodium or potassium salt of the sulfonic acid was treated with a large excess of concentrated phosphoric acid. The sulfonic acid was decomposed, sulfuric acid released as bisulfate, and the hydrocarbon completely recovered Experiments with benzene, *m*-xylene, and naphthalene and its hydrides indicated that this new method allow a very easy separation; the monosulfonic acids decomposed in this manner were in proportion to the ease with which they are formed (Friedel and Crafts, 1889ab).

Crafts also discussed the catalytic effects that occurred during the hydrolysis of sulfoconjugated acids with HCl and other strong acids (Crafts, 1901, 1907). His results indicated that the rate of reaction instead of being proportional to the concentration of the catalyst, increased 35 times when a solution of 38 wt % HCl was used instead of one 19 wt %. Addition of zinc chloride resulted in a further increase in the rate. These results indicated that the catalysis of the reaction was due not to the hydrogen ions but to the joint action of HCl and water. The above conclusion was supported by the results of about 150 experiments on the hydrolysis of *m*-xylene sulfonic acid, $C_8H_9SO_3H$, with HCl (gas) of concentrations varying between 13 and 43 wt %, or with or without addition of sulfuric acid, nitric acid, or zinc chloride The experiments were carried on in sealed tubes heated chiefly to 100°C (Crafts, 1901).

The experimental results pointed to a remarkable relation between the rate constant and the concentration of HCl, the reaction promoter. For HCl concentrations between 13 and 31 wt %, the rate increased fourfold for each successive increment of 6 wt % HCl. Since the sulfonic acids had nearly a strong affinity as HCl, Crafts thought that they might autocatalyze the reaction, and the decomposition might be related to the concentration. Additional experiments confirmed this assumption (Cross, 1918).

In his second paper on the subject (Crafts, 1907) Crafts gave a detailed and quantitative description on the rate of hydrolysis of the sulfonic acids derived from toluene, *m*- and *p*-xylene, mesitylene, pseudocumene, trichloro-and bromobenzene, and naphthalene, and the amino acids. The catalyzing agents were HCl, HBr, HI, and H_2SO_4, in concentrations rising from 0.03 to 12.5 mol/L and at temperatures ranging in intervals of 10° from 80° to 218°. His results indicated that the rate of hydrolysis of sulfoconjugated acids with strong acids such as HCl, HBr, and H_2SO_4, progressed in a geometrical progression when the catalyst concentration was increased in an arithmetic progression (Crafts, 1907).

Thermometry

Crafts published two summarizing papers on his work on thermometry, one in French and one in English (Crafts, 1883ab). In the first one he gave a general review of all the work on thermometry, followed by a detailed description of the preparation and stability of pure naphthalene and benzophenone, as well as the experiences done with an air thermometer to determine their boiling points in the pressure range 85 to 1800 mmHg (Crafts, 1883a). In the second paper he described in great detail specific subjects such as calibration of mercury thermometers, the value of the degree, depression and rise of the zero point (Crafts, 1880bc, 1882b), the preparation and calibration of thermometers (Crafts, 1882d, 1883a, 1888b), corrections to be applied to mercury thermometers to bring them to the true temperature as measured by a hydrogen thermometer (Crafts, 1878, 1882c, 1888b), problems associated with thermometers having a limited scale, expansion of glass (Crafts, 1880b), apparatus for measuring vapor pressures, purification of mercury (Crafts, 1888a), influence of pressure, and application to the determination of the boiling and melting point of a substance (Crafts, 1880e, 1882a).

It was a well-known fact that a mercury thermometer left unused for some time, suffered a temporary drop of its zero point of several tenths of a degree if it was heated to about 100°C. Similarly, a prolonged exposure to a high temperature resulted in a contraction of the bulb and an elevation of the mercury column on the scale. Crafts studied this problem in detail and published several memoirs where he suggested how to handle this problem (Crafts, 1880bc, 1882b). In a paper published in 1880 (Craft, 1880b) he compared eight thermometers, four built of French crystal and four built of German sodium glass free of lead. Here he reported the zero point, the position of the zero point one hour after the heating, and the temperature and time elapsed between two observations of the zero. Analysis of the results indicated that the zero point rose more rapidly and farther in the thermometers made of crystal, that the elevation of the zero time was faster at the beginning and possibly tended to a limit for a very prolonged heating at a given temperature, and that the zero point, raised by prolonged heating at a high temperature, remained fixed at the new height when the instrument was kept at the ordinary temperature, and the effect produced by the high temperature rendered the thermometer more stable under the influence of any inferior temperature. The maximum effect observed was an elevation of 26.4°C after heating the thermometer for a total period of 263 hours at 355°C. The experiences were stopped before achieving the maximum effect in order to see if the elevation remained constant (Craft, 1880b).

In a following note (Crafts, 1880c) Crafts quoted many experiences showing that the pressure had a negligible effect on the permanent elevation of the zero point of the thermometer. Glass heated by a lamp and exposed for a long time to the action of heat decreased its volume as a result of an internal work. He then went on to say that the theory exposed by César Despretz (1791-1863) (Despretz, 1837) to explain the temporary depression of the zero point could be also used to explain the permanent elevation of the zero, and also to account for the anomalous effect of heat that produced two opposite effects: "Every time that the molecules of a substance experiment a displacement caused by a mechanical cause like pressure, traction, or torsion, by a physical cause such as an increase or decrease of the temperature, they do not return to their original positions once the cause is eliminated. That is, if the volume is decreased or increased in a substantial amount by any force, it remains increased or decreased for a long time after the force has ceased its action". In other words, according to Despretz's theory the glass particles separated by glass blowing did not return immediately their normal position at a lower temperature (hysteresis effects in glass). During a certain period of time, perturbations were observed, and the glass could remain for a long time in a tension state at room temperature. The action of heat at a given temperature (355°C for example) increased the mobility of the particles, favored their return to the normal position, and originated a contraction, but the glass on cooling from the latter temperature, retained part of the displacement that occurred at 355°C. Heating again to a temperature below 355°C (300°C for example), a new contraction took place, and thus successively, such that the slow cooling that produced all these effects on the glass particles, would provide the longest approach to the normal state, and hence, a largest stability. Another of Craft's conclusions was the Johann Pernet's law (Pernet, 1879) that between 0 and 100°C the depressions of the zero are proportional to the squares of the temperatures, was invalid at high temperatures (Crafts, 1880c).

In a following paper Crafts again analyzed the question of the variation of the expansion coefficient of glass (Crafts, 1880d). If the bulb of the thermometer contracted in a permanent manner then all the mercury scale was displaced in the scale by a certain number of degrees and each reading was corrected accordingly, but if the expansion coefficient varied, the distance between two fixed points changed accordingly and the graduation became incorrect. Crafts reported the variations of the points 00 and 100°C observed in seven thermometers, which had been heated at 355°C for a long period of time. The results showed that the original interval of 100°C had increased between 0.5 to 0.9°C. This was an important question because if we assumed that the irregularities in the expansion coefficient originated from different degrees of tension produced during the blowing of the bulb, then these could be made to disappear by the treatment indicated here (Crafts, 1880d).

All physics books contained a table of the corrections to apply to all mercury thermometers (Crafts, 1882c), which had been prepared by Victor Regnault (1810-1878) around 1850 for use with his instruments. Regnault had indicated the inconvenience of using his tables for instruments of a different origin since the march of the reading of a thermometer changed according to the composition of the glass and the treatments it has experienced. Regnault's warning had been neglected when classing laboratory thermometers into two categories according if their glass contains or not lead oxide; one set of corrections applied for the crystal of Choisy-Roi and the other to common glass manufactured in France and Germany. Crafts used a hydrogen thermometer to compare fifteen thermometers, seven manufactured by Baudin, seven manufactured by the Alvergniat brothers, and a German soda glass thermometer manufactured by Muller in Bonn. Crafts's paper tabulates the average corrections to be added to the readings of the 15 thermometers to obtain the true temperature measured with a gas thermometer. The results indicated that the march of thermometers manufactured in Paris closely followed that of the ordinary glass thermometer used by Regnault, but that they differed substantially from the ones made from Choisy-le-Roi crystal, which contained almost a double percentage of lead oxide. In general, the variation of the readings between 2000 and 300°C were seen to be very similar for the French crystal thermometers and the German soda glass ones that do not contain lead (Crafts, 1882c).

For a long time gas thermometers had been used to measure high temperatures, particularly because there their readings overlapped those of the Kelvin scale. Unfortunately, at high temperatures the precision of gas thermometers left much to be desired. The progress of organic chemistry in the last years had resulted in the discovery of a large number of new compounds for which little information was available about their physical properties, particularly their boiling points, when these were above 340°C. The main reason for this was the lack of instruments appropriate for the measurement of high temperatures, able to wok with very small amount of a substance. In this paper, Crafts restricted himself to temperatures below 400°C, trying to prove that certain substances could be prepared with a degree of purity high enough so that their the boiling point could be used as fixed thermometric points, and allow an easy and accurate calibration of the instrument in the high temperature range. The thermometers employed were a mercury thermometer and a nitrogen gas one. The basic idea was the physical principle that a pure liquid will always exert the same vapor pressure at a given temperature. For his purposes, Crafts selected naphthalene and benzophenone, which could be boiled for hours without any trace of decomposition. Both could be prepared extremely pure by repeated crystallization until the melting point not varied by more than 0.05°C. According to Crafts "naphthalene has a value almost equal to that of water for establishing temperatures" (Crafts, 1913b; Crafts and Meier, 1880a).

Crafts also mentioned that no thermometric scale could exceed the degree of precision by which the ice point and the temperature of condensation of water had been determined. The pertinent value was of the order of 0.001°C. Clearly, the precision of the measurement would depend simultaneously of the thermometric apparatus used, the constancy of the vessels, and the measure of the boiling pressure. The mercury and nitrogen gas thermometers allowed a precision of 0.01°C and the barometer of 0.01 mmHg. Considering the experimental results, Crafts believed that the overall accuracy of his results was about 0.05°C (Crafts, 1913b).

The first part of the paper was devoted to discuss the purity and inalterability of naphthalene, the study and measurement of the pressures, measurement of the temperature using first a gas thermometer and then a nitrogen gas one, and correlation of the results. A very detailed description, accompanied by drawings, is given of every piece of equipment used. Atmospheric nitrogen was selected for the gas thermometers because it could be obtained easily and did not corrode the equipment. The fixed point zero was determined by submerging the reservoir of the thermometer in ice, carefully ground and finely grated, and constantly sprinkled with distilled water. Similarly, the fixed point 100 was determined in a specially built apparatus, well protected from radiation (Crafts, 1913b).

Crafts utilized an equation proposed by Pierre Chappuis (1855-1916) (Chappuis, 1888), to calculate the value of the expansion coefficient α of nitrogen between 64.11 and 271.48 K. Over 200 measurements of the variation of the vapor pressure, P, of naphthalene with the temperature (temperatures 171 to 270°C and pressures 231 to 2,149 mmHg), led to the following regression formula:

$$P = 62.816 + 2.0509(T - 130) + 0.038169(T - 130)^2 + 0.0002122(T - 130)^3 + 0.0000011264(T - 130)^4$$

with P in mmHg and T in K.

Craft's results agreed closely with those of Ludwig Holborn (1860-1926) and Fritz Henning (Holborn and Henning, 1905), published afterwards, where the temperatures were measured by a resistance thermometer (Cross).

A following paper (Crafts, 1915) was devoted to a revision of Victor Regnault's (1810-1878) tables and Broch and Wiebe calculations, concerning the vapor pressure of water, and to put in evidence several errors present in Regnault's data, particularly the one related to the movement of the zero point. The analysis was very important because Regnault's tables were widely used, particularly in the thermodynamic analysis of steam engines. In this memoir Crafts reported very detailed data on his measurement of the vapor pressure of water between 135 and 228°C, as well as a comparison with Regnault's data and the corrections to be applied to the latter.

In the second part of this paper Crafts discussed the application of three well know empirical equations (Dühring, 1878; Crafts, 1913a, and Ramsay and Young, 1886) to describe the relation between vapor pressure and temperature. To do so he used the data available in the literature for nine substances (water, acetic acid, ethanol, benzene, fluorobenzene, naphthalene, hexane, and hexamethylene) and concluded that none of them was general enough to fit all the compounds.

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