



Auguste Scheurer-Kestner. Contribution to the atomicity of iron

Auguste Scheurer-Kestner. Contribución a la atomicidad del hierro

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Resumen

Se sabía que las sales normales de los óxidos superiores podían hacerse más o menos básicas y seguir siendo solubles. Auguste Laurent había postulado que un mismo cuerpo podía tener dos masas atómicas diferentes siempre que se tuvieran en cuenta las funciones que realizaba, por ejemplo, Fe^2 (ferrosus = 28) y $\text{Fe}^{4/3}$ (ferricum = 18,66). Scheurer-Kestner demostró que cuando el hierro se disuelve en ácido nítrico hasta la saturación, el resultado siempre es un nitrato de hierro básico y la basicidad depende de la concentración del ácido como sal férrica. Para demostrar la naturaleza hexatómica del hierro, Scheurer-Kestner preparó y determinó las propiedades de una variedad de poliácidos y acetónitratos férricos, y mostró que, aunque todos ellos estaban bien definidos y cristalizados, no se prestaban a la representación racional conservando el antiguo masa atómica del elemento.

Palabras clave

Atomicidad, fierro, óxidos superiores; sales de fierro.

Abstract

It was known that the normal salts of the higher oxides could be made basic and still be soluble. Auguste Laurent had postulated that the same body could have two different atomic masses if the functions it performed were considered, for example, Fe^2 (ferrosus = 28) and $\text{Fe}^{4/3}$ (ferricum = 18.66). Scheurer-Kestner proved that when iron was dissolved in nitric acid to saturation, the result was always basic iron nitrate and the basicity depended on the concentration of the acid as a ferric salt. To demonstrate the hexatomic nature of iron Scheurer-Kestner prepared and determined the properties of a variety of ferric polyacid and acetol nitrates and showed that although all of them were well defined and crystallized, they did not lend themselves to rational representation while retaining the old atomic mass of the element.

Keywords

Atomicity; higher oxides; iron, iron salts.

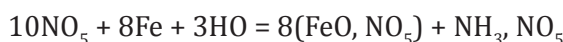
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In what follows attention must be paid to the fact that Scheurer-Kestner sometimes used the old nomenclature, for example, water = HO

Atomicity

In 1858, J. M. Ordway published a long paper describing the properties of sesquisalts (sesqui = 1.5) (Ordway, 1858) where he stated that the normal salts of the higher oxides, that is, those containing more than one equivalent of oxygen to one of metals, could be made basic and remain soluble. It also seemed that the soluble compounds, with rare exceptions, appeared to be incapable of crystallization; a gemlike character being their peculiar distinguishing feature. By spontaneous evaporation they became tough, shining, transparent masses, the less basic of them again being soluble on pure water. Hence, to obtain crystals of the normal salts, an excess of base had to be carefully avoided. Ordway described five different procedures to make salts basic: (1) digesting the hydrated oxide with the normal salts, or with less than the equivalent of acid; (2) by direct oxidation to make a soluble salt with less than the normal quantity of acid. For example, reacting ferrous sulfate with half its weight with nitric acid of specific gravity 1.2. This resulted in a rapid oxidation of the ferric salt with evolution of nitric oxide and a red liquid containing ferric oxide, sulfuric acid and nitric acid; (3) expulsion of a portion of the acid from a normal salt by means of a moderate and long heating; (4) removal of a portion of the acid by another base in the form of an insoluble salt, as in a double decomposition; and (5) neutralization of part of the acid of a normal salt by a more powerful base, the whole remaining in solution. For example, gradual addition of dilute ammonia to a solution of ferric nitrate produced precipitation until $\frac{7}{8}$ of the acid was combined with ammonia (Ordway, 1858).

According to Scheurer-Kestner, the reaction between nitric acid and iron was sometimes excessively lively, sometimes, on the contrary, slow, and difficult; the difference due mainly to the density of the acid used (Scheurer-Kestner, 1859ab). It was long known that nitric acid having a relative density of 1.034 produced only ferrous oxide nitrate and no gas was given off; the hydrogen forming ammonia with the elements of nitric acid. As a result, the product of the reaction was a mixture of ferrous nitrate and ammonia nitrate. Acid of relative density 1.073 dissolved iron rather slowly with a noticeable evolution of gas. This time the product of the reaction was a mixture of ferrous oxide nitrate oxide and ferric oxide nitrate, accompanied by a significant amount of ammonia. A more concentrated acid, for example of relative density 1.115, produced only ferric oxide nitrate, and no ammonia. The production of the latter took place as long as there was formation of a ferrous salt, according to the equation (Scheurer-Kestner, 1859ab):



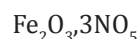
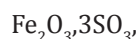
When the only product was ferric oxide nitrate, this salt was far from having a constant composition; it was found that the quantities of iron dissolved in proportion to the acid employed were very variable. For example, allowing the acid to act on the metal for some time, more or fewer basic salts were formed which appear as jelly in the liquid, a jelly that dissolved in water when left to macerate for twenty-four hours at 40 °C. The formation of these sub-salts interfered with the preparation of neutral ferric oxide nitrate and could be avoided by removing the iron when the reaction began to subside, that is, when the nitric acid had been already saturated. Doing so, most of the time a partly basic salt was produced, which remained dissolved (Scheurer-Kestner, 1859ab).

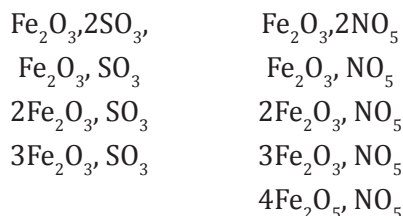
Scheurer-Kestner analyzed the different liquors formed as follows: He took two samples of identical weight of each liquid and treated the first with ammonia to precipitate the iron oxide. The precipitate was then calcined and weighed. The second sample was boiled for twenty minutes with freshly precipitated calcium carbonate. The resulting calcium nitrate was precipitated with ammonium oxalate; the weight of the calcium oxalate dried at 100 °C on a filter of known weight filter gave, by calculation, the weight of the acid contained in the liquor. The results indicated that the freshly precipitated calcium carbonate decomposed completely, even the insoluble iron sub-nitrates (Scheurer-Kestner, 1859ab).

Scheurer-Kestner found that by using the acid of relative density 1.332 and adding to it a suitable quantity of iron, he was able to obtain a ferric solution of relative density 1.580 which deposited on cooling beautiful rectangular prisms with four sides, colored brown by the mother liquor interposed; but which become almost colorless on drying on blotting paper. He also observed that the iron was also attacked by even more concentrated acid (i.e., relative density 1.384). but when the liquor approached saturation, the iron became shiny and passive state. By this and other experimental procedures, he was able to prepare the whole series of iron nitrates, determine their formula, and some of their properties (Scheurer-Kestner, 1859ab).

To sum up, these experiments showed that when iron was dissolved in nitric acid to saturation, the result was always basic iron nitrate and the basicity depended on the concentration of the acid (Scheurer-Kestner, 1859ab).

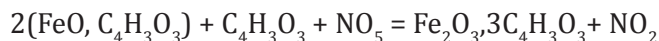
Scheurer-Kestner summarized his results as follows (Scheurer-Kestner, 1858, 1859ab): (1) A nitric acid of relative density 1.034 produced with iron only ferrous oxide nitrate and ammonia; an acid of 1.073 gave a mixture of ferrous and ferric oxide nitrates and ammonia nitrate, and an acid with a relative density of 1.115 produced only ferric oxide nitrate and no ammonia; (2) the latter nitrate was not a pure neutral nitrate, it was a mixture of neutral nitrate and several different basic nitrates; (3) the quantity of basic salts formed, as well as the heat released by the reaction, were approximately in direct proportion to the concentration of the acid employed; (4) the neutral salt with three acid atoms could only be obtained by using quantities of acid and iron corresponding to the equation $4\text{NO}_5 + 2\text{Fe} = \text{Fe}_2\text{O}_3,3\text{NO}_5 + \text{NO}_2$; (5) the neutral salt thus obtained crystallized alone with 18 equivalents of water. The neutral nitrate, $\text{Fe}_2\text{O}_3,3\text{NO}_5,18\text{HO}$, crystallized alone; (6) sesquibasic and tribasic nitrates were non crystallizable and their presence hindered the crystallization of the neutral nitrate; (7) the neutral nitrate was not precipitated from its aqueous solution by nitric acid, which simply discolored it. The sesquibasic and tribasic nitrates were, on the contrary, precipitated by nitric acid; (8) boiling with water decomposed each of the three salts mentioned. The neutral nitrate, on decomposing, gave a salt which had the formula $2\text{Fe}_2\text{O}_3,\text{NO}_5,\text{HO}$, a formula that could be also interpreted as $\text{Fe}_2\text{O}_3,\text{NO}_5,\text{Fe}_2\text{O}_3,\text{HO}$. The sesquibasic nitrate gave a body of formula $3\text{Fe}_2\text{O}_3,\text{NO}_5,2\text{HO} = \text{Fe}_2\text{O}_3,\text{NO}_5,2(\text{Fe}_2\text{O}_3,\text{HO})$. The tribasic nitrate gave a body of formula $4\text{Fe}_2\text{O}_3,\text{NO}_5,3\text{HO} = \text{Fe}_2\text{O}_3,\text{NO}_5,3(\text{Fe}_2\text{O}_3,\text{HO})$; (9) the complete series of iron nitrates contained the following terms: (a) $\text{Fe}_2\text{O}_3,3\text{NO}_5$, neutral nitrate; (b) $\text{Fe}_2\text{O}_3,2\text{NO}_5$, sesquibasic nitrate; (c) $\text{Fe}_2\text{O}_3,\text{NO}_5$, tribasic nitrate; (d) $2\text{Fe}_2\text{O}_3,\text{NO}_5,\text{HO}$, from neutral nitrate; (e) $3\text{Fe}_2\text{O}_3,\text{NO}_5,2\text{HO}$, from sesquibasic nitrate; and (f) $4\text{Fe}_2\text{O}_3,\text{NO}_5,3\text{HO}$, from tribasic nitrate; (10) the complete series of iron nitrates, except one, had their correspondents in the series of iron sulfates:





and (12) salts of similar constitutions also existed in the nitrate series of lead and mercury: HgO, NO_5 , $2\text{HgO}, \text{NO}_5$, $3\text{HgO}, \text{NO}_5$, PbO, NO_5 , $2\text{PbO}, \text{NO}_5$, and $3\text{PbO}, \text{NO}_5$, but all these salts were insoluble (Scheurer-Kestner, 1858, 1859ab).

In his next paper, Scheurer-Kestner repeated that certain ferric salts were often prepared by oxidizing a mixture of suitable proportions of the ferrous salt and the acid (Scheurer-Kestner, 1859c). In this manner, it was possible to prepare ferric sulfate and ferric chloride by oxidizing with nitric acid the corresponding ferrous salts mixed with the proper amounts of sulfuric acid or HCl. Reacting a mixture of boiling nitric acid and ferrous acetate in the presence of an excess of acetic acid resulted in a rapid oxidation and a clear solution colored dark red. But to achieve completion required an amount of nitric acid well in excess to that required by the equation:

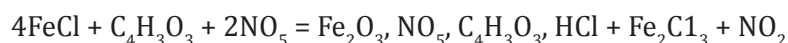


Experience indicated that full oxidation did not take place before the second equivalent of nitric acid had been added (Scheurer-Kestner, 1859c).

Using sufficiently concentrated liquors, followed by cooling of the product, resulted in the walls of the reactor being lined with beautiful blood red needles, which could be purified by separation, washing with ether, dissolution in water at 100 °C, recrystallization, washing with ether, and drying under a bell with sulfuric acid. Analysis of the purified crystals indicated that they contained, by weight, 27.73% Fe_2O_3 , 16.68% C_8 , 4.45% H_{12} , and 4.99% N, corresponding to the formula $\text{Fe}_2\text{O}_3, \text{NO}_5, 2\text{C}_4\text{H}_3\text{O}_3, 6\text{H}_2\text{O}$. Upon boiling, an aqueous solution of this solution decomposed yielding a mixture of nitric acid and acetic acid and a precipitate of pure iron oxide. The addition of an excess of acetic acid retarded this decomposition, allowing the liquors to be concentrated under gentle heat to crystallize them.

According to Scheurer-Kestner, this salt could also be prepared by the direct action of acetic acid on the water-soluble basic iron nitrate $\text{Fe}_2\text{O}_3, \text{NO}_5$, during several days at moderate heat, followed by addition of an excess of acetic acid, and evaporation. Heating immediately after the addition of the acetic acid, resulted in the decomposition of the basic nitrate. Heating the mixture for some time to 100 °C in a sealed tube, decomposed the salt immediately, like basic iron nitrates, producing a clear solution by transparency and cloudy by reflection. According to Scheurer-Kestner, addition of a further equivalent of nitric acid, induced crystallization of a coarse and darker new salt, containing 32.47% Fe_2O_3 , 29.23% C_4 , and 4.26% H, to which Scheurer-Kestner was unable to establish a rational formula (Scheurer-Kestner, 1859c)

Scheurer-Kestner found that a solution of ferrous chloride in acetic acid and oxidized by nitric acid, provided yellowish-red crystals containing, by weight, 14.55% chlorine and 32.31% iron oxide, according to the reaction (Scheurer-Kestner, 1859c):



Scheurer-Kestner wrote that Auguste Laurent (1807-1853) had postulated that the same body could have two different atomic masses as long as the functions it performed were considered (Scheurer-Kestner, 1861). Thus, Laurent adopted two different atomic masses for iron, noting that "when Fe^2 (ferrosium = 28) entered into a combination, it imprinted certain properties on it which made it immediately recognized, even without analysis; and when it was $\text{Fe}^{3/2}$ (ferricum = 18.66), which entered a combination, it likewise imprinted on its characteristic properties which made it recognizable as a ferric salt" (Laurent, 1854; page 121). The properties of the chemical combinations of both species of iron, as well as the amounts of iron displaced by equal quantities of electricity, were substantially different. Scheurer-Kestner mentioned that Charles Adolph Würtz (1817-1884) initially rejected these ideas, but eventually accepted them. He compared ferric hydrate, $\text{Fe}^{\text{vi}}\text{H}_6\text{O}_6$ to glucose, and considered ferricum ($\text{Fe}^{\text{vi}}=112$) as hexatomic, analogue to saccharyl, $(\text{C}_6\text{H}_6)^{\text{vi}}$ (Würtz, 1860; Scheurer-Kestner, 1861b).

Scheurer-Kestner wrote that reacting in suitable proportions ferric hydrate and a monoatomic acid or hydracids (nitric acid, acetic acid, HCl), for a few days at 40 °C, yielded compounds able to crystallize when the solutions obtained were sufficiently concentrated. The resulting salts were very labile, particularly above 40 °C. To avoid this inconvenience, he developed two alternative methods, which were faster and allowed the immediate preparation of solutions sufficiently concentrated to crystallize: (1) taking as a starting point a ferrous salt in a very concentrated solution, or even in crystals, adding thereto the acid intended to enter combination, and oxidizing the mixture by nitric acid. The resulting liquors usually gave up crystals during their cooling; and (2) making the salts obtained act on each other or in combining an acid with a basic ferric salt of an acid different from the first (Scheurer-Kestner, 1861b).

To demonstrate the hexatomic nature of iron, Scheurer-Kestner prepared and determined the properties of ferric tetraceto-nitrate, tetraceto-dinitrate, diaceto-tetranitrate, triaceto-nitrate, triacetate dichloride, and triacetate. His starting material was ferric hydrate of a determined composition synthesized from crystalline ferric nitrate prepared by the method he had described before (Scheurer-Kestner, 1859).

For example, for preparing ferric tetraceto-dinitrate, the ferrous salt method was found to be the easiest and quickest. A solution of ferrous acetate of relative density of 1.250 was heated to 80 °C and then mixed, drop-wise, with ordinary, non-smoking nitric acid. A very lively exothermic reaction took place, which brought the mixture to boiling. Upon cooling, the walls of the vessel become covered with fine blood red needles. The product was purified by solution in water at 100 °C, followed recrystallization. The purified salt was found to be deliquescent, thermal labile, and smelling of both acetic acid and nitrous vapors. It was very soluble in water and in alcohol. Chemical analysis indicated that it contained, by weight, 19.40% iron, 16.68% carbon, 4.45% hydrogen, and 4.99% nitrogen, corresponding to the formula $\text{Fe}^{\text{iv}}(\text{C}_2\text{H}_3\text{O})^{3/4}(\text{NO}^2)^{1/2}, \text{O}^6 + 6 \text{H}_2\text{O}$ (with $\text{fe} = 28$, $\text{Fe}^{\text{vi}} = 112$, $\text{C} = 12$, $\text{N} = 14$, $\text{H} = 1$) and representing ferric tetraceto-dinitrate (Scheurer-Kestner, 1861b).

Scheurer-Kestner wrote that ferric tetraceto-dinitrate, diaceto-tetranitrate tetraceto-nitrate, and triaceto-nitrate decomposed in boiling water, releasing acetic and nitric acid, and depositing iron oxide. This mode of decomposition by boiling water was clearly different from that experienced in the same circumstances by iron nitrates, which gave up, instead of pure iron oxide, more basic salts (Scheurer-Kestner, 1861b).

In a following paper, Scheurer-Kestner repeated his finding that leaving a solution of an iron nitrate to itself for a long time, turned it sometimes jelly and appeared to be cloudy (Scheurer-Kestner, 1859b). Addition of water eliminated the turbidity and produced a liquid limpid by transparency and cloudy by reflection, a phenomenon very similar to the effect of heat on ferric acetate reported by Léon Péan of Saint-Gilles (1832-1863) (Péan of Saint-Gilles, 1856). It was assumed that this allotropic modification of iron oxide was the result of boiling a solution of ferric acetate for a long time at 100 °C. Scheurer-Kestner decided to test this hypothesis on neutral iron nitrate and the two soluble basic nitrates that he had prepared previously (Scheurer-Kestner, 1859a). Samples of these salts were enclosed in glass sealed tubes and immersed in boiling water for a long time. After a few hours of treatment, the color of the two basic salts had changed from reddish brown to brick red, and the solution, limpid by transparency, appeared cloudy, seen by reflection. The internal liquid did not smell like nitric acid but showed other changes. For example, addition of a drop of HCl, sulfuric acid, or of a solution of sodium or potassium sulfate resulted in a precipitate, a result not produced by the unheated solution (Scheurer-Kestner, 1859b).

After ten hours of boiling, analysis of a sample of the precipitated tribasic nitrate $\text{Fe}_2\text{O}_3\cdot\text{NO}_5$, indicated that it contained, by weight, 9.88% of Fe_2O_3 , 17.60 of NO_5 17.60%, and 72.52% water, that is, the iron oxide and nitric acid were found in the ratio 1:1.781, against 1: 0.68 in the original salt. After 72 hours of exposure to heat, the filtrate exhibited the composition of iron nitrate at 3 acid equivalents and remained as such afterwards. Hence, the two basic salts were the only ones capable of being modified (Scheurer-Kestner, 1859b).

Drying of the precipitate in a current of dry air resulted in the formation of small black plates insoluble in concentrated acids, but very soluble in pure water. Dissolved in water, they reproduced a solution cloudy by reflection and limpid by transparency, which did not react with ferrocyanides and sulfocyanides as proper of iron salts, but was precipitated by acids and sodium sulfate, reproducing the soluble iron oxide containing, by weight, 89.88% of Fe_2O_3 and 10.12% OH, corresponding to the formula $\text{Fe}_2\text{O}_3\cdot\text{HO}$. These results indicated that heat exerted on the two basic nitrates an action analogous to that which it produced on ferric acetate, except that while ferric acetate was completely decomposed into ferric oxide and acetic acid, the basic nitrates were split into oxide and neutral nitrate. Scheurer-Kestner found that light acted on these bodies as heat, and hence, this agent was responsible for the decompositions, which are sometimes produced in solutions exposed to air for some time (Scheurer-Kestner, 1859b).

In 1858 J. M. Ordway reported that he had prepared a crystallized ferric nitrate containing 6 molecules of water of formula $\text{Fe}^{\text{vi}},6\text{NO}_2,\text{O}_6 + 6\text{H}_2\text{O}$ (Ordway, 1858), and in 1861 Robert Wildenstein published the synthesis of another ferric nitrate having the composition $\text{Fe}^{\text{vi}},6\text{NO}_2,\text{O}_6 + 12\text{H}_2\text{O}$ (Wildenstein, 1861). The anhydrous part of these two new nitrates was very the same as the one that Scheurer-Kestner had synthesized previously, $\text{Fe}^{\text{vi}},6\text{NO}_2,\text{O}_6 + 18\text{H}_2\text{O}$ (Scheurer-Kestner, 1858); they differed only in the amount of water they contained (and consequently in the proportion of ferric oxide, represented by the numbers 27.02, 22.86, and 19.80. This difference was too large to attribute it to an analytical error, a fact that led Scheurer-Kestner to reinitiate his work on the subject to verify if these compounds were truly new nitrates, and identify their origin (Scheurer-Kestner, 1862).

Scheurer-Kestner repeated that the crystals that he had analyzed were the product of the reaction of iron with nitric acid having a relative density of 1.28 to 1.33. Cooling

the resulting liquor resulted always in the precipitation of many crystals of ferric nitrate with 18 molecules of water; cooling the liquor, if the reaction was carried with a slight excess of nitric acid to keep the basic salts in solution to avoid their being an obstacle to crystallization origin (Scheurer-Kestner, 1862).

Wildenstein had reported that his crystals came from a commercial product prepared by the direct dissolution of iron in nitric acid with a density of 1.260. About 150 liters of the mother solution had been left alone for 18 months and provided 10 kg of crystals containing 12 water molecules (Wildenstein, 1861).

Scheurer-Kestner suspected that the mother liquor of Wildenstein was probably basic since commercial ferric nitrate was basic because it was normally prepared by evaporation of the raw solution to the relative density of 1.530. His basic approach was to determine if the difference in composition was a result of the crystallization technique. For this reason, he redissolved a known amount of his 18-molecule water crystals and evaporated it slowly under a bell in the presence of sulfuric acid. The resulting colorless prismatic crystals were found to contain 18 molecules of water. This result meant the solutions of ferric nitrate provided, either by cooling, or by slow crystallization, or in the presence of basic nitrates, the same crystals containing 18 molecules of water. The next procedure consisted in evaporating the solution in a water bath, producing a supersaturated liquid. Here the result was different, Cooling the resulting syrup in ice, yielded up a crystalline mass which, separated from the mother liquor, gave on analysis, a composition corresponding to the formula $\text{Fe}^{\text{vi}},6\text{NO}_2,\text{O}_6 + 2\text{H}_2\text{O}$. The liquid separated from these crystals gave up after a few hours' small colorless prisms, which when analyzed, had an overall composition corresponding to the formula $\text{Fe}^{\text{vi}},6\text{NO}_2,\text{O}_6 + 12\text{H}_2\text{O}$, identical the salt prepared by Wildenstein, and which also came from a solution evaporated in a water bath. According to Scheurer-Kestner, his results proved that the solutions of ferric nitrate generally produced crystals containing 18 molecules of water, but that under certain circumstances, and especially when the solutions were *supersaturated*, the salt formed may contain only 12 or even only 2 water molecules combined. He added that he had failed in all his attempts to prepare Ordway's salt containing 6 molecules of water (Scheurer-Kestner, 1862)

The last section of this paper was devoted to the use of the diffusion concepts of Thomas Graham (1805-1869) to the separation and purification of substances, which Graham called colloidal (Graham, 1861). Graham wrote that the diffusive mobility exhibited by liquid substances appear to be wide as the scale of vapor pressures. A large group of substances (i.e., hydrated silicid acid, hydrated alumina, and some metallic peroxides) exhibited a relatively low diffusivity, marked out by the absence of the power to crystallize, which was very slow in the extreme. These substances distinguished also by the gelatinous character of their hydrates. Many times, these characteristics could be used to separate mixtures. Graham mentioned, for example, the case of alumina binacetate. Keeping a solution of this compound in a closed vessel at 100 °C for several days liberated most of the acetic acid, without any simultaneous precipitation of alumina. One way of achieving this separation was by boiling off the acetic acid. The same result could be achieved by dialyzing a solution of alumina acetate that had been altered by heat (Graham, 1861).

Another example was a solution of hydrated ferric oxide prepared by saturating a solution of ferric chloride with hydrated ferric oxide, added in small quantities at a time, so long as the precipitated oxide continued to redissolve on stirring (as described by Ordway

and Scheurer-Kestner). The red liquid obtained was already a colloidal hydrochloride of ferric oxide, which to be separated required to be dialyzed for a sufficient time. According to Graham, put in a dialyzer it took 19 days to reduce the amount of HCl present to 1.5%, representing one equivalent of acid to 30.3 equivalent of ferric oxide, that dialysis of the original dissolution of ferric hydrate en ferric chloride had been transformed into a dissolution of ferric hydrate. almost pure, in water (Graham, 1861).

Scheurer-Kestner repeated this dialysis experiment of Graham using as a dialyzer a glass sleeve lined at its lower part with an ordinary bladder submerged in pure water (he was unable to obtain the vegetable parchment used by Graham). He introduced into the dialyzer 300 g of a solution of basic ferric nitrate of composition $\text{Fe}^{\text{vi}},4\text{NO}_2,\text{H}_2\text{O}_6$, containing 4.95 g of ferric oxide, and left the whole alone under visual observation for twenty-five days, while sampling the liquid in the sleeve on several occasions. During this period, he noticed that a large part of the pure water was introduced by endosmosis into the dissolution of the ferric nitrate, while the liquid surrounding the sleeve gradually took on a mixture of nitric acid and neutral ferric nitrate.

The results were presented in a table showing the date of the sample, and the amounts of ferric oxide and nitric acid, in actual amounts, and as % of the solids. The results indicated that (1) the basicity of the nitrate increased from time (the relative acidity decreased from 57.44% to 21.5%); (2) it was possible to obtain ferric nitrates containing a larger excess of ferric oxide, (3) the composition of the latter approached the formula $5\text{Fe}^{\text{vi}},4\text{NO}_2,\text{O}_6$; (4) after three days the interior and exterior liquids exhibited the following compositions:

TABLE 1: Composition of liquid phases (Scheurer-Kestner, 1863).

	Ferric oxide in 100 parts of nitric acid
Internal liquid	60.3
External liquid	35.6
Neutral nitrate	40.38

and (5) neutral ferric nitrate was therefore broken down by dialysis into basic salts, which remained in the dialyzer, while a mixture of neutral ferric nitrate and nitric acid crossed the membrane from the inside to the outside (Scheurer-Kestner, 1862).

In a previous paper about the atomicity of iron, Scheurer-Kestner tried to demonstrate that in ferric salts iron could be considering as playing the role of an hexatomic element. For this purpose, he synthesized and described the properties of a variety of iron polyacid salts of this element, which although well-defined and crystallized, did not lend themselves to rational representation while retaining the old atomic weight of the element (Scheurer-Kestner, 1861). He added that in a recent work, Hugo Schiff (1834-1915) (Schiff, 1862) had pointed out that by taking the number 112 for the equivalent of ferricum, it was necessary to double the formulas of alums, while by using the number 56 (corresponding to triatomic ferricum) it was possible can represent the molecule of ferric salts containing 112 of iron by writing twice the radical Fe^{iii} (= 56). In this way, these compounds could be formed by the condensation of two atoms of the triatomic ferric radical in one (Scheurer-Kestner, 1863).

Scheurer-Kestner believed this assumption was wrong because it would give the sulfate an inadmissible formula. To justify his argument, he went on synthesize, determine the formula, and describe the properties of a varieties of iron salts, among them ferric dichlorotetracetate, ferric triacetate-dinitrate, basic ferric acetate, ferrous and ferric

formiate, basic ferric formiates, ferric formio-nitrate, ferric dichloroformiate, ferric triacid salts, ferric fluorides (Scheurer-Kestner, 1863).

For example, ferric dichlorotetracetate was prepared by dissolving one molecule of ferric hydrate in a mixture of two molecules of HCl and four of acetic acid. The resulting liquor, evaporated over sulfuric acid, led to the crystallization of a red-yellow salt, which dried in the air without losing water of crystallization. Chemical analysis of the crystals indicated that they contained, by weight, 23.3% iron, 19.8% carbon, 3.9% hydrogen, and 14.7% chlorine, corresponding to the formula $[\text{Fe}''', 4(\text{C}_2\text{H}_3\text{O})_2]_2\text{O}_3 \cdot \text{Cl}_2 + 3\text{H}_2\text{O}$, that is, ferric dichlorotetracetate, a body analogous to Schiff's chromic acetodichloride. This salt was very soluble in water and in alcohol; it decomposed easily acetic acid, which was released as ferric dichlorotriacetate, a more basic salt which often crystallized from the above solutions, when brought to boiling or evaporated in a water bath. Ferric dichlorotetracetate, treated with silver nitrate, furnished ferric tetracetodiazotate, $[\text{Fe}''', 4(\text{C}_2\text{H}_3\text{O})_2 \cdot 2(\text{NO}_2)_2]_2\text{O}_6 + 6\text{H}_2\text{O}$ (Scheurer-Kestner, 1863).

Ferric hydrate freshly precipitated, dissolved easily in formic acid; in the presence of an excess of hydrate the result was soluble basic salts. Ferric formiate was found to be more stable than ferric acetate; it formed very brilliant yellow crystals, soluble in water and little soluble in alcohol. Elemental chemical analysis indicated, by weight, 27.9% iron, 17.7% carbon, and 2.0% hydrogen, corresponding to the formula $[\text{Fe}''', 6(\text{CHO})_2]_2\text{O}_6 + \text{H}_2\text{O}$. Iron filings dissolved slowly in fluorhydric acid of relative density 1.07. Evaporation of the resulting liquor yielded green prisms of ferrous fluoride strongly attached to the bottom of the capsule. This salt was little soluble in water and more soluble in hydrogen fluoride. Elemental analysis indicated that they contained, by weight, 23.5% iron, 60.9% water, and 15.6% fluorine (by difference), corresponding to the formula $\text{Fe}''\text{F}_2 + 8\text{H}_2\text{O}$ (Scheurer-Kestner, 1863).

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