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Etienne Francois Geoffroy's table of relations and the concept of affinity

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Summary. The paper describes Geoffroy's table of proportions. The context in which it was developed is discussed, and subsequent tables, particularly those of Bergman, are dealt with at some length. The impact that such tables, known as affinity tables, had during the 18th century, and the reasons of their vogue receding with the birth of modern chemistry at the time of Lavoisier and Dalton are analysed.

Introduction

To appreciate the novelty and impact of the table of relations "rapports" in French (Fig. 5), introduced in 1718 by Geoffroy [1] it is worthwhile to try and understand which were the dominant concepts, or as we would say now the paradigm, of chemistry at that time.

We can for that purpose read Nicolas Lemery's "Cours de Chymie" first published in 1675 [2] and still a standard text in 1730, not really to be outdated before the publication of Macquer's "Eléments de Chymie-Théorique" (Fig. 2) in 1749 [3].

After making the remark that most authors who wrote on chemistry did so with such obscurity that they seem to have endeavoured not to be understood, and to have but too well succeeded, Lemery goes on by defining chemistry as "an art that teaches how to separate the various substances that are found in mixtures (mixtes, in French)". He adds "I mean by mixtures naturally occurring matter ("les choses qui croissent naturellement") namely minerals, plants and animals".

Indeed the main purpose and time consuming occupation of chemists, often referred to as "artistes" in no deprecating sense in the French texts, was to analyse every possible sample of matter. As soon as the 17th century analysis of waters was a common pursuit, but as late as the end of the 18th century, Klaproth, Kirwan, Rouelle, and even in his early days Lavoisier, devoted much if not all their time to the analysis of minerals, and of all kind of organic substances.

But what were the constituents into which mixtures had to be resolved in order for an analysis to be performed?

They were designated in French by "principes" and we shall use the word "principle" in English.

Lemery starts by stating that the first principle that one may accept in the making of mixtures is an "universal spirit" that being present everywhere produces various effects according to the various matrices or pores of the earth in which it is found enclosed. But Lemery follows up immediately

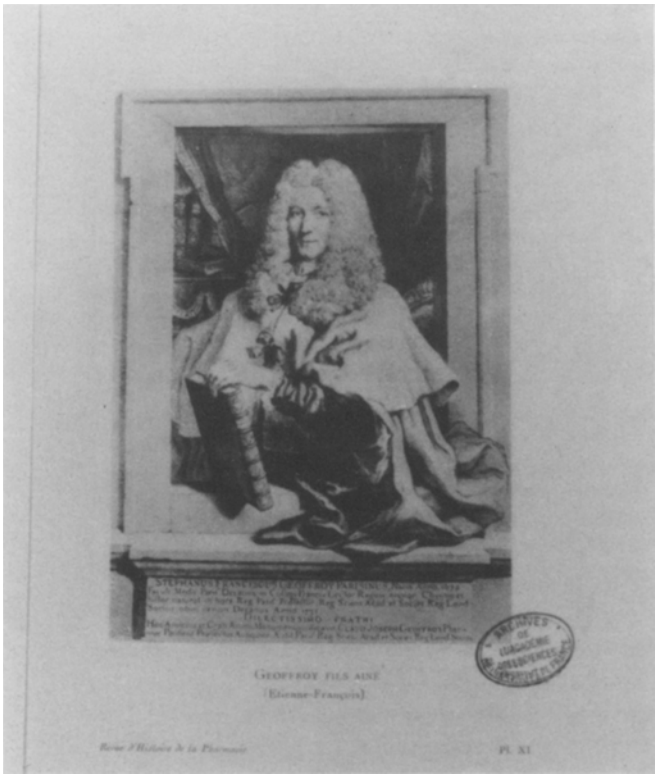

Fig. 1. Portrait of Etienne Francois Geoffroy, by permission of the archives of the French Academie of Sciences

with the comment that this principle being of a somewhat metaphysical nature, and not being perceived by the senses, it is well to establish sensible ones.

He states that when analysing mixtures chemists found five substances and concluded to five principles to wit: water, spirit, oil, salt, and earth. Of which spirit, oil and salt are active and water and earth are passive i.e. do not act by themselves but may accept, and foster the action of active principles such as oils; and he gives the example of vitriol oil that being diluted in water is more active than when concentrated.

The influence of the Aristotelian concepts is obvious in this classification, though fire is no longer considered as an element, but also those principles are to be considered as generic terms.

For instance Lemery refers to mercury as to a spirit and the first of active principles. "Sulfur" is an oil for Lemery

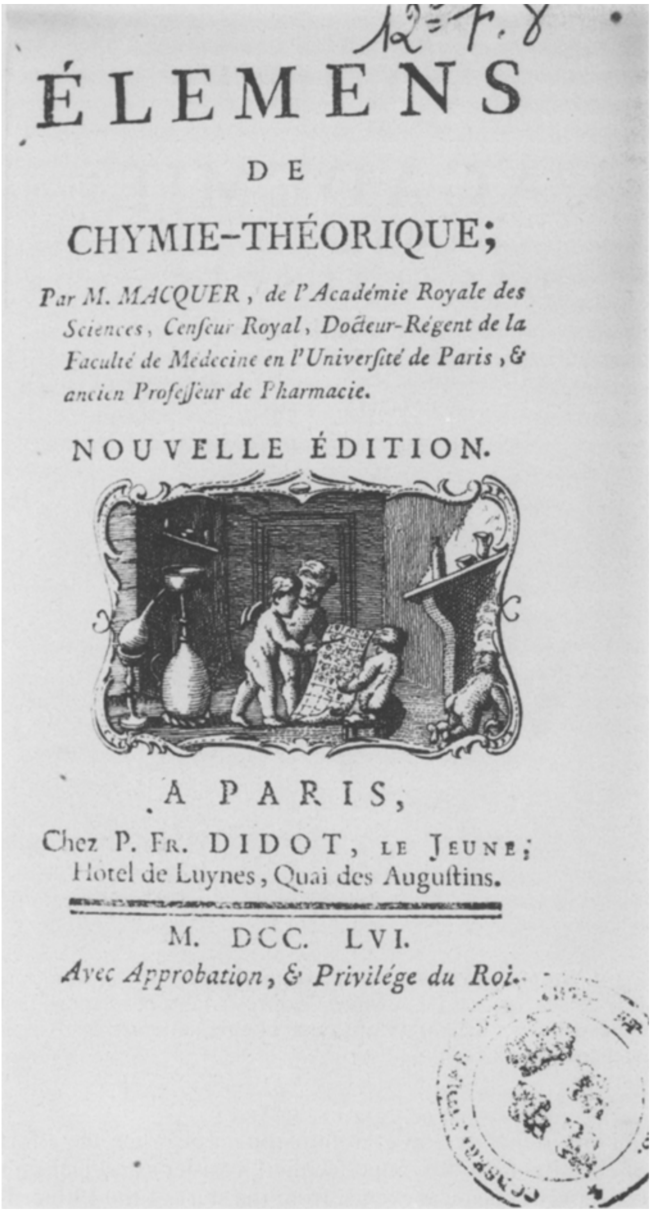
ÉLEMENS
DE
CHYMIE-THÉORIQUE;
Par M. MACQUER, de l'Académie Royale des Sciences, Censeur Royal, Docteur-Régent de la Faculté de Médecine en l'Université de Paris, & ancien Professeur de Pharmacie.
NOUVELLE ÉDITION.
A PARIS,
Chez P. Fr. DIDOT, le Jeune; Hôtel de Luynes, Quai des Augustins.
M. DCC. LVI.
Avec Approbation, & Privilége du Roi.

Fig. 2. From page of Macquer's epoch making treatise of chemistry [3] from the library of Conservatoire National des Arts et Métiers

and has little relation to the element now designated by the same word; and Geoffroy himself very clearly explained in his "tractabus de materia medica", translated into French as "Traité sur la matière médicinale" [4], how when wine is analysed by distillation one finds successively an ardent water or spirit, an insipid water or phlegm, an acid liquor (which is found also in vinegar) named spirit or mercury, finally an oil or sulfur. The dry residue (after further extraction) is an earth known as caput mortuum.

This illustrates the difficulty that one meets with when reading those old papers. One constantly must wonder whether the author refers to a general principle or to a specific substance, and in the latter case whether this substance is or not the same as the one that bears the same name today.

Interestingly, Lemery points out that the principles of chemistry are only principles inasmuch as we are unable to analyse matter any further. He also wonders, and this is a question that Berthollet will address one century later, whether what is extracted from a mixture was present within this mixture under the same form before extraction.

It should also be remembered that today's metals were in the 17th century considered as compounds, the most recent theory at the time of Geoffroy being that they were a combination of "calces" (the modern oxides) and phlogiston. This complex nature of metals was of course what justified in the past alchemists in their search of a reactant that could change metals into gold. And though Stahl's "sublime theorie" of phlogiston has nothing to do with alchemie, the idea that there could be a relation between the seven metals that had been isolated by the ancients (gold, silver, mercury, copper, iron, tin and lead) and the planets, and subsequently with illnesses affecting various parts of the body (the head for the moon, the liver for mercury, etc.) was still alive. Even later Macquer writes that "though there is no proof to support this idea he does not dare say that it is absolutely wrong".

Also by neglecting or overseeing the fact that air was a reactant, and a weighable one, the premature use of the balance by a chemist like Van Helmont lead him to erroneous conclusions. By watching a willow twig planted in a pot grow from an initial five pounds into a 160 pound tree with not other external supply than water he concluded, quoted by Geoffroy, that the salt and sulfur principles it contained came from the water and for a little part from the earth, of which a few ounces had disappeared.

Finally though Lemery was very careful to stick to facts, as we have seen when he discards the concept of universal spirit, he enters into explanations of how the different principles act, and he is both influenced by theoretical Cartesian concepts and by observations from which however his conclusions must today be termed non-sequiturs.

From Geoffroy's writings one can find that he essentially shared the same idea, which is the reason why they are mentioned here.

"Earth and water", writes Geoffroy, "are not sufficient to form mixed matter; movement and the power to (re)act must be present also, this subtle principle may be considered as the peripatetian's fire or as Descartes's subtle matter".

Chemistry should give an idea of the nature and "figure" i.e. geometry, of the elementary "petits corps" which in the Cartesian terminology were small bodies that together with movement were the basis of Descartes explanations of physical phenomena.

One thus had to accept that those small bodies had figures that explained their nature and reactions. Acids for instance consisted of particles equipped with points. Differences between the sharpness of those points were the reasons for differences in strength of acids.

Such a concept was not purely abstract, experience seemed to support this view as one could feel the points of acids on the tongue when tasting them, and one could see the points when acids were made to crystallize.

Newton's conception of forces acting between distant objects seems to have been ignored by Geoffroy, but he must have known of the dispute between Gassendi, who contended that the interval between "petits corps" was void of matter, and Descartes who maintained that such bodies

Fig. 3. Portrait of de Boërhave from the archives of the French Académie des Sciences

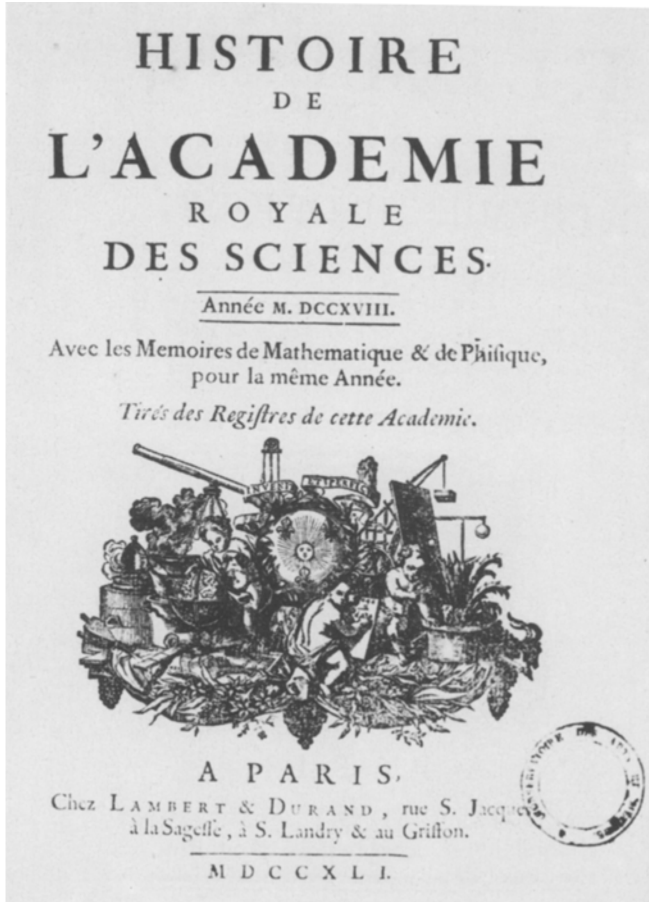

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Fig. 4. Front page of the volume of the History of the Académie Royale des Sciences [1] in which Geoffroy's table of relations first appeared, from the library of Conservatoire Nationale des Arts et Métiers

reacted with one another through subtle matter joining them. Clearly Geoffroy followed Descartes.

To illustrate how difficult it was to stick to positive ways of thinking let us mention that Boyle, who wrote in 1666 "The sceptical chemist", and developed the idea that chemical phenomena were due to purely mechanical interactions of very small particles, also wrote in 1679 (or before: it was translated that year in French) a book whose title at least is a very anthropomorphic description of chemical reactions:

"Experiments and observations on the fight resulting from mixing bodies". (Recueil d'expériences et observations sur le combat qui résulte du mélange des corps).

Other authors like Boërhave (Fig. 3) preferred to compare chemical reactions not to fights but to lovemaking [5].

The table of relations

It is in this context that in 1718 Geoffroy established and published in the Mémoires de l'Académie Royale des Sciences (Fig. 4) his "table des différents rapports observés en chimie entre différentes substances" that was to have so great an impact on chemistry throughout the 18th century, only to fall into oblivion, and even into contempt, when the effort of chemists focussed on perfecting Lavoisier's and Dalton's concepts of chemical events, from the start of the 19th century on.

Who was this Etienne Francois Geoffroy, who signed Geoffroy l'aîné, in order to distinguish himself from his younger brother who was a pharmacist and succeeded to their father[1], as Etienne Francois should have done if he had not stubbornely resisted, in order to become a medical doctor, but a doctor devoted to study the scientific foundation of his art: chemistry?

We know about his life because in the French academy the duty of the secretary was to write the praise of academicians who passed away. Fontenelle did write praises of high literary value, and at the same time quite informative and accurate.

Geoffroy wrote in 1704 his thesis himself, though apparently at that time the president of the jury of the candidate was expected to write it. Remarkably this thesis, that was written in Latin, had to be translated into French at the request of ladies, specially of ladies of the highest rank in

[1] Hence the caption on this portrait "Geoffroy son, the elder"

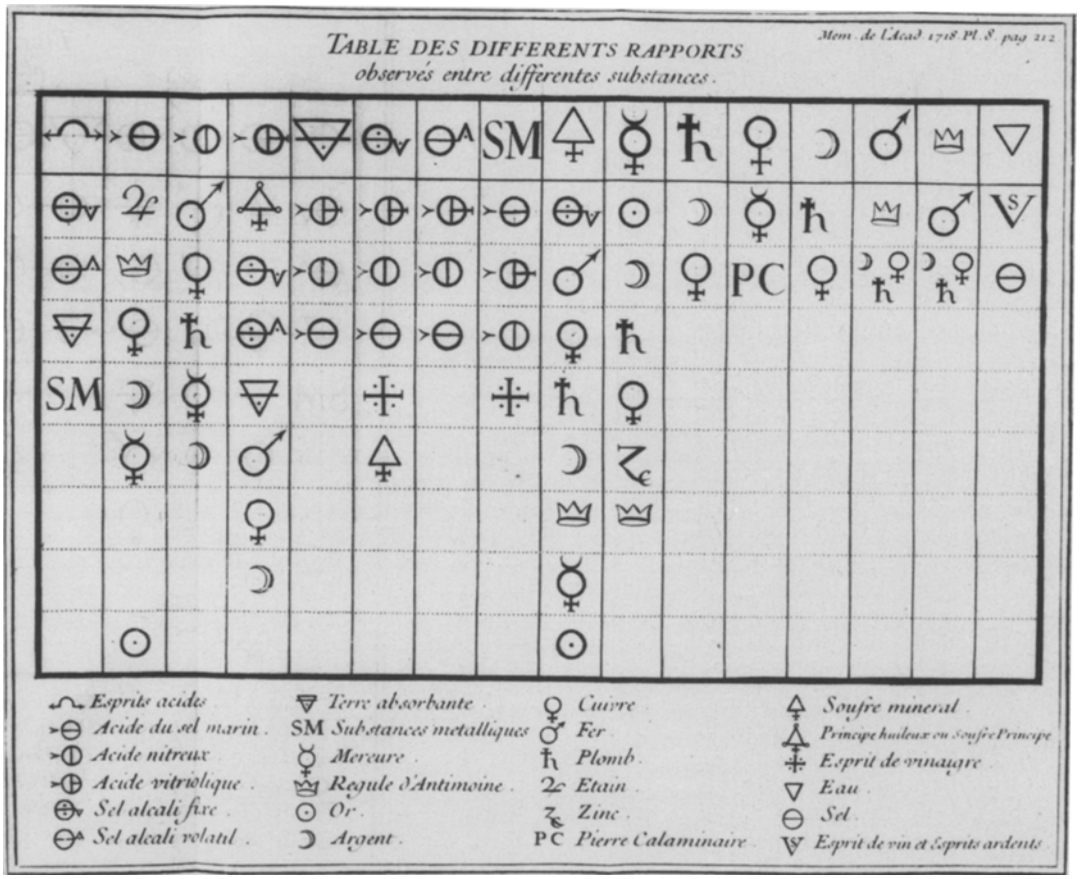

Fig. 5. The original table of relations by Geoffroy from [1]. Because they were colored, gold, copper, iron and antimony were solar metals, and their symbols included a full circle. Metals other than gold were more or less imperfect and their representation show either a cross or an arrow to indicate it. Silver and other lunar metals, tin and lead, were white. They are represented by a half circle, sometimes difficult to recognize, to which in the case of metals other than silver imperfection signs are added. These original rules quoted by Hassenfratz in [18] also explain the symbol of mercury a metal both solar and lunar and imperfect. However, these rules were forgotten gradually and signs became arbitrary

the court. When one merely reads the title "Whether the beginning of man was to be a worm?", one may wonder whether Geoffroy was a forerunner of Darwin and in that case why ladies were so eager to read his thesis.

In fact what he describes as "worms" are those little "animals" found in sperm and known nowadays as spermatozoons. These "animals" had only been discovered by Hartsoeker around 1675 and published, with the help of Huygens, in 1678. So touchy was the subject that at first those "animals" were said to have been discovered in saliva by Hartsoeker who only revealed the truth when another chemist claimed also to have observed them in saliva! Anyway, Geoffroy describes very accurately how a spermatozoon from a male fertilizes the egg of the female. He discusses the number and activity of spermatozoons in the semen of young boys, of mature and old men. He also describes the woman's role in the conception of the fetus, and his rendering of facts is astonishingly accurate, and ahead of his time, as can be seen by the statement of Voltaire years later that it is not known how children are conceived. No wonder that, as Fontenelle puts it, "ladies wished to be enlightened on mysteries the theory of which they ignored" [6].

Other remarkable quotations from his work could be made. I will only cite those words that could have influenced Lavoisier: "One is never so sure to have resolved a mixture into its true constituents as when, with the same constituents, one has been able to recompose it."

To introduce his table of relations Geoffroy observes that when several substances are mixed together one of these will always combine with a certain other one, preferably to all others. He explains further that among substances that are enclined to combine, when two bodies are effectively combined, some substances when added or mixed with these bodies will cause them to separate ("let go" in his words). Other substances will neither separate them nor combine, like the preceding ones, with either of the two. Though as he excuses himself he has not been able to study all possible combinations, he proposes that "every time that two substances that have a tendency to unite are combined, if a third one appears, that has more relation to one of these two, it combines with that one forcing the other one to let go".

On this basis he drew his table where substances employed in chemistry are represented by the symbols in use at his time (Fig. 5).

On a first row one finds sixteen such substances. The first one concerns acid spirits in general whereas the three following ones are respectively the acids of marine salt, of nitre, and the vitriolic acid. Similarly after the eighth substance, which is a metallic substance in general, one finds mineral sulfur[2], mercury, lead, copper, silver (note the moon like symbol), iron, antimony; finally one finds water. Under each substance other substances are disposed in columns. In each column the one that has the most "relation" with the substance at the top is written down first. Therefore any substance will detach from the one at the head of the column all those that are below it. Conversely it will be separated by those above it.

As an experienced professor Geoffroy gives a detailed example of how to make use of his table, and he chooses to demonstrate how it enables to understand the preparation of calomel.

The usual preparation consisted in mixing calcinated vitriol (iron sulfate), with marine salt and mercury first dissolved in "esprit de nitre" (nitric acid) and then evaporated. By distillation nitrous vapors are observed to escape, mixed with some "spirit of salt", a white deposit, which is calomel, forms at the top of the vessel and a reddish residue remains at the bottom which he identifies as colcotar, or safran de Mars (ferrous oxide).

The table shows that: a) acids combine more readily with "absorbing earths" (here it will be sodium) than with metals; b) the fifth column shows that vitriolic acid combines more readily with these earths than the acid from marine salt.

Consequently vitriolic acid will let go from the metal in vitriol to combine with the earth from marine salt.

The acid from marine salt would evaporate because it is volatile, however, as shown by the eighth column it will attack metallic substances; in the present case both mercury combined with nitric acid and iron combined with vitriolic acid. Liberated nitric acid finds nothing to combine with, since sodium (the earth from marine salt) unites more readily with vitriolic acid; it consequently evaporates and decomposes into yellow nitrous vapors.

His demonstration obviously would not be accepted today, but it enables Geoffroy to rationalize an, up to his time, entirely empirical process. He explains further why, though one could dispense with nitric acid and use pure mercury in the preparation, mercury "divided" by the acid reacts more readily; and also why, if one starts with mercury nitrate, vitriol is not indispensable. The reason is that nitric acid having more relation with the earth from marine salt will liberate the acid from the marine salt and enables it to react with mercury.

Finally, calomel can be prepared by a wet route by dissolving mercury in nitric acid and pouring into the solution marine salt, or even by pouring directly spirit of salt (or acid from marine salt) over mercury dissolved in nitric acid.

The table of proportions serves as a guide for these last reactions in a similar way as above.

The fate of Geoffroy's table

Geoffroy himself warned that separations predicted by his table were not always perfect due to a variety of causes, but nevertheless the rules that it summarized could be considered constant.

When submitted to be read at the academy the historian commented highly on this table [7]. He stressed the predicting value of the table and how pleasing to the mind it was to have achieved if not "the certainty of mathematics" at least an imitation of their order. Interestingly, when stating that explanations for substitutions predicted by the table are not known he adds "here sympathies and attractions would come in à propos, if they were anything". The next echo we have of how the table was received is two years later when three objections were raised and mentioned also in the history of the Academy [8], along with the answer by Geoffroy [9]. Two of these objections are said to be due to Geoffroy's younger brother. Essentially, the place of quicklime in the columns was contested because it could cause ammonia to be evolved from salts of "volatile alkali", which it should not be able to do, as limestone is an "absorbing earth" and therefore is below alkalis in the columns of acids.

The answer was that quicklime is not limestone and, though he could not prove it at the time, Geoffroy claimed that it contains an alkali stronger than ammonia.

A similar question was raised with respect to the action of iron filings that also can evolve ammonia from its salts though metals are less strongly attached to acids than alkali in the table. The less convincing answer was here that filings are not massive iron, and furthermore are usually digested in ammonia salts for 24 h before starting the reaction mentioned.

But soon after that the use of the tables spread in France, specially under the influence of Macquer who reproduced them in his treatise. And so fundamental did they seem that the article "Chymie" of Diderot's Great Encyclopedia [9] reproduces them with a few additions by Rouelle. On the page where they are printed (Fig. 6) one can see the picture of a chemical laboratory in the middle of the 18th century, and each of the persons represented has a role, even the physicist discussing with the chemist. Strangely however, the author writes that what physicists have written on chemistry is very imperfect because of the absence of a detailed comparison with facts, and he criticises even Boyle, Newton, Boërhave and others, on this ground [10].

Incidentally in France since the 17th century, chemists seemed to take a dim view of physicists. Le Fevre pretends that when asked about the composition of a substance a physicist will only answer that it must be made from parts having a finite dimension, but however the reverse could also be true. And he claims that physicists contrary to chemists fear to soil their hands with coal and are content to read their thesis and then to boast of their degrees, as chemists stick to their furnaces and analyse matter [11].

The success of the tables was even greater outside France. They were reproduced and followed by "improved" tables all over Europe. One finds a detailed account of the publication and contents of such tables in [12–14]. Their list is reproduced in Table 1 from [12] with the addition of Lavoisier's and Guyton de Morveau's tables.

The followers of Geoffroy

After Geoffroy the word relation (for the French "rapport") was abandoned.

Geoffroy had purposely picked that word in order to avoid affinity, that might have anthropomorphic implications, and refrained from using attraction that could imply adhering to Newton's conception of forces acting between distant objects.

[2] In addition Geoffroy has a symbol for principe huileux or soufre principe that, according to Partington, is similar to phlogiston

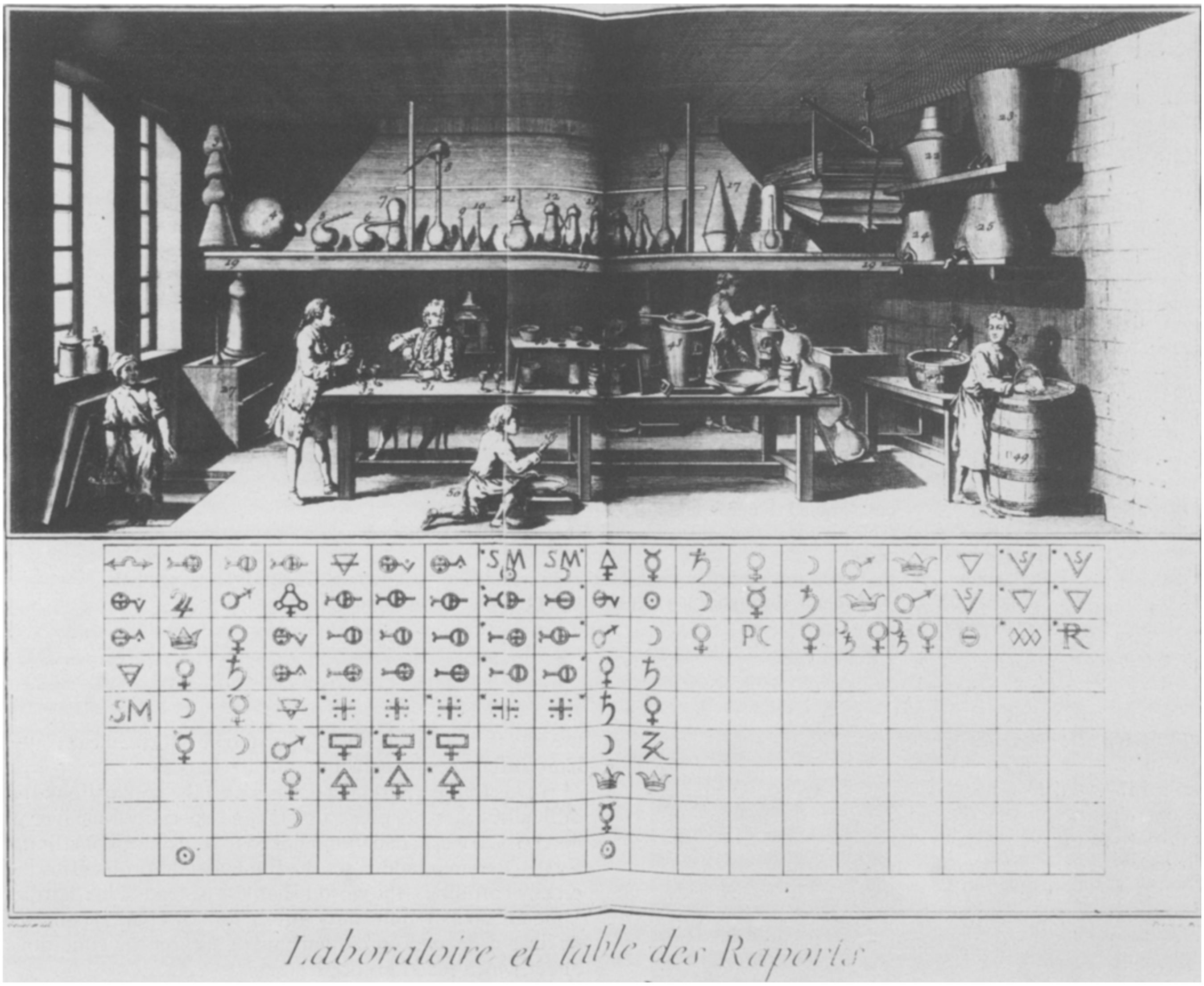

Fig. 6. Page of the "Encyclopédie ou dictionnaire raisonné des sciences des arts et métiers" par une société de gens de lettres, mis en ordre par M. Diderot, Paris 1753. vol. III of Recueil de Planches — under the heading chimie-laboratoire. This encyclopedia was known as "the great encyclopedia" in France. Photograph courtesy of the library of Conservatoire National des Arts et Métiers

Followers of Geoffroy either like the French did not load the word affinity with a connotation of sentiments that was no longer to be feared due to progress in chemistry, or like Bergman (Fig. 7), they were explicitly Newtonians and as Fourcroy puts it since the progress of science had assigned those supposed rapports to attraction forces established by nature this expression fell into oblivion [15].

However, the firm foundation of the tables remained that they were built from facts and observations and proposed no interpretation. Given the tables one could understand reactions or predict behaviours, one did not explain either.

It is within that scope that successive builders of tables tried to improve on Geoffroy's.

First they included more and more substances as from his own words Geoffroy himself would have tried to do. This did not improve very much the original table and on the contrary made their use unwidely when as many as 59 substances could finally be listed. Shortened versions of the more lengthy tables then appeared!

Major changes are to be looked for in other directions. I will comment mainly on Bergman's work [16], because of the great importance that this "dissertation on selective attractions" had up to the Lavoisier revolution that brought an end to his influence, because Bergman based his explanations of chemical facts on the phlogiston theory that was rejected, and because the concept of affinity was no more the driving force behind fruitful research.

Unlike Geoffroy, Bergman starts by a discussion of chemical forces. He writes that attraction is an universal property, whose causes are not investigated. But Bergman distinguishes long range attractions from short range attractions. In the first case, as between stars, objects can be assimilated to dimensionless points. When considering chemical elements this is no longer the case and the shape of substances reacting with one another plays a role because every point of each body attracts points of the others.

This enables one to understand why forces may be specific of each substances, and it also reconciles the tenets

Table 1. Tables of affinity and similar tables in the 18th century. Reproduced from Duncan [12]

Date of issue	Author	Description
1718	Geoffroy	16 columns, uses alchemical symbols
1730	Grosse	19 columns, symbols
1749	Clausier	not in columns, but 78 lists of substances in order of affinity, written in words
1751	Gellert	28 columns, representing order of increasing solubility, not decreasing affinity, symbols
1756	Rüdiger	15 columns of substances that combine, and 10 supplementary columns of those that do not, symbols
1758	Limbourg	33 columns, symbols
1762	Marherr	120 columns each showing the order of affinity of only two substances with a third, symbols
1763	Rouelle	19 columns, mainly derived from Geoffroy, symbols
1763	Spielmann	28 columns, symbols
1769	Demachy	20 columns and appendices, symbols
1773	unknown	'ouvrage' printed at the Imprimerie Royale, referred to by Demachy but untraced
1773	De Fourcy	36 columns
1775	Erxleben	36 separate lists, in words
1775	Bergman	one table for the wet way and one for the dry one, eventually extended to 59 substances, symbols
1777	Weigel	not in columns, distinguishes wet and dry ways, and reactions involving more than two substances, shows product of reactions, words
1781	Wiegleb	not in columns, distinguishes wet and dry way, and reactions involving two, three or more substances, words
1783	Lavoisier	table limited to one column that of "oxygine"
1786	Guyton de Morveau	table limited to five acids and seven bases but giving numerical values and "enabling to solve 490 affinity cases"
1788	Berkenhout	shortened version of Bergman's table, 36 columns for wet way and 25 for dry way, symbols
1790	Gergens and Hochheimer	40 columns, distinguishing wet and dry ways where appropriate, words

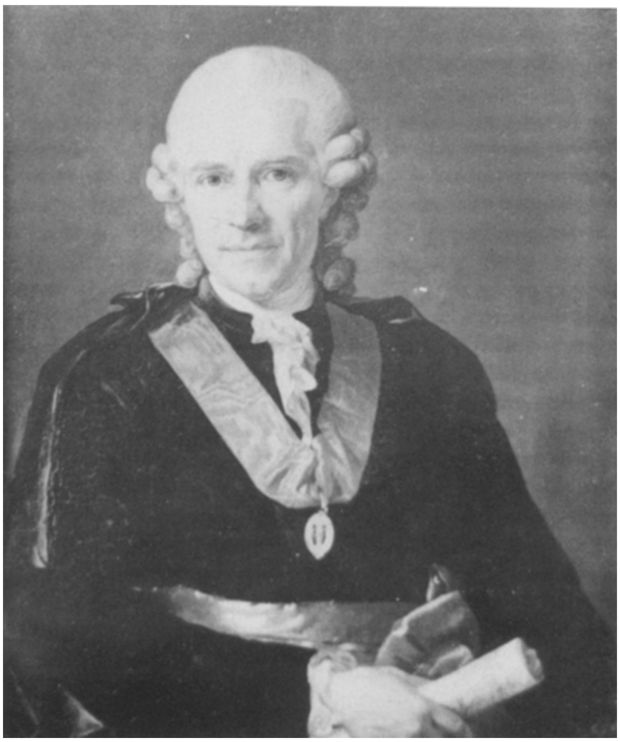

Fig. 7. Portrait of Bergman, from the archives of the French Académie des Sciences

of Newtonian physics with the affirmation of Cartesianism (though not explicitely so in Bergman's writing) that the figure of chemical elements has a determining influence on the way they interact. Indeed, Guyton de Morveau calculated later differences in attraction due to shapes.

In his treatise Bergman discusses all the implications and difficulties that his predecessors, and specially Macquer in his classical work, had found linked to the concept of affinity. Firstly Bergman addresses the fundamental problem: is the order of affinities (the word I shall use instead of his "attraction" for sake of uniformity throughout this paper) constant or does it depend on circumstances, i.e. on the conditions under which reactions occur?

The answer to this question is in fact the subject of eleven chapters of his book where a definition of different kind of affinities is to be found as was first proposed by Macquer. The simple, or single, affinity occurs when of three substances two combine and expel the third one. Double affinity is met with when two compounds, each consisting of only two principles, exchange these constituents in the reaction. The number of participants in a reaction is not the only criterium of differences in kind of affinities. The nature of the interaction itself is taken into account. Thus affinity of aggregation, affinity of solution or fusion, and many other ones, are defined. For instance, the first one relates to the case when the only change is an increase of the amount of substances whose nature remains unchanged.

The table of affinities consists of 59 columns, among which 25 for the acids, 15 for the metals, 3 for alcohols, and in addition to other categories such as earths, sulfur, spirit of wine, etc. one finds also one column for each of the following substances: vital air, phlogiston, the matter of heat, water.

Even more fundamental perhaps is the introduction of two sets of affinities, one in the dry way the other in the wet way.

The difference between the order observed in the two sets may be assigned to the action of heat, to which a chapter is

Table 2. Dates of birth and death of chemists and principal persons mentioned in this paper

Aristotle	–384––322 before present ERA
Bergman	1735–1784
Berzelius	1779–1848
Boërhave	1668–1738
Dalton	1766–1844
Boyle	1627–1691
Descartes	1596–1650
Diderot	1713–1784
Dumas	1800–1884
Fontenelle	1657–1757
Fourcroy	1765–1809
Gassendi	1592–1655
Gellert	1713–1795
Geoffroy	1672–1731
Guyton de Morveau	1737–1816
Hartsoeker	1656–1795
Hassenfratz	1755–1827
Huygens	1629–1695
Kirwan	1733–1812
Laplace	1749–1827
Lavoisier	1743–1794
Lemery	1645–1715
Le Fevre	1610?–(1669–1674)?
Macquer	1718–1784
Newton	1642–1727
Rouelle	1703–1770
Stahl	1660–1734
Van Helmont	1577–1644
Voltaire	1694–1778
Wenzel	1740?–1793

Fig. 8. Portrait of Guyton de Morveau from the Archives of the French Académie des Sciences

devoted, as the wet way is followed at room temperature and the dry way at an elevated one.

As Lavoisier later remarked, in fact the action of heat implies that an affinity table is only valid at a given temperature.

Bergman in addition to variations caused by heat discusses a number of "irregularities" which he calls apparent ones, namely those due:

– to double affinities;

– to successive modifications in the substances (these irregularities are similar to those explained by Geoffroy when discussing the reaction of quicklime with saltammonia);

– to solubility; this kind of affinity had been treated rather exclusively by Gellert (see Table 1);

– to three substances combining;

– to a given excess of one or the other of the principles; it is interesting to note that when discussing this "irregularity" Bergman refers explicitly to "the amount of one component that is necessary to saturate another when both are combined". He was on the way to, but never arrived at, a law of defined proportions.

Having dealt with the various types of exceptions Bergman comments on his table.

For Bergman phlogiston and heat were weighable substances, and he describes his way of calculating their weight in a given reaction. Vital air strangely he deems difficult to classify because it barely reacts unless fostered by double affinities or by a large excess of heat.

In contrast to Geoffroy, Bergman not only describes facts on which the construction of his table is founded but interprets them in the light of concepts of the chemical nature of matter and of chemical reactions.

For instance, he explains the precipitation of gold from solutions by another metal not by the greater attraction of the acid for that other metal but because phlogiston attaches itself more readily to the calx of gold (thus producing the metal) than to the calces of other metals.

In view of all the possible irregularities listed, and to cover reactions in which known substances took part, Bergman could easily calculate that more than 30,000 experiments were still required to make his table complete, a task for which he requested the help of all other chemists.

Finally, Guyton de Morveau's long article in "Encyclopédie Méthodique" de Panckouke (not to be identified with Diderot's Encyclopédie of which it was partly an abridged version), expands the state of the art on the subject in 1786, taking all preceding efforts into consideration [18] (Table 2).

Guyton de Morveau (Fig. 8) who with Lavoisier, Berthollet and De Fourcroy was to publish in the following year the paper on chemical nomenclature that was to be a corner stone of modern chemistry [18], devotes much of the space of his review to quantitative considerations. This was new though diagrams such as the one presented here (Diagram 1), where numbers characterize forces acting between components, have their origin in the qualitative ones that one finds not only in Bergman's dissertation but in some of his predecessor's work. But Guyton de Morveau integrates in addition Macquer's idea that "there is a mutual exchange (of elements) each time that the sum of activities that each of the principles of both compounds has with the principles of the other surpasses the sum of activities that the principles forming the two initial compounds have, when forming the initial compounds".

In the example shown on the diagram the initial compounds "vitriol de potasse" (potassium sulfate) and "nitre d'argent" (silver nitrate) show a total affinity of 9 + 2 = 11. Potassium plus nitric acid show an affinity of 8, vitriolic acid and silver calx (the hypothetic dephlogistonated silver that combined with acids) are assigned an activity of 4. Consequently, vitriolic silver and potassium nitrate should form when vitriol de potasse and nitre d'argent are mixed, because 8 + 4 = 12 is greater than 11.

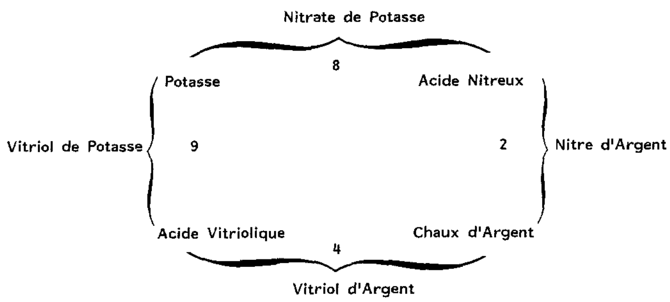

Diagram 1. Diagram of double exchange

The largely unsolved problem is to assign a priori values to the affinities that could enable to predict the course of reactions, instead of picking numbers that "explain" them. An attempt to produce such sets of values is given by tables such as the one in Fig. 9 given in the article.

Guyton de Morveau also interprets reactions as Bergman did. The latter did so exclusively with the help of phlogiston which, for instance, he introduces as the fourth component in exchanges involving apparently only three constituents. Guyton de Morveau refers also to Lavoisier's ideas and in parallel to the loss of phlogiston as the cause of formation of calces he gives the fixation of "air vital" by the metals.

Progress in chemistry also shows up in his work by the fact that the influence of concentrations on apparent affinities is recognised, and that notions of neutralization and saturation are clearly distinguished. Here the influence of Kirwan is acknowledged.

The determination of affinity however remains a problem. Bergman had apparently relied on the original concept based on displacement of principles by one another, and was certain that for instance mercury and silver were precipitated from vitriolic and nitrous acids by an addition of copper. Guyton de Morveau who had studied extensively adhesion, considered it as due to a form of affinity that could be measured by other means and seemed ready to follow Kirwan who stated "the affinity of an acid with the amount of base that lacks (to achieve saturation) is in the ratio of this quantity to the total amount of base with which it can combine". A difficulty, among others, that this concept met with at the time was that the quantitative composition of many compounds was not well known. The table of composi-

TABLE des expreſſions numériques des affinités de cinq acides & de ſept baſes.

N. B. Cette Table eſt la même que celle qui ſe trouve à la page 558 de ce volume. Ayant été obligé, depuis qu'elle eſt imprimée, d'en rectifier quelques nombres, j'ai penſé qu'il ſeroit plus commode de la retrouver ici toute entière. On ne ſera pas étonné de ces changemens, ſi l'on a ſaiſi le principe ſur lequel ces rapports ſont établis, & ſur-tout ſi l'on fait attention que les nombres placés dans ces 35 caſes doivent répondre déjà à 490 ſymboles ou cas d'affinités. (*Voyez page 609*).

	Acide ſulfurique	Acide nitrique	Acide muriatique	Acide acéteux	Acide carbonique
Baryte	66	62	36	28	14
Potaſſe	62	58	32	26	9
Soude	58	50	31	25	8
Chaux	54	44	24	19	12
Ammoniaque	46	38	21	20	4
Magnéſie	50	40	22	17	6
Alumine	40	36	18	15	2

Fig. 9. Table of numerical values of affinities by Guyton de Morveau from [16], library of Conservatoire National des Arts et Métiers

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TABLE des Proportions des parties constituantes dans quelques sels, suivant MM. Bergman, Wenzel & Kirwan.

NOMS DES SELS.		Suivant Bergman. Ils tiennent pour 100 : Acide.	Base.	Eau.	Suivant M. Wenzel. Acide.	Base.	Eau.	Suivant M. Kirwan. Acide.	Base.	Eau.
Méphite	de barote	7	65	28						
	de chaux	34	55	11	43,2	55,7	1,1	32,42	55,92	11,66
	de magnésie	25	45	30	32,5	41,7	25,8			
	d'alumine	76,92	23,08					26	74	
	de potasse	20	48	32	30			22,457	77,543	
	de soude	16	20	64	40			20	35	45
	ammoniacal	45	43	12	53,7			53	44	3
Vitriol	de barote	13	84	3						
	de chaux	46	32	22	59,8	40,2		29,44 39	32 42	38,56 19 séché
	de magnésie	33	19	48	30,63	16,87	52,5	23,75 45,67	19 36,54	57,25 17,83 séché
	d'alumine	38	18	44	9,06	11,66	79,28	23,94 42,74	18 32,14	58,06 25,02 séché
	de potasse	40,5	51,5	8	45,25	54,75		28,51	66,32	5,2
	de soude	28	16	58	55,73	44,27		13,19 29,12	21,87 48,60	64,94 22,28 séché
	ammoniacal				58,75	41,25		51,42	48,58	
	de zinc	40	20	40	53,81	46,19		23,92	76,08	
	de fer	39	23	38	57,83	42,17		27,03	72,97	
	de cobalt				61,08	38,92		21,74	78,26	
	de nickel							23,82	76,18	
	de plomb	30,08	69,92		30,24	69,76		19,53	80,47	

Eeee ij

Fig. 10. Table of compositions of various salts as determined by Bergman, Wenzel and Kirwan. From [16], library of Conservatoire National des Arts et Métiers

tions of a series of salts established by such great chemists as Kirwan, Wenzel and Bergman illustrates the point (Fig. 10).

This practical difficulty was not of course the fundamental reason why stoichiometry could not be a measure of affinity but simply it was not the right parameter to use.

Here the difference in foresight of simply very great chemists like Kirwan, and geniuses like Lavoisier reveals itself.

Lavoisier and Laplace, the great mathematician, wrote in 1783 in a communication on heat, as quoted by Guyton de Morveau, "equilibrium between heat, that tends to separate molecules that build substances, and mutual affinities (between those molecules) may provide an accurate means for the comparison of affinities". Thermodynamics were in germ in the mind of the authors of this sentence and hopes to, one day, be able to calculate in advance the course of chemical reactions were expressed at the time.

Practical uses of tables of affinity

It is not certain that affinity tables have been used in the way that Geoffroy describes in his original paper, nor in the fashion found in Guyton de Morveau's review where he explains how to use his numerical values to find a preparation of pure silver nitrate from starting materials consisting of impure commercial nitrous (meaning nitric) acid, and silver from non-descript origin or allied with copper, or how to prepare copper acetate from commercially available "vitriol de cuivre" and lead acetate. One is not convinced that he does not propose more a rationalization than a prediction tool.

Moreover, objections seem to have been raised to Guyton de Morveau's numerical values of affinities, specially by Scheele who pointed out precipitations by carbonic acid that looked impossible to conciliate with them. Hassenfratz [19] gave ingenious interpretations of those difficulties and showed how to use "correctly" the numbers and predict the observed precipitations.[3]

Nevertheless Dumas could accuse the tables to have misled chemists. He cites the case of the preparation of caustic soda. During the French revolution, in order to palliate the shortage in this chemical, a new fabrication process was sought. By looking at affinity tables baryte was thought to be able to decompose marine salt, and fabrication of baryte was undertaken and pushed to the point where dozens of tons of this substances were prepared; all in vain as the predicted reaction does not take place [22].

Table 3. Tableau des affinités du principe oxygine avec les differentes substances avec lesquelles il est susceptible de s'unir principe oxygine

Principe inconnu de l'acide marin, ou principe muriatique
Substance charbonneuse
Zinc
Fer
Principe inflammable aqueux
Regule de manganese
Cobalt
Nickel
Plomb
Etain
Phosphore de kunckel
Cuivre
Bismuth
Regule d'antimoine
Mercure
Argent
Regule d'arsenic
Sucre
Soufre
Air nitreux
Principe de la chaleur
Or
Acide marin fumant du commerce
Acide nitreux/Chaux de mangenese

The end of research on affinities

As soon as 1783 Lavoisier had summarized the shortcomings of affinity tables, he himself had a hand at a partial table limited to the affinity of oxygen (Table 3) [20].

He remarked that the effects of heat that enabled the oxides of mercury to be formed at one temperature and

[3] He argued that a substance could be extracted from two salts in contact by an acid having for this substance an affinity greater than only the difference of its affinities in the two salts

COMBINAISONS DE L'ACIDE SULFURIQUE.

TABLEAU des combinaiſons de l'Acide ſulfurique ou Soufre oxygéné avec les baſes ſaliſiables dans l'ordre de leur affinité avec cet acide, par la voie humide.

NOMENCLATURE NOUVELLE.

Combinaiſons de l'acide ſulfurique avec :

Nos.	*Noms des baſes.*	*Sels neutres qui en réſultent.*
1	La baryte	Sulfate de baryte
2	La potaſſe	Sulfate de potaſſe
3	La ſoude	Sulfate de ſoude
4	La chaux	Sulfate de chaux
5	La magnéſie	Sulfate de magnéſie
6	L'ammoniaque	Sulfate d'ammoniaque
7	L'alumine	Sulfate d'alumine ou alun.
8	L'oxide de zinc	Sulfate de zinc
9	L'oxide de fer	Sulfate de fer
10	L'oxide de manganèſe	Sulfate de manganèſe
11	L'oxide de cobalt	Sulfate de cobalt
12	L'oxide de nickel	Sulfate de nickel
13	L'oxide de plomb	Sulfate de plomb
14	L'oxide d'étain	Sulfate d'étain
15	L'oxide de cuivre	Sulfate de cuivre
16	L'oxide de biſmuth	Sulfate de biſmuth
17	L'oxide d'antimoine	Sulfate d'antimoine
18	L'oxide d'arſenic	Sulfate d'arſenic
19	L'oxide de mercure	Sulfate de mercure
20	L'oxide d'argent	Sulfate d'argent
21	L'oxide d'or	Sulfate d'or
22	L'oxide de platine	Sulfate de platine

NOMENCLATURE ANCIENNE.

Combinaiſons de l'acide vitriolique avec :

Nos.	*Noms des baſes.*	*Sels neutres qui en réſultent.*
1	La terre peſante	Vitriol de terre peſante, ſpath peſant.
2	L'alkali fixe végétal	Tartre vitriolé, ſel de duobus, arcanum duplicatum.
3	L'alkali fixe minéral	Sel de Glauber
4	La terre calcaire	Sélénite, gypſe, vitriol calcaire.
5	La magnéſie	Vitriol de magnéſie, ſel d'Epſom, ſel de Sedlitz.
6	L'alkali volatil	Sel ammoniacal ſecret de Glauber.
7	La terre de l'alun	Alun.
8	La chaux de zinc	Vitriol blanc, vitriol de Goſlard. Couperoſe blanche, vitriol de zinc.
9	La chaux de fer	Couperoſe verte, vitriol martial, vitriol de fer.
10	La chaux de manganèſe.	Vitriol de manganèſe.
11	La chaux de cobalt	Vitriol de cobalt.
12	La chaux de nickel	Vitriol de nickel.
13	La chaux de plomb	Vitriol de plomb.
14	La chaux d'étain	Vitriol d'étain.
15	La chaux de cuivre	Vitriol de cuivre, couperoſe bleue.
16	La chaux de biſmuth	Vitriol de biſmuth.
17	La chaux d'antimoine	Vitriol d'antimoine.
18	La chaux d'arſenic	Vitriol d'arſenic.
19	La chaux de mercure	Vitriol de mercure.
20	La chaux d'argent	Vitriol d'argent.
21	La chaux d'or	Vitriol d'or.
22	La chaux de platine	Vitriol de platine.

Fig. 11. Table of the combinations of sulfuric acid with bases arranged in the order of affinities in the wet way. The new nomenclature is used in this table. For comparison the treatise gives also the table with the old nomenclature [24]

decomposed at another, those of the attraction of water, or of its decomposition were not taken into account. The division of tables in two parts one for the dry and one for the wet way was only a partial solution to the problem. Finally, the tables did not express the variations in affinities due to the variations in degree of saturation. In spite of this he presents the combinations of sulfuric acid in his "Traité élémentaire de chimie" (1789) in the order of the affinities (Fig. 11).

The exhaustive work on affinities by Guyton de Morveau practically marked the end point of research in the field.

So diverse had become the notion, so numerous the parameters to consider in order to achieve a consistent picture of chemical reactions interpreted in the light of affinities that understandably, when the concepts of Lavoisier and those of Dalton opened the way to a new kind of researches bearing immediate results of practical value, the effort on affinity declined.

Already in his treatise on Chemistry [21] Thenard devotes a mere 10 pages, out of more than 3000, to the concept of affinity. He starts by enumerating seven parameters influencing affinity among which one finds the relative amounts of reacting substances and temperature as well as "electrical state", specific weight. Those are probably the less satisfactory pages of a book that, as early as 1827 expanded the atomic theory, Berzelius's electrochemical scale and notations, etc. Thenard concludes, after Berthollet, that the old concept of affinity as found in Bergman was wrong, as the claim that a greater affinity of A for B than that of B and C would mean a complete separation of B from C under the action of A.

Finally, ten years later Dumas (Fig. 12) in a lecture at the Collège de France refuted the concept of affinity altogether [22].

He does this in what appears a somewhat prejudiced manner. He criticizes Geoffroy on the ground that his "rapports" are disguised attractions which is precisely what Geoffroy tried to avoid.

He also criticizes theoretical interpretations of Geoffroy's followers and specially Bergman in trying to emulate

Fig. 12. Portrait of Dumas. From the archives of the French Académie des Sciences

Newton in the science of molecular movements as a general explanation of chemistry. This is a distorted view of Bergman's work but Dumas repeatedly objects to physicists' ideas when trying to explain chemical phenomena. On the other hand, he had for Boërhave, whom he credited with the first usage of the word affinity, admiring words for sticking to facts without being carried away by his imagination. He even likes his comparison of the aptitude of two chemical bodies to unite, or react, or dissolve, with a marriage. Dumas found the sentence "they act magis ex amore quam odio"[4] very poetic.

More scientifically, the reasons of Dumas for rejecting affinities were of two natures in addition to being misleading in some cases. Firstly, a pupil of Berthollet, he followed partly the ideas of his master who assigned to precipitation and volatilisation the role that was previously thought to be that of affinity. Even more important for him was the role of electrochemical forces that had been discovered by Davy for whom he professed an immense admiration, going to the point of quoting his interpretations because "even if they are wrong they are so beautiful". He recognized that Berzelius's views were however more realistic; in any case electrical forces enabled to forgo the concept of affinity.

[4] More by love than by hate

Conclusion

Firstly with respect to Geoffroy, I would like to quote from Fourcroy [15] the following remark: "Great men are recognized as much by the fact that their writings contain no stupic proposition as by the advances they have made." By this criterion Geoffroy was a really great man.

Then let us remark that the rise and fall of the popularity of the affinity concept took place in less than eighty years. These were the years preceding immediately the foundation of modern chemistry. In retrospect, and being able to form an opinion less biased than that of Dumas who was involved in the heated controversies accompanying the change of paradigm in chemistry at the beginning of the 19th century, one may perhaps advance the following view:

The effort put by many of the very best chemists of the 18th century in trying to conceptualize the experimentally founded notion of affinity or attraction was a major factor in the progress of chemistry, and the concept was of great pedagogical value.

By bringing experimental facts together in an orderly fashion, and by compelling chemists to find explanations to "exceptions" and "irregularities" the construction of affinity tables was an important factor of progress in chemistry. It led to new experiments, and to establish the role of "circumstances" of reactions, such as temperature, etc.

Theoretical discussions to justify adopted arrangements and to explain reactions were not fruitless; by failing to give satisfactory answers, even after the most subtle interpretations, unsatisfactory theories had finally to be abandoned.

Finally, one can consider that the publication of Geoffroy's table of relations marks the start of the evolution of chemistry, conceived as the art that teaches how to separate substances found in mixtures, to chemistry conceived in a modern sense as the science of reactions.

Caveat. In many instances I have put between quotation marks sentences translated from the French. English speaking readers may be found in A. M. Duncan [13, 14] and in Goupil. The reader interested in the subject should refer to them. He should also for a general survey of chemical philosophy in France during the 17th and 18th centuries consult H. Metzger [23]. Partington [25] is an invaluable source of information.

Acknowledgements. I am indebted to Professor Th. D. Burns for sending me the paper by A. M. Duncan on elective attractions by T. Bergman that introduced me to Duncan's work.

I thank Mrs. Nicole Glynn for finding and sending me Duncan's articles on the tables of affinity, Dr. E. Grison for pointing out Hassenfratz's work, the librarian of Conservatoire National des Arts et Métiers, Mrs. B. Hirsch librarian at the public library of Versailles for their help in finding many original documents.

The permission to reproduce pages of books at Conservatoire National des Arts et Metiers and portraits from the collections of the French Academy of Sciences is gratefully acknowledged.

Characteres Chemici præcipui

⊖ Sal in genere.
\+ acidum; c. concentratum; d. dilutum.
\+m. Acidum minerale.
Acidum Vitrioli.
c. concentratum; d. dilutum.
Acidum Nitri; a.n. phlogisticatum.
Aqua fortis.
Acidum Salis; a.s. dephlogisticatum.
Aqua Regis.
Acidum fluoris mineralis.
Acidum arsenici.
\+v. Acidum Vegetabile.
Acidum tartari.
Acidum Sacchari.
Acetum destillatum.
Acetum.
\+a. Acidum animale.
Acidum urinæ; phosphori.
Acidum Formicarum.
Acidum aëreum; atmosphæricum.
⊖ Sal alcalinus.
⊖p. Sal alc. purus (causticus).
⊖v. Alcali fixum vegetabile.
⊖vm. Alcali fixum minerale.
Alcali volatile.

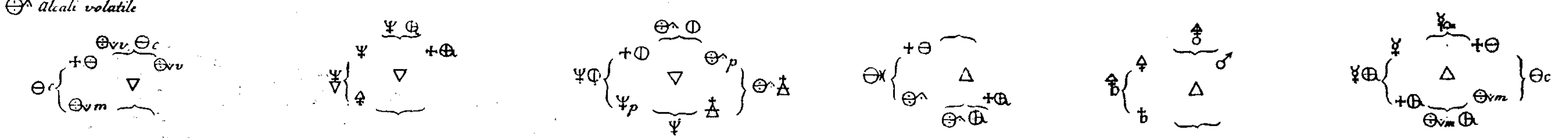
Sal neutralis.
Nitrum.
⊖c. Sal communis.
Tartarus; r. ruber; a. albus; p. purus.
Borax.
Sal ammoniacus.
Sal medius terrestris cum acido.
Magnesia vitriolata (Sal amarus, Anglic.)
Alumen.
Sal medius terrestris cum alcali.
Alcali volatile magnesia saturatum.
Sal medius metallicus cum acido.
Vitriolum cupri (v. Coeruleum)
Vitriolum ferri (v. viride.)
Vitriolum zinci (v. album.)
Luna nitrata (crystalli lunæ)
Mercurius Sublimatus corrosivus.
Mercurius præcipitatus albus.
Plumbum acetatum (Saccharum saturni)
Cuprum acetatum; Cupr. acet. purum.
Aurum regalisatum.
Sal medius metallicus cum alcali.
Alcali volatile cupro saturatum.
Sal sedativus.

Terra.
Lapis.
Arena.
Calx; p. pura (ustulata.)
Calx vitriolata (selenites, gipsum)
Terra ponderosa.
Magnesia.
Argilla.
Terra Silicea.
Crystallus.
Vitrum.
Fel vitri.
Minera.
m. Calx metallica.
Aurum fulminans.
Turpetum minerale.
Arsenicum album.
Vitrum plumbi.
Magnes.
Metallum.
Cinis.
Urina.
▽ Aqua.
Aër; n. nudus.

△ Ignis.
Phlogiston.
Sulphur.
Phosphorus.
Pyrophorus.
Carbo.
Oleum unguinosum.
Oleum empyreumaticum.
Oleum essentiale.
Æther.
Spiritus vini. R.s. rectificatissimus.
Alcali phlogisticatum.
Hepar alcalinum; Hepar terræ pond.
Hepar calcis; Hepar magnesiæ.
Sapo.
Saccharum.
Resina.
Gummi; Gummi-resina.
Metallum Sulphuratum.
Mercurius sulphuratus (cinnabaris)
Stannum sulphuratum (aurum musivum)
Arsenicum sulphuratum (auripigm., realgar)
Antimonium sulphuratum (ant. crudum)
Ferrum sulphuratum (pyrites)

☉ Aurum (Sol)
Platina.
☽ Argentum (Luna)
☿ Hydrargyrus (Mercurius)
♄ Plumbum (Saturnus)
♀ Cuprum (Venus)
♂ Ferrum (Mars)
♃ Stannum (Jupiter)
Vismutum.
Niccolum.
Arsenicum.
Cobaltum.
Zincum.
Antimonium.
Magnesium.
Argentum auratum.
Cuprum auratum.
Ferrum auratum.
Argentum cupro foetum.
Cuprum arsenicatum (metallum album)
Orichalcum.
Orichalcum argentatum.
Stannum plumbo foetum.
♂ Chalybs.

Retorta.
Recipiens.
Cucurbita; Alembicus.
Crucibulum.
re. Evaporare; tio. Evaporatio.
re. Digerere; tio. Digestio.
re. Coquere, ebullire.
re. Destillare.
re. Incinerare.
re. Calcinare.
re. Sublimare; Sublimatum.
re. Pulverisare; pulvis.
re. Solvere; tio. Solutio.
re. Præcipitare; Præcipitatum.
re. Fundere; io fusio.
Residuum, Caput mortuum.
Mensis.
Dies; Nox; Nyctemeron.
Hora.
Libra medica = ℥12 = ʒ96 = ℈288 = 5760 gran = 7410 ; i.
℥j = ʒviij = ℈XXIV = gr. 480 = 618 ass.
1 lb Libra mercatoria = 32 lod = 8848 ass = 6872 2330 gran
1 lod = 4 quint = 276½ ass = 214,7573 gran.
1 gran = 1,2875 ass; 1 ass = gr. 0,7767.



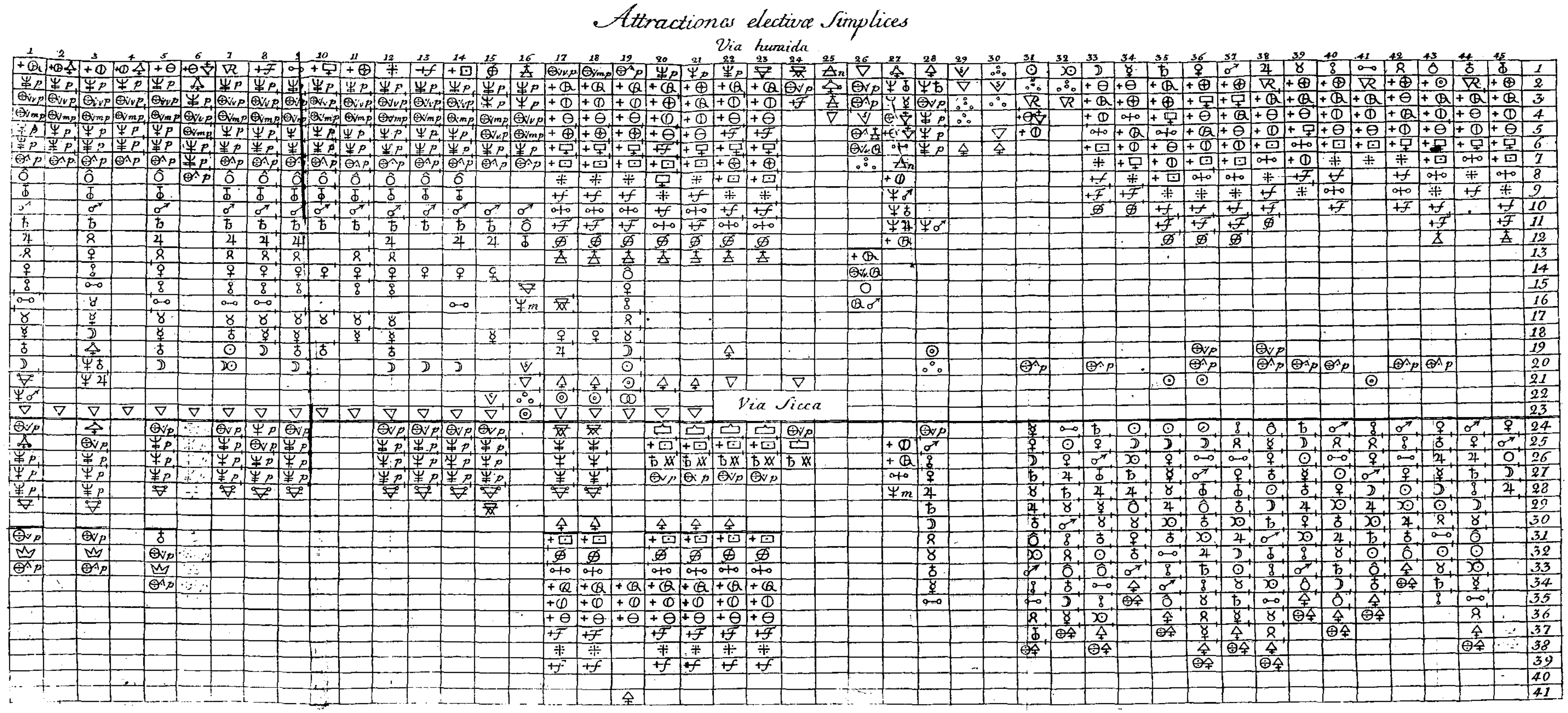


Fig. 13. Bergman's table of elective attractions and table of symbols. (Documents given to the author by Pr. L. Niinistö)

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A thorough study of affinity tables and of the work of Bergman can be found in A. M. Duncan [13, 14]. The reader interested in the subject should refer to them. He should also for a general survey of chemical philosophy in France during the 17th and 18th centuries consult H. Metzger [23]. Partington [25] is an invaluable source of information.

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