Symbolism of Arrows

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Chemistry: A Panoply of Arrows**

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abstract art · chemical equations · history of chemistry · Klee, Paul · symbolism in chemistry

Dedicated to Professor Michel Verdaguer

The arrow[***] is used in almost every field of human activity. In mythology and art it makes up the armory of Apollo and Diana, representing the light of the supreme powers. It symbolized the sunbeam, both in Greece and in precolumbian America. But, because of its shape, it has undeniable phallic associations.[2] Diana, the Roman goddess of the hunt (Artemis in Greek mythology), daughter of Zeus and Leto, and twin sister of Apollo, was represented as carrying a golden bow and arrows. Arrows were also used by Cupid, the Roman god of love, beauty, and fertility, and by his Greek alter ego, Eros. In Christian iconography the martyred Saint Sebastian is shown pierced by myriad arrows; he survived, only to be beaten to death by order of Emperor Diocletian.

The origin of the arrow as a weapon is lost in antiquity, yet every archaeological museum in the world has a collection of prehistoric arrowheads. Many pictures of arrows can also be found in prehistoric cave paintings.[3] Among them, we may focus on a hunting scene found on the walls of the Valltorta caves in Spain (Figure 1). It is interesting to note that the arrowheads do not indicate direction, as we would expect. The arrows the hunters are preparing to shoot have no heads, and it is up to the observer to interpret the drawing on the basis of experience. The arrows fly from the bow to the target (a deer), not in the opposite direction. But the arrows sticking out of the deer are shown with their heads pointing in the "wrong" direction, probably a deliberate decision of the artist to make the simple line recognizable as an arrow.

Figure 1. Hunters equipped with bow and arrows, depicted in the prehistoric paintings in the caves of Valltorta (Castelló, Spain).

The great variety of arrow shapes has attracted widespread attention.[4] A typical arrow consists of a shaft, a nock (or notch) and feathering, and a head, point, or tip. But arrows can differ in the composition and shape of nock, the number and length of the feathers, the type of wood used for the shaft, the material used for the head (e.g. obsidian, agate, jasper, bronze, wood), and the shape of the point.

Today arrows are omnipresent symbols. Traffic signs are an obvious example; the arrows indicate where drivers must go, where they cannot go, or where they might like to go. In chemistry, different sorts of arrows have played—and still play—a wide variety of roles, especially in chemical equations. However, little attention has been paid to arrows in chemistry, with one recent exception.[5] There have been two articles on chemical equations; one deals only tangentially with the issue of the arrows,[6] and the other is inaccurate regarding their introduction in chemical equations.[7] The present Essay reviews the concepts associated with arrows, their power as tools of abstraction and representation, and the subtle variations of meaning depending on the context, from the point of view of chemical symbolism.

1. Chemical Equations

Arrows were among the plethora of symbols used in alchemy and early chemistry (Figure 2), until Hasenfratz and Adet proposed a new system of symbols.[8] While the symbols of the alchemists were hardly standardized, there was a broad

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[***] **ar·row** *n.* **1.** a slender, straight, generally pointed missile or weapon made to be shot from a bow and equipped with feathers at the end of the shaft near the nock, for controlling flight. **2.** anything resembling an arrow in form, function, or character. **3.** a linear figure having a wedge-shaped end, used in maps, architectural drawings, etc., to indicate direction or placement.[1]

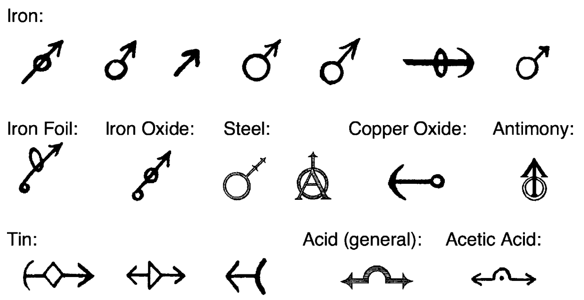

Figure 2. Some arrows used by alchemists and early chemists as symbols of chemical substances as noted by Murúa[10] and De Saporta.[11]

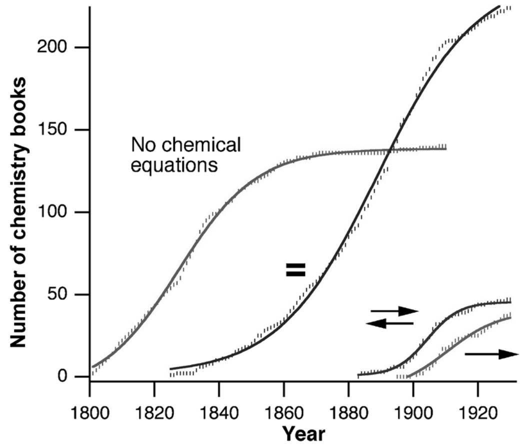

Figure 3. Evolution of the cumulative number of chemistry books that used (from left to right): no chemical equations, chemical equations with the equals sign only, equations with double arrows for equilibrium reactions and the equals sign for the rest, and equations with single arrows.

consensus in representing both iron and its associated planet, Mars, by a combination of arrow and circle. The extensive collection of alchemical symbols presented in the *Encyclopédie* of Diderot and D'Alambert (1751–1772) included, besides the symbols shown in Figure 2, arrows to represent operations such as purification or stratification, and substances such as phlegm, alum, minium, and urine. However, following the adoption of alphabetical atomic symbols in 1814 as proposed by Berzelius,[9] these arrows disappeared from chemistry texts. A long evolution was required before arrows returned to chemistry, which began with the use of equations to represent chemical reactions.

It was Lavoisier who first proposed a sort of chemical equation,[12] connecting reactants and products with an equals sign, in the description of the fermentation of sugars [Eq. (1)].[13] He added that the substances undergoing fermentation and the products of the reaction form part of an algebraic equation, which can be used to calculate their proportions. However, it was a long time before the use of chemical equations became common practice. An extensive survey of books on chemistry published in the nineteenth century (Figure 3; see the Supporting Information for a full list) tentatively identified the fifth edition of Thénard's *Traité de chimie élémentaire, théorique et pratique* (1827)[14] as the first text to include a chemical equation using the equals sign as proposed by Lavoisier. The equation refers to the generation of hydrogen in the reaction of zinc with sulfuric acid [Eq. (2), where the dots above the atomic symbols represent oxygen atoms]. Later, such equations were used by other authors, such as Baudrimont, who showed them only at the very end of his book [Eq. (3)],[15] Turner used quite similar equations intercalating the word "yield" between reactants and products [Eq. (4)].[16] Again, Thénard in a new edition of his treatise, wrote equations with an updated formulation of the reagents [Eq. (5)].[17] Two early users of chemical equations, Reid[18] and Guérin-Varry,[19] adopted the equals sign, albeit in nonbalanced equations. For some time, however, well-known authors such as Berzelius and Raspail, did not include chemical equations in their books,[20] and only around 1860 did equations begin to appear in practically all chemistry books (Figure 3).

$$2\,H\dot{H} + Zn + 2\,\dddot{S} = 4\,H + \ddot{Zn}\,\dddot{S} \qquad (2)$$

Ammoniaque.		Iode.		Hydriodate d'ammoniaque.		Iodure d'azote.	
$4\ NH^3$	+	$6\ I$	=	$3\ (NH^3 + IH)$	+	$I^3\ N$	(3)

1 eq. perox. iron & 2 eq. chloride of tin		yield	1 eq. sesquiox. tin & 2 eq. chlo. iron		
2 Fe+3O	2(Sn+Cl)		2 Sn+3O	2(Fe+Cl)	(4)

$$\textit{moût de raisin} = \textit{acide carbonique} + \textit{alkool} \qquad (1)$$

$$H^2O + SO^3 + Zn = H^2 + ZnO \cdot SO^3 \qquad (5)$$

A few decades later, in 1884, Van't Hoff proposed in his book *Étude de Dynamique Chimique*[21] that the equals sign should be replaced by a double arrow, ⇄, to stress the reversibility of some reactions. In that way, the concept of chemical equilibrium, the dynamic balance of opposing reactions, was incorporated into the formalism of the chemical equation. In the first part of his book, Van't Hoff used the equals sign for chemical equations, and only in the chapter on chemical equilibrium did he introduce the double arrow for the reaction of dissociation of N_2O_4 [Eq. (6)]. However, he did not explain its meaning, as if it were already an established convention. In an appendix he stated that a

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$$N_2O_4 \rightleftarrows 2\,NO_2 \qquad (6)$$

chemical equilibrium had been expressed "by the following symbol", in reference to the double arrow.

The introduction of the double arrow was later explicitly explained by Van 't Hoff in his 1901 Nobel Lecture as well as in a series of lectures at the University of Chicago in June 1901.[22] It was used in equations referring to the reaction of methanol and formic acid to give water and methyl formate:

"This can be illustrated in the formula by introducing the sign for a reversible reaction instead of the sign of equality:

$CH_4O + CH_2O_2 \rightleftarrows H_2O + C_2H_4O_2$

Such transformations, then, take place in either direction: the final state being known as chemical equilibrium."

During a transition period some authors combined the equals sign with the double arrow, while others continued to use only the former. The latter group included authors such as Remsen, Perkin, Ramsay, and Moissan (see the Supporting Information). There are, however a few remarkable exceptions. In 1884, the same year as Van 't Hoff's proposal, Eugenio Mascareñas published a summary of his lectures at the University of Barcelona,[23] in which he commented on the existence of chemical equilibria: "*… this circumstance must be represented in the formulae by means of a special sign. The one proposed by J. H. Van 't Hoff, seems to us highly acceptable, since it indicates the possibility of the opposite reactions and the equilibrium state that the conditions of the experiment determine.*" The two examples presented by Mascareñas are shown in Equation (7). Although subsequent pages contain few equations, none of which includes double arrows, he used them consistently in later, expanded versions of the book.[24] Double arrows appeared much later in research papers,[25] although in the absence of a more systematic search, the first appearance of the double arrow in a chemistry journal cannot be established. Further examples can be found in textbooks

$$\begin{array}{l} CO_3\,Ca \rightleftarrows CO_2 + CaO. \\ \text{Agua líquida} \rightleftarrows \text{Vapor ácueo.} \end{array} \qquad (7)$$

by Holleman[26] and Newth,[27] published in 1900 and 1902, respectively.

Arrhenius, Nernst, Hofmann, and several others[28,29] continued to use the equals sign for years thereafter, but were careful to draw a double arrow whenever a reversible reaction was discussed. Resistance to the new symbolism was voiced by Hildebrand,[30] who introduced the double arrow as follows in a chapter on equilibrium:

"It is frequently desirable to express in the equation for a reaction the fact that the reaction is reversible. This is done by substituting a double arrow, ⇄, for the equality sign.

Since nearly all reactions are reversible, however, the double arrow sign is in reality somewhat superfluous, except, perhaps, where it is desired to emphasize the fact of reversibility. In view of these facts we will not ordinarily use it in the following pages."

Nevertheless, Hildebrand illustrated the concept of equilibrium and the use of the double arrow with an example from real life:

"We may illustrate this important point by imagining a Western celebration in which a large number of cowboys are to ride wild horses. Now in order to have fifty mounted cowboys it would be necessary to have more than fifty cowboys and fifty horses present, for we will assume that cowboys are constantly being unhorsed.

Man + Horse ⇄ Mounted Horse"

In contrast, in his 1904 review of Pattison Muir's book, Alexander Smith complained that the double arrow was seldom used.[31]

Van 't Hoff's double arrow was modified in 1902 by Hugh Marshall,[32] who removed the inner barb of each arrow. This created the half-headed double arrows, ⇌, which have since been further simplified to ⟶. In justifying his proposal, he noted that single arrows were being used in organic chemistry "*to indicate merely the stages and methods by which a substance can be produced from some other substance as a starting point. In such cases, as no attention is paid by the bye products (sic), there is nothing of the nature of an equation involved.*" Thus, he proposed the use of arrows to indicate sequences of reactants and products, and that we should reserve the equals sign for ordinary equations merely for the purpose of calculations, not implying that the substances on one side of the equation are converted into those on the other side. For chemical equations he proposed four symbols, as shown in Equations (8)–(11).

$$KClO_4 \rightleftharpoons KCl + 2\,O_2. \qquad (8)$$

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2. \qquad (9)$$

$$\begin{array}{l} CuCl_2,\ 2\,H_2O + 2\,K_2CuCl_4,\ 2\,H_2O \\ \overset{56^{o}}{\rightleftharpoons} 2\,KCuCl_3 + K_2CuCl_4,\ 2\,H_2O + 4\,H_2O \end{array} \qquad (10)$$

$$CuCl_2 + H_2S \rightleftharpoons CuS + 2\,HCl, \qquad (11)$$

The half-headed double arrow is sometimes modified by using shafts of different length, representing the displacement of the equilibrium to one side of the reaction or the other.

2. The Single Arrow

The single arrow used today in chemical equations was adopted after the double arrow. However, an early application of the single arrow to represent chemical reactions was introduced by Gustavus D. Hinrichs, professor at the University of Iowa, who also contributed to the development of the periodic system along with Mendeleev. In a book published in 1874,[33] he represented the steps presumably involved in chemical reactions by combining the shape and layout of branches with the directionality of arrows (Figure 4). Hindrich's extensive use of arrows is all the more remarkable, since such symbols were not being used by

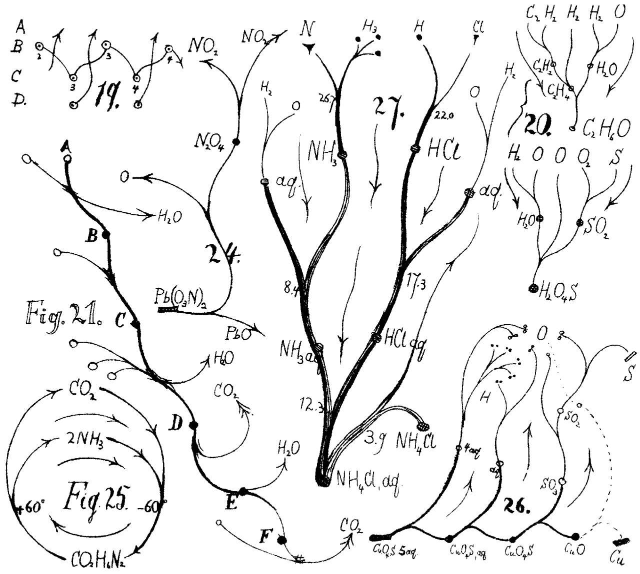


Figure 4. An early use of arrows to represent chemical reactions in a textbook by Gustavus D. Hinrichs. Some of the reactions represented are the synthesis of ethanol (20), the oxidation of an alcohol (21), the dissociation of lead nitrate upon heating (24), the reversible dissociation of ammonium carbonate (25), the dissociation of copper sulfate (26), and the formation of ammonium chloride from its constituent elements (27).

chemists at that time. When, then, did the arrow become a standard symbol for chemical equations?

From a survey of chemistry journals and books published around the end of the nineteenth and the beginning of the twentieth centuries (see the Supporting Information for more details), we can tentatively conclude that the equals sign was almost exclusively used to describe chemical reactions until approximately 1890. In the German journal *Berichte der Deutschen chemischen Gesellschaft*, single arrows appeared as far back as 1894.[34] These were "sequential arrows" used to indicate that one organic compound (to the right of the arrow) could be obtained from another one (to the left), without including other reagents or by products. Those sequential arrows should not be confused with proper reaction arrows, as later pointed out by Marshall when he introduced the half-barbed arrow. They were not intended to replace the equals sign, as is evident from the coexistence of the two symbols in the same paper. Sequential arrows became common around 1899–1900, especially among organic chemists. They can also been found in other periodicals such as the *Journal of the American Chemical Society* and the *Bulletin de la Societé Chimique de Paris.* So it is not surprising that in 1902 Marshall attempted to differentiate those arrows used to establish a qualitative connection between the starting materials and final products of a reaction, from those meant to convey the quantitative meaning associated with a chemical equation.[32]

Almost without being noticed, some authors began to include chemical equations with the single arrows in research papers.[35] Initially, arrows of different styles were used, the most common ones in the *Journal of the American Chemical*

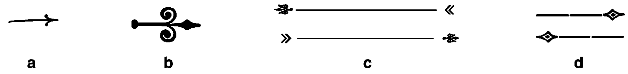


Figure 5. Several arrow designs used in chemical equations around 1900. References: a) Ref. [38]; b,c) Ref. [36]; d) Ref. [37].

Society being feathered arrows, ⤜. However, arrows with other sophisticated shapes also appeared at the beginning of the twentieth century, some of which are shown in Figure 5.[36–38] Feathered arrows were also used for a time to indicate the direction of the galvanic current produced by a chemical reaction.[39] Gradually, only the simpler and more stylized arrows were used in chemical equations.

Among the chemistry books analyzed here, the first to include single arrows for chemical equations is *Essentials of Chemistry for Secondary Schools* published by John C. Hessler and Albert L. Smith in 1902.[40] Let us recall that the single arrow appeared one year later in the collection of the lectures[22] given by Van't Hoff to the University of Chicago in 1901. Since both Hessler and Smith were based in Chicago and the former was an Instructor in Chemistry at the university, it is likely that their decision to use the chemical arrow was inspired by Van't Hoff's lectures there. In any event, Hessler and Smith presented a thorough discussion of the symbols used in chemical equations and their meanings. The innovative character of such symbolism was stressed by a Publisher's note: "*Instructors in Chemistry need not be told that it is now the custom of lecturers on this subject to use the arrow interchangeably with, and more often in place of, the equality sign. This is done in this book. It makes the equation plain, and, to the chemist, means more than does the usual (old) sign of equality.*" Other books that incorporated arrows in subsequent years are listed in the Supporting Information. It is important to stress here that the first use by Wilhelm Ostwald of a split arrow of the style proposed by Marshall [Eq. (8)] apparently corresponds to a book published in 1907,[41] which was translated into English two years later.[42]

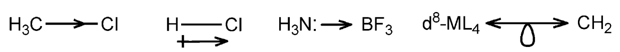
The reluctance to adopt the new symbolism is exemplified in a review of Alexander Smith's *General Inorganic Chemistry*, published in 1906.[43] Amidst a highly laudatory comment, Lawrence Bigelow wrote:[44] "*…the substitution of a single arrow for the equality mark is an innovation which the reviewer frankly doesn't like.*"

The adoption of the arrow in chemical equations to replace the equals sign does not represent just the choice of an alternative symbol, but constitutes a significant conceptual step forward. While the equals sign, as used in mathematical equations, suggests a symmetric relationship between the chemicals on both sides, the arrow introduces a sense of direction and clearly differentiates reactants and products. As noted by Kolb,[6] in a chemical equation the left term is equivalent to the right term only in terms of mass and number of atoms of each element, and therefore the strictest sense of the term "chemical equation" is actually a misnomer. Newth, who still used the equals sign, also noted the different meaning that the + sign has on the two sides of the equation: while on the left it means "reacts with", on the right it only implies the simultaneous appearance as products of the reaction, often forming a mixture.[27] A similar observation was made by Roscoe and Schorlemmer[45] when commenting on the decomposition reaction of potassium chlorate to give potassium chloride and oxygen: "*the sign + connects the two products and signifies 'together with'*."

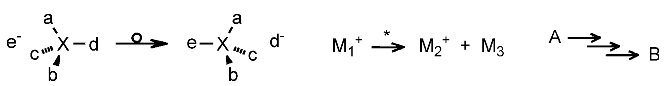
3. Other Horizontal Arrows

The concept of resonance[46] popularized by Pauling in 1933 in three of his series of articles on *The Nature of the Chemical Bond*[47] and later in the book with the same title had been introduced by the German chemist Fritz Georg Arndt (1885–1969) in 1924,[48] who also proposed the use of a double-headed arrow to represent resonance structures. The same author introduced the reversible arrows for tautomerism. Note that the same symbol is used to represent alternative descriptions of the electronic structure of the same molecule (resonance) and a chemical process that interconverts two species (tautomerism), typically the interconversion of two isomers through a simultaneous shift of a double bond and a proton.

Other uses of horizontal arrows in chemistry are only briefly noted here. A mid-head arrow represents an inductive effect or bond polarization in a molecule, with the head pointing to the most electronegative element of the bond (**1**). A crossed arrow (**2**) is commonly used to indicate the direction of the dipole moment in a molecule, with the head pointing to the negative pole and the tail representing a + sign (even though IUPAC recommends defining a dipole moment in the opposite direction). A single arrow connecting a Lewis lone pair and a Lewis acid represents a covalent coordinative bond (**3**), which paradoxically is expected to have a dipole moment that should be represented by an arrow pointing in the opposite direction. A double arrow with a dangling lobe (**4**) was proposed by R. Hoffmann to indicate isolobal analogies, a concept that refers to the similar symmetry, energy, and occupation of molecular orbitals in apparently dissimilar fragments.[49] According to the *IUPAC Gold Book*, the occurrence of a Walden inversion during a chemical transformation can be indicated in the chemical equation by



1 **2** **3** **4**



5 **6** **7**

the symbol shown in **5** instead of a simple arrow pointing from reactants to products. Also, when a fragmentation reaction is written with an asterisk above the arrow (**6**), it means that the reaction has been confirmed by the observation of a metastable peak in a mass spectrum. Finally, multiple arrows (**7**) are used as an ellipsis for several intermediate steps in a chemical reaction.

The most recent addition to the panoply of arrows for chemical equations is the retrosynthetic arrow, ⇒, introduced by E. J. Corey in 1971. This arrow points from products to reagents, and is of use in the design of accessible reaction steps that may lead back to simple, affordable reagents.[50] The direction of this arrow has the opposite meaning to the single arrow: the compound to the left of the arrow can be obtained from that on the right. This symbol also provides an example of how an arrow can lose its iconic character, since one would hardly imagine a physical arrow with two shafts and a single arrowhead.

4. Vertical and Diagonal Arrows

In chemical equations we also use vertical arrows to indicate the evolution of a gas, ↑, or the formation of a precipitate, ↓. The origin and the date of the introduction of vertical arrows in chemical equations are uncertain. An early example corresponds to a high school textbook on physics and chemistry published in 1862 by Manuel Rico and Mariano Santisteban, professors at the Universidad Central in Madrid. In the first two editions of their book, they made extensive use of feathered horizontal arrows in textual representations of chemical reactions to indicate the evolution of a gas.[51] In later editions they appended up-pointing diagonal arrows for gaseous reaction products, and down-pointing diagonal

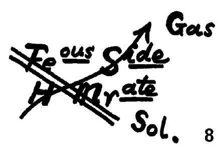
$$\mathrm{Cu+2SO^3{=}CuO,SO^3+SO^2}\nearrow. \qquad (12)$$

$$\mathrm{NaO,2(BoO^3)nHO+HCl{=}NaCl,nHO+2(BoO^3,3HO)}\swarrow. \qquad (13)$$

arrows for the formation of precipitates or crystals in chemical equations [Eqs. (12) and (13)].[52] The convention associated with such a symbol was explained in a footnote, thus suggesting that it was not a common practice at that time: *We use the arrows to indicate in the chemical formulae the bodies that evolve in gaseous form (↗), and those that precipitate from liquids in chemical reactions (↙).*

Three decades later, diagonal arrows reappeared in books written by Hinrichs[53] and Mermet.[54] The former book is a collection of 100 lectures on inorganic chemistry. At the end of lecture 28, which is devoted to the chemical reaction, we find the following note:

"*Diagrams of Reactions should be written out in the simplest possible manner. The essential features of the reactions should be specially marked, namely insolubility, volatility, etc. The substances actually taken are written one above the other; the* DETERMINING REACTION *is now marked by one heavy line terminating in an arrow, and the* CONSEQUENT REACTION *is marked by a light double line. For gases and vapors, the line should be drawn upwards; for precipitates the line should be drawn downwards, as shown in the few instances here given.*"



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In a variety of chemical equations represented by Hinrichs, the formulae of the reactants are thus written on top of each other and the products are indicated by diagonal lines connecting the components of the reaction products, as in the reaction of ferrous sulfide and hydrogen chloride, or "hydrogen muriate", shown in **8**.

Soon after Hinrichs, Walker and Ullmann represented the evolution of gases such as HCl with diagonal arrows.[55] Also noteworthy is the presence of vertical arrows in a high school textbook written by Adam in 1903,[56] for the author takes care to define the symbols to be used for chemical reactions throughout the book:

⇄ *indicates a reaction that can give the reverse reaction;*
↗ *indicates the evolution of a gas;*
↷ *indicates the distillation of a liquid or a solid (sic);*
↓ *indicates a precipitation.*

There was apparently a long "induction period" before the vertical arrows were generally adopted as standard symbols, as in, for example, books by Stähler[29] and Smith.[57] The latter made extensive use of them, and also felt it necessary to present a definition of the vertical arrows, under the heading Chemical Equilibrium: "*When this relative completeness is due to precipitation or volatilization, the fact will be indicated with vertical arrows.*" Smith also used the up-pointing arrow to indicate a reactant that is dissolved. Combined, the up- and down-pointing arrows constitute the reflux arrows, ↓↑, sometimes annotated with the reaction conditions and the solvent used, above or below the reaction arrow. Although the present study does not claim to be comprehensive, the fact that no similar arrows were found for the years between Rico–Santisteban and Hinrichs suggests that the former may be regarded as an isolated case and not


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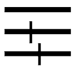
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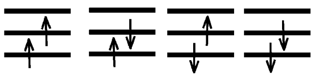
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representative of common practice at that time. Also the fact that Smith included a definition in his textbook indicates that it was seen as a recent incorporation to the symbolism of chemical equations.

The concept of electron spin is also closely associated with up- and down-pointing arrows (**9**). A significant step forward in terms of abstraction consists in removing the arrowheads that indicate the electronic spin, as done in **10**. This scheme implicitly represents all descriptions of two electrons in two orbitals of a degenerate set, which amounts to a total of 36 spin orbitals or, more precisely, to the 15 spin orbitals that obey the Pauli antisymmetry principle (four of them shown in **11**). In this way, a huge amount of information is beautifully encoded in the amazingly simple diagram **10**, which illustrates what is probably the most abstract version of an arrow and takes us back to some of the prehistoric arrow drawings (Figure 1).

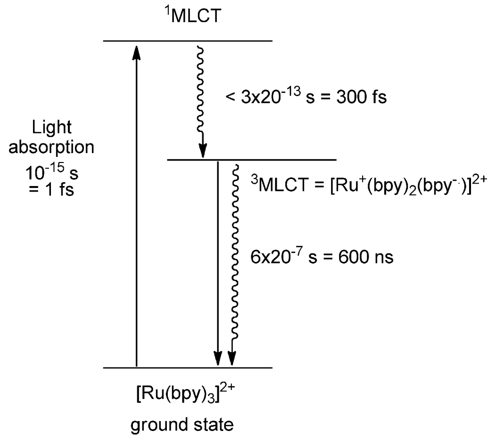


Figure 6. A typical Jablonski diagram indicating radiative (straight arrows) and nonradiative (wavy arrows) transitions.[58]

5. Photons, Excitation, Relaxation, and Wavy Arrows

Photophysical processes such as nonradiative relaxation or luminescence are represented by different sorts of arrows in Jablonski diagrams (Figure 6). Radiative processes, whether absorption or emission of light, are generally indicated with straight arrows. In contrast, radiationless transitions, termed "intersystem crossing" or "nonradiative decay", are generally

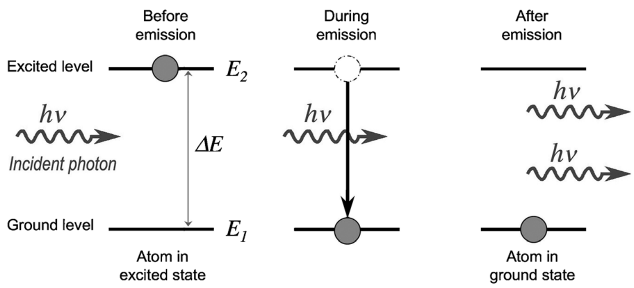
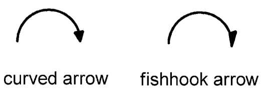


Figure 7. Schematic depiction of the stimulated emission of radiation that takes place in lasers (adapted from Wikimedia Commons).

indicated with wavy arrows ⟿, although intersystem crossings can also be represented with dashed arrows. This seems a paradoxical choice, because we tend to associate wavy arrows with the wave nature of light, as used in a diagram of stimulated emission of radiation (Figure 7). This may be reminiscent of the nomenclature of Hassenfratz and Adet, who proposed a vertical wavy line to represent light.[8] In nuclear physics, the radiation emitted by a decaying nucleus is also represented by a wavy arrow, while the nuclear reaction itself is represented by a straight arrow.

6. Curved Arrows and Cycles

The representation of electron rearrangements through curved arrows (**12**) is essential in describing reaction mech-



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anisms in organic chemistry. This symbol, also called the "curly arrow", indicates displacement of electron pairs and was introduced by Sir Robert Robinson in 1922[59] to explain the reactivity of hexatriene. Arthur Lapworth simultaneously published a paper with curved arrows representing rather the motion of "partial valencies", a concept that was less successful.

The fishhook arrow (**13**) replaces the curved arrow when one wishes to refer to a shift of only one electron, typically for homolytic cleavage of a bond that generates two radicals. This symbol was introduced by Carl Djerassi and co-workers to explain electron-impact-induced fragmentation patterns in the mass spectra of organic compounds.[60] There has been a recent attempt to introduce a bouncing curved arrow[61] to replace curved arrows in some cases, although it is probably too early to guess the possible fate of such a symbol.

Accustomed as we are to curved arrows, it is hard to realize the degree of abstraction implicit in these symbols. First of all, it seems quite obvious that most of the iconic content of the straight arrow is lost in its curved analogue. The latter does not represent a physical object at all, and the very notion of hunters or warriors trying to throw a curved arrow would make us smile. To better understand the curved arrow in chemistry we should consider the arrowed parabolas that represent the trajectory of a projectile. In this symbol the arrowhead indicates direction, but the shaft is replaced by a curve that describes trajectory. In spite of the geometrical similarity between the ballistic arrow and the curved arrow, the curve in the latter is not meant to describe a trajectory. It is only one way of connecting the departing and end points of an electron-pair displacement. For attempts to represent truly three-dimensional phenomena in chemistry we can turn to studies of reaction mechanisms, in which we can see, for instance, the choreography of concerted atomic motions in con- or disrotatory electrocyclic reactions represented by curved arrows.

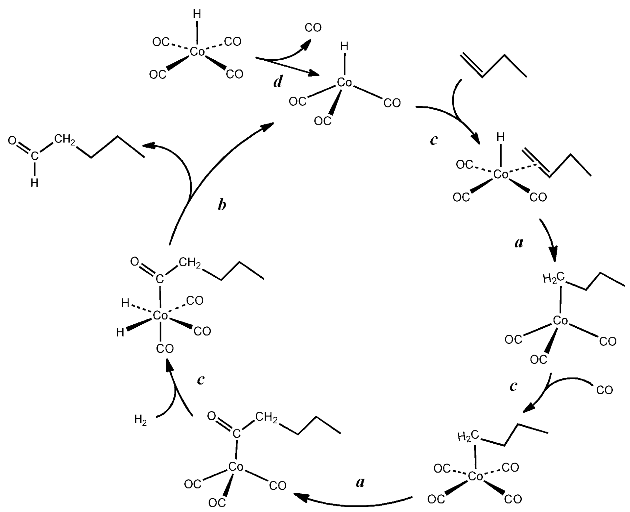

Figure 8. Typical scheme for a catalytic cycle, representing the hydroformylation of olefins in the presence of $[HCo(CO)_4]$, commonly known as the oxo process. Here the labels ***a–d*** indicate curved arrows with different meanings.

Another type of curved arrow is used to describe every proposed step in a catalytic cycle. Let us consider as an example the reaction of hydroformylation of olefins using a cobalt catalyst, commonly known as the oxo process (Figure 8). Each curved arrow in such a cycle may have one of several possible meanings depending on its context: ***a***: single curved arrows mean A→B within the cycle; ***b***: bifurcating arrows mean A→B+C, where C is a product of the reaction while A and B are intermediate species; ***c***: merging arrows correspond to steps of the type A+B→C, where A is a reactant but B and C are intermediates; and ***d***: bifurcating arrows leading out of the cycle indicate the evolution of a reagent that is not a stoichiometric product of the reaction to form the catalytically active species from the precatalyst. Even though I have used straight arrows to represent steps of types ***a–c*** for simplicity in the previous sentences, it must be stressed that the use of curved arrows in the cycle is not a merely decorative choice. They clearly show that those steps take place within a catalytic cycle, not in a stoichiometric reaction.

7. Arrows We Share with Physicists and Artists

Besides their extensive use in chemical equations, arrows have been assigned a variety of other meanings in chemistry. For instance, several authors used arrows to indicate electron sharing and chemical bonding, some of which, now obsolete, have been discussed in a classical book devoted to symbols and formulae in chemistry.[62] Similar to convention in mathematics and physics, arrows are also extensively used to represent all kinds of vectors, notably coordinate axes and displacement vectors that indicate distortions or vibrational modes. They are also used as indicators of motion or flux in diagrams of experimental setups, such as the air flow in an air bath[63] or water circulation in a distillation column, poetically described by Roald Hoffmann:[64]

You can see inside
every vessel
without reflections, without getting wet,
and explore every link
in a copper condenser.
Flames are outlined cypresses
or a tulip at dawn,
and some Klee arrows
help to move gases and liquids the right way

It may be interesting to establish parallels between the use of simple and double-headed arrows in chemistry and elsewhere, particularly in art. One such analogy can be found in the comment made by Tufte[65] about the cover of the book *Cubism and Abstract Art*, published by Alfred H. Barr, Jr. in 1936. On that cover, a diagram showing the relationships between the different trends in modern art uses arrows to indicate the influence of one art style on another (e.g., fauvism on expressionism, or dadaism on surrealism). Tufte remarks that there are no paired arrows, ⇄, and criticizes Barr for not using these or double-headed arrows, ↔, which would signal mutual influences among art styles. The similarity between the arrows proposed by Tufte and the ones used in chemical equations may not be merely a coincidence, since

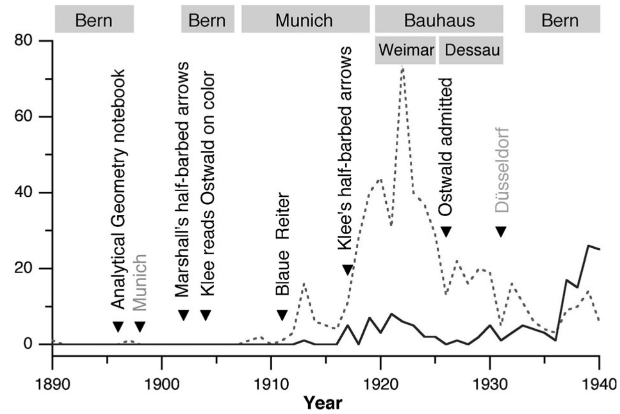

Figure 9. Chronology of Paul Klee's production of artworks incorporating half-barbed arrows (continuous line) and other types of arrows, including spears and harpoons (dashed line). Events relevant to the comparison of the use of arrows in chemical equations and in Klee's artwork are signposted (see text).

the author analyzed a variety of scientific graphic materials, including Pauling's *General Chemistry*.

Since the use of arrows in art is epitomized by Paul Klee, it is pertinent here to consider his works from a chemist's point of view. In general, his arrows are intended to suggest motion, force, equilibrium, or tension, akin to the meanings attached to arrows in physics. But in Klee's hands, they may also be converted into a window, a chimney, clock hands, weathervanes, lightning, mind, time, space, cause, effect, creation, or cosmic forces.[66] Arrows are present in nearly 700 of his works throughout his career, as seen in the yearly distribution of Klee's arrow-containing works (Figure 9; see the Supporting Information for a full list). Although the largest production corresponds to Klee's Bauhaus years (1920–1931),[67] reaching a peak in 1922, the chronology presented here shows clearly that his systematic use of the arrow as a pictorial element occurred before he joined the Bauhaus. The chronology also suggests that Kandinsky may have influenced Klee's use of arrows, since the first peak in his arrow production occurred after he had joined the Blaue Reiter movement led by Kandinsky and Franz Marc. In addition, schemes in which arrows figure prominently are very common in his notebooks from the Bauhaus period.[68]

According to J. Daniel,[69] Klee was more interested in representing formation and motion than shapes, and for that reason he used arrows profusely in his paintings. In Klee's own words, "*Thus form may never be regarded as solution, result, end, but should be regarded as genesis, growth and essence.*"

More interesting from a chemist's viewpoint is the appearance of what could be interpreted as half-barbed arrows ⇀ in a significant portion of Klee's works. Well over 100 such works (see the Supporting Information for a full list) appeared from 1913 until his death in 1940 (Figure 9). Disguised half-barbed arrows appear in several works as part of figurative elements: insect stings, fishhooks, hands, feet, noses, trees, sails, axes, or flags. In other cases, these arrows can be detected amidst other abstract elements without an obvious figurative function. Finally, there is an important group of works in which the half-barbed arrows are clearly present, with roles similar to those of his full arrows.

One could hypothesize that Klee's half-barbed arrows stem from spears or harpoons, but these objects are much less common in his work and appear only as weapons. In contrast, his half-barbed arrows play similar roles to the full arrows, indicating motion or direction. Fishhooks, present in an early series of four watercolors featuring fish,[70] are another possible origin of the half arrows. A possible influence from chemistry books seems a reasonable hypothesis, given Klee's well-known interest in science. Aichele has suggested that he might have been familiar with Ostwald's *Lehrbuch der allgemeinen Chemie*, which was then in general use as a Gymnasium text.[71] During his high school time, Klee doodled in his geometry, physics, and chemistry notebooks. It is not strange, therefore, that Klee incorporated symbols

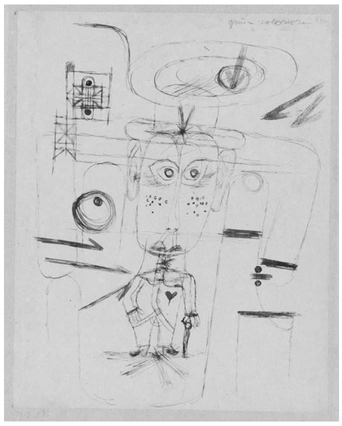

Figure 10. *Bedrängter kleiner Herr* (*Little Gentleman in Distress*) by Paul Klee, 1919, 133, pen on paper on cardboard. Zentrum Paul Klee, Bern, Livia Klee Donation. Reproduced with permission.

used in physics and chemistry classes into some of his drawings, although we must not forget that half-barbed arrows were introduced in chemistry somewhat later. What is undeniable is that half-barbed arrows first appear in Klee's work in 1913 (if we consider some of the many lines that appear in an untitled etching (catalogue number 1081) as half-barbed arrows). This is well after they had been introduced in chemistry by Marshall and subsequent textbooks.[29,42,72] Klee's half-barbed arrows became fully recognizable as independent symbolic elements a few years later, initially in his *Little Gentleman in Distress* (Figure 10), and frequently afterwards in his works (*Station L112*, *Stormy Ride*, *The Trombone Sounds*, and many more, listed in the Supporting Information). Given the timeframe (Figure 9) and Paul Klee's interest in scientific advances, it might well be that his adoption of half-barbed arrows as pictorial elements had been influenced by their presence in chemical equations following Marshall's proposal, though this is only a hypothesis.

A personal influence from Ostwald in his discovery of half-barbed arrows should also be ruled out, since Klee and Ostwald joined the Bauhaus was after this (1920 and 1926, respectively), and they had not yet met at the time when these symbols began to appear in Klee's work. Although we know that Klee read Ostwald's book on color in 1904 and did not find it interesting,[73] this fact is unlikely to have had any connection with his use of half arrows.

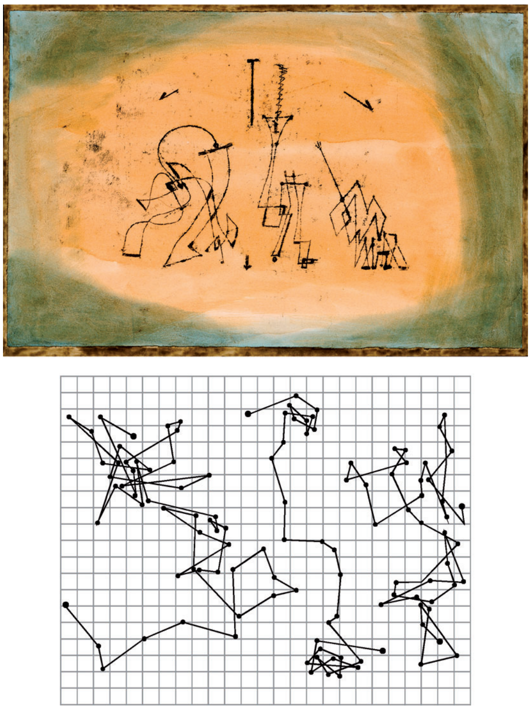

Figure 11. Top: *Abstract Trio* by Paul Klee, 1923, watercolor and transfered printing ink on paper, The Berggruen Klee Collection. Copyright: The Metropolitan Museum of Art/Art Resource/Scala, Florence. Bottom: Diagram of the observation of Brownian motion by Jean Perrin.[74]

In the context of this Essay, Klee's *Abstract Trio* is the work that most caught my attention, since it clearly shows how he used scientific graphic material as a source of inspiration. It has been proposed[71] that the proto-Cubist drawings produced by Klee in 1912, in particular his illustrations for Voltaire's *Candide*, were influenced by Jean Perrin's depiction of Brownian motion which earned him the 1926 Nobel Prize in Physics. However, it seems to me that the painting *Abstract Trio* is much more evidently inspired by Perrin's diagram, as seen by comparing the two works (Figure 11). Each of Perrin's Brownian trajectories is converted in Klee's hands into one of the musicians of the trio.

Since Klee was an accomplished violinist, it might not be merely fortuitous that he added half-barbed arrows to this creation, since they are similar in appearance to a musical quarter note and to an eighth rest. This can be seen in a pictorial example of a three-part movement by J. S. Bach that is reproduced in his pedagogical notebooks.[68] Hence, the half-barbed arrows could in this case represent both musical notes and the direction of the propagation of the sound from the instruments of the trio, conveying a sense of stereophony. It is probably relevant that this painting was created in the period after the first stereophonic transmission through a telephonic line by Clément Ader in 1881 and before the first stereophonic radio broadcast by the BBC in 1925. Another remarkable aspect of the leftmost member of the trio is that what may be perceived as a saxophone also has the silhouette of a curved half-headed arrow. This and other less obvious arrows present in *Abstract Trio* are more clearly seen in the preparatory drawing (*Theater of Masks*, 1922), in which the underlying structure of dots and lines imitating Perrin's graph is more visible. It is interesting to note that the same Alfred H. Barr, Jr., who filled the cover of his book on abstract art with arrows, bought the *Abstract Trio* in 1930 and owned it for fifty years.[75]

8. Summary and Outlook

Historically, arrows were first connected to chemical knowledge as alchemical symbols representing elements or compounds. The different sorts of arrows now used in chemistry, however, are not successors of the alchemical arrows but have evolved independently after a century of chemistry without arrows. During this period a crucial event was the adoption of "chemical equations" for the simplified and quantitative description of chemical reactions (ca. 1833), which had been invented much earlier by Lavoisier (1787) and made use of formulae with the atomic symbols established by Berzelius (1814). Arrows appeared for the first time in chemical equations when Van 't Hoff wanted to emphasize the fact that some reactions are reversible and proposed to replace in those cases the equals sign by two arrows pointing in opposed directions (1884). Only one decade later the single arrow started to be used in chemical equations, although a deeper analysis is probably needed before a definitive date and name can be established as a departing point. It must be said, however, that Van 't Hoff and Marshall played crucial roles in the dissemination and standardization of the new symbolism, and that Hessler and Smith are outstanding candidates for the title of first textbook authors who introduced the single arrow for chemical equations. A preliminary timeline for the incorporation of those symbols in chemical equations is presented in Figure 12, where some of the authors who contributed to their use are also noted.

It is important to stress that the symbols discussed here were only accepted by the chemical community at a specific time, when the knowledge and the nomenclature were ripe for their introduction. In that respect, Lavoisier and Hinrichs were precursors for the introduction of the chemical equation and the reaction arrow, respectively, although their proposals were practically ignored for decades. An analysis of the incorporation of such symbolism in chemistry texts (Figure 3) shows that after the introduction of each particular symbol

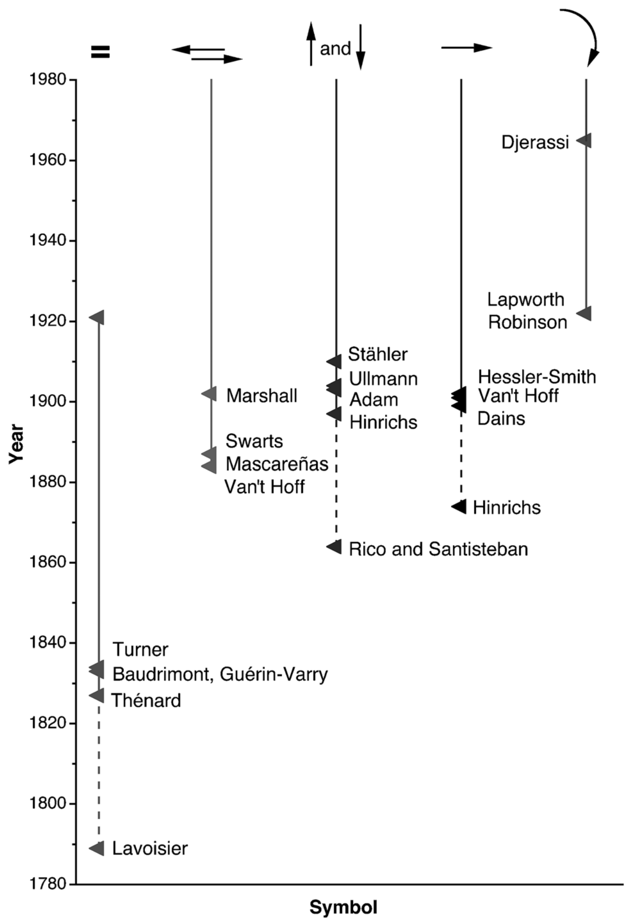

Figure 12. Timeline for the incorporation of different types of symbols into chemical equations; the names of some of the pioneers in the use of each type of symbol are noted. The dashed lines connect the very first use of a particular symbol, which probably did not have direct influence its adoption, with the onset of more generalized use (see also Figure 3).

there is an induction period in which its use grows slowly, reaching its plenitude and replacing the earlier symbols only after several decades.

The variety of meanings that a simple symbol such as an arrow may have is astounding. It is evident in a simple analysis of the variety of traffic signs based on arrows, but also in the many uses within the field of chemistry reviewed here. In chemistry, for instance, a vertical arrow can either mean the evolution of a gas from a chemical reaction or the positive spin of an electron, depending on whether it appears in a chemical equation or in an orbital energy diagram. We have also seen that a curved arrow, commonly used to indicate electron shifts in organic molecules, may have different meanings when it is inserted in different places within a catalytic cycle. Last but not least, a wavy arrow may represent opposite concepts depending on the context in which it is used, either emitted light or radiationless decay. The tremendous power of the arrow as a symbolic element is also shown by the radically different meanings attached to subtle changes, such as its horizontal, up-pointing, or down-pointing position within a chemical equation. The horizontal chemical arrow has a higher information content than the equals sign in a mathematical equation, and it endows different meanings to the plus signs on the left- and right-hand sides of the equation. These were undoubtably key factors in the final replacement of the equals sign by an arrow in the chemical literature.

In this Essay I have tried to show how the arrows in chemical equations convey much more information than the strictly iconic sense, and that they carry a significant degree of abstraction. It is not unlikely that scientists progressively exposed to abstract art at the beginning of the twentieth century were more prepared to accept chemical equations with arrows and vice versa. While the arrow is a ubiquitous symbol that chemistry shares with many fields of knowledge and of visual communication, the half arrow seems to be more specifically a chemical symbol. The frequent use of half arrows as pictorial elements by Paul Klee is therefore remarkable and supports the idea of a concurrent incorporation of abstraction in chemistry and art, reflected in the chronological parallelism shown here. A particularly relevant case corresponds to the attendant half arrows in Klee's *Abstract Trio*, which was unmistakably inspired by the plots with which Perrin recorded his observations of Brownian motion. In his interpretation Klee masterfully combined aesthetics, representation, music, and science. To quote William Blake (out of context), one could conclude that both modern chemistry and abstract art have been developed "*with intellectual spears, and long winged arrows of thought*".

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[1] *Webster's Encyclopedic Unabridged Dictionary of the English Language*, Gramercy Books, New York, **1996**.
[2] J. E. Cirlot, *Diccionario de símbolos*, Siruela, Madrid, **2001**. For an English translation see *A Dictionary of Symbols*, Philosophical Library, New York, **1962**.
[3] A. Leroi-Gourhan, *L'art pariétal. Langage de La préhistoire*, Editions Jérôme Millon, Grenoble, **1992**.
[4] C. Miles, *Indian and Eskimo Artifacts of North America*, American Legacy Press, New York, **1963**.
[5] A. Lakshminarayanan, *Resonance* **2010**, *15*, 51.
[6] D. Kolb, *J. Chem. Educ.* **1978**, *55*, 184.
[7] W. B. Jensen, *J. Chem. Educ.* **2005**, *82*, 1461.
[8] J.-H. Hassenfratz, P. A. Adet in *Méthode de Nomenclature Chimique* (Eds.: L.-B. Guyton de Morveau, A.-L. Lavoisier, C.-L. Berthollet, A.-F. Fourcroy), Cuchet, Paris, **1787**.
[9] J. J. Berzelius, *Ann. Phil.* **1814**, *3*, 51.
[10] A. Murúa y Valerdi, *Mem. Acad. Cienc. Artes Barcelona* **1916**, *12*, 283.
[11] A. De Saporta, *Les theories et les notations de la Chimie Moderne*, J.-B. Baillière et Fils, Paris, **1889**.
[12] H. M. Leicester, *Panorama histórico de la química*, Alhambra, Madrid, **1967**.
[13] A. Lavoisier, *Traité élémentaire de Chimie*, *Vol. 1*, Cuchet, Paris, **1789**.
[14] L.-J. Thénard, *Traité de chimie élémentaire, théorique et pratique*, 5th ed., Crochard, Paris, **1827**.
[15] A. Baudrimont, *Introduction a l'Ètude de la Chimie par la Théorie Atomique*, Louis Colas, Paris, **1833**.
[16] E. Turner, *Elements of Chemistry*, 5th ed., John Taylor, London, **1834**.

[17] L. J. Thénard, *Traité de chimie élémentaire théorique et pratique*, 6th ed., Crochard, Paris, **1834**.
[18] D. B. Reid, *Rudiments of Chemistry*, William and Robert Chambers, Edinburgh, **1836**.
[19] R.-T. Guérin-Varry, *Nouveaux élémens de chimie théorique et pratique*, F.-G. Levrault, Paris, **1833**.
[20] J. J. Berzelius, *Tratado de Química*, translated from the 5th ed., Ignacio Boix, Madrid, **1845**; F.-V. Raspail, *Nouveau système de chimie organique*, 2nd ed., Baillière, Paris, **1838**.
[21] J. H. Van't Hoff, *Études de Dynamique Chimique*, Frederik Muller, Amsterdam, **1884**.
[22] J. H. Van't Hoff, *Physical Chemistry in the Service of the Science*, The University of Chicago, Chicago, **1903**.
[23] E. Mascareñas, *Introducción al Estudio de la Química. Compendio de las lecciones explicadas en la Universidad de Barcelona,* Crónica Científica, Barcelona, **1884**.
[24] E. Mascareñas, *Elementos de Química General y Descriptiva*, Pedro Ortega, Barcelona, **1903**; E. Mascareñas, *Elementos de química general y descriptiva*, 2nd ed., Pedro Ortega, Barcelona, **1913**.
[25] W. D. Bancroft, *J. Phys. Chem.* **1896–7**, *1*, 337; A. E. Taylor, *J. Phys. Chem.* **1896–7**, *1*, 1; S. W. Young, *J. Am. Chem. Soc.* **1897**, *19*, 851.
[26] A. F. Holleman, *Lehrbuch der anorganischen Chemie*, Veit, Leipzig, **1900**.
[27] G. S. Newth, *A Text-Book of Inorganic Chemistry*, Longmans, Green, and Co., London, **1902**.
[28] S. Vila Vendrell, *Tratado teórico-experimental de Química General y Descriptiva, con aplicación a la Medicina*, Farmacia e Industria, Agustín Bosch, Barcelona, **1915**; S. Arrhenius, *Theorien der Chemie*, Akademische Verlagsgesellschaft, Leipzig, **1906**; W. Nernst, *Theoretische Chemie vom Standpunkte der Avogadroscehn Regel un der Thermodynamik*, 6 ed., Ferdinand Enke, Stuttgart, **1909**; F. A. Philbrick, E. J. Holmyard, *A Text Book of Theoretical and Inorganic Chemistry*, Dent and Sons, London, **1932**; F. S. Taylor, *Inorganic and Theoretical Chemistry*, 8th ed., William Heinemann, London, **1947**; K. A. Hofmann, *Lehrbuch der Anorganischen Chemie*, Vieweg, Braunschweig, **1919**.
[29] A. Stähler, *Einführung in die anorganische Chemie*, J. J. Weber, Leipzig, **1910**.
[30] J. H. Hildebrand, *Principles of Chemistry*, Macmillan, New York, **1918**.
[31] A. Smith, *J. Am. Chem. Soc.* **1904**, *26*, 1175.
[32] H. Marshall, *Proc. R. Soc. Edinburgh* **1902**, *24*, 85; H. Marshall, *Z. Phys. Chem.* **1902**, *41*, 103.
[33] G. Hinrichs, *The Principles of Chemistry and Molecular Mechanics*, Egbert & Fidlar, Davenport, Iowa, **1874**.
[34] E. Bamberger, *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 914; H. Schiff, A. Ostrogovich, *Ber. Dtsch. Chem. Ges.* **1894**, *27*, 960.
[35] C. Hoitsema, *Z. Phys. Chem.* **1898**, *25*, 686; F. B. Dains, *J. Am. Chem. Soc.* **1899**, *21*, 136; R. Wegscheider, *Z. Phys. Chem.* **1900**, *35*, 513; J. Stieglitz, *J. Am. Chem. Soc.* **1901**, *23*, 797; T. W. Richards, N. Stull, *Z. Phys. Chem.* **1902**, *41*, 544; H. L. Wheeler, T. B. Johnson, *J. Am. Chem. Soc.* **1902**, *24*, 680.
[36] Anonymous, *An. Soc. Esp. Fis. Quim.* **1906**, *4*, 339.
[37] Anonymous, *An. Soc. Esp. Fis. Quim.* **1906**, *4*, 453.
[38] E. Piñerúa, *An. Soc. Esp. Fis. Quim.* **1904**, *2*, 141.
[39] A. Findlay, *Practical Physical Chemistry*, **1915**; G. M. Smith, *J. Am. Chem. Soc.* **1905**, *27*, 540.
[40] J. C. Hessler, A. L. Smith, *Essentials of Chemistry*, B. H. Sanborn & Co., Boston, **1902**.
[41] W. Ostwald, *Prinzipen der Chemie: Eine Einleitung in alle chemischen Lehrbücher*, Akademische Verlagsgesellschaft, Leipzig, **1907**.
[42] W. Ostwald, *The Fundamental Principles of Chemistry*, Longmans and Green, London, **1909**.
[43] A. Smith, *General Inorganic Chemistry*, The Century Co., New York, **1906**.
[44] S. L. Bigelow, *J. Am. Chem. Soc.* **1906**, *28*, 1081.
[45] H. E. Roscoe, C. Schorlemmer, *A Treatise on Chemistry*, D. Appleton, New York, **1901**.
[46] F. Arndt, E. Scholz, P. Nachtwey, *Ber. Dtsch. Chem. Ges.* **1924**, *57*, 1903.
[47] L. Pauling, J. Sherman, *J. Chem. Phys.* **1933**, *1*, 679; L. Pauling, J. Sherman, *J. Chem. Phys.* **1933**, *1*, 606; L. Pauling, G. W. Wheland, *J. Chem. Phys.* **1933**, *1*, 362.
[48] P. Cintas, *Angew. Chem.* **2004**, *116*, 6012; *Angew. Chem. Int. Ed.* **2004**, *43*, 5888; E. Campaigne, *J. Chem. Educ.* **1959**, *36*, 336.
[49] R. Hoffmann, *Angew. Chem.* **1982**, *94*, 725; *Angew. Chem. Int. Ed. Engl.* **1982**, *21*, 711.
[50] E. J. Corey, *Q. Rev. Chem. Soc.* **1971**, *25*, 455.
[51] M. Rico, M. Santisteban, *Manual de Física y elementos de Química*, 1st ed., Eusebio Aguado, Madrid, **1856**; M. Rico, M. Santisteban, *Manual de Física y elementos de Química*, 2nd ed., Eusebio Aguado, Madrid, **1858**.
[52] M. Rico, M. Santisteban, *Manual de Física y Química*, 3rd ed., Eusebio Aguado, Madrid, **1862**.
[53] G. Hinrichs, *Introduction to General Chemistry*, C. G. Hinrichs, St. Louis, **1897**.
[54] A. Mermet, *Manipulations de Chimie: Métalloïdes*, Paul Dupont, Paris, **1899**.
[55] F. Ullmann, *Travaux pratiques de chimie organique: méthodes de préparation des substances organiques*, Dunod, Paris, **1904**; J. Walker, *Elementary Inorganic Chemistry*, George Bell & Sons, London, **1901**.
[56] F.-E. Adam, *Leçons de Chimie*, Ch. Delagrave, Paris, **1903**.
[57] A. Smith, *Introduction to Inorganic Chemistry*, 2nd ed., George Bell and Sons, London, **1916**.
[58] A. Vlček, Jr., *Coord. Chem. Rev.* **2000**, *200–202*, 933.
[59] D. O'Hagan, *Chem. World* **2010**, *April*, 54; W. O. Kermack, R. Robinson, *J. Chem. Soc. Trans.* **1922**, *121*, 427.
[60] H. Budzikiewicz, C. Djerassi, D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds*, Holden-Day, San Francisco, **1965**.
[61] A. R. Straumanis, S. M. Ruder, *J. Chem. Educ.* **2009**, *86*, 1389.
[62] R. M. Caven, J. A. Cranston, *Symbols and Formulae in Chemistry. An Historical Study*, Blackie & Son, London, **1928**.
[63] E. Sauer, *J. Am. Chem. Soc.* **1894**, *16*, 31.
[64] R. Hoffmann, *Gaps and Verges*, University of Central Florida Press, Orlando, FL, **1990**.
[65] E. R. Tufte, *Beautiful Evidence*, Graphics Press, Cheshire, Connecticut, **2006**.
[66] M. L. Rosenthal, Ph.D. thesis, The University of Iowa (Iowa), **1979**.
[67] D. Chevalier, *Paul Klee*, Flamarion, Paris, **1979**.
[68] J. Spiller, *Klee: The Thinking Eye*, 2nd ed., George Wittenborn Inc., New York, **1964**.
[69] J. Daniel, Senior Honors Thesis, Ohio State University **2007**.
[70] F. P. Gianadda, *Klee*, Martigny, **1985**.
[71] K. P. Aichele, *Leonardo* **1993**, *26*, 309.
[72] W. McPherson, W. E. Henderson, *An Elementary Study of Chemistry*, 2nd ed., Ginn and Company, Boston, **1906**.
[73] P. Klee, *Tagebücher 1896–1918*, Dumont Buchverlag, Köln, **1957**.
[74] J. Perrin, *Rev. Sci.* **1911**, *49*, 774.
[75] S. Rewald, *Paul Klee. The Berggruen Klee Collection in The Metropolitan Museum of Art*, The Metropolitan Museum of Art, New York, **1988**.

