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THE EQUATION OF REACTION: A CLUSTER OF OBSTACLES WHICH ARE DIFFICULT TO OVERCOME

ABSTRACT: At the beginning of upper secondary school (age 16), when pupils encounter changes in matter, they have to be able to recognise a chemical reaction. They must understand the underlying concepts, must know how to represent the phenomena and have a knowledge of the "language" used to communicate the nature of what has happened. The Chemical Equation enables them to relate what is happening in the bulk situation with the underlying atomic and molecular changes. To do this requires a large measure of abstraction. We would be deceiving ourselves if we believed that pupils would be able to accomplish, without difficulty, an intellectual process, which took centuries for scientists to construct. In this article, the various stages of the historical development of the concepts implicit in the Chemical Equation will be set out and the consequent pupil difficulties will be analysed.. [*Chem. Educ. Res. Pract.*: 2004, *5*, 327-342]

NOTE: This is the English version of a previous paper in French published in this Journal (Laugier & Dumon, 2004).

1. POSITION OF THE PROBLEM

The pupils who enter Upper Secondary School (15-16 year-olds) have been taught about chemical changes. They have been introduced to the concepts of *chemical substance* (identified by its proprieties), *molecule* (consisting of atoms) and *atom* represented by a positively charged nucleus surrounded by electrons. They have to know that, during a chemical reaction, the disappearance of reactants and the formation of products corresponds to the rearranging of atoms within new molecules. The total mass is conserved during the transformation. Equations have been introduced as soon as the first reactions were met, and the rules for balancing these equations (preservation of the atoms during the reaction, preservation of the charge whenever ions occur) have been taught. But when the pupils manage to "master" these rules, what meaning do they give them? What understanding of the chemical change do they build when they are following the rules? Are they doing this with any understanding?

National evaluation

In 1995, the French Ministry of Education published a study on the pupils' knowledge at the end of Grade 4 (of French lower secondary school). Chemistry came out worse than physics. Generally speaking, at the end of Grade 4, pupils do not seem to have mastered the language of chemistry. It is on mechanical tests that they obtain their best results. But not all of them know the basic rules and symbols or, when they know them, they do not grasp their meanings well. Therefore, whereas most pupils can associate the name of an element or molecule to its chemical symbol, only 40% can produce the chemical formula of a compound with a clear understanding of its composition and fewer than 20% succeeded in the reverse operation.

The pupils' opinion

A questionnaire with 23 items, nine of which concerned chemical symbolism, was given to 112 pupils. Interviews with ten of them were conducted to clarify and supplement the answers. We shall produce a summary of the analysis which emerged (Laugier & Dumon, 2000a):

- The pupils understand that a chemical formula enables one to know precisely the nature and the proportion of atoms that constitute a compound, but they also think that the chemical formula is merely a shorthand for the name of a substance.
- For a majority of pupils, quote, "*in school we spend too much time writing equations of reaction with formulae*". However, they believe that they can balance a chemical equation, because it is an operation that merely relies on simple arithmetic, but, for them, that ability does not mean they have understood what the equation of a reaction is. This evidence is consistent with the results of the 1995 evaluation.
- For some pupils, in a chemical reaction, there is no conservation of molecules but the nature of the atoms is indeed conserved. Contrary to this, opinions differ on the conservation of the number of atoms (54% against and 46% for).

Of the ten pupils interviewed, half relied on the equation of a reaction to represent a chemical change. This relatively satisfactory result hides the fact that none of those who mention the equation of a reaction could read it correctly at either the macro- or microscopic levels. They simply knew it must be written, but they did not know how to use it to represent a chemical reaction.

This use of chemical symbolism seems to constitute, for a pupil entering Upper Secondary School, a real stumbling block: *"I found chemical formulae, equivalents, balancing... very hard in school"*. It is on the matter of the use of equation of reaction that most protests focus*: "It is hard to balance", " the balance sheet of a chemical reaction was my problem, well, I can't cope", "equations of reaction are too abstract. For me, seeing letters and numbers move does not mean anything"*. Julien agrees: *"I have a certain difficulty in manipulating it,... my approach to these equations is somewhat blurred."* Notwithstanding such difficulty, that same pupil knows that this equation could help him: "*I must say that if the experiments we have actually done could be translated with the help of equations, well, then, they would be clearer".*

It can thus be concluded that the pupils who enter Lycée, though they seem to know the rules which render the balancing of equation of a chemical reaction possible (conservation of atoms and not of molecules), find it really difficult to use them. The symbolism of chemical language cannot be related to reality, even if at the same time they

have a clear belief that it could help them to have a better understanding of a chemical change.

Chemical changes in Grade 5

Grade 5 corresponds to the end of the introduction to chemistry, which began in Grade 3. The experimental field has been considerably enlarged. It now covers chemical reactions between compounds, be they molecular, ionic or in a solution. Chemical species (pure compound) can be described on two levels:

- that of an observed macroscopic phenomenon, through their physical properties (appearance, colour, state and so on) and through their characteristic properties such as how they can be extracted, synthesised and identified.
- that of an imaginary microscopic phenomenon, "seen" through a model of matter (characteristics of particles and their organisation).

In physical change (the changing of state) the particles of the model remain unchanged, but in a chemical change (chemical reaction), they are reorganised and modified. A new concept, the element, is introduced to characterise what is conserved in a chemical reaction (molecules and atoms are modified). Its definition makes this concept both macroscopic (it regards all identical nuclei) and microscopic (characterised by its atomic number). As the concept of element and the periodic classification are added, the model of an atom gets more complex (two sorts of particles in the nucleus to explain isotopy and the distribution of electrons in electronic shells to explain the classification in columns in the periodic table).

The symbolic level allows the move between the macroscopic and microscopic levels of description of chemical change. The place of an element in the periodic table makes it possible to predict the charge of a monatomic ion and the number of bonds that it can establish. The use of the octet rule and of the Lewis model makes it possible for chemical species to be represented by their formulae (either primary or semi-developed). The equation of a reaction, associated to the concept of the mole allows for the balance sheet of the chemical reaction to be rationalised in terms of quantity of matter. Stoichiometric coefficients are not a mere mathematical means for balancing the equation of a reaction; they give a new meaning in terms of proportion ratios.

Barlet and Plouin (1994) refer to the equation for a reaction as an integrating concept. It is integrating when it enables one to describe experimental observation of a very large number of chemical entities, but it only makes sense when used at the atomic and molecular level. The passage from the observable to the notional implies mastering concepts of three levels (Johnstone, 1982, 1991):

- the microscopic level (atom, element, molecule, ion, atomic and molecular masses);
- the macroscopic level (chemical species, simple compounds, composite compounds, molar mass);
- the symbolic level (symbols of elements, formulae of chemical species, stoichiometric coefficients).

The last of these makes it possible to *"transfer from an invisible chemical entity to collection of chemical entities, which have visible and bulk properties"*. The chemical equation *"presents multiple views. It rests on the explicit, and suggests the implicit. It*

presupposes many notions about how the reactions take place and the teacher often jumps from one to the other without mentioning it".

The functions of equations are complex and the mastering of them implies a high degree of abstraction. It would then be an illusion to believe that, whereas it took scientists centuries to build it, pupils would be able to use it to establish mass balance easily (an expected ability at the end of Grade 5).

We shall describe the different steps of the historic development of the concept of the reaction equation, then analyse the problems met by the pupils in coming to terms with the different levels of complexity of chemical change.

2. HISTORIC APPROACH: THE DIFFERENT STAGES OF THE DEVELOPMENT OF THE CONCEPTS ASSOCIATED WITH CHEMICAL CHANGE

At the end of Grade 5, a pupil who meets changes of matter must be able to recognise a chemical reaction, understand its underlying concepts, know how it can be represented, be fluent in the language which allows for the communication of the knowledge it covers, and must know how to use it to achieve a balance of matter. Behind the objectives defined for the teaching of chemistry, is the whole thinking of philosophers and scientists (about matter and its transformation) over a period of two thousand years (Laugier & Dumon, 2001; Dumon, 2004).

Macroscopic level

Until the time of Lavoisier, compounds were studied only in their tangible state and identified by a few analytical characteristics. What distinguished mixing from chemical combination had been recognised (Boyle, 1661), but the study was confined to acids, alkalis, salts, oxides, organic compounds extracted from animal and vegetable matter, and so on. Lavoisier was responsible for devising the first precise methodological tools for the study of chemical change:
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- *"[...] it can be considered a principle that, in any operation, there is an equal quantity of matter before and after the operation, that the quality and quantity of the principles are the same, that there are only changes, modifications.[...]"*
- *" One is compelled to suppose, in any chemical transformation, a real equality(or equation) exists between the principles of the compounds studied and those which are drawn from the process of analysis. So, because the grape must produces carbonic acid and alcohol, I can say:*
    grape must = carbonic acid + alcohol".

Moreover, Lavoisier developed analytic techniques for the study of the composition of compounds. He introduced the notion of element as *"[...] the last term of analysis"* (in fact the simple compounds), reformed the vocabulary of chemistry, but he did not care about the symbolism of formulae which he considered as *"mere notes devised to lighten the mind's operations".*

At the beginning of the nineteenth century, after Wenzel's work, Richter developed quantitative analysis of salts and established the notion of *"stoichiometry"* (1792), as well as the *"Law of proportional numbers"* and the notion of *"chemical equivalent"* attached to it. This work was completed by Proust (from 1797 to 1807) with the idea of *"definite proportions"* in which chemical substances combine. With these studies, chemists were convinced that each element can be given a coefficient implying that, in each compound, the

ratio of the weight of combined elements will equal the ratio of their coefficients or a simple multiple of this ratio.

At this fist level, chemical change can be defined as a process of modification of the nature of the substance present, a process during which the mass is conserved, as well as the "elements" that constitute the compound. Substances are pure compounds that are characterised by their physical and chemical properties.


Atomic-molecular level

In 1808, Dalton was the first to see the link between macroscopic, which is accessible to measurement and experiment, and imagined microscopic. He devised the hypothesis that the constancy of mass proportions is due to the existence of particles, the atoms, belonging to each element. For him, a particle is attached to each element and a symbol as well as an atomic weight attached to each particle. These symbols allow the building of formulae that underlie the number of associating particles. With Dalton, atoms became genuine physical entities: there are as many atoms as elements and these atoms are indestructible and unalterable. It is the properties of these atoms which give the compounds their macro properties.

As early as 1813, Berzelius proposed to turn Dalton's symbols into letters which led him to representing the formulae of chemical compounds that resemble ours of today.
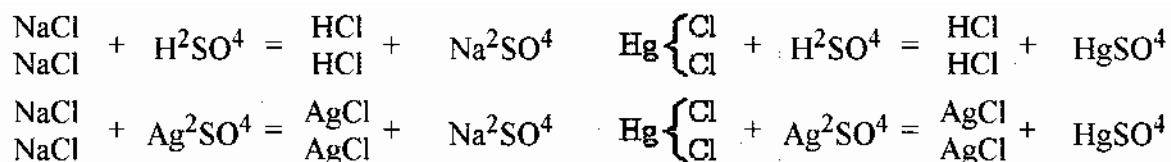
In his dictionary of natural sciences, Chevreul (1818) established the relationship between a simple compound, an element - an atom and a composite compound and proposed an interpretation of the compound's chemical individuality based on atomic theory: *"in a **simple compound** there are only atoms of one identical nature. In a **composite compound**, there are as many different natures as there are **elements**."*

One of the first to use Berzelius's symbols to symbolise the writing of the chemical transformation was Thenard, in 1836, from whom we borrow the following example of the action of sulfuric acid on a metal:

$$\textit{Formule atomique.}$$

$$H^2 O + S O^3 + Zn = H^2 + (Zn\ O, S\ O^3).$$
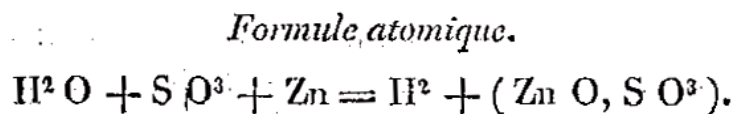
However, the concept of atom as used by Thenard was not that of a microscopic particle. For him as for most chemists in the XIXth century, it refers to the chemical atom: the smallest quantity of matter in an element that enters a combination. Now, as far as distinguishing atom from molecule, this seemed inconceivable to most chemists, at a time when the undecomposable character of the atom as the ultimate particle of matter rendered it impossible to dissociate. Primary formulae depending on the system of underlying atomic weight made chemists direct their efforts to obtaining more and more precise determination of these weights (or of equivalent weights, i.e. mass ratios in which the different elements combine), but with the use of different conventional references (O = 100; H = 1 and so on), thus different formulae.

The distinction between *atom* and *molecule* (defined as the unit of chemical substance) initiated by Avogrado (1811), then reused by Gaudin (1833), became effective only after Cannizzaro's work. In his 1858 class of chemistry in Genes, he proposed formulae that are very similar to the ones we use today, while taking Gerhardt's scale of atomic weights:

$$\begin{matrix} NaCl \\ NaCl \end{matrix} + H^2SO^4 = \begin{matrix} HCl \\ HCl \end{matrix} + Na^2SO^4 \qquad Hg\begin{cases} Cl \\ Cl \end{cases} + H^2SO^4 = \begin{matrix} HCl \\ HCl \end{matrix} + HgSO^4$$

$$\begin{matrix} NaCl \\ NaCl \end{matrix} + Ag^2SO^4 = \begin{matrix} AgCl \\ AgCl \end{matrix} + Na^2SO^4 \qquad Hg\begin{cases} Cl \\ Cl \end{cases} + Ag^2SO^4 = \begin{matrix} AgCl \\ AgCl \end{matrix} + HgSO^4$$

The theory of atomicity (Kekulé, 1857; Cooper, 1858) and the interpretation of isomeric phenomena lead to representing of chemical substances as developed formulae (Cooper, 1858; Boutlerov, 1859; Crum Brown, 1861; Loschmidt, 1861) with spatial representation (Paterno, 1869; Le Bel, 1874; Van't Hoff, 1874).

At this second level of development, chemical change becomes a process of reorganisation of the "atoms" (units of indivisible matter) of the original substances, through which the number and identity of atoms are preserved.
This change is symbolised by an equation. The substances can be simple or composite compounds, made of atoms (either identical or different) united by "chemical bonds"(the nature of which is not specified), within molecules, where atoms are distributed according to specific spatial arrangements or as gigantic structures (metals - crystals).

Physical-chemical level

The end of the XIXth and the beginning of the XXth centuries saw a coming together of physics and chemistry, and with it came a model of chemical change which draws from both subjects, in the microscopic as well as the macroscopic domains.

At the microscopic level

The distinction between *"simple compound"* and *element* and their relationship with the concepts of atom and molecule was still unclear. Mendeleev (1879) addressed this problem: *"a **simple compound** is something material that owns physical properties and is capable of chemical reactions. The statement "simple compound" corresponds with the idea of molecules (...). The name "element" must be kept to characterise the material particles that form simple and combined compounds and that determine the way they behave from the physical and chemical points of view. The word "element" calls for the idea of atom.* Thus element becomes an abstract concept that replaces atom in the writing of chemical formulae.

The concept of atom underwent a radical evolution. Under the influence of physicists who were concerned with the kinetic theory of gases (Clausius, 1869; Maxwell, 1873; Bolzmann, 1897) and following Perrin's works (1909, 1913) and on the determination of

Avogadro number, the atom went from being the *"smallest quantity of matter involved in combining"* to that *of "smallest particle with an actual identity"*. But at the very moment when the reality of atoms was difficult to challenge, discoveries were made which transformed the concept of the atom from an indivisible entity to a *"particle made of other particles"*.

The study of cathode rays by J.J. Thomson (1897) led to the hypothesis of the existence of small negatively charged particles charged within atoms, the electrons. To interpret the deflection of a rays by matter, Rutherford proposed a hypothesis on the structure of atom (1911) according to which the atom 's positive charge and its mass are concentrated into a very tiny volume (10 000 times as small as the atom's) in the centre of the atom and the electrons occupy the space outside the nucleus; thus the atom is mainly empty space! The number of positively charged units was then identified (1914) as **the atomic number**, a name used by Moseley in 1913 when he studied the X-ray emission spectrum of the elements (simple compounds). In 1919, Rutherford asserted that the unit of positive charge is the H^+ ion, which he named **"proton"**. The search for an answer to the enigma posed by the existence of isotopes (the elements which have different masses but identical properties) led Chadwick (1932) to reveal the existence of a new subatomic particle: the **neutron**.

From 1916 chemists developed a model of the atom in accordance with Mendeleev's periodic table, and were able to interpret the variable valence of elements and the bonding between atoms. This opened the way to the search for electrons in the atom. This is how Kossel set out the basis of the relationship between the atomic structure and the chemical behaviour of atoms (1916). For him, the atomic number, which underlines the place of each element in Mendeleev's periodic classification, is nothing but the number of electrons of the corresponding atom and equals the number of positive charges of the nucleus. He introduced the notion of **"valence electrons "** which determine the properties of the atom and the progressive filling of shells by adding electrons. On this basis, Kossel recognised the mechanism of ionisation as the loss or gain of electrons so as to acquire the same configuration as the rare gas nearest in the classification.

In the same year, Lewis proposed an atomic model that depended on postulates that resemble Kossel's, but with some refinement such as the atom's tendency to reach 8 electrons on its outside layer, and the fact that chemical bonding is achieved when *"two electrons are held in common by two atoms"*. He represented the core of each atom in a compound with the use of the element symbol and the electrons situated on the outside sphere with that of pairs of dots.

In 1919, Langmuir proposed an extension of Lewis's model by the introduction of the notion of shells and of subshells (complete with two electrons) and produced the **"octet rule"**, according to which the maximum number of electrons on the outside shell is 8 (two for the first row).

Between 1922 and 1924, a great deal of the research was published concerning the counting of the energy sub-levels associated to the K, L, M ... levels of energy of the X-ray spectra: Bohr (1922 & 1924); Landé (1924), Sommerfeld (1923), Robinson (1923), de Broglie and Dauvillier (1924).

It was only at the end of the first quarter of the XXth century, once the development of Bohr's model had established the variables on which the state of electrons in atoms (kinetic and magnetic moment, spin) depends, was it possible to establish the exact electronic structure of all the elements in Mendeleev's table. With the four quantum numbers n, l, m, s, the elements could be described in shells, subshells and quantum levels.

On this third level, chemical change is seen as a process that makes electrons of the atom's valence shells become involved and that atoms are held together by covalent bonding within molecules or in the form of ions. When the atoms reorganise, some bonds break while others form.
The equation reaction symbolises the balance of what happens on the microscopic scale when molecules or atoms collide.
Atoms are made up of subatomic particles. They are represented by the symbol of the corresponding element, its atomic number, a mass number, and they have a certain electronic structure. The number of bonds (or the ion charge) that can be made by an atom depends on the structure.

On the macroscopic level

In the XVIIIth century, as an answer to the question on the nature of the action that a compound can exert on another, the idea of affinity was introduced: it consisted of a relational concept that resulted more or less from "magical" forces and led to the idea of complete reaction always going in the same direction.

Berthollet (1803) recognised that reactions are not necessarily complete but they arrive at a state of **static equilibrium** in which reactants and products coexist. But, during the first half of the XIXth century, the conception of incomplete reactions, which depend on the experimental conditions, and the direction of which can be reversed, directly opposed the conception of chemical phenomena as complete reactions.

From the 1850s, the chemists' attention became concerned with two new experimental domains: the reactions of organic chemistry and the reactions of *"dissociation"* of gaseous compounds at high temperature. The limited character of these reactions raised further questions. Sainte-Claire Deville (1855, then 1864) then Berthelot and Péan de Saint-Gille (1862 and 1863), while using thermodynamics, proposed an explanation, at macroscopic level, of two opposed reactions leading to a final state of chemical equilibrium. It is a stable state which is reached in a certain length of time (i.e reactions are no longer instantaneous) and in which net reactions no longer occur. Williamson (1852, 1854) adopted a molecular view, thus giving chemical equilibrium a **dynamic aspect.** This dynamic state is no longer considered a state of rest, but a state where both the forward and the backward reactions happen simultaneously.

Guldberg and Waage (1864 then 1867), taking the dynamic aspect into account, proposed an empirical law when they introduced the concept of *"active mass"* (what is today named concentration). They established that total reactions are only a special form of a few reactions. After Van't Hoff 's and Arrhenius 's work, (1884 and 1887 respectively), the law was validated and applied to gaseous equilibrium and acid-base equilibrium.

The thermodynamic interpretation of equilibrium and the forecast of the evolution of a chemical system were proposed by Gibbs (1876) and Helmotz (1882) on the basis of *free energy* (G). The study on the influence of physical and chemical factors (temperature, pressure on the one hand and concentration on the other hand) on the equilibrium change was done by Van't Hoff (1884) and Le Chatelier put forward his *"**principle of moderation**"* in 1884.

For a long time, mass was considered as the characteristic variable of the amount of matter of different substances involved in a chemical system. In 1893, the notion of the "mole" first appeared. In fact, Mol. was the German short for "Molekül" used by Oswald to

denote *"the weight in grams that is numerically equal to the normal or molecular weight of a given substance"*.

Chemists at the time used the notion of **"gram-molecule"** as a laboratory tool to prepare solutions. Gibbs, although he used the mass of different chemical species to characterize the composition of thermodynamic systems, suggested that the notion of equivalent should be used for preference in certain cases. Thermodynamicists used the term "mole" as *"the quantity of substance whose weight in grams numerically equals the molecular weight"*. But when defined in this way, it is ambiguous. It represents both an individual mass and a group of discreet entities equalling Avogrado's number, at atomic level. In 1958 IUPAP, then IUPAC in 1967, suggested that the mole should be defined as the quantity of matter that contains as many elementary entities as atoms in a mass of isotope of reference (16 g of ^{16}O isotope according to IUPAP; 0.012 kg of ^{12}C for IUPAC). In 1971, the mole became *"the unit of the quantity of matter"*.

To represent the variation of the quantity *matter* during a chemical change, another variable of composition was necessary. In 1917, Jouquet used the chemical variable *x* to define the composition of a thermodynamic system. This variable was labelled **"degree of advancement"** with a value between 0 and 1, by De Donder in 1920, then Prigogine and Defay (1944). Balesdent seems to be the one who suggested the term of **"advancement"** to express the state of advancement or extension of the reaction from an arbitrary origin: *x* = 0 when *t* = 0.

At this level, the third in the macroscopic level, chemical change develops quickly and generally leads to a state of equilibrium where reactants and products coexist.
Chemical change, which occurs, between collections particles is modelled with the help of a reaction equation which allows for the conservation of elements. And the equation allows for balance. in mass and or a balance in terms of energy with the use of the advancement variable.
The mole is the tool that makes it possible to go from the microscopic description of the chemical reaction to its macroscopic description.

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3. A DIDACTIC APPROACH

Many researchers have been interested in the ideas pupils have about chemical changes, and in the problems they encounter in the different levels of comprehension. Their work has been analysed by different authors (Fillon, 1997; Barker, 2000; Laugier & Dumon, 2000; Furio, Azcona, & Guisasola, 2002).

To grasp the full meaning of a reaction equation, the pupil must be able to move from the *observed experimental situation* (the tangible phenomena, at *macroscopic level*: what can be seen, touched or felt); to the domain of the *model* where the behaviour of substances is described in terms of non-visible and molecular things (at *microscopic level*: atoms, molecules, ions, structures); finally, all the above must be translated through equations (register of *symbolic representations*: elements, formulae, equation, mole and so on). (Johnstone, 1982, 2000; Larcher, 1994). But the pupils cannot build a representation of the objects of the model from their knowledge of the sensory world. A molecule of water is not a tiny part of a drop of water. Thus many chemical concepts cannot be learnt logically, at least not in terms of a clear consequence derived from an initial accepted idea and/or the

interpretation of an empirical evidence (Taber, 2001). In chemistry there is no "perfect" chemical reaction in which *"the model approximates to experimentation"*.

To illustrate the pupils' difficulties in understanding equations, let us take two examples of chemical change studied at lower-secondary school level: the combustion of domestic gas and the action between hydrochloric acid and iron. They will first be introduced to a word equation similar to Lavoisier's:

(1) methane +dioxygen $\rightarrow$ carbon dioxide + water.
(2) iron + hydrochloric acid $\rightarrow$ dihydrogen + iron chloride.

If one adopts the model of "the two worlds", as Tiberghien (1994) and Le Maréchal (1999a) suggest, to study the difficulties of making sense of models in chemistry, these representations already belong to the *"rebuilt world"* of chemists. Indeed in the *"real world"* the first attempt at writing about the reactions will correspond to *"domestic gas burns with the production of flame and heat"* and the second one *"iron is attacked by the solution and results in the production of a gas bubbles and the solution turns greenish"*.

To understand these primary representations, one must first master the concept of chemical change (substances turn into new substances: and this the objective to be reached), admit that gas is a chemical substance (which is far from generally admitted among pupils), know that different substances can be identified by specific tests, know of the chemical nomenclature and then one is already in the domain of models. Indeed, to go from Dalton's *"swamp gas"* to Hoffmann's methane (1865) or from Van Helmont's *"sylvester gas"* to the present carbon dioxide, many explanatory models of chemistry have been necessary and the dioxygen, dihydrogen, carbon dioxide labels lie on the knowledge of the atomic composition of molecules, which was not easy. Finally, if the proof for the existence of ions in an aqueous solution goes as far back as Faraday (1834), Kossel produced the model of ionic bonding in 1916. It then can be said that, with Le Maréchal (1999b), chemistry does not content itself with giving a possible description of interaction between the objects of real world, but it changes the objects and works on those new objects in a theoretical approach.

One can only wonder how a pupil at lower secondary level, who can no longer rely on the model of the *spherical atom* (which is completed in Grade 4 with the existence of a positively charged nucleus around which electrons move while the whole is neutral) can grasp the meaning of the compact models of H_2O, O_2, CO_2, CH_4 molecules he is faced with.

Why O_2 for oxygen (sorry! I mean, dioxygen)? Why does carbon always behave the same: a tetrahedral molecule for CH_4 methane and linear molecule for carbon dioxide CO_2? Why a bent molecule H_2O for water? Why can iron in a solution be found in the form of ions Fe^{2+} and Fe^{3+}, and copper and zinc only under the form of Cu^{2+} or Zn^{2+}, and silver Ag^+? Why is sulfate ion written SO_4^{2-} and carbonate CO_3^{2-}?
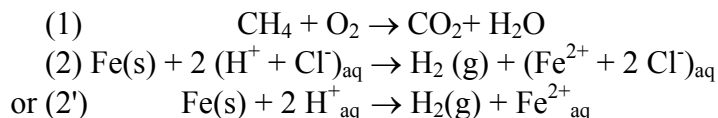
As nothing can allow for the building of such different representations, it is no surprise that pupils cannot master the models easily and that they build other representations, for instance:

• the CO_2 molecule is in fact one carbon atom and one dioxygen molecule (C..O_2);
• copper hydroxide is represented by CuO, H_2O (because when heated the two substances are recovered separately; also, one must take account of the fact that this is the notation adopted around the 1830, on the basis of very similar arguments); copper hydroxide is also represented as CuOH [and not $Cu(OH)_2$] analogous to $CuSO_4$, because there are Cu^{2+} ions in both substances.

The fact that the pupils do not possess the concept of "valence" which is only presented in Grade 1 in Upper Secondary School, hinders their grasping the "rule" of definite

proportions, and as a consequence the atomic composition of substances: so, they conclude that chemical formulae are just a shorthand for the name of substances.

Let us consider now the representation of transformations by using formulae. They are translated into the following:

$$(1) \qquad CH_4 + O_2 \rightarrow CO_2 + H_2O$$
$$(2)\ Fe(s) + 2\ (H^+ + Cl^-)_{aq} \rightarrow H_2\ (g) + (Fe^{2+} + 2\ Cl^-)_{aq}$$
$$or\ (2')\qquad Fe(s) + 2\ H^+_{\ aq} \rightarrow H_2(g) + Fe^{2+}_{\ aq}$$

Equation (2') is the "simplified" form of equation (2), which only considers the reactive species (a form recommended by the French Official Instructions). But how are pupils supposed to know this?

These representations were first used in 1827 by Thenard (= used to replace $\rightarrow$) to indicate the conservation of matter (the mass) and atoms (thought to be chemical at the time) during chemical change. It is also the objective they are given at lower secondary school level. The coefficients they are preceded with, help to "adjust" the number of atoms of each sort within the products with that of *reactants*. In Grade 1, Upper Secondary, they turn into stoichiometric numbers and they indicate the proportions (in terms of matter quantity) in which reactants can react and products are formed.

This equation must not be confused with a mathematical equation, because in the transformation there is no equality between the two sides but simply the conservation of masses, atoms and electric charges (and not that of volumes or molecules). Consider the question asked by Laugier and Dumon (1994): "*Imagine a chemical reaction in which all gases and their volumes are measured under the same conditions of temperature and pressure.*

> *1litre of compound X + 1litre of compound Y → 1litre of compound Z*
> *Is such reaction likely?*"

The percentage of right answers varies from 0% in Upper Secondary Grade 1 to slightly more than 10% in Grade 2 and in first year university. For the majority of pupils and students, the chemical equation reads in terms of conservation of volumes and, as a university student put is: "*1+1 =2 is easy as pie*".

This is then is a problem for pupils, and is added to the difficulty they feel when asked to make sense of the indexes in formulae and of the coefficients (and to differentiate between these two numbers!). We can understand the following pupil's commentary: "*the equations are too abstract for me. Seeing moving numbers and letters does not mean anything*".

The second problem is that equations are supposed to represent the conservation of atoms. If this is clear for equation (1) above, it is not so for equation (2). Indeed, the iron atom is not unchanged. Its nucleus is no longer surrounded by 26 electrons, but by 24 when it changes into the Fe^{2+} ion (the same goes for H^+ and H in H_2). The pupil must then be able to differentiate between iron as an object visible in real world, iron as a chemical substance (a simple compound of atomic structure) and iron in the ion state, a non-visible microscopic particle at the model level. As the notion of chemical element, *a concept included into a theoretical structure* (Martinand, 1986) will only be approached in Upper Secondary, Grade 1, the differentiation will prove tricky. And even at that level, (Le Maréchal, 1999b), the pupils meet problems in linking iron as a tangible thing with the two concepts of chemical substance and element from the reconstructed world. This is no surprise as this linking of the

"simple compound", of the element with the concepts of atom and molecule, made by Mendeleev in 1879, cannot be understood if one does not possess a vast knowledge of chemical reactions. As Bachelard points out (1973, p. 38): *"There exists behind the chemical phenomenon as seen by observation, a new level of abstractionî which is intangible but which is necessary to understand the experiment"*. The element must undergo a change of existence if it is to become an abstract concept in the written chemical formulae: a heavy task for pupils!

This inability to master the symbolic level leads the pupils to look for other solutions. For instance, when interpreting the reaction of reduction of copper oxide by carbon, Fillon (1997) observed that pupils look for symmetry, either from language, or from the writing of formulae. So, instead of writing the reaction that has been studied through experiment in the form:

$$2\ CuO + C \rightarrow 2\ Cu + CO_2,$$
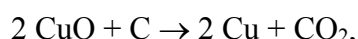
their reasoning goes the following way:

copper **monoxide** + carbon $\rightarrow$ **carbon monoxide** + copper

$$\underline{Cu}\ O + C\ \rightarrow\ CO + \underline{Cu}$$
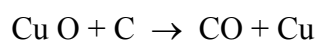
Thus chemical language hinders the pupils. This also was verified when experimenting on the de-hydration of copper hydroxide (Laugier & Dumon, 2003). When trying to find the name of the substance coming off, a pupil proposed: *"Well, there had to be water and copper oxide since they cannot be separated, therefore the green-blue precipitate was copper hydro oxide."*

Besides, when pupils manage to adjust the coefficients of an equation of reaction, many of them fail to link the two levels (Yarroch, 1985). At the highest level of understanding, a pupil grasps the different meanings of chemical symbols and of numeric coefficients whereas at the lowest level they cannot go beyond a mere mathematical manipulation of signs. This discrepancy between managing to balance an equation and understanding its meaning in the macroscopic and microscopic levels has been largely confirmed by other research such as Savoy and Steeples' (1994) or Huddle and Pillay's (1996).

Finally, at the end of Upper Secondary Grade 1, the pupil is supposed to be able to use the equation to achieve a balance sheet of matter. On his own, if he is to succeed, he must circulate, from the macroscopic to the microscopic so as to determine what proportions are necessary for the substances to react, then go back to the macroscopic as they use the concept of mole (the unit of matter quantity) to determine the necessary matter quantities. Indeed, in the symbolical register, the concept of mole allows for the reading of an equation of reaction in both registers, macroscopic and microscopic. Let us take a simple example: the reaction of water synthesis. Writing $2H_2 + O_2 \rightarrow 2H_2O$ can mean that the synthesis of two water molecules is done through the reaction between two molecules of dihydrogen and one molecule of dioxygen. But if it is represented by $H_2 + 1/2\ O \rightarrow H_2O$, the chemist will see at once that they are situated in the macroscopic register because the strictly mathematical equivalent "$1/2\ O_2 = O$" bears no physical signification. The $1/2$ coefficient means that to synthesise water, quantities of O_2 and H_2 must be put together at half the amounts. We have observed (Laugier & Dumon, 2003) a very strong resistance from the pupils to that move between the levels when they are to read an equation of reaction. Their reading jumps

between the macroscopic level (volume and mass) and when, under the teacher's very narrow guidance, they have to read it at microscopic level, they are unable to go back into the macroscopic level.

Furthermore, a Swedish study (Tulberg, 1994) shows that most students do not distinguish between molar and atomic masses and they conceive the mole not as a quantity of matter but as a number of particles. When the word "quantity" is used about an equation of reaction, the students understand it as the synonym for the number of moles, the molar mass or the volume. Such confusions, to which difficulties in manipulating numbers are added, are at the root of the pupils' difficulties when they are required to link the ratio of the different element masses to the composite formula (Schmidt, 1990).

4. IMPLICATIONS FOR TEACHING

In face of this inventory of problems, should one be discouraged? Not in the least! As Barlet (1999) and Johnstone (1999, 2000) put it, this is what makes chemistry special, gives it its charm, according to some, and at the same time, raises the difficulty of the teaching it (taking into account the pupils' cognitive capacities). This lies in the necessity for switching between *macroscopic* and *microscopic*; between the *observable* and the *model*; between the *concrete* and the *abstract*. Well then, let us be aware of the difficulties and let us challenge them by making pupils confront the dialectics of modelisation-experimentation through frequent and explicit linking of both levels.

According to Barlet (1999), *"the use of mental models is the means of ordering and rationalising the behaviour of many chemical species"*. Contrary to the modelling in physics, it has an explanatory rather than a predictive function. As the models refer to a limited experimental field, the modelling can only be subject to revision. It is only through a to and fro movement between experimentation and modelling that the models can be refined and become more useful in fitting a greater number of experimental situations.

To help pupils engage in such modelling, our first hypothesis that the *"approach to scientific teaching can only be made but through the establishing what belongs to the empirical level and what to the modelling level"* (Orange, 2003). The problem then is to have pupils confront obstacles, among those we have already mentioned, in problem-situations (Laugier & Dumon, 2000b, 2003). Such theories were developed with reference to Martinand's modelling scheme, or to Brousseau's theory of didactic situations (1998). The progression of activities during the different steps is organised in the respect of **action** phases that allow pupils to *"build their own representation of the situation which turns into their model for taking their decisions"* in the process of interaction with one another; of **formulation** phases that lead to the making of a common language for all the members of the group to understand; of **validation** by confronting the group's propositions to other pupils' opinions and/or to the experiment. We would be deluding ourselves to believe that pupils are able to build, on their own, the concepts or models which took chemists centuries to establish, one should insist, with Lemeignant and Wreil-Barais (1988), on the importance of guidance (in the form of help to the pupils) during the activities. They consist of "*suggesting procedures that are near what they can already do and direct them to the more sophisticated procedures*".

Our second hypothesis is that *"the teaching of science must show <u>how</u> contents have been developed"*. The point is to provide pupils with the means of understanding how science works and to recognise which questions *such* concepts answer. In short, the point is to <u>give meaning </u>to scientific knowledge.

For instance, working on historical texts that show the evolution of models over the years to interpret changes in materials (Laugier & Dumon, 200c) allows the pupils to discover:

- What the activity of modelling corresponds to: the model is not the description of reality at microscopic level, but corresponds to the idea that can be made from the changes observed at the macroscopic level. Chemists in response to their own questions have built the models or concepts.
- What are its essential characters: its explanatory power, its hypothetical and alterable character, its indirect link with reality and its limited validity.

During these activities, pupils have to look for the information about modeling that can be derived from them.

- What are the physical objects in the situation?
- What are the phenomena that can be observed?
- What are the purposes of models developed in science?
- What relationship exists between the experimental and theoretical fields?

We have observed that, during such activities where class debate is important, the pupils construct questions about things they had not thought of before. How can we represent a change in matter? What is a model ? How does the chemist choose the purpose of a model? What limitations are there on models? These are questions that belong to the core of scientific activity. To formulate the questions and examine the possible answers, they have been led to jump between the two levels and the development of this skill is an essential whenever a chemical reaction is to be represented.

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REFERENCES

Bachelard, G. (1973). *Le pluralisme cohérent de la chimie moderne*. Paris: Vrin.

Barker, V. (2000). Beyond appearances : Student's misconceptions about basic chemical ideas. *Report for the Royal Society of Chemistry* [http://www.chemsoc.org/networks/learnnet/miscon.htm]

Barlet, R. (1999). L'espace épistémologique et didactique de la chimie. *L'Actualité Chimique.* Avril, 23-33.

Barlet, R. & Plouin, D. (1994). L'équation bilan en chimie. Un concept intégrateur source de difficultés persistantes. *Aster*. n°18, 27-55.

Brousseau, G. (1998). *Théorie des situations didactiques*. Grenoble : La pensée sauvage.

Dumon, A. (2004). *La modélisation de la matière et des substances chimiques : Une approche historique*. Ouvrage collectif à paraître, Belin, Paris.

Fillon, P. (1997). Des élèves dans un labyrinthe d'obstacles. *Aster*. n° 25, 113-141.

Furio, C., Azcona, R. & Guisasola, J. (2002). The learning and teaching of the concepts amount of substance and mole: A review of the litterature. *Chemistry Education: Research and Practice, 3*, 277-292. [http://www.uoi.gr/cerp]

Huddle, P. A. & Pillay, A. E. (1996). An in-depth study of misconceptions in stoichiometry and chemical equilibrium at a South Africa University. *Journal of Research in Science Teaching, 33*, 65-77.

Johnstone, A. H. (1982). Macro and microchemistry. *School Science Review, 64*, 377-379.

Johnstone, A. H. (1991). Thinking about thinking. *International Newsletter on Chemical Education,* No. 6, 7-11.

Johnstone, A. H. (2000). Developing student's understanding of chemical change - What should we be teaching? *Chemistry Education: Research and Practice, 1*, 77-90. [http://www.uoi.gr/cerp]

Larcher, C. (1994). Point de vue à propos des équilibres chimiques. *ASTER*, n°18, 57-62.

Laugier, A. & Dumon, A. (1994). Les obstacles à la conceptualisation de la réaction chimique en classe de seconde. In *Actes du 4ème séminaire de recherche en didactique des sciences physiques* - AMIENS - octobre 1994.

Laugier, A. & Dumon, A. (2000a). Travaux pratiques en chimie et representation de la reaction chimique par l'equation-bilan dans les registres macroscopique et microscopique : Une etude en classe de seconde (15 – 16 ans). *Chemistry Education: Research and Practice, 1*, 61-75. [http://www.uoi.gr/cerp]

Laugier, A. & Dumon, A. (2000b). Mise en œuvre d'un curriculum constructiviste en classe de chimie de seconde : qu'en pensent les élèves ? *In Actes du 3ème congrès international : Actualité de la Recheche en Education et Formation,* Université Bordeaux 2, 15p.

Laugier, A. & Dumon, A. (2000c). Histoire des sciences et modélisation de la transformation chimique. *Bulletin de l'Union des Physiciens*, n°826, vol. 94, 1261-1284.

Laugier, A. & Dumon, A. (2001). D'Aristote à Mendeléev ; 2000 ans de symbolisme pour représenter la matière et ses transformations. *L'Actualité Chimique,* mars, 38-50.

Laugier, A. & Dumon, A. (2003). A la recherche des obstacles épistémologiques à la construction du concept d'élément chimique par les élèves de seconde. *Didaskalia*, n°22, 69-97.

Laugier, A. & Dumon, A. (2004). L' équation de réaction: Un nœud d'obstacles difficilement franchissable. *Chemistry Education: Research and Practice, 5,* 51-68. [http://www.uoi.gr/cerp]

Lemeignant, G. & Weil-Barais, A. (1988). Gestion d'activités de modélisation en classe. *ASTER.* n° 7, 121-141.

Le Marechal, J. F. (1999a). Design of chemistry labwork activities aiming basic chemical concepts. In *Actes of Fourth European Science Education Summer School,* pp. 68-80. Marly le Roi, 1998.

Le Marechal, J. F. (1999b). Modeling student's cognitive activity during the resolution of problems based on experimental facts in chemical education. In J. Leach & A.C. Paulsen (eds.), *Practical work in science education*, pp. 195-209.

Martinand, J. L. (1986). *Connaître et transformer la matière*. Berne : Peter-Lang.

Martinand, J. L. (1995). Introduction à la modélisation. In *Didactique des disciplines techniques.* ENS Cachan, LIREST, pp. 126-138.

Orange, C. (2003). Investigation empirique, construction de problème et savoirs scientifiques. In C. Larcher et M. Goffard (eds), *L'expérimental dans la classe*. Paris : INRP.

Savoy, L.-G. & Steeples, B. (1994). Concept hierachies in the balancing of chemical equations. *Science Education Notes*, *75*, 97-103.

Schmidt, H.-J. (1990). Secondary school student's strategies in stoichiometry. *International Journal of Science Education*, *12*, 457-471.

Taber, K. S. (2001). Building the structural concepts of chemistry: Some considerations from educational research. *Chemical Education Research and Practice, 2*, 123-158. [http://www/uoi/gr/cerp]

Tiberghien, A. (1994). Modeling as a basis for analysing teaching-learning situations. *Learning and Instruction*, *4*, 71-87.

Tulberg, A., Strömdahl, H., & Lybeck, L. (1994). Students' conceptions of 1 mole and educators' conceptions of how they teach 'the mole'. *International Journal of Science Education*, *16*, 145-156.

Yarroch, W.L. (1985). Student understanding of chemical equation balancing. *Journal of Research in Sience Teaching, 22*, 449-459.