Chemistry: Bulgarian Journal of Science Education | *Volume 25 Number 5, 2016* | *Природните науки в образованието*

Curriculum Matters
Учебно съдържание, планове, програми и стандарти

STUDY OF THE APPROPRIATION BY THE PUPILS OF SECOND BACCALAUREATE YEAR OF KNOWLEDGE OBJECTS RELATING TO ACID-BASES TITRATIONS

Ali Ouasri
Centre Régional des Métiers de l'Education et de la Formation, Rabat, Morocco

Abstract. This article aims to study the difficulties of the Moroccan high school pupils in teaching of the acid-base topic. Based on others similar context, particularly the Tunisian one, we have firstly carried out a classification of the knowledge objects relating to acid-base titrations in the empirical register and in the register of models. The analysis of the written productions of the pupils in situation of solving problem showed that the Moroccan pupils in classes of second Baccalaureate encountered difficulties to appropriate the knowledge objects relating to weak acide-strong base titrations and to adapt these knowledge as well as with the empirical register and with the register of models.

Keywords: acid-base titration, design, empirical register, knowledge object, register of models

Introduction

The resistance of certain conceptions and the difficulty of changing them during a teaching process are two problems persisting into didactic of sciences. The prescientific conceptions that pupil developed regarding to a "knowledge object" seem to be an obstacle to the acquisition of the scientific theory about this object. The Yves Chevallard's anthropological approach about the report with the knowledge indicates that a particular knowledge can live in different institutions and give sens to the extra- scholar sources of the knowledge. The didactic is distinguished compared to the other disciplines since it treats only particular knowledge such as the square root in mathematics or the lightning in physics. The theorization of Chevallard has been characterized by the fact that particular knowledges exist only inside institutions. The objects of knowledge would exist if they were recognized by an institution where they constituted its institutional objects. One indicates by the institution the school, the class but also the family.

The scientist knowledge is not considered as an alone source of knowledges; others referents are considered as differents knowledge sources. The institutions were distinguished by the way with which they are projected inside each subject and by the sens that this one assigned to them. In an institution, the knowledge lives through the questions to which the subject can answer but also through the problems that they make it possible to solve.

The entry of a person in a physics classroom confronts him with knowledge with which he should maintain a report as the institution defined it. The pupil will be confronted with two types of reports: a personal report which he already developed during its passage by others institutions and a scholar institutional report which he should develop, under the requirement which ensure the good performance of this institution. When the personal report of a pupil with a particular knowledge becomes similar to the report defined by institutions, the learning is then reached. The concept of "object" is regarded as being the first basic concept of the anthological approach of Chevallard (1989; 2003). This general concept within the meaning of Chevallard "all is thus object" includes the declaratory and procedural knowledges related to a discipline like chemistry, and in particular to acid-base titrations (chemical entities, symbolic notations, theoretical register, register of models, empirical register).

In chemistry, the world of theories and models consists primarily of entities whose nature and behavior are described in a symbolic language. It cannot be apprehended in terms of clear consequences deduced from the experimental observations (Taber, 2004). Since the conceptual structuring of this knowledge needs time during learning (Taber, 2004), the learner tend to build alternative conceptions to give sens to such abstract concepts. The representations built during the adaptation of the old conceptions to the new scientific ones are suitable for the evolution and can appear in a given context.

The causes of student difficulties with acid-base chemistry have been ascribed to the existence of certaines alternatives conceptions or misconceptions (Demerouti et al., 2004; Demirciogli, 2005); other authors (Furio-Mas et al., 2005; Kousathana et al., 2005) related the these difficulties to the models used in acide-base chemistry. Based on these reported literatures, it seems to us that Moroccan pupils may have many difficulties to understand what is happening to the pH values during titrations; for this reason we are interested in pupils understanding of some acide-base concepts and in their appropriation of the objects of knowledge corresponding to acide-base titrations.

In this article, we carry out a study on the knowledge that built some Moroccan pupils in class of second baccalaureate year to describe acid-base titrations. We start by presenting the problem that consist to study how Moroccan pupils appropriate certaines knowledges relating to acide-base titrations, ie understand what happened during titration stages. In the conceptual framework, we present what it acts the teaching of acid-base titrations in the Moroccan high school, and we try to classify the objects of knowledge relating to acid-base titrations in two registers (the empirical referent and the register of the models) to describe what is "modeling and models" in general, and the modeling of the evolution of a chemical system involved in acide-base titrations. Next, we describe the methodology and the questionnaires of research; the adopted methodology allows to definite the target population as well as the methods of the investigation and the instruments of data collection. In the end, we try to discuss the results that we have got on the pupils of the second Baccalaureate year class in the solving problem situation relating to the weak acid-strong base titrations.

Problem

Acid-base titrations are common experimental activities that are realized by pupils in high school chemistry courses. The topic has been a regular component of introductory chemistry curricula and receives wide coverage in introductory texts and related laboratory manuals (Dingrando et al., 2002; Wilbraham et al., 1996). The most frequently conducted titrations involve neutralization of strong acids with strong bases, with pupils being required to calculate the unknown's concentration using this method. Some introductory texts (Dingrando et al., 2002) extend the topic to include details of titration curves. The treatment of these curves in introductory chemistry classes is usually non-mathematical and is often included to determine the most appropriate indicators to use in particular titrations.

Generally, little searches in didactic of chemistry were devoted to the knowledge objects relating to acid-base titrations (Nakhleh & Krajcik, 1993; Ouertatani & Dumon, 2008; Sheppard, 2006). According to Sheppard (2006), the American students had difficulties with acid-base chemistry and were unable to understand acide-base concepts involved in titrations such as neutralization, pH, strength and the theoretical description of acids and bases; the difficulties stemmed from a lack of understanding of some underlying chemistry such as the nature of chemical change and the particulate matter nature.

Two types of difficulties in the learning titrations by pupils were retained: difficulties in the comprehension of the titration courses and difficulties in the representations related to the technique adopted in titration: follow-up by pH-meter, conductimetric follow-up and colored indicator. The difficulties of pupils are studied in situations of solving problems treating stoichiometry and reagent limiting which lead to determine the concentration of the chemical species to be titrated. Moreover, each type of titration is succeptible to generate specific didactic effects in terms of representations and acquisition of knowledge.

The study of titrations involves the concepts of chemical change, chemical reaction, stoichiometry, degree of advancement of reaction and limiting reagent. Some of these concepts have been studied in relation with pupil's representations (Anderson, 1990; Stavridou & Solomonidou, 1889; 1994) - these studies showed that pupils encountered generally important difficulties in the comprehension of these concepts, and thus highlighted the importance of construction, stage by stage, of the concepts of chemical change and chemical reaction during the teaching of chemistry.

Practically, the equivalence remains accessible by pupils from a simple change of solution color, by a pH jump. But the theoretical comprehension of equivalence is not also obvious. The suggested experiments in the programs of first and second Baccalaureate years for the titrations teaching aimed only to determine the concentration or the amount of a chemical species at the equivalence. The focusing on this objective of equivalence is limited too much, since this neglects the possibilities of theoretical deepening by the pupils on chemical change, chemical reactions and other concepts which acid-base titrations utilized.

With this intention, it seems to us important to carry out some situations analyses to see how the Moroccan pupils in class of second Baccalaureate year can appropriate certain knowledges aimed by the teaching of acid-base titrations. Our study is only limited to one titration type that has been taught in this class; this titration is of methanoic acid (weak acid) by a solution of sodium hydroxide (strong base). The process of the titration is carried out according to successions of chemical changes before the equivalence where this process is finished with the total consummation of the limiting reagent.

Thus, we propose to study the comprehension by the pupils of titrations, not only to determine the concentration, but to understand what happened in the titration from the first addition of the titrating solution until the addition in excess of this solution. For this, we consider the equivale*n*ce as an opportunity of seeing how the pupils could appropriate certain knowledge objects relating to the concepts of chemical change and chemical reaction. The distinction between these two concepts seems to be very useful in the analysis of the knowledge to be taught or in the interpretation of the difficulties encountered by the pupils during the teaching-learning of titrations.

To interpret the pH-metric curve of the chemical system evolution during the successive additions of the sodium hydroxide solution to a methanoic acid solution, that is a complex process, the pupils should connect a certain number of knowledge objects of the empirical referent (nature of the solutions, presence of the chemical entities, concentrations, volumes,…) to the world of the models (succession of the different chemical reactions, the modeling and symbolization of these reactions, $K = f(pH)$,….) or to the world of theories (chemical equilibrium, chemical equilibrium constant,….); this requires a complex production on behalf of the pupils.

Indeed, it is interesting to ask certain questions which are essential in several contexts (Tunisia, Morocco and other countries) during the teaching of titrations: (i) which are the knowledges objects that the pupil should mobilize to be able to model the titration of a weak acid by a strong base; (ii) which are the knowledges objects of which misses the pupils to carry out a correct comparison of the empirical register with the world of the theories, and which are the identified prescientific designs for the pupils.

To study the difficulties encountered by the pupils in their training of certain knowledge relating to acide-base titrations, we proposed to them to solve one problem in the acid-base titration topic (Appendix). The solving of the problem type requires some capacities to made connection between the empirical world and its objects and the world of the theories and models and their objects. The pupils are brought to answer to the questions revealing critters of acquisitions of certaines knowledge.

Concepts used in teaching of the acid-base topic

Dosing and titration

The dosing consist to determinate a concentration, or an amount, of one solution (or of a chemical species in a solution). The method used in dosing can be of chemical or physical characters. The dosings are based on a physical property of the species to be dosed (pH-metric, conductimetric and spectrophotometry dosings). The titration being as a typical case of dosing aims to determinate of an unknown solution concentration by using another solution of a known title, by a chemical change carried out between the species to be titrated and the titrating species. It thus acts of a chemical method which based on the chemical reactivity of the substance to be titrated and not on its physical properties. The chemical reaction taking place during the titration should be total, fast and selective. Generally, one speaks about volumetric, colorimetric and gravimetric titration.

Evolution of a chemical system during a titration

The chemical reactions that have been used during titrations can be of acid-base, oxydo-réduction, precipitation and complexation types. The titration may be considered as successive consummations of the chemical species in the solution to be titrated at the time of the successive additions of the titrating solution until the equivalence will be realized. The titration may be described according to three stages: (i) before the equivalence, the chemical species to be titrated changes completely and instantaneously with each addition of the titrating solution; (ii) the equivalence is realized with the addition of titrating solution so that the amount of the added species is equal to the initial amount of the species to be titrated; (iii) after the equivalence, the titrating chemical species is in excess.

Chemical change and chemical reaction

The titration involved chemical change and chemical reaction concepts. So, it is important to specify in which case, one or other concept could be used. The chemical change corresponds to the chemical system evolution from an initial to a final state, whereas the chemical reaction involves only the chemical species which are effectively consumed (reagents) or appeared (products). The reaction symbolized by a chemical equation is regarded as being a model leading to explain the evolution of a chemical change that can be modeled by one or more chemical reactions.

The total chemical change is modeled by a chemical reaction that is carried out only in one direction. In the Moroccan context, it is only in class of second Baccalaureate year that the conceivers of the chemistry program introduced the concept of no total chemical change that was modeled by a chemical reaction with two directions (direct and opposite directions). The concept of degree of advancement of reaction (extent of reaction) and the table of advancement are taught quantitatively to determine the final composition of the chemical system starting from its initial composition and the chemical equation of chemical change.

The teaching of acid-base titrations in Moroccan high school

In the Moroccan high schools, there are three years (classes): the trunk commun class, the first and the second Baccalaureate classes. The acide-base titrations make a good part of the chemistry taught in classes of first and second Baccalaureate years.

Acid-base titrations in the first Baccalaureate year programs

In the chemistry program of first Baccalaureate year that has been set up in 2005, the measurement of the physical amounts sizes (concentration, pressure and volume.) is conceived for the quantitative studies of a chemical change by using the table of advancement, maximum degree of advancement and the composition of the reactional mixture at a given moment or at a final state. This program is interested simply to acid-base titrations involving strong acid-strong base chemical reactions.

To determine the amount during a dosing, one is often confronted with the equivalence and the table of advancement.

The equivalence is defined as the system state in which the titrated reagent becomes limiting; before the equivalence the limiting reagent is the titrating one.

The table of advancement is introduced to describe the chemical system during titration in the class of first Baccalaureate year. In this class, the reaction between the hydrochloric acid solution (strong acid) and a soda solution (strong base) is conceived to be as an experimental support to introduce the concept of equivalence in titrations. The chemical reaction corresponding to this dosing is written by the chemical equation:

$$H_3O^+ + HO^- \rightarrow 2H_2O \qquad (1)$$

One reaches the equivalence when: $n(H_3O^+)_{(initial)} = n(HO^-)_{(versed\ at\ equivalence)}$; this may be when: $C_A V_A = C_B V_{B,E}$

Acid-base titrations in the second Baccalaureate year programs

In the chemistry program of second Baccalaureate year, acid-base titrations are introduced to study the “chemical equilibriums: incomplete chemical changes”. Two new dosings were thus studied there: (a) the dosing with PH-metric technique that involves acid-base reactions (strong acid/strong base, weak acid/strong base dosing); the pH = F (V) curve representing the variation of pH according to the volume of the added titrating solution is used to determine the concentration of the titrated solution; (b) the acid-basic titration with colored indicator which was to be suitably selected to detect the equivalence.

Then, these acid-base dosings constitute an opportunity for the pupils of second Baccalaureate year to reconsider the definition of a total chemical change and the determination of the maximum degree of advancement of a reaction. However, the titration of an acetic acid solution (weak acid) by a soda solution (bases strong) presents some problems. The equation of the reaction relating to the chemical change made in this titration is:

$$CH_3COOH + HO^- \rightleftarrows CH_3COO^- + H_2O \qquad (2)$$

This reaction with two directions (equilibrium) generates certain confusions at the pupils who had already learned that the reactions of dosing must be total. In the context Tunisian (Ouertatani & Dumon, 2008), the equation of the reaction of the titration of an acetic acid solution by a soda solution, Eq (2), is introduced as being the result of the displacement of the equilibrium of acetic acid ionization into water in consequence of the consummation of H_3O^+ ions according to the reaction (Eq. (1)).

The formalism may let the pupils generalize that the reaction of titration is always considered the Eq (10 whatever the acid (or the base) concerned during titrations. Thus, the generalization at the pupils of the relation $C_A V_A = C_B V_{B,E}$ at the equivalence would be reinforced. In the Moroccan context, the chemistry program of second Baccalaureate year, the introduction of Eq (1) to explain the titration of acetic acid by soda is not explained more by the fact that the addition of OH^- ions coming from soda involves successive displacements of the equilibrium carried out between acetic acid and water. Here are thus some problems which we will discuss in this article through the analysis of acquisition of the pupils, in situation of resolution of problems, some knowledge relating to titrations, in particular with acido-basic titrations.

Knowledge objects relating to acid-base titrations in Moroccan high schools: referents involved in teaching acid-base titrations

Empirical referent

According to Lhoste (2006), the empirical register contains objects, phenomena and daily experiments, ie the elements that one can check by an observation or a measurement; these elements correspond to what there is to explain, but they are not made up for all. For Martinand et al. (1992), the "empirical referent" is not made up only of objects, phenomena or actions on the objects and interventions on the phenomena; but also of descriptions, of the rules of actions involving the knowledges which find an empirical statute only after one conceptual elaboration. According to Martinand et al. (1992), the empirical referent contains generally three elements: (1) *phenomenotechnique*: is related to knowledge of rule of assembly, of the security conditions, of instrumental know-how of the implementation of manipulations; (2) *phenomenography:* is corresponding to the initial description of the phenomena concerned with some anterior conceptualizations; (3) *phenomenology:* is relating to the description second of phenomena in terms of concepts, models and theories shared by a community of scientists.

Register of models

The models can be regarded as intermediaries between the theoretical and experimental aspects of knowledge. According to Fourez et al. (1997), a model is regarded as a scheme, an image or an organized speech which represents the complexity of the approached situations. Larcher (1996) indicates that a model is a hypothetical construction in answer to a questioning. The register of models contains elements relating to an organization and/or to a more or less imagined fonctionement. These elements suggested solutions to explain the elements of the empirical register (Lhoste, 2006). According to Walliser (1977), a register of models includes semantic components (a convenient semiography to represent the elements of the model), syntactic (the elements of the model maintain between-them relations that have been related to its method of construction) and pragmatic (which make it possible to question, to represent, to envisage, to invent and to explain the empirical referent).

The models can be formal "remain purely symbolic and make it possible to emit some general properties of the system" (Walliser, 1977); in the chemistry, it is the case of the equation of reaction and the representation of the chemical formulas. The models can be also digital "give digital values and make it possible to calculate the value of certain variables by knowing others" (Walliser, 1977); it is the case of the curves of dosing or of the relation at the equivalence $C_A V_A = C_B V_B$.

Modeling

The process of modeling connects two worlds: (A) The experimental world that Robardet & Guillaud (1994) called "experimental field of reference", that Tiberghien (1994) named "worlds of the objects and events"; for Walliser (1977) it is "the empirical field". Martinand (1992) indicates this world by "empirical referent or empirical register" about which concepts, models or theories speak. This world consists of objects of reality and phenomena as well as practices on these objects and these phenomena (phenomenotechnique, phenomenography and phenomenology); (B) The word of theories, models and symbolic notations: Martinand (1994) involved "cognitive matrix" to refer to the theoretical aspects and the models of studied material situations and to allow the construction of a representation of the new objects and observed phenomena. For Le Marshal (1999), he speaks about objects and rebuilt events.

The modeling is not a simple comparison of the various registers to find a solution; it consists to make these registers in relation to lead to problematization that may be identified taking in account the empirical constraints and the conditions of a model possibility. Indeed, the comparison of the various "knowledge objects" described using the various "symbolic languages" may allow to the conceptualization of the studied phenomenon as we will specify it in our present study about the classification of some knowledge objects relating to the titration of acetic acid by sodium hydroxide.

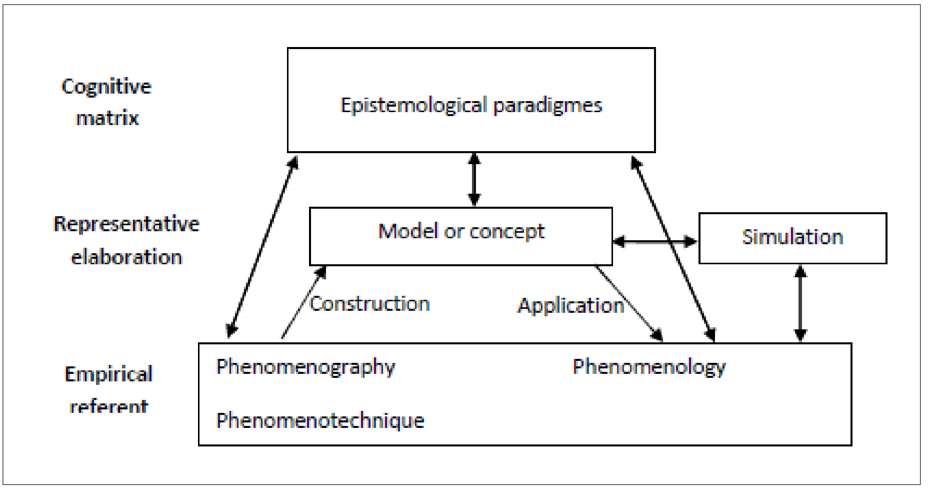


Fig. 1. Diagram of modeling (according to Martinand, 1994)

Fig. 1 distinguishes an initial knowledge which allows the construction of the model (phenomenography) of a second description that may be made possible by the use of the model which is projected on the empirical referent (phenomenography); this makes it possible to locate simulation activities which correspond to an exploration of the model. The cognitive matrix, including the epistemic paradigms and the theoretical and the semiotics resources, makes it possible to describe what is available and mobilizable, that must be brought in accordance with the requirements of the task.

The modeling of acid-base titrations aims to compare the empirical register with the world of theories, models and symbolic notations that are able to describe the system in an abstract language. Such a language could be defined as a coherent and structured system of concepts that have been connected between them by a number of organization rules which can be translated in the form of literal relations, laws, curves, diagrams, equations digital (Robardet & Guillaud, 1994; Walliser, 1977).

Analysis of knowledge objects relating to acid-base titrations

A chemical change is defined as the chemical system evolution between an initial state and a final one. For a change which stops when at least one of the reagents is exhausted (limiting reagent), the chemical reaction is introduced as being a model symbolized by an equation of reaction. It is a question here of differentiating what Davous et al. (2003) called "phenomenologic description" and "modeling description". At the empirical level, the pupils are brought to observe and describe an experimental fact: a chemical change which represents the evolution of the chemical system of the initial state in a final state. The introduced model of the chemical reaction indicates the stoichiometry in which the various chemical species (reagents and products) appear and disappear during the chemical conversion.

Knowledge objects according to the empirical referent

In the case of titration of methanoic acid by a solution of soda of a known concentration, which is the experimental situation (physical situation) around which our questionnaire of research is built, the knowledge objects, succeptible to be connected, according to Martinand are: (i) *phenomenotechnique*: the use of glass materials, the colored indicators, the pH-meter; (ii) *phenomenography*: the equivalence is reached when the indicator changes its color (color change) or when one reached the equivalent point of the curve pH = f(V_{versed}); the equivalence coordinates point is determined by the method of tangents; (iii) *phenomenology*: at the equivalence the acid and base amounts were put in presence in the proportions that were indicated by the stoichiometric coefficients ($n_A = n_{B\ added}$); the curve of pH follow-up of titration represents the variation of the pH (thus of the concentration in H_3O^+) according to the versed volume of soda.

Since the Moroccan context is near similar to the Tunisian one, we state that the world of the theories which could be mobilizable by the pupils contains the following knowledge objects (Ouertatani & Dumon, 2008): (I) *the sizes*: amount (mole), molar concentration and pH = -Log [H_3O^+]; (II) *the model of Brönsted*: an acid is a species being able to liberate a proton H^+ to give it to another species; a base is a species that is likely to collect a proton being coming from another species which is the acid; (III) the acidic-basic equilibriums and their associated sizes (K_A and pK_A); (IV) the Autoprotolyse constant of water $K_e = [H_3O^+][HO^-] = 10^{-14}$ at 25 °C; (V) the prevision of the reactions those are likely to occur between the chemical entities present in solution; (VI) the knowledge of the operation of the color indicators like the acid-conjugate base couples HIn/In^- (color change); (VII) the concept of equivalence.

Knowledge objects in the register of models

Formal representations

The chemical entities formula: HCOOH, NaOH, $HCOO^-$, H_3O^+, H_2O, HO^-.

The equations symbolizing the acid-bases reactions that involved $HCOOH/HCOO^-$; H_3O^+/H_2O et H_2O/OH^- acid-bases couples are:

$$HCOOH_{(aq)} + H_2O_{(aq)} \rightleftarrows HCOO^-_{(aq)} + H_3O^+_{(aq)} \quad (3)$$

$$HCOOH_{(aq)} + HO^-_{(aq)} \rightleftarrows HCOO^-_{(aq)} + H_2O_{(aq)} \quad (4)$$

$$2H_2O_{(aq)} \rightleftarrows H_3O^+_{(aq)} + HO^-_{(aq)} \quad (5)$$

The digital figurations

The curve of pH-metric follow-up, the relation $C_A V_A = C_B V_B$, the relation allowing to calculate pH.

The table of advancement which allows to the interpretation of the curve evolution of titration during successive additions of the solution titrating.

The syntax of the model interpreting the titration curve

(a) At initial state, the methanoic acid reacts with water according to Eq. (3); (b) The equation of the reaction of titration is Eq. (4); (c) Before equivalence, the methanoic acid is in excess (HO^- is the limiting regent), the entities H_3O^+, HCOOH and $HCOO^-$ coexist in solution; (d) At equivalence the methanoic acid reacted completely with the versed sodium hydroxide: the acid and base amounts that have been reacted are equal: $n(HCOOH)_{(initial)} = n(HO^-)_{(versed\ at\ equivalence)}$, i.e. $C_A V_A = C_B V_{B,E}$. The majority entity is $HCOO^-$ ion that is the weak conjugate base of the HCOOH acid. A jump of pH is observed and the pH with equivalence is higher than 7

$$pH = 7 + \frac{11}{22}(pK_A + Log\ [HCOO^-]_{eq}); \quad (6)$$

(e) After equivalence, they are OH^- ions in excess (change of limiting reagent) which fixe pH. The autoprotolyse equilibrium of water makes it possible to find pH value from the relation:

$$pH = 14 + Log\ [HO^-]_{eq} \quad (7)$$

Method

Target population

The population to which we subjected the problem to be solved (questionnaire) contains pupils of three classes of second Baccalaureate year. One class is of Mathematical Sciences and contains 20 pupils, while the two other classes are of Life and earth sciences: one comprises 29 pupils and the other 23 pupils.

The three classes profit from six to eight hours of course of Physical and Chemistry per week. As in all the Moroccan high schools, a weekly program of continuous teaching, from 8 h at 6 h, with a pause of two horses from 12:00 to 14 h, is adopted within these high schools. The choice of this population (classes of second Baccalaureate year) is primarily based on the fact that we want to study titration by follow-up pH of a weak acid (methanoic acid) with a solution of sodium hydroxide (strong base). It is a titration which utilizes the concept of chemical equilibrium. This concept being not taught in Morocco before the class of second Baccalaureate year constitutes for pupils an innovation that merits be analyzing and studying.

Methodology and questionnaire

We seek by this study to evaluate the performances of three groups of Moroccans pupils on the articulation of the knowledge elements related to two worlds: empirical referent and register of the models. Indeed, three questions can accompanied this problem: (I) at which levels the pupils would be able to connect the different symbolic figurations with the rules, the laws and the theories of the chemical language; (II) do the pupils follow the logical approaches to solve the problems, and/or do use the prescientific conceptions; (III) is the modeling of the anterior phenomena well conceptualized by the pupils.

To study this problem and seek to validate or invalidate our hypotheses, we carried out some activities on pupils of the three classes of which one comprises pupils of mathematical sciences. Indeed, we submitted a questionnaire to 72 pupils (three classes) six weeks after the end of the teaching of the acid-base theme in order to make sure that the answers given to our questions did not result from a simple memorizing of recently learned knowledge.

The questionnaire (Appendix) contains six questions referring to the titration of a methanoic acid solution by a sodium solution. The answers given by the pupils are classified in various categories which correspond either to the independent answer (question 2) or to answers being based on dependent ideas (questions 1, 3, 4, 5 and 6).

The percentages of the answers calculated for each type (category) are characteristic of our pupils (target) and can be generalized to other populations only with much of precaution. The questions that are referring to a digital figuration [curve of titration pH =f (V)] belong to the register of the models. The physical situation of the empirical register that are determining the conditions of elaboration of the curve is described by the use of the chemical species names in solution or their symbol, and also by sizes which characterize these chemical species (volumes, concentrations).

Among the objectives of the problem questions submitted to the pupils, we cite: (I) The first question consists to evaluate the pupils description of an event of the empirical register (particular titration) using the symbolic language of chemistry by the modeling of a chemical acid-base reaction within the framework of the Brönsted theory; (II) The second question would lead to see whether pupils are delighted to use the formula $C_A V_A = C_B V_{B,E}$ (object of the digital model) while reasoning on amounts at equivalence; (III) The third question consists to evaluate the pupil's description of the system during titration while referring to the curve of titration and quoting the chemical species concerned; (IV) The fourth question: the point A corresponding to the beginning of the titration reaction must be placed at the beginning of the curve, the point B indicating the end of the titration is the point of equivalence, beyond who's the variation of the pH is due to the excess of the added soda hydroxide solution; (V) The fifth question consists to evaluate if pupils are able to evoke the concept of chemical equilibrium in relation with the titration reaction representing a no total chemical change. It is to be recalled that the reaction between methanoic acid and soda leads to an equilibrium (non total change) whereas the pupils know already that the reaction of titration is always total; (VI) The sixth question purpose to evaluate the capacity of the pupils to make the choice of the color indicator which is appropriate to carry out this titration by a change of color.

Results and discussions

Question 1

The Table 1 presents the different types of answers that are relating to question 1 in accordance with the formalism of Brönsted. The questions 1.1 and 1.2 concerning the writing of the two half acid-base equations are introduced to simplify the establishment of the dosing equation and illustrate the concept of chemical equilibrium.

Table 1. Pupils responses concerning the writing of the reaction of dosing

Type of answers		N	Percentage (%)
Equation of acid + water :	$HCOOH(aq) + H_2O(aq) \rightleftarrows HCOO^-(aq) + H_3O^+(aq)$	66	91.67
Dissolution of the soda:	$NaOH(aq) \rightarrow Na^+(aq) + HO^-(aq)$	20	27.77
Reduced equation of titration:	$HCOOH + HO^- \rightarrow HCOOH^- + H_2O$	61	84.72
Complete equation : Acid + base water	$HCOOH + NaOH \rightarrow HCOONa + H_2O$	0	0
	$HCOOH + NaOH \rightarrow HCOO^- + Na^+ + H_2O$	0	0
Total of acceptables writings		**61**	**84.72**

Others responses	Simple addition of chemical species	4	5.55
	Error in the the reagents and products formula	3	4.17
Total of non satisfactory writings		7	9.72
Non answers		4	5.56
Total		**72**	**100**

One can state that the majority of pupils (91.67%) have answered to the question relating to the writing of reaction of a weak acid with water. But, it is noted that only 27.77% of the pupils are able to answer to the question about the dissolution of soda in water. One states that 84.72% of the pupils are able to give an acceptable writing of the requite equation of the acide-base titration; and that even if they are mistaken in the second half acid base reaction that is the equation of dissolution of soda in water: ($NaOH_{(aq)} \rightarrow Na^{+}_{(aq)} + HO^{-}_{(aq)}$).

Concerning the non acceptable answers that present 9.72 %, it seems generally that pupils make errors in the writing of the reagent and/or the products (nature, charges of ions), this indicate that these pupils encountered difficulties at the symbolization level, ie that they are not appropriating the knowledge object in the register of models. Whereas others pupils (5.56 %) did not give any answer; this may be explained by the fact that these pupils have serious difficulties not only at the register model, but at the empirical referent.

It is important to note that pupils being able to give acceptable responses (84.72 %) use the reduced equation with the Brönsted formalism and not the complete equation to formulate the equation of dosing; these results are nearly comparable with the results obtained in the Tunisian context (Ouertatani & Dumon, 2008).

For the question 1 that concerns the treatment of writing of the reaction of titration, one can say that the majority of the pupils are able to write correctly the chemical reaction by using the rules of the symbolic language within the framework of the Brönsted formalism. But, we remark that even the pupils who were mistaken in modeling of the reaction of dissolution of soda in water reach to give correctly the equation of the titration reaction.

Question 2

This question is very close to that appearing in the studies of Meyer & Doucet (1988) and of Ouertatani & Dumon (2008). It aims to see whether the pupils are delighted to use the formula $C_A V_A = C_B V_{B,E}$ that imply that at equivalence the methanoic acid has reacted with the added sodium hydroxide with equal amounts. The answers of the pupils are gathered in Table 2.

Table 2. The pupil's responses about the determination of the soda amount that must be added to reach the equivalence

Answers types	**N**	**Percentage (%)**
Correct table of advancement	30	41.66
Correct Volume Vb of Soda	46	63.88
To realize the equivalence, it is necessary to add:		
(a) less than 0.0003 mol	4	5.55
(b) 0.0003 mol	36	50
(c) more than 0.0003 mol	6	8.33
(d) No answers	26	36.11
Total	72	100

For the establishment of the table of advancement, we note that only 30 pupils (41.66 %) have answered to this question, whereas 46 pupils (63.88 %) were able to determine graphically the volume of added soda at equivalence. Compared with the rate (84.72 %) obtained for the correct writing of the reduced equation of acide-base titration (question 1), we state that several pupils cannot writ correctly the table of advancement in which the equation of titration is usualy introduced.

Concerning the amount of soda that must be added to realize the equivalence, we state the rate of good answers (50 %) is less than the value 63.88 % that present the percentage of pupils being able to give the added volume at the equivalence and more than 41.66 % which present the rate of pupils who have given the correct table of advancement. One can remark the value of 50% is nearly identical to that obtained on the others pupils in the in the Tunisian context (Ouertatani & Dumon, 2008). The pupils that have given a good answers justified their answers by using that at equivalence $n_{acid.} = n_{base} = 0.0003$ mol.

But, the pupils who did not answer correctly to this question are those which made miscalculations or those which retained formula $C_A V_A = C_B V_{B,E}$ without putting it in relation to the amounts in presence at equivalence. Others pupils did not give answers, even if this question is preceded by the table of advancement that would have to help the pupils to connect between the formula $C_A V_A = C_B V_{B,E}$ and the amounts at equivalence.

Generally for the second question, the half of pupils has reached to give what we regard as a good answer (0.003 ml) with the help of the table of advancement, whereas others do not put any link between $C_A V_A = C_B V_{B,E}$ relation and the amounts of the chemical species involved in the reaction.

Question 3

The goal of this question is to evaluate the abilities of pupils to describe what happened during acide-base titration by determination of the chemical entities that were present in solution, before during and after equivalence and also to use their pre-receipt concerning the chemical change and the limiting reagent. The analysis of the pupil's productions showed that any completely correct answer was given. Although curtains pupils could give correctly the limiting reagents, they were however mistaken in the enumeration of the chemical species that were present in solution. Among the mistakes made by the pupils for this question, one can distinguish: (a) Before equivalence, the chemical species that existed in solution are: HCOOH, HCOO-, HO^-, Na^+, H_2O » as if there is no reaction before equivalence; (b) At the equivalence, the present chemical species in solution are: $HCOO^-$, Na^+, H_2O, even if they consider that the reaction of titration is total; (c) After equivalence, the present species in solution are: $HCOO^-$, Na^+, HO^-, H_2O.

These answers indicate the difficulties that pupils have with the concept of chemical change and neutralization that were taken place in the acid-base titration; this was already stated in several studies that have classified the student explanations of chemical change into five categories (Anderson, 1990; Hesse & Anderson, 1992). Among these categories, it seems that the Moroccan pupils description of neutralization fall generally into the displacement and modification categories in which the products are displaced reactants and modified forms of the reactants, respectively. It is clear that as even after teaching-learning process pupils did not understand what signified the chemical change and neutralization, despite being familiar with these concepts.

Question 4

The curve of titration presents the variation of pH during successive additions V_B(added) of the soda to the methanoic acid solution. The interpretation of the relation of the digital figuration with the syntax elements of the model was one of the objects of acide-base titrations teaching. Indeed, the point A that is corresponds to the beginning of the reaction of titration must be placed at the beginning of the curve; the point B indicating the end of titration is the point of equivalent. Beyond B, there is no more reaction of titration, and the variation of the pH is due to the excess of the added soda solution. The Table 3 gives the various categories of answers of the pupils to this question.

Table 3. The different pupils answers about the curve parts corresponding to the reaction of titration

Answers types	N	Percentage (%)
Beginning of the curve to the equivalence (correct answer)	9	12.5
The curve part corresponding to the sudden jump of pH	10	13.89
The beginning of the curve to the end of jump of pH	8	11.11
At the equivalence point	6	8.33
The entire curve	21	29.17
No answers	18	25
Total	72	100

This question aims to help the pupils to establish a report between the chemical system and the curve of acide-base titration. As it is shown in Table 3, the pupils could give the good answer only with one small percentage (12.5%) and without any justification; any pupil could give the correct interpretation of this question. This result seems to be less than the results obtained by Naija (2004), Ouertatani & Dumon (2008) and Sheppard (2006). The different explanations of the titration curve revealed that a majority of pupils had non-scientific alternative ideas on neutralization, pH and chemical reaction involved in acide-base titration.

To account for the sudden jump in pH, approximately 14% of pupils described the titration reaction as suddenly starting to occur when pH jumped; whereas 11.11% of pupils considered that the titration take place from the beginning of the curve until the end of the jump of pH. The pupils that explain the titration as is happened at equivalence point present 8.33 % while those that considered the titration realized along the entire curve present 29.17%.

Indeed, the difficulties of interpretation revealed from the pupil's explanation may be due to: (a) The confusion at the pupils between the concepts of equilibrium and equivalence (6 pupils) "the reaction reached the equilibrium state when the amount of base is equal the amount of acid $n_{NaOH} = n_{HCOOH}$; V = 15 mL et pH = 8"; (b) The pupils justify their answer "the entire curve" by "the reaction finished when the pH became constant"; (c) The comparison of the digital figuration with the elements c, d and e of the syntax model involving the chemical entities that are presents in solution, is carried out only by one small proportion of pupils.

It appears that pupils present a subjacent reasoning of geometrical type that is related to the curve shape. At the perceptible event "jump of pH" is associated a "cause" which is the starting of titration reaction. This reasoning may be described as it is a causal reasoning. One can conclude that a majority of pupils have difficulty to articulate the register of the model and the model of theory; they have a confused reasoning about the limiting reagent change (HO^- before equivalence and HCOOH after equivalence) (register of the model) and the interpretation of an acid-base reaction in term of chemical equilibrium (field of the theory).

Question 5

The aim of this question is to evaluate the pupils capacity to put in relation one digital figuration, that is an object of the register of the model, with the world of the theories (as chemical equilibriums) and the element a, b, c, d (question 2.3) of the model syntax. The obtained results are gathered in Table 4 on six answers types. From these responses, we can state that: (i) The correct answer "all points of the curve" is given only by five pupils (6.94 %) who distinguish the equilibrium notion from the equivalence one. To answer correctly to this question, one pupil must understand that the chemical equilibriums take place at the time of the successive additions of the sodium hydroxide solution during the titration; (ii) 36.11 % of pupils consider that the chemical equilibrium occurred at equivalence. The justification given by the pupils showed that the chemical equilibrium state corresponds to the equality of acid and base amounts that have been reacted "because at equivalence there is $n_{acide} = n_{base}$"; (iii) 18 % of the pupils related the equilibrium state to the jump of pH; these pupils believe that the reaction of titration occurs in this pH zone. The two responses (the jump of pH and the equivalence point) may be due to a geometrical reasoning. For these pupils (54.15 %), the chemical equilibrium is associated to the equality of acid and base amounts that have been reacted; there is here an ambiguity between the equilibrium notion and the equivalence one, this later seems to be more present the reasoning of the pupils; (iv) 38.39 % of the pupils were not able to give any answer for this question; this implies that a good part of pupils encountered important difficulties to understand the chemical equilibrium and to distinguish this notion from the equivalence one.

Table 4. Pupils responses about the points of the curve where was realized the chemical equilibrium

Answers types	N	Percentage (%)
All point of the curve (correct answer)	5	6.94
The equivalence point	26	36.11
The part of curve corresponding to jump of pH	13	18.05
No answers	28	38.89
Total	72	100

It is concluded that the pupils have adapted neither the concept of equilibrium, nor the elements of the syntax of the model relating to acid-base equilibriums that take place in titrations. That's why the majority of pupil's responses correspond to the d element of the question 2.3 (I don't know answer). Thus, the comparison of the digital figuration with the world of theories and models seems to be not realized for all the pupils.

Question 6

This question aims to evaluate the capacity of the pupils to choose the suitable color indicator to realize the acid-base titration. To answer to this question the pupils may take as reference the pH value at equivalence that can be deduced from the digital figuration and the world of theory (zone of color change of an indicator). The obtained results concerning this question are gathered in Table 5.

Table 5. Pupils responses concerning the choice of a suitable color indicator

Answers types	N	Percentage (%)
Indicators of pKA < 7	4	5.55
Indicators of pKA > 7	10	13.88
Blue of bromothymol (BBT)	14	19.44
Red of phynol (correct answer)	27	37.50
No answers	17	23.61
Total	72	100

The percentage of the pupils that could give the good answers of 37.5%; these pupils justify their response by: "the indicator zone of change contains the pH value at equivalence". Thus, we note that the comparison of the color change of an indicator (event of empirical referent) with its zone of change (event of the world of the theory) and the pH at the equivalent point (size of empirical referent) is controlled by 37.5% of the pupils. On the other hand, we state that 19.44 % of pupils were near to give a correct answer since they consider the BBT as the suitable indicator for this titration; while 23.61 of the pupils can' not give any answer for this question; this implies that a good part of pupils encountered important difficulties to understand the chemical equilibrium and to distinguish this notion from the equivalence one.

Conclusions

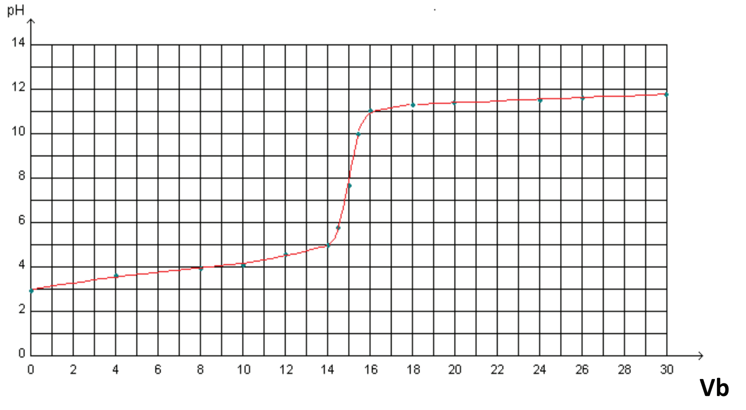
This study illustrates some conceptual frameworks in relation with the teaching of acid-base titrations through the solving problems activities. The classification of some knowledge objects relating to acid-base titrations in the empirical register and in the register of the models were done in comparison with the Tunisian context that is similar to the Moroccan one. The appropriation of acide-base titrations by the pupils in classes of second Baccalaureate year was studied with an aim of highlighting certain difficulties that encountered the pupils to adapt the knowledge objects relating to weak acid–strong base titrations, on the empirical register and the register of models.

Generally, pupils of second Baccalaureate year have encountered many difficulties on solving problems treating acid-base titrations. The analysis of some difficulties indicates that: (A) Several pupils have not a clear design of what the equation of a chemical reaction represents, did not control the concept of the chemical equilibrium and then have difficulties to identify the chemical species present in the studied chemical system and the evolution of their concentration during an acid-base titration; (B) The non-control of the concept of limiting reagent and the non interpretation of the reaction of titration as an equilibrium chemical put the pupils in the incapacity to connect the empirical referent with the world of the theories and models in order to interpret the shape of a curve of pH-metric titration and to describe what occurs correctly during titration: (C) The pupils used some extracts of the world of theories and models that they memorized without true appropriation, for example: the equivalent point is reached when $C_A V_A = C_B V_{B,E}$; the jump of pH characterizes the time when the titration reaction is finished.

Appendix

Titration of a methanoic acid solution (weak acid) by a soda solution (strong base) problem suggested to the pupils

We realized a titration of V_a = 20 cm^3 of methanoic acid solution HCOOH of concentration C_a = 0.015 mol/l, by the soda solution NaOH with C_b = 0.02 mol/l; then we obtained following graph:



1) The equation of dosing reaction

1.1. Knowing that the methanoic acid is a weak acid, write the equation of the reaction of this acid with water.

1.2. Write the equation of dissolution of soda in water.

1.3. Deduce the equation of dosing reaction of the methanoic acid by a soda solution, then give the two couples acid/base that have been interacted and their corresponding half-equation

2) Table of advancement and equivalence point

2.1. Give the table of advancement corresponding to this chemical change

2.2. Determine the volume Vb of the soda solution that is versed at the equivalence and calculate the concentration Ca of the soda solution

2.3. To realize the equivalence, it is necessary to add:

a) Less than 0,0003 mol; **b)** 0,0003 mol; **c)** More than 0,0003 mol; **d)** I don't know to answer.

3) Give the chemical species in solution and specify the limiting reagent in the following cases: Before the equivalence; during the equivalence; after the equivalence

4) Indicate the part of the curve corresponding to the reaction of this acide-base titration. One indicates on the curve the item (A) as the beginning of this reaction and the item (B) as the end of this reaction. Justify your choice.

5) In which points of the curve can you say that there is a chemical equilibrium? Justify your answer.

6) By using the table below, choose the color indicator that is suitable for this colorimetric titration. Justify your choice

Color indicator	Color		pKA	Zone of turne
	Acide form	Basic form		
Blue of thymol	Red	Yellow	1.5	1.2 - 2.8
Helianthine	Red	Yellow	3.7	3.2 - 4.4
Red of methyl	Yellow	Red	5.1	4.8 - 6.0
Blue of bromothymol	Yellow	Blue	7.0	6.0 - 7.6
Red of phenol	Yellow	Red	7.9	6.8 - 8.4
Phenolphtaleine	Incolor	Rose	9.4	8.2 -10.0

REFERENCES

Anderson, B.R. (1990). Pupils' conceptions of matter and its transformations (age 12 – 16). *Stud. Sci. Educ., 18*, 53 – 85.

Chevallard, Y. (1989). Le concept de rapport au savoir (pp. 211 – 235). In: *En séminaire de didactique des mathématiques et de l'informatique*. Grenoble: Institut Fourier.

Chevallard, Y. (2003). Approche anthropologique du rapport au savoir et didactique des mathématiques (pp. 81 – 104). In: Maury, S. & Caillot, M. (Eds). *Rapport au savoir et didactiques, education et sciences*. Paris: Fabert.

Davous, D., Dumont, M., Feore, M.C., Fort, L., Gleize, R., Mauhourat, M.B., Zobiri, T. & Jullien, L. (2003). Les nouveaux programmes de chimie au lycée. *L'actualité chimique*, Février 2003, 31 – 44.

Demerouti, M., Kousathana, M. & Tsaparlis, G. (2004). Acid-base equilibria, part 1: upper secondary students' misconceptions and difficulties. *Chem. Educator, 9,* 122 – 131.

Demircioglu, G., Ayas, A. & Demircioglu, H. (2005). Conceptual change achieved through a new teaching program on acids and bases. *Chem. Educ. Res. Pract., 6,* 36 – 51.
Dingrando, L., Gregg, K.V., Hainen, N. & Wistrom, C. (2002). *Chemistry*: *matter and change.* New York: Glencoe/McGraw-Hill.
Furió-Más, C., Calatayud, M.L., Guisasola, J. & Furió-Gómez, C. (2005). How are the concepts and theories of acid-base reactions presented: chemistry in textbooks and presented by teachers. *Int. J. Sci. Educ., 27,* 1337 – 1358.
Fourez, G., Englebert-Lecomte, V. & Mathy, P. (1997). *Nos savoirs sur nos savoirs*. Bruxelles: De Boeck Université.
Hesse, J.J. & Anderson, C.W. (1992). Students' conceptions of chemical change. *J. Res. Sci. Teaching, 29***,** 277 – 299.
Kousathana, M., Demerouti, M. & Tsaparlis, G. (2005). Instructional misconceptions in acid base equilibria: an analysis from a history and philosophy of science perspective, *Sci. & Educ., 14,* 173 – 193.
Le Maréchal, J-F. (1999). Modeling student's cognitive activity during the resolution on problems based on experimental facts in chemical education (pp. 195-209). In: Leach, J. & Paulsen, A.C. (Eds.). *Practical work in science education*. Dordrecht: Kluwer.
Larcher, C. (1996). La physique et la chimie, sciences de modèles (pp. 160-178). In: Toussaint, J. (Ed.). *Didactique appliquée de la physique-chimie*. Paris : Nathan.
Lhoste, Y. (2006). La construction du concept de circulation sanguine dans un débat scientifique en classe de 3ème: problématisation, argumentation et conceptualization. *Aster*, No. 42, 79 – 107.
Martinand, J.-L. (1994). Introduction à la modélisation : *communication présentée à lam conférence, Actes du séminaire de didactique des disciplines technologiques* (pp. 126-138). In: Seminar of technological disciplines didactic. Cachan.
Martinand, J.-L., Astolfi, J.-P., Chomat, A., Drouin, A.-M., Genzling, J.-C., Larcher, C., Lemeign, G., Meheut, M., Rumelhard, G. & Weil-Barais, A. (1992). *Enseignement et apprentissage de la modélisation en science.* Paris: INRP.
Martinand, J.-L., Genzling, J.-C., Pierrad, M.-A., Larcher, C., Orange, C., Rumelhard, G., Weil-Barais, A. & Lemeignan, G. (1994). *Nouveaux regards sur l'enseignement et l'apprentissage de la modélisation en science.* Paris: INRP.
Meyer, R. & Doucet, J. (1988). Un équilibre très instable. *Bulletin de l'union des physiciens.* No. 708, 1211 – 1220.
Naija, R. (2004). *Apprentissage des réactions acido-basiques: mise en évidence et remédiation des difficultés des étudiants lors d'une*

séquence d'enseignement expérimental, Thèse de l'Université Lumière, Lyon 2.
Nakhleh, M.B. & Krajcik, J.S. (1993). A protocol analysis of the influence of technology on student's actions, verbal commentary, and thought process during the performance of acid-base titrations. *J. Res. Sci. Teaching, 30,* 1149 – 1168.
Ouertatani, L. & Dumon, A. (2008). L'appropriation des objets de savoir relatifs aux titrages acide-base par les étudiants tunisiens. *Didaskalia,* No. 32, 9 – 40.
Robardet, G. & Guillaud J.-C. (1994). *Eléments d'épistémologie et de didactique des sciences physiques, de la recherché à la pratique.* Grenoble: IUFM.
Sheppard, K. (2006). High school students' understanding of titrations and related acid-base phenomena. *Chem. Educ. Res. Pract., 7*, 32 – 45.
Stavridou, H. & Solomonidou, C. (1989). Physical phenomena – chemical phenomena: do pupils make the distinction. *Int. J. Sci. Educ., 11,* 83 – 92.
Stavridou, H. & Solomonidou, C. (1994). Les transformations des substances, enjeu de l'enseignement de la réaction chimique. *Aster,* No. 18, 77 – 95.
Taber, K.S. (2004). Learning quanta: barriers to stimulating transitions in student understanding of orbital ideas. *Sci. Educ., 89*, 94 – 116.
Tiberghien, A. (1994). Modelling as a basis for analyzing teaching-learning situations. *Learning & Instruction, 4*, 71 – 87.
Walliser, B. (1977). *Systèmes et modèles*. Paris: Seuil.
Wilbraham, A.C., Staley, D.D. & Matta, M.S. (1996). *Chemistry.* Menlo Park: Addison-Wesley.

✉ **Prof. Ali Ouasri**
Département de Physique-Chimie
Centre Régional des Métiers de l'Education et de la Formation
Madinat Al Irfane, Souissi,
BP 6210 Rabat, Morocco
E-mail: aouasri@yahoo.fr