Learning about stoichiometry: from students' preconceptions to the concept of limiting reactant

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Abstract: We have studied students' previous conceptions and the effects of the usual teaching about the concept of limiting reactant. Previous work revealed two apparently contradictory conceptions held by students: *both reactants are totally converted* at the end of the transformation whatever the proportions, and *only one reactant is converted* whatever the proportions, with an active agent/passive object representation. We examined students' explanations about various experimental problems to see whether one kind of problem leads preferentially to one conception or the other. We investigated grade 10 students at the beginning and at the end of the school year in order to study the impact of teaching stoichiometry on students' conceptions. The results show that the conception *both reactants are totally converted* is quite strong in those problems where reactants are in the same physical state, and is more in competition with the conception: *only one reactant is totally converted* when the reactants are in a different physical state. It seems that teaching has little effect on wrong answers, but mainly leads to a shift from no answers to good answers. [*Chem. Educ. Res. Pract.*, 2007, **8** (4), 362-375.]

Keywords: stoichiometry, chemical change, chemical reaction, limiting reactant, students' conceptions, teaching effects.

Introduction

This paper deals with the construction of notions of stoichiometry. Many papers (Frazer and Servant, 1986, 1987; Schmidt, 1990; Huddle and Pillay, 1996; Boujaoude and Barakat, 2000; Arasasingham et al., 2004) explored students' difficulties in solving stoichiometric problems. Moreover, Stamovlasis et al. (2004, 2005) demonstrated that competence in algorithmic problem solving is independent of competence in conceptual questions. These results demonstrate the limits of usual teaching of stoichiometry through the use of formulas and algorithms.

According to the "Ingenierie Didactique" framework (Artigue 1988), in order to elaborate fruitful teaching strategies, different types of a priori analyses are needed, which include the analysis of students' conceptions, their difficulties in understanding, and the analysis of the effect of the usual teaching on students' conceptual development.

We can find similar preoccupations in the "Educational Reconstruction" framework (Duit, 2005). In this framework, great importance is given to the analysis of the referent scientific knowledge, and to the students' conceptions in the process of educational reconstruction.

Understanding the notion of limiting reactant or surplus of reactant can be considered as a basic step in understanding stoichiometry. It is part of the meaning of the concept of chemical change and it is part of the distinction between chemical change and physical transformations, what research about conceptions demonstrates to be a significant step towards the understanding of chemical change (Méheut et al., 1985; Stavridou and Solomonidou, 1989; Andersson, 1990; Tsaparlis, 2003). In such a prospect, we are interested in studying students' previous conceptions and the effect of the usual teaching about the notion of limiting reactant.

Students' difficulties with stoichiometry

Difficulties in learning about stoichiometry

In an investigation involving French grade 10 students, Laugier and Dumon (2000) analyzed students' answers during a teaching sequence concerning reactions between two solutions: sodium hydroxide and copper sulphate. They reported that 88% of the students thought that there are neither copper ions nor hydroxide ions left at the end. For these students, all the ions have reacted; they didn't envisage a possible surplus of a reactant in such a case. In a previous study using questionnaires about limiting reactants (Gauchon 2002), we found that 68% of the students (grade 10 or later) say that the reaction between chalk and hydrochloric acid solution stops when there is no more chalk, whatever the quantities of chalk and hydrochloric acid. So, it seems that when beginning to learn about chemical reactions, students explain and interpret the final state of a chemical change in different ways, depending on experimental situations.

Frazer and Servant's study (1987) underlined another level of understanding among first year university students. They noted that students can be inclined to use a ratio equal to one between the amounts of matter of reactants whatever the transformations. It seems that these students have developed some idea of proportion between reactants but they can't consider any other ratio but one. Is this only due to the incapacity to use another ratio or is this linked with previous conceptions about chemical changes?

These examples suggest different levels of understanding of stoichiometry. It seems that this notion needs to be built step by step, probably against strongly established conceptions.

Problems with reactant ratios

Laugier and Dumon (2000) showed that when students feel the need to take into account proportions in a chemical change, another difficulty may appear. Spontaneously, they think of 'appropriate' volumes or 'appropriate' masses. They have to understand that the quantities to be taken into account are amounts of matter that implies the use of the mole concept.

Frazer and Servant (1986, 1987) noted that even among first year university students, a lot of mistakes in problem solving are due to confusion between different chemical quantities. Concentration, mass or volume are often used instead of the amount of matter. Frazer and Servant's observations are similar to some of Schmidt's research results (1990); he found that many students failed to establish relationships between different variables (amount of substance, mass, molar mass …).

Stoichiometry and balancing equations

In their study, Frazer and Servant (1986, 1987) noted that 27% of students succeeded in solving stoichiometric problems, and 22% (of the total) interpreted and correctly used balanced equations, inferring that successfully writing a balanced equation and in interpreting correctly stoichiometric coefficients provides the basis of success in solving problems.

Other pieces of research reported difficulties in correctly interpreting a balanced equation. The different representational levels included in a balanced equation are very difficult to distinguish for students. For example, grade 10 students (Laugier and Dumon,

2000) found it hard to understand that just one script, the balanced equation, can represent many experimental situations. Thus, at the end of a chemical change, students are surprised to find compounds that do not appear in the right hand side of the balanced equation.

The authors of the French chemistry curriculum for upper secondary schools also warned teachers that some students consider that chemical equations imply the use of stoichiometric quantities of reactants only (Ministère, 2000). Moreover, they stress that balanced equations may make students interpret chemical equation at a microscopic level only.

Limiting reactant and surplus of reactant

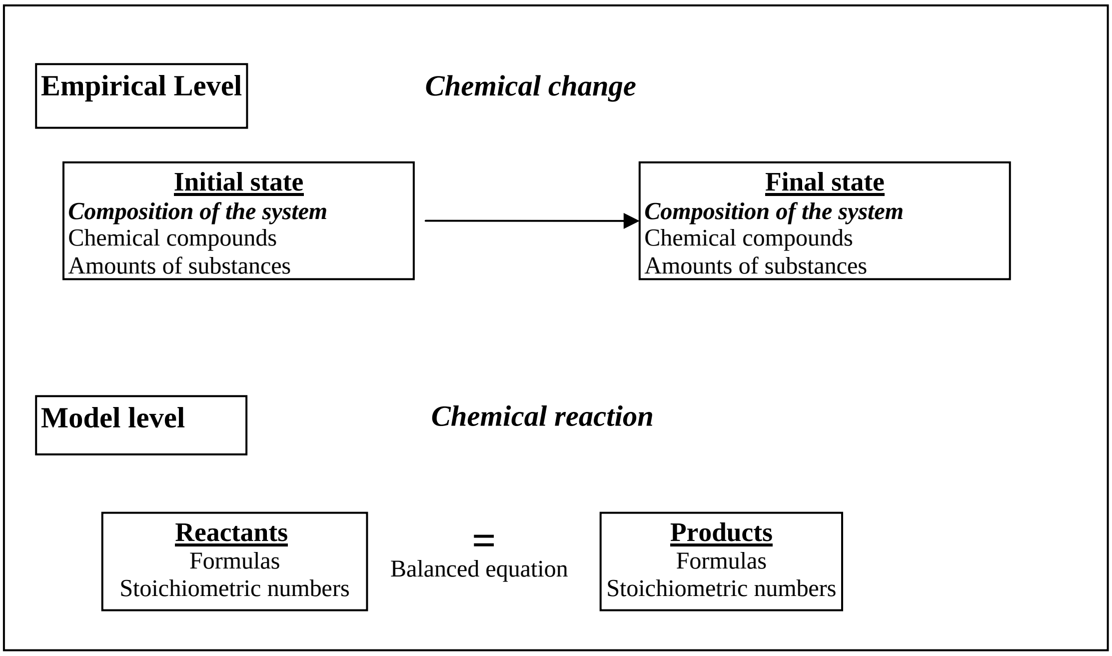
According to research results, success in solving stoichiometry problems is very low when reactants are mixed in any proportion. Identifying the limiting reactant appears to be a major obstacle. Thus, Arasasingham et al. (2004) demonstrated that the students have great difficulty determining the final state of a system from the initial composition using the chemical equation, whatever the proposed method: algorithmic or using symbolic representations. Boujaoude and Barakat (2000) reported that the students chose the limiting reactant randomly, without really justifying their choice. For example, they chose the one whose 'amount of matter' is given in the question, or the one whose mass is given, or from a comparison between the different molar masses.

Huddle and Pillay (1996) reported more systematic mistakes. A few students claimed that the limiting reactant is the compound with the smallest stoichiometric coefficient in the balanced equation. Other students decided that the limiting reactant is the one whose 'amount of matter' is the smallest. One student even wrote: *"limiting reactant = least number of moles"*. We suppose that these students generalize from the case of an equimolar reaction; such thinking can be reinforced by the teaching, when using an algorithmic approach to stoichiometry in particular cases such as equimolar reactions.

Context of the study

Our research took place at the beginning of the teaching of chemical changes in French secondary schools (grade 10). In the French chemistry curriculum, a chemical change is defined as the evolution of a chemical system from an initial state to a final state. At grade 10, only complete chemical changes are considered. In the final state one reactant at least is missing: the limiting reactant. In this approach, the chemical reaction is presented as a model, symbolized by a balanced equation. Using a general account of modelling, as presented for example by Tiberghien et al. (1995), or a more specific one, as presented by Kermen (2005), we can analyse this part of grade 10 French chemistry curriculum content as follows (Figure 1)

Figure 1. Modelling a chemical change in grade 10 French curriculum



At an empirical level, students have to observe and describe an experimental event, a ‘chemical change’: the evolution of a chemical system from an initial state to a final state. They have to characterize the substances present in the initial state and the ones present in the final state, and to quantify the amounts of these substances. At grade 10, only reactants can be found in the initial state, and the final state can include products and surplus reactants. Teaching introduces a model, the chemical reaction, represented by a balanced equation between reactants and products. The model allows the explanation of the macroscopic evolution of the chemical system. It gives the stoichiometry in which the different chemical compounds appear and disappear during the chemical change. According to the experts’ group: “*the purpose is, above all, to enable students, mostly by an experimental approach, to understand that a chemical change does not need the reactants to be in particular proportions in the initial state*” (Ministère 2000, p.126).

However, the experiments recommended in curricular documents and those presented in textbooks are mainly qualitative. Only one experimental activity clearly focuses on the notion of limiting reactant: the study of the results of mixing two solutions (copper sulphate and sodium hydroxide) in various proportions.

Research questions

We have seen earlier that much research deals with students’ difficulties in solving stoichiometry problems. The tasks used in these studies imply mainly an algorithmic treatment, and the authors often stress that an adequate representation of the problem appears to be lacking. And the results of the research make clear how the students’ pre-conceptions of chemical phenomena can be obstacles for elaborating adequate representations of stoichiometric problems.

From the literature (Laugier and Dumon, 2000) and a previous study (Gauchon, 2002), we note two conceptions that seem to contradict each other. Thus, for chemical changes involving two solutions (Laugier and Dumon, 2000) the following conception appears: both reactants are totally converted at the end of the transformation, whatever the proportions. For chemical changes involving a solid and a solution (Gauchon 2002), another conception appears: only one reactant is totally converted, whatever the proportions, with an ‘active agent/passive object’ representation (Brosnan, 1990) and/or because of a physical transformation.

So we decided to examine student explanations of various situations: reactants in the same physical state, or reactants in different physical states. Further, we asked whether one kind of problem leads preferentially to one conception or the other. We investigated students at the beginning and at the end of grade 10 year in order to look at the impact of teaching on students’ conceptions.

Methodology

Collecting data

We used paper and pencil tests. We questioned students, before and after the teaching of stoichiometry, about the composition of a chemical system at the end of a transformation in order to investigate the two conceptions described above. We investigated students’ understanding of four problems that are suggested in the French chemistry curriculum (grade 10).

Two problems involve reactants in the same physical state:

Problem 1: copper oxide (solid) and carbon (solid);

Problem 2: sodium hydroxide solution and copper sulphate solution.

Two problems involve two reactants in different physical states:

Problem 3: chalk (solid) and hydrochloric acid solution;

Problem 4: iron (solid) and copper sulphate solution.

The forms of the questions are given in the Appendix.

The description of the situations reports observable events that students may note during an experiment. A parallel work showed that giving more complete description of the experiments had no significant influence on the answers (Grisard, 2006).

The students had to answer multiple choice questions; the possible answers were devised from a previous enquiry with open questions (Gauchon 2002). We selected the most frequent answers; so the students had to choose from four options. Two answers favour one reactant; the third one mentions that both reactants are totally converted together; and the fourth one considers that one or the other reactant is totally converted at the end of the chemical change. A last heading called ‘other answer’ enables the students to develop their own answer if they wish. Moreover, the students had to justify their answers.

Samples

We questioned 116 grade 10 students from four classes of a secondary school before they have studied stoichiometry (58 about problems 1 and 3, 58 about problems 2 and 4). We questioned 177 grade 10 students, from six classes of another secondary school after they have studied stoichiometry (92 about problems 1 and 3, 85 about problems 2 and 4).

In each class, half of the students were questioned about problems 1 and 3 and half of them about problems 2 and 4. So there is no doubt about the equivalence of the populations when discussing the results. The conclusions about the effects of teaching will need to be treated with more caution. Both samples can be considered as reasonably representative of the average population of grade 10 French students, because they represent two similar ‘typical’ urban secondary schools in medium sized towns with catchment areas of similar socioeconomic status.

Results

Table 1. Reactants in the same physical state: the distribution of answers**.**

Question / Type of answer selected	Problem 1 **Two solids** (CuO and C)		Problem 2 **Two solutions** (NaOH and $CuSO_4$)	
	% Before N=58	% After N=92	% Before N=58	% After N=85
only one reactant converted	10.5	15	20.5	18
both reactants totally converted	34.5	30	33	36
limiting reactant	22.5	48	15.5	35
other answer	3.5	2	3.5	4
do not know or *no answer*	29	5	27.5	7
Total	100	100	100	100

Analysis of answers for reactants in the same physical state

As Table 1 shows, before teaching, the rates of no answer are rather high (29%, 27.5%). The rates of good answers (22.5%; 15.5%) are low, which is not really surprising because the notion of limiting reactant has not yet been studied. If we examine the wrong answers, we can observe that the type of answer "*both reactants were totally converted"* is the one most often selected and with similar rates in both problems (34.5%; 33%). The type of answer "*only one reactant was converted*" scored lower: 10.5 % (5.2% for copper oxide and 5.2% for C) and 20.5% (13.5% for copper ions and 7% for hydroxide ions).

After teaching, the rates of 'no answer' (5%; 7%) are lower and good answers are higher: 48% (problem 1) and 35% (problem 2). Wrong answers are chosen with similar ratios in both problems: 15% (8% for copper oxide and 7% for carbon) and 18% (7% for copper ions and 11% for hydroxide ions) for the type *"only one reactant was converted"*, and 30% and 36% for the type *"both reactants were totally converted"*; This last type of answers score high for those problems in which the reactants are in the same physical state.

As mentioned before, the students had to explain their choice. Before teaching, many students (near half of them) did not justify their choice (see Table 2). After teaching, justifications were much more numerous, but they were often paraphrases of the chosen answer. Nonetheless, we can draw three categories of explanations.

Table 2. Reactants in the same physical state: the distribution of explanations.

Question / Explanation category	Problem 1 **Two solids** (CuO and C)		Problem 2 **Two solutions** (NaOH and $CuSO_4$)	
	% Before N=58	% After N=92	% Before N=58	% After N=85
one reactant favoured	5	8	12	6
reactants convert in order to make up products	17.5	28	21	31
limiting reactant or *surplus of reactant*	14	43	3.5	32
other justification	20.5	13	17	16
no justification	43	8	46.5	15
Total	100	100	100	100

We named "*one reactant favoured*" explanations corresponding to the answers *"only one reactant was converted"*. These explanations do not take into account stoichiometry. Some imply a conception ‘passive object/active agent’, for example: “*Because copper oxide transforms carbon*”. Other explanations refer to physical changes or dissolution phenomena rather than chemical change: “*Because copper sulphate dissolves in sodium hydroxide solution*”

Kinds of explanations entitled “*reactants change in order to generate products*” are linked with answers “*both reactants were totally converted*”. Here are some examples of justifications:

- “*before the reaction stops , reactants need above all to generate products*”
- “*[...]because both solids undergo a change*”

Finally, the category of explanations *limiting reactant or surplus of reactant* is linked with answers *limiting reactant*. No reactant is favoured in these justifications.

- “*because there is obviously one limiting reactant and one in surplus.*”
- “*a reaction stops when at least one of the reactants is missing*”

Some of these justifications are quite comprehensive and mention the various possibilities

- “*If one compound is totally converted or if both compounds are converted together then the reaction stops.*”
- “*The reaction stops when one or both reactants disappear*”

So the distribution of the explanations in the various categories fits well with the distribution of the answers. We have also established that there is a strong coherence between answers and associated justifications.

Analysis of answers for reactants in different physical states

Chalk and hydrochloric acid solution

Table 3. Chalk and hydrochloric solution: the distribution of answers and explanations.

Problem 3. one solid and one solution ($CaCO_3$ and HCl)		
Type of answer selected	% Before N=58	% After N=92
only one reactant was converted	43	44
both reactants were totally converted	15.5	12
limiting reactant	22.5	36.5
other answer	3.5	0
‘do not know’ or no answer	15.5	7.5
Total	100	100
Explanation category	% Before N=58	% After N=92
one reactant favoured	38	36
reactants are converted in order to form products	10.5	14
limiting reactant or *surplus of reactant*	19	29
other justification	8.5	7
no justification	24	15
Total	100	100

Before teaching, the rate of ‘no answer’ is lower (15.5%) than for problems 1 and 2. We can assume that this kind of reaction is rather well known to students because they studied the reactions between hydrochloric solution and various materials in grade 9. But the score of good answers is low too (22.5%). If we have a look at the wrong answers, the type '*only one reactant was converted*' represented 43% of the answers, of these 36% chose chalk and 7% chose hydrochloric acid.

After the teaching of stoichiometry the rate of good answers (36.5%) was higher than before. The type of answer *"only one reactant was converted"* was given by 44%, and chalk was named in 32.5% of the answers. Thus, in this case, many students identified the absence of the solid reactant in order to explain the end of the transformation. Their justifications often indicated an 'active agent/passive object' representation. For example: *"hydrochloric acid solution eats away chalk"*. We could also observe that a few students do not see the chemical system evolution as a chemical change but rather as a dissolving phenomenon or as a physical change: *"[the reaction] stops when chalk disappears from its solid state"; "as we know, chalk melts"*.

Iron and copper sulphate solution

Before teaching, the rate of 'no answer' is important (19%) and good answers are low (17.5%). If we have a look at wrong answers, the type *"both reactants were totally converted"* was predominant with 34.5%, unlike with problem 3. The type *"only one reactant was converted"* appeared with 24%, including 19% identifying iron.

Table 4. Reactants in different physical states (iron and copper sulphate solution); the distribution of answers and explanations.

Problem 4: **Reaction between solid and solution** (Fe and $CuSO_4$)		
Type of answer selected	% Before N=58	% After N=85
only one reactant was converted	24	34
both reactants were totally converted	34.5	23.5
limiting reactant	17.5	38
other answers	5	0
'I do not know' or no answer	19	4.5
Total	100	100
Explanation category	% Before N=58	% After N=85
one reactant is favoured	12	27
reactants are converted in order to form products	15.5	17
limiting reactant or surplus of reactant	15.5	27
other justification	17.5	10
no justification	39.5	18
Total	100	100

After the teaching of stoichiometry, the rate of good answers (38%) was higher than before. With regard to wrong answers, the category *"only one reactant was converted"* was predominant with 34%, preferentially iron (about 26%); In this case again, the lack of solid was favoured. The explanations were similar to those reported in the situation with chalk. For example, one student explained *"a solid often dissolves in a liquid until it disappears"*. The category *"both reactants were totally converted"* appears with 23.5%.

Discussion

As argued previously, both samples (before and after teaching) can be considered as representative of the average population of grade 10 French students. Moreover, teaching contents and activities are very precisely defined by curricular documents and school books, so differences between schools are small. That is why, in our opinion, differences between 'before' and 'after' results can be attributed to the effects of teaching. Nevertheless, these results should be considered as preliminary, to be confirmed by further investigations in France and in other countries; this would allow the assessment of their general value and to identify possible effects of different ways of teaching this subject.

Rates of good answers (see Table 5) were similar for all problems before the teaching of stoichiometry. They scored a bit higher for the students who have been questioned after the concept has been studied.

Table 5. The distribution of answers to the different problems.

Question / Type of answer	Reactants in the same physical state				Reactants in different physical states			
	Problem 1		Problem 2		Problem 3		Problem 4	
	%Before	%After	%Before	%After	% Before	% After	% Before	% After
good answer	22.5	48	15.5	35	22.5	36.5	17.5	38
wrong answer	48.5	47	57	58	62	56	63.5	57.5
no answer	29	5	27.5	7	15.5	7.5	19	4.5

It is really notable that even after studying stoichiometry, about half (47-58%) of the students were not at ease with the notion of limiting reactant, and the rates of wrong answers were very similar for both samples, before and after teaching. It seems that teaching had little effect on wrong answers but allowed a shift from 'no answer' to good answers.

For wrong answers, the students' way of thinking depends on the situation. The next table (Table 6) represents the distribution of wrong answers in the various problems.

Table 6. The distribution of wrong answers according to the problem.

Question / Type Of answer	Reactants in the same physical state				Reactants in different physical states			
	Problem 1		Problem 2		Problem 3		Problem 4	
	%Before	%After	%Before	%After	%Before	%After	%Before	%After
one reactant was converted	22	32	36	31	69	79	38	59
both reactants were totally converted	71	64	58	62	25	21	54	41
other answer	7	4	6	7	6	0	8	0

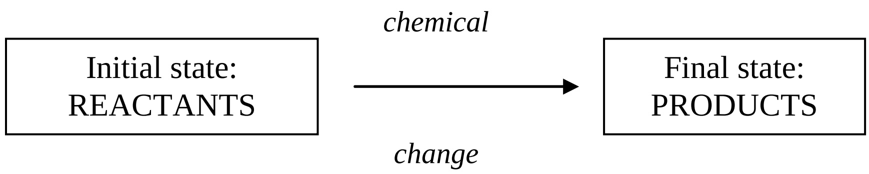
For problems 1 and 2, we can note that the conception *"both reactants are totally converted whatever the proportions"* appears with high score for students questioned before and after teaching.

For problem 3, the answer *"only one reactant was converted"* (preferentially the solid one) remains in a large majority among students questioned before (69%) and after (79%) teaching. Problem 4 shows more mixed results. Comparing the answers of students questioned after and before teaching, we can see fewer answers of the type *"both reactants are totally converted"* and more of the type *"only one reactant disappeared"*.

For both reactions between the compounds in the same physical state, the conception *"both reactants are totally converted"* clearly emerges. From this point of view, we note some quite interesting sentences: *"The end of the reaction is shown by the change of both reactants, indeed, two products already transformed can not transform again*" *"[...] because in the mixture, we mix copper sulphate with sodium hydroxide solution. Thus all the ions react because they are all reactants."; "They (Cu^{2+} and OH^{-}) are reactants then when they react together, they change into copper hydroxide*"

We can establish a parallel between such justifications and a diagram (Figure 2) we found in a French secondary school book (Durandeau et al., 2000, p.235).

Figure 2. A confusing representation of a chemical change



Such a schematization results from a superposition of empirical and model levels, as presented in Figure 1. The initial state of the system is confused with the left side of the chemical equation, the final state with the right one. No information is given about the reactants in surplus in the final state. To write on this diagram solvent and other chemical compounds which do not react might make students have a less limited view of the chemical system.

Conclusion and perspectives

These results illustrate the way conceptions depend on situations. If the conception *"both reactants are totally converted"* is favoured when reactants are in the same physical state, this would be in competition with the conception *"only one reactant is totally converted"* when a solid is one of the reactants. It is interesting to observe for Problem 4 that teaching seems to reinforce the conception: *"Only one reactant is totally converted"*. This study demonstrates that the conception *"both reactants are totally converted"* seems to be the most common one. As stated before, students' explanations often show confusion between the empirical level of the chemical change and the model level of the chemical reaction, and teaching (the rough schema in the textbook, for example) may reinforce this confusion. To distinguish clearly those two levels must be part of the teaching strategy in order to support students' conceptual development.

The results of the post-test make us suspect that both conceptions are deeply rooted, because they remain clearly present even after studying stoichiometry with a quantitative treatment. These results illustrate the discrepancy between the purpose of the curriculum "*to enable students, mostly by an experimental approach, to understand that a chemical change does not need the reactants to be in particular proportions in the initial state"* (Ministère 2000, p.126) and such conceptions. Therefore, teaching strategy must take into account the students' pre-conceptions before introducing a quantitative treatment of stoichiometry. The results presented here can be used to design teaching-learning situations addressing students' conceptions, by asking students to make predictions and then to make them compare their predictions with those of others (socio-cognitive conflict), and to compare them to the experimental facts (cognitive conflict).

The results appear to show that teaching has little effect on wrong answers but mainly allows a shift from 'no answer' to good answers. Piaget's theory proposes two kinds of situations favouring the evolution of cognitive structures: contradictions and gaps (Piaget 1975). Here, it seems that usual teaching doesn't bring to the surface students' conceptions, so these conceptions are not modified, but it does allow students who 'didn't know' to adopt a correct conception. This hypothesis has to be confirmed by further studies.

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Appendix

Problem 1

Copper oxide (solid) and carbon (solid) are mixed in a test tube. If the mixture is heated (this reaction needs a supply of energy), formation of copper and carbon dioxide is observed. The heating does not stop.

In your opinion, the chemical change stops when:

□ All the copper oxide is used up
□ All the copper oxide and all the carbon are both totally used up
□ All the carbon is used up
□ All the copper oxide or all the carbon is used up
□ Other answer: ……………………………………………………………………
□ I do not know

Please, explain your answer: ……………………………………………………………………

Problem 2

Sodium hydroxide solution and copper sulphate solution are combined in a beaker. Copper hydroxide precipitate is formed.

In your opinion, the chemical change stops when:

□ All the hydroxide ions are used up
□ All the hydroxide ions and all the copper ions are both totally used up
□ All the copper ions are used up
□ All the hydroxide ions or all the copper ions are used up
□ Other answer: ……………………………………………………………………
□ I do not know

Please, explain your answer: ……………………………………………………………………

Problem 3

Chalk (calcium carbonate) is put into a hydrochloric acid solution. Calcium carbonate and hydrochloric acid react. Emission of carbon dioxide gas is observed.

In your opinion, the chemical change stops when:

□ All the hydrochloric acid is used up
□ All the hydrochloric acid and all the chalk are both totally used up
□ All the chalk is used up
□ All the hydrochloric acid or all the chalk is used up
□ Other answer: ……………………………………………………………………
□ I do not know

Please, explain your answer: ……………………………………………………………………

Problem 4

The reaction between iron (solid) and copper sulphate solution produces iron ions in solution and copper (solid). Some iron filings are put in a copper sulphate solution.

In your opinion, the chemical change stops when:

□ All the iron is used up
□ All the copper ions and all the iron are both totally used up
□ All the copper ions are used up
□ All the copper ions or all the iron are used up
□ Other answer: ………………………………………………………………
□ I do not know

Please, explain your answer: ……………………………………………………………