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Teaching and Learning Chemical Thermodynamics in School

Jean-François Le Maréchal*
UMR I.C.A.R., INRP, CNRS, Université de Lyon, France
E-mail: lemarech@ens-lyon.fr

Rania El Bilani
UMR I.C.A.R., INRP, CNRS, Université de Lyon, France
E-mail: raniaelbilani@yahoo.fr

Abstract

The hypothesis that a better representation of energy is important to help students understand the founding knowledge in chemical thermodynamics is formulated. A simple model is used to help students with such a representation: as the chain energy model. The benefit of this model can be anticipated on the basis of the known pre-university students' conceptions, which are reviewed in this article. An innovative teaching sequence involving the chain energy model is then designed, analyzed and evaluated. This teaching sequence involves an experimental work and a computer simulation to introduce chemical thermodynamic concepts such as bonding energy, heat of reaction or changes of states, from both microscopic and macroscopic viewpoints.

Keywords: Science education, teaching sequence, energy, chemical reaction, conception.

1. Introduction

Teaching and learning thermodynamics involves concepts that concern most scientific domains such as physics, biology, earth science, and of course chemistry. Everyday life is also a sphere of activity of thermodynamics, for example the melting of ice cubes or the heating of one's home. Such a multiplicity of uses of thermodynamic concepts provides a large choice for finding examples in teaching. However, learning these concepts is often a difficult challenge as they may be used with different meanings. As a case in point, heat and temperature are currently used with the same meaning in many everyday life situations, whereas in thermodynamics, their meanings are clearly distinct.

Teaching thermodynamics is a long process. In most countries where science is taught at school, teaching thermodynamics begins in primary school with the first notion of temperature. Then, heat is usually involved through the change of state of water in lower secondary school. Later, the first uses of energy are introduced in mechanics, electricity, and in chemistry in upper secondary school. Finally, all these concepts continue to be taught from the principles at university level. In this process, two complementary approaches can be used in teaching: conceptual understanding and problem solving. Chemical educators have often assumed that success in solving mathematical problems should indicate mastery of a chemical concept (Nakhleh and Mitchell, 1993). However, Nurrenbern and Pickering (1987) and Pickering (1990) have found little connection between solving an algorithmically based problem and understanding the chemical concept behind that problem.

The research in thermodynamics education is separated into physical thermodynamics, which was recently reviewed (Paik et al., 2007), and chemical thermodynamics that is the purpose of this article. This article first presents the main difficulties that research in science education has found in teaching and learning chemical thermodynamics, then the main ideas that give possible explanations to these difficulties are reviewed, and finally, a possible way to tackle theses difficulties in the case of transferring few concepts from physical to chemical thermodynamics is described within an experimental context assisted by a simulation artefact.

* Author to whom correspondence should be addressed.

2. Difficulties in Teaching and Learning Chemical Thermodynamics

Many teaching and learning difficulties in chemical thermodynamics have been observed at all levels (Goedhart and Kaper, 2002). The review of these authors deals with more than 70 research articles related to heat and energy in chemical changes. In most studies, students' difficulties are pointed out. One of the earliest recognized difficulties has been the confusion of heat and temperature (Erickson and Tiberghien, 1985). This study showed that 25% of students between the ages of 12 and 16 said that there is no difference between these two concepts, and that this percentage did not decrease with teaching. Energy of chemical bond has also been much studied (for example Boo, 1998) and is involved in our third task below. In these reactions, the energy of bond breaking and making is the central phenomenon to be taken into consideration, which corresponds to gas phase reaction. Students' conceptions relative to more complex interactions, such as the solvent solute bonds, have also been documented (Ebenezer and Frazer, 2001; Çalýs et al., 2005).

In schools, burning is often used as a prototypical chemical change, in contrast to physical changes. Although considering that combustion produces energy seems evident, several authors report that students may view heat as the causal agent of such a reaction (for example: Watson et al., 1997; Boo, 1988). In Boo's study, 85% of grade 12 students thought that chemical reactions need an external, active causal agent, and viewed the heat supplied to start the reaction as the driving force of the reactions concerned. The reason for this inversion in the cause / effect relation can be attributed to the fact that heat is often necessary (for kinetic reasons) to run chemical reaction, event combustions. This may explain frequent confusion between exo- and endothermicity (De Vos and Verdonk, 1986; Galley, 2004).

The concepts of chemical bond and the energetic of its making / breaking have been much investigated as they are in relation to the energy social demand. Barker and Millar (2000) probed the progress of 16 year old students who took the Salter Advanced Course (SAC) where many units were proposed from a context-based approach. The SAC proposed to teach chemical concepts from the context approach. For example, in "The Atmosphere" unit, students were introduced to bond breaking; in the unit "Developing Fuels", they learned about the thermicity of bond making / breaking, Hess' Law; and in the "Using Sunlight" unit, enthalpy change of combustion was used to compare hydrogen and petrol. This study has shown that after the 20 months of the SAC, over 30% of the students could not describe the energy of methane burning from a bond making / breaking point of view.

In their study, Boo and Watson (1998) have found that even though students in year 12 (grade 12) were able to predict the type of change involved in terms of the relevant reactants and products, they would poorly perform in the energetic aspect of chemical reactions. For example, the study has shown that even after a year of chemistry instruction, 48% of the interview sample held the conception that bond breaking releases energy. In a similar study, Boo and Watson (2001) have found that only 29% of the students in year 13 reasoned that the reactions were exothermic, based on the principle that the bonds made were stronger than the bonds broken.

In 2003, Greenbowe and Meltzer claimed that calorimetry has received little attention in chemical education, although it is one of the more elementary applications of thermochemical concepts. In their study, they focused on the primary conceptual difficulties faced by college chemistry students in their initial study of calorimetry. One of the difficulties stems from the reactants that must be viewed in two distinct ways: as the entity that releases heat, and as part of the mass that gains heat. This study also pointed out that students have difficulty making the inference that the heat 'absorbed by' the chemical reaction is equal in magnitude but opposite in sign to the heat 'absorbed by' the solution.

In order to improve teaching, Teichert and Stacy (2002) investigated the effects of intervention discussion sections on student learning. They have found that in group discussions, students that had been coached by graded students to express their understanding and try to clarify their ideas among contradictory debate performed significantly better. Among a large body of conceptions, they found that students had some trouble with sign conventions in energy exchanges.

Energy is a unifying concept in physics, and its teaching can no longer be viewed as a notion that looks different to learners in different science domains. For example, incoherence occurs when learners are told that breaking a chemical bond costs energy in chemistry courses, whereas 'high-energy bonds' store energy in ATP when biology is concerned (Boo and Watson, 2001; Galley, 2004). Further along, at the university level, giving meaning to the differences between free energy, enthalpy and Gibbs energy is not easy, nor is the introduction of entropy. At such a level, introducing thermodynamics concepts relies primarily on the use of mathematics, for example partial derivatives, which is not possible at school level. How can teaching thermodynamics occur at lower levels?

3. Teaching and Learning

Two important kinds of learning have been observed: conceptual learning and problem solving abilities. On one side, conceptual learning deals with concept understanding, such as the distinction of heat and temperature. On another side, problem solving involves the uses of strategies and algorithms. Although both kinds of learning are not independent, it has been shown that high problem solving abilities do not necessarily develop good conceptual learning (Nakhleh and Mitchell, 1993). In the case of thermodynamics, where a high level of precision is required, concepts such as heat and energy are precisely defined. Heat is one of the possible ways energy can be transferred from one system to another. Heat is more a flow of energy than energy. However, the first principle, in the case of when no pressure forces are active, can be stated as $\Delta U = Q$. A good problem solving student who efficiently uses this relation may be convinced that heat is energy, and has therefore a poor conceptual understanding.

To try to improve students' learning in the field of chemical thermodynamics, we hypothesized that a simple model of energy could be helpful. We introduced an innovative and performing approach called "energy chain" (Gaidioz et al., 1998) in our teaching sequence. Energy chain is a model derived from Feynman's considerations on energy. This model states that energy is a quantity that belongs to systems and has the following properties: conservative, storable, transferable. Energy is stored in energy reservoirs and is transferred by means of the following ways: heat (Q), work (W) or rays (R). It is transformed into energy transformers. Any situation involving energy can therefore be represented with a chain, as in the example of a battery and a bulb (*Figure A1*). Such a model of energy has been used in many different researches (Baker and Lund, 1997; Devi et al., 1996).

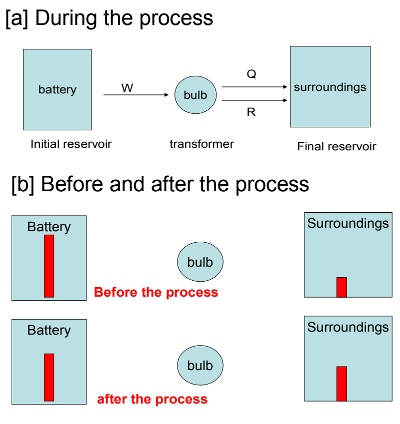

Figure A1 – Representations used in the model of the energy chain

The conservative property of energy is expressed as $W = Q + R$ in *Figure A1[a],* or by the fact that the sum of the sizes of the bars in the diagram of *Figure A1[b]* is the same before and after the process. Teaching situations, where students had been working with this model, have been shown to induce conceptual learning on the energy concept (Robinault and Tiberghien, 1998).

4. A Case Study in Chemical Education

The rest of this article focuses on a case study that illustrates the above general research results. The aim of this case study has been to elaborate a teaching sequence for introducing chemical thermodynamics according to the curriculum of the second year of upper secondary school. We worked with 17 year old students who had been taught energy in physics with the energy chain model. This model was used with chemical systems to introduce the notions of heat of reaction and energy of chemical bonds. The curriculum also asked to compare heat of reaction and heat of change of state. The innovative character of this sequence relies on the pedagogical intention to involve both conceptual and problem solving approaches. This sequence makes use of laboratory experiments as well as a computer simulation. Four tasks were designed for this sequence. They are briefly presented below and the resulting learning is assessed. TABLE I summarizes these tasks.

TABLE I. OVERVIEW OF THE FOUR TASKS OF THE TEACHING SEQUENCE DESCRIBED BELOW

1st task (40 min)	Paper & pencil	Test on energetic chain model Recall of the model
2nd task (1h20 – 1h50)	Laboratory	Work about energy transfers involved in an acid/base reaction
3rd task (1h)	Simulation	Micro- and macroscopic points of view of combustion reactions Introduction of bond energy and energy of reaction
4th task (30 min)	Paper & pencil	Questionnaire about change of state, using many of the concepts developed in the previous task

4.1. First task

The first task lasted for 40 minutes; its first part aimed at testing students' prior knowledge on energy concepts, and reactivating notions related to the energetic chain model. Indeed, students had been taught this model and its use in physics a month before, with the same teacher. Questions such as: make a sentence with heat, one with energy, one with temperature, and one with all three concepts, were proposed. Then, as a second part, a brief summary of the model of the energy chain was provided, including representations as in *Figure A1*. The reactivated knowledge was then solicited by questions such as: how the conservation is represented in the energy chain; explain why such representations [several representations had been reproduced] account for the cooling of a system. Then the definition of an isolated system was given and a few questions relating the definition with representations were proposed. Finally, as a third part, a few questions from the first part were repeated to assess the effect of the reintroduction of the energy chain model.

We found that most students had only a few memories of the energy chain at the beginning of the test. Indeed, most sentences that were produced used the words temperature, energy and heat as in everyday situations, and not as they should be used in terms of the energy chain model. However, getting students to read the model was efficient. For example, a student could write the following sentence before being reminded of the model:

There is more energy when temperature rises and heat becomes unbearable.
and then, once the model was reminded of:
The loss of energy as heat makes the temperature of the surroundings increase.
For another student, these sentences were:
[Before] – *Energies released heat that made temperature vary.*
[After] – *The temperature of the surroundings can vary if the system transfers energy.*

Such observations are in agreement with the difficulties in learning concepts related to energy; however, the effectiveness of the energy chain model was quite helpful. For example, to the question "Propose a sentence using the word *energy* and *temperature*, 4 out of 31 answers (14%) distinguished the two notions before recalling the energy chain, and 6 (20%) after. Then, to the question: "Propose a few words qualifying energy, 18 out of 31 answers (58%) improved their proposals. Among the proposals were words such as kinetic, potential, force, power, electric, and others from the physics class, and not from everyday life. Other words such as transfer, reservoir, heat, isolated system were proposed and clearly taken from the energy chain model. After such a task, the use of the vocabulary of the model could be considered reactivated in students' mind.

4.2. Second task

The second task took place one week after the first one and lasted for 1h20 – 1h50, according to students. It was based on a classical calorimetry experiment that students performed by themselves. It consisted of a semi-quantitative study of an exothermic acid base reaction. The writings of each of the 17 pairs of students were collected and the answers to questions analyzed. Two pairs of these students were videoed during this task, and the analysis of the transcription of the video helped to understand the process of answering the questions.

Students measured the temperature of hydrochloric acid in an insulated test tube for 2 min – a tube in a Dewar flask filled with styrofoam chips – before adding a few pellets of sodium hydroxide, while monitoring the temperature. Then they repeated the experiment in a non-isolated test tube. The novelty of this teaching situation lies in the questioning that went along with the experiment in relation to the energy chain model. In the interpretation of this experiment, only two energy processes had to be considered: (i) the energy of the chemical reaction and (ii) the possible energy transfer from the system to its surroundings. In this questioning, students were not involved in a distinction between energy of the chemical reaction and energy of a chemical phenomenon as Ebenezer and Frazer (2001) unsuccessfully tried.

The most innovative questions of the task dealt with the representation of energy in the experiment. Students were asked to represent the energy of the first chemical system and of the surroundings when adding the base, after one minute, then after four minutes. They were then asked to do the same with the non-insulated system. Using the model in the case of the insulated system would lead to the representation of a constant value of energy, whereas confounding energy and temperature would lead to an energy that would increase and decrease as did the temperature. A conflicting situation is important to give students a chance to interact with the model and to promote conceptual change (Hewson and Hewson, 1984; Laburu and Niaz, 2000).

The last part of the experiment dealt with the exothermicity of the reaction and the computation of the heat transferred from the chemical system to the environment. Students were told that the heat of reaction is a tabulated value Q, which is related to the energy ΔE transferred from the chemical system to its surroundings for an extent ξ of the reaction by $\Delta E = \xi \times Q$ (ΔE in J, ξ in mol, and Q in $J.mol^{-1}$). Finally, students were asked to determine

ΔE in both experiments, after indicating the initial and final states that should be considered. Although this computation is classic, having students make explicit the initial and final states was expected to provoke interesting discussions involving the energy chain model.

Analysis of the students' reports showed that, on the one hand, the classic computation was correct, so were the closed questions involving the model. On the other hand, the answers to the open questions involving energy proved to be unclear. To understand the students' reasoning behind these questions, analysis of the transcription of the videos was then undertaken. In the following, significant utterances of a pair of students – named Ali and Mike (pseudonyms) – are shown to enlighten the kinds of difficulties students may face.

To the question: "For each experiment, what can be said from the energy of the system during the reaction?" Ali immediately answered: *I'd say that it rises then decreases, doesn't it? I'd say energy rises when hydroxide is added, and then decreases after the end of the reaction.* Ali had seen temperature going up and down, and clearly could not discriminate energy and temperature. The heat / temperature confusion largely described in the literature is the same for energy / temperature.

Mike took some time to agree, as if he were not convinced by Ali's answer, but not having a better proposition, he accepted it. Mike and Ali should have used the model they had with the text of the task to answer. For example, they could have considered one of their previous answers about the insulated system, as they did recognize that the Dewar of the first experiment was an insulated system, whereas the ordinary tube of the second was not. Instead, their everyday life knowledge that associates an increase of heat (then of energy) and an increase of temperature was used as an interpretation of the experiment.

Later, Ali seemed to have some concern with the main characteristic of the insulated flask as he said:

Ali – My experiment is not quite successful.

Mike – Wait.

Ali – The insulated system should not exchange energy.

Mike – With the surroundings.

At that point, Ali realized that the temperature / should have kept still in the Dewar, and he felt embarrassed by the conflict with their observations. After a short discussion that did not help much, Mike suddenly claimed: *Yes, it heats up, yes it loses energy, the system[with the Dewar] loses energy because it is transferred to the surroundings.*Then both students spent some time representing the evolution of the energy of both systems as in *Figure 1*.

At that point, Mike proposed a real interpretation, most certainly partial, as an observation (the decrease of temperature) was reformulated in terms of the model. Such behavior is a key step in scientific reasoning, and Mike could do it because he involved altogether the data of an experiment, the text of a model, a set of appropriate questions, a relevant system of representation, and a colleague to talk to. This is, in our opinion, how students can construct scientific knowledge. Unfortunately, the situations that are often proposed are not rich enough. The classic experiment of the acid / base reaction above, followed with a calorimetric device, often leads to a short algorithmic calculus that most of the students successfully perform, but probably without a real construction of conceptual knowledge.

Ali's utterance latter made clear another difficulty, while both students were representing the exchange of energy. He said: *But the surroundings, it exchanges nothing.*

One of the major difficulties in understanding energy conservation is probably the role of the surroundings. The materiality of it is difficult to comprehend. The energy chain model proposed to the students is worth representing it and its energy, but still, the relation to the experiment resists learning. Not having conceptualized the surroundings led Ali to say: *There is a problem, with the conservation of energy…*
Ali accepted the conservative property of energy, but watching the decrease of the temperature, he was uncomfortable with this loss of energy that had no place to go.

Successful algorithmic problem solving in calorimetry does not prove that the widespread thermochemical misconceptions are not active (Greenbowe and Meltzer, 2003). In our case, not only the observed students managed to solve the computational part of the task, but they also had a fruitful explicit reflection about energy transfer. The fundamental conservative property of energy was involved, probably due to the clear demand of using the energy chain model.

Neither in the video nor in the written reports was the idea that the energy would come from the release of energy stored in the crystal as observed by Liu et al. (2002). Such a difference with Liu's study may be explained by the fact that ours was in the context of an acid-base reaction whereas Liu's focused on dissolution.

4.3. Third task

The third task was organized around a simulation that presents both micro- and macroscopic viewpoints of the heat of reaction. On one side, a window with the microscopic viewpoint could display the molecules that correspond to a combustion reaction of an organic reagent (for example ethanol) chosen from among a list of eight. The number of molecules corresponded to stoichiometric proportions ($2\ C_2H_5OH + 7\ O_2$), and an animation showed the evolution of the energy of this system (in 10^{-18} J), with the same representation as in *Figure 1*, as the chemical bonds were successively broken. Then, when all bonds were broken, atoms were reorganized and new bonds formed to give the products ($4\ CO_2 + 6\ H_2O$). The energy of the system was still represented step by step and became negative. On another side, a window with a macroscopic viewpoint could display a quantitative evolution of the molar amount of matter and the energy ΔE exchanged with the surroundings for the same reaction. The energy was $\Delta E = 0$ for any extent of reaction if the system was insulated, and $\Delta E = \xi \times Qr$ if not. The evolution of both the energy and temperature of the system and the surroundings were also qualitatively represented as in *Figure 1.*

Students were first asked to observe the microscopic animation, where they could watch the energy of the system getting higher each time a bond would break, and propose a definition for the energy of a chemical bond. Such a question puzzled students as they had little knowledge of chemical bonding. As an example, a pair of students answered this question by improving their proposals step by step (students are names At and Me, and each of their intervention is numbered):

Me9: energy that increased
Me13: it is in 10 to the power minus 18 joule
Me29: you have a given energy for a given bond
At38: it is not the same energy for every bond
Me55: there is a given energy
Me65: E is the sum of the energy of the bonds
Me67: each bond has a specific energy
At70: the energy of the bond is the energy that is freed for each bond that breaks

Just as this pair of students did, 6 other pairs over 17 (41%) elaborated correct theoretical elements establishing a relation between energy and bond breaking. This example shows that during the long process of proposing a definition for the energy of a chemical bond students had to get over several steps: the sign of the evolution of energy; the fact that different bonds have different energy values; and the relation between each bond and the total energy. Later in the task, students also have to deal with the meaning of a negative value for the energy. During this work, the main attributes of the simulation that seemed to have provided an efficient hint to students were the simultaneity of bond making / breaking with the value of the energy of the system, and the possibility of students dealing with the values of the energy of the system and the bonds. We observed that 17 pairs of students (77%) could elaborate a quantitative model with the help of the computer.

In our opinion, working with positive and negative values of energy may be a step in having students care about the sign of an energy exchange, as it has been noticed to be a common error (Greenbowe and Meltzer, 2003). Moreover, linking the evolution of the energy of the system with the breaking and making of chemical bond can be profitable for avoiding having a high percentage of students believing that molecules store energy which is released when the bonds are broken (Barker and Millar, 2000; Boo, 1998).

During the second part of the task, students were asked to anticipate the animation for studying the reaction $H_2 + Cl_2 \rightarrow 2\ HCl$. All students correctly found that both the H–H and Cl–Cl bonds had to break down, then an H–Cl bond had to form, but we noticed that at least one group of students spent some time on the (uninteresting) question of which of the H_2 or Cl_2 bonds would break first. Finally, students were successively tested on their ability to work out the heat of combustion of methane from the values of the bond energy. In this case, a conceptual understanding (that had been done with the animation) could lead to problem solving ability. This success may be related to the fact that the conceptual understanding learning involved processing numerical data. In this question, 14 pairs of students (80%) correctly wrote that the reaction of Cl_2 with H_2 was exothermic. Considering that the students discovered this reaction during this question, the understanding of the energetic of this reaction can be considered good and may be due to the efficiency of the teaching sequence and the use of the computer representations.

The third part of this task focused on a macroscopic viewpoint of the energy of a chemical reaction. Students should have involved concepts of insulated (or not) systems, energy and temperature, during the previous laboratory session, while they were introduced to the heat of reaction. Heat of reaction had been introduced through the $\Delta E = \xi \times Qr$ relation at the end of the second task, and was now involved again here after having been introduced from a microscopic perspective with the simulator. All students worked out the calculus and 14 pairs (82%) managed to correctly predict the energy of the reaction. Unfortunately, the evolution of energy and temperature in the system and the surroundings was not correctly predicted. However, the animation, close to an animated representation of *Figure 1.b*, rapidly convinced the students of their mistakes.

It has long been recognized that students get mixed up with the concept of heat and temperature (Erickson and Tiberghien, 1985) in primary school and, in college, Thomas and Schwenz (1998) have identified "No heat occurs under isothermal conditions" with a conception. In our case, the opposite conception was observed; our students expressed the idea that temperature cannot rise if there is no heat supply. It can indeed if an exothermic reaction occurs in an insulated device.

The conclusion of this part is that the microscopic / macroscopic relation was not too difficult, solving problems could be numerically done, but managing the basic concepts of energy and temperature was again difficult. However, the analysis by students of their own mistakes was promising.

4.4. Fourth task

The last task dealt with changes of state, in a nine question questionnaire, intending to involve the knowledge of the previous tasks. It followed the curriculum prescription, asking to compare the energy involved in breaking intermolecular bonds (changes of state) and intramolecular bonds (chemical reactions). Analysis of students' reports showed that, in this task, several students could spontaneously use several key elements of knowledge introduced during the teaching sequence, such as the concepts of insulated system or heat of reaction. Nevertheless, basic knowledge on the representation of the states of matter was as incorrect as described in the literature for much younger pupils (Johnson, 1998b). For example, the representations of liquid and gas samples of ethanol were found incorrect *(Figure 2).* The hybrid representations of *Figures 2a* and *2c* indicate that for many students, molecules are not the substance, but in the substance (Johnson, 1998a). These drawings also show that many students represented the liquid with molecules that are not in contact, for the liquid to pour, unlike the solid. For most representations, molecules in the gas phase are too close to each other compared to the liquid phase (*Figures 2b* and *2d*) (Gabel et al., 1987). In addition, one representation of the gas state (*Figure 2d*) deeply disagrees with the model of the ideal gas that had been taught the previous year.

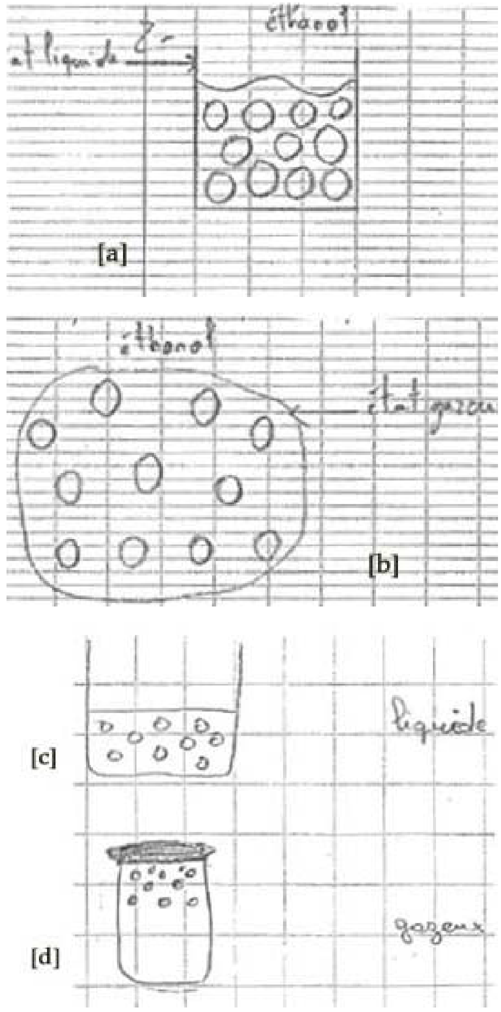

Figure 2. Students drawings for a change of state: [a] and [b] come from one student, and [c] and [d] from another one. Translation of the students words: éthanol / ethanol; état gazeux / gas state; liquide / liquid; gazeux / gaseous.

5. Conclusion

Teaching and learning thermodynamics are long and difficult processes, and students' conceptions are difficult to change. This article emphasizes the difficult discriminations of energy and temperature and several of its consequences on conceptual learning. Thus, an innovative teaching sequence was designed and its evaluation is promising, although students still had difficulties. The novelty has been to create the proper conditions for students to involve an appropriate model in conflicting situations. The model has been helpful for confronting students with several conceptions beyond the important energy / temperature confusion. Conceptions such as the exo- / endothermic aspect of chemical reactions, or the energy involved in breaking / making bonds, have been involved in relation to the chain energy model. In addition, a new kind of reflections with calorimetry has been proposed, which is all the more interesting because of the little attention that this technique has received in chemical education so far. The chain energy model can of course be used in many other fields, as long as a global viewpoint on energy is required, whatever the level of education might be.

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