Margarita KOUSATHANA and Georgios TSAPARLIS
University of Ioannina, Department of Chemistry

STUDENTS' ERRORS IN SOLVING NUMERICAL CHEMICAL-EQUILIBRIUM PROBLEMS

ABSTRACT: Chemical-equilibrium problems are among the most important and at the same time most complex and difficult general-chemistry problems. In this paper, errors made by the students, while solving such problems, are discussed. These errors are of two kinds: (i) 'random' errors caused by hastiness, or by thoughtlessness, or by an overload of working memory, or by field dependence or a combination of the above factors. (ii) 'systematic' errors that are caused by misconception(s) or by a difficulty in understanding of the underlying theory, concepts, or processes. Students in their final upper-secondary school year (age 17-18), attending an elective chemistry course, participated ($N =$ 120-148, depending on the question). The errors that were detected were categorised into five categories: (1) the equilibrium constant; (2) stoichiometry; (3) heterogeneous equilibria; (4) the direction of a reaction which is not at equilibrium (the disturbance of the chemical equilibrium); (5) gas equilibria and the ideal-gas law. [*Chem. Educ. Res. Pract. Eur.*: 2002, *3*, 5-17]

KEY WORDS: *problem solving; chemical-equilibrium problems; misconceptions; errors in chemical-equilibrium problem solving; misconceptions in chemical-equilibrium problem solving*

INTRODUCTION

A number of researchers have addressed students' misconceptions (or alternative conceptions) about chemical equilibrium. Griffiths (1994) published a review of students' chemistry misconceptions and identified twenty misconceptions about chemical equilibrium. A similar review was published by Garnett, Garnett, and Hackling (1995). Most of the misconceptions are related to conceptual aspects not entering in numerical chemical-equilibrium problems, such as the dynamic character of chemical equilibrium, the rates of the forward and the backward reaction, extent versus rate of reaction, or the effect of a catalyst.

Long ago, Johnstone, MacDonald, and Webb (1977) studied the conceptual difficulties of chemical equilibrium, and attributed them to the inherent abstract nature of the topic; this abstract nature leads to "tacit assumptions" on the part of the student, about which the teacher is quite unaware, and which account for misconceptions like left and right sidedness, the reversed-arrow symbol, and catalysis in general. At about the same time, Wheeler and Kass (1978) reported five misconceptions with twelfth-grade students. Misconceptions among senior secondary students were reported later by Hackling and Garnett, too (1985, 1986). Gorodetsky and Gussarsky (1986, 1988) identified a number of misconceptions among seventeen- and eighteen-year-olds by using various evaluation methods. Cachapuz and Maskill (1989) worked with fifteen-year-olds and used word

association tests to detect misconceptions with chemical equilibrium, and the application of Le Chatelier's principle in particular.[1] Banerjee (1991) studied both pre-service students and teachers, and reported three misconceptions. Quilez-Pardo and Solaz-Portoles (1995) examined the misapplication of Le Chatelier's principle by students and teachers. [1]

Tyson, Treagust, and Bucat (1999) used a two-tier test, coupled with interviews from a case study, to explore students' understanding of what happens when reaction mixtures at equilibrium are disturbed. Three levels of explanation can be used at the secondary level: (i) (the qualitative statement of) Le Chatelier's principle; (ii) the (quantitative) equilibrium law; (iii) the (qualitative) consideration of changes that occur to the rates of the forward and the backward reactions (collision theory). According to the findings, it did not appear that one explanation is better than the other, while language (that is, the use of terms such as 'equilibrium position' or 'equilibrium balance') turned out to be a key factor, causing misinterpretations by students. Care should also be taken to identify not only the similarities but also the differences between physical and chemical equilibrium.

According to Pedrosa and Dias (2000), language used in textbooks may give rise or reinforce student alternative conceptions about chemical equilibrium; by using some of the students' alternative conceptions already identified, and available in the literature, they devised an instrument to analyse chemistry textbooks used in secondary and tertiary education. On the other hand, students' reasoning first of incomplete chemical conversions, and then of chemical equilibrium was related to the historical development of these concepts by Driel, De Vos, and Verloop (1998); the study revealed similarities and differences between students' reasoning and 19th-century scientists. It is remarkable that most of the students reasoned in macroscopic terms, but only few related the observed phenomena to their corpuscular conceptions.

As we shall see in this work, the study of chemical-equilibrium numerical problem solving reveals not only some of the known from the literature misconceptions, but also some misconceptions that are characteristic of the problems themselves. All these misconceptions lead to 'systematic' errors in the solution of the problems. In addition, there are a number of 'random' errors.

Chemical-equilibrium problems are among the most important, and at the same time most complex and difficult general chemistry problems. It is not then surprising that many researchers have dealt with them from a number of perspectives. Camacho and Good (1989) studied the problem-solving behaviours of experts and novices engaged in solving chemical-equilibrium problems, and reported that unsuccessful subjects had many knowledge gaps and misconceptions about chemical equilibrium. Wilson (1994) examined the network representation of knowledge about chemical equilibrium, and found that the degree of hierarchical organisation of conceptual knowledge (as demonstrated in concept maps constructed by the students) varied, and that the differences reflect achievement and relative experience in chemical equilibrium. Similar findings have previously been reported by Gussarsky and Gorodetsky (1988). On the other hand, a conclusion, which applies to the students in general, is that by Gabel, Sherwood, and Enochs (1984), whose subjects used algorithmic methods without understanding the concepts upon which the problems were based. Niaz (1995) has compared student performance on conceptual and computational problems of chemical equilibrium and reported that students who perform better on problems requiring conceptual understanding also perform significantly better on problems requiring manipulation of data, that is, computational problems; he further suggested that solving computational problems before conceptual problems would be more conducive to learning.

Tsaparlis, Kousathana, and Niaz (1998) examined the effect on student achievement of the manipulation of the logical structure as well as of the mental demand (*M*-demand) of

these problems (see below). In addition, they studied the relationship between student achievement in the problems and a number of cognitive variables, namely, developmental level, working-memory capacity, functional mental capacity and degree of field dependence/independence of students. Of the cognitive factors studied, developmental level played the most important role, especially as the logical structure of the problem increased. The other three cognitive variables had an effect, too, with working memory capacity leading. The findings were mainly attributed to the fact that the problems were rather algorithmic exercises for the students, because of familiarity and training.

Furio *et al.* (2000) used four qualitative tasks on chemical equilibrium, all involving Le Chatelier's principle, and concluded that the procedural knowledge used by twelve-grade as well as by first- and third-year chemistry students (in Spain) in answering these tasks was very poor. Students apply mechanically reasoning based exclusively on Le Chatelier's principle, even when a solid is added to a heterogeneous system at equilibrium or an inert gas is added to a homogeneous system at equilibrium. These authors maintained that students demonstrate a memoristic 'fixedness' of reasoning, that is a standard method that has been used ('fixed') previously in similar problems, and which hinders the students' reflection of new situations.

Voska and Heikkinen (2000) developed a 10-item pencil and paper, two-tier diagnostic instrument, the *Test to Identify Student Conceptualizations* (TISC), and used it to identify and quantify chemistry conceptions students use when solving chemical-equilibrium problems requiring application of Le Chatelier's principle. They administered the test to students attending a second-semester university general chemistry course, after the students received regular course instruction, concerning equilibrium in homogeneous aqueous, heterogeneous aqueous, and homogeneous gaseous systems. Eleven prevalent incorrect student conceptions about chemical equilibrium were identified by *TISC*. Finally, Niaz (2001) tried a number of alternative sequences of statements related to the external addition of a reactant to a system in chemical equilibrium, and argued that one particular sequence facilitated some students to generate and resolve a cognitive conflict.

In this work, we discuss errors made by Greek senior high school students, when solving numerical chemical-equilibrium problems.[2] Before proceeding, let us clarify what we mean by 'systematic' and 'random' errors':

- *'Systematic' errors* are caused by *learning difficulty* or *difficulties*, that is, by difficulties or failures in understanding of the underlying theory, concepts, or processes. According to Kempa (1991, cited in Furio *et al*, 2000), a learning difficulty exists whenever a student fails to grasp a concept or idea as a result of: (i) the nature of ideas/knowledge possessed by the students or (ii) the inadequacy of such knowledge in relating to the concept to be acquired. Using more standard terminology, we can assume that we have here what have been termed as *alternative conceptions* or *misconceptions*.
- *'Random' errors* are caused, not by lack of relevant knowledge or by a misconception, but by *hastiness*, or by *thoughtlessness*, or by an *overload of working memory*, or by *field dependence*. It may also be caused by a combination of the above factors. In other words, the student must be able to correctly answer the relevant question if the question is given to him (or to her) separately or his (her) attention is specially drawn to it by the teacher. Camacho and Good (1989) and Furio *et al* (2000) speak of 'fixedness' of reasoning (see above).

A note of caution should be added here: the possibility exists that what might be a random error for one student may be a systematic one for another. Hence, the actual

distinction between the two types of errors is not always clear. A qualitative study that would probe in depth students' reasoning behind the errors is more appropriate for making definite the above distinction.

The logical schemata in chemical-equilibrium problems

We consider it useful to have in mind the logical schemata that enter the problems that were used in this study, so that the errors that will be revealed are placed in better context. The logical structure of a problem is specified by the number of *operative schemata* entering the problem (in the Piagetian sense, Tsaparlis, Kousathana, & Niaz, 1998). On the basis of their analysis, as well as of previous work on this topic (Hackling & Garnett, 1985; Niaz, 1995) Tsaparlis, *et al.* (1995a, 1998) arrived at the following schemata of chemical-equilibrium (molecular equilibrium):

Schema 1. The process of establishment of the chemical equilibrium.
Schema 2. The condition of chemical equilibrium.
Schema 3. The case of gaseous systems, with use of partial and total pressures as well as of K_p.
Schema 4. The disturbance of the equilibrium and the establishment of a new equilibrium.

Various general chemical schemata enter these problems, too, such as the ideal gas equation, Dalton's law of partial pressures, and the density of a mixture. In addition, a general schema that enters most chemical-equilibrium problems is stoichiometry.

For instance, in problem 1 in Appendix 2 three schemata enter: (1), (3) (ideal-gas equation), and (2) (Tsaparlis & Kousathana, 1995; Tsaparlis, Kousathana, & Niaz, 1998). On the other hand, in problem 2 four schemata are involved: (1), (3) (ideal-gas equation), (2), and (4).

METHOD

The sample of this study consisted of students from four urban, mixed, state upper secondary schools in the Athens Greater Region. Depending on the question, the number of students varied from 120 to 148. They were in their final upper-secondary school year (age 17-18), and attending an elective chemistry course which led to the university entrance examinations for science, engineering, and agricultural and health-science, tertiary education departments.

An instruction on chemical-equilibrium problems, designed by the authors, and delivered by different teachers, the second author being among them, was given to the students. An integral part of the project was the device and testing of a method for teaching problem solving in chemistry. According to this method, students were taught first the schemata that enter the problems. Afterwards, when solving example problems, students were called to try to identify the schemata that enter each particular problem, and then to separate and write down on a diagram the data according to the relevant schema. The detailed solution of the separate schemata, with the entering steps, followed.

The students were each tested in nine composite problems, each having just one question. Appendix 2 has two examples of the problems used. Before this testing, students were given a preliminary test, consisting of nine questions/exercises (see Appendix 1). These exercises tested in simple form all the schemata and steps entering the nine composite problems; in addition, they included some extra questions that aimed at some other relevant

concepts. Students' answers to the preliminary test were reviewed by the teachers and returned to the students. An in-class discussion followed about the errors made and their teacher gave relevant recommendations and guidelines to the students.

RESULTS AND COMMENTS

We present below the errors, together with percentages of students who demonstrated the errors, in answering the set questions and problems. Note that the remaining percentage refers to students who *have not made* the errors.

In our presentation, we make an attempt to distinguish between 'random' errors and misconceptions on the basis of the above distinction. As a rule, random errors should also be characterised by low frequencies. On the other hand, misconceptions may appear with both low and high frequencies. We repeat that this distinction may be not always sound. For example, failure to set up the correct expression for the chemical-equilibrium constant in the case of non 1:1 stoichiometries is considered as 'random' error. This is also supported by the low frequency of this error (5% in our sample). On the other hand, it may be the case with some students that such an error reflects a misconception. For this reason, we have labeled some cases as 'random' errors or misconceptions. The Table summarises our findings.

The equilibrium constant

(1: *'random' error*) Failure to set up the correct *equilibrium expression* (the expression for the chemical-equilibrium constant). This error is rare, and occurs only in the non 1:1 stoichiometries, e.g. $N_2 + 3H_2 \rightarrow 2NH_3$. (5.0% of the students failed to set up the correct K_c expression in question 6b of Appendix 1.)

(2: *'random' error*) Failure to use *concentrations* in the equilibrium-constant expression (number of moles is used instead). Thus, 21.6% of the students made this error in question 7 (Appendix 1). This is a very serious error, which may be caused by the useful practice (at least in Greece) of working out the solution to the problem with number of moles (instead of concentrations). It is likely that this practice overloads students' working memory. Students should be urged to work systematically, by applying always the final step "*convert to concentrations*", before writing the K_c expression.

(3: *misconception*) An *increase* in *temperature* always *increases* the value of the *equilibrium constant*. In a relevant question (question 9e, Appendix 1), 62.5% of the students were found to possess this misconception. The reason for this widespread misconception may lie in the so-called "*kinetic proof of the law of chemical equilibrium*", where one equates at equilibrium the rates of the forward and the backward reaction. But from chemical kinetics, students know that an increase in temperature always results in an increase of the reaction rate. Note that a misconception ("*increasing temperature increases amount of product*") has been reported by Gorodetsky and Gussarksy (1986).

Stoichiometry

(4: *'random' error or misconception*) Errors in the calculation of *molar masses*. Thus, 8.8% of students made errors in question 1 (Appendix 1).

TABLE. *Students' errors in solving numerical chemical-equilibrium problems found in this study (percentages of students who made the errors in parentheses).*

THE EQUILIBRIUM CONSTANT

1. Failure to set up the expression for the chemical-equilibrium constant. *(5.0%)*
2. Use of number of moles instead of concentrations. *(21.6%)*
3. An increase in temperature always increases the value of the constant. *(62.5%)*

STOICHIOMETRY

4. Errors in the calculation of molar masses. *(8.8%)*
5. In the case of stoichiometries other than 1:1, errors in the stoichiometric amounts of the substances which react or are produced. *(25.0%)*
6. Failure to identify substances which are present in excess of the stoichiometric amounts. *(72.5%)*
7. The yield of the reaction is estimated from the relative amount of a reactant, which has reacted, even in cases when the particular reactant is present in excess of the stoichiometric amount. *(70.0%)*

HETEROGENEOUS EQUILIBRIA

8. Inclusion of "concentrations" of solids (in general, of species which are outside the phase in which the reaction occurs). *(17.6%)*

9. Le Chatelier's principle applies in all systems, including heterogeneous equilibrium systems. *(71.7%)*

THE DIRECTION OF A REACTION WHICH IS NOT AT EQUILIBRIUM OR THE DISTURBANCE OF CHEMICAL EQUILIBRIUM

10. Failure to correctly predict the direction of the reaction in the case of random initial amounts of reactants and products. *(50.0%)*
11. The position of equilibrium does not change if equal numbers of moles of a reactant and a product are added to a system which is at equilibrium. *(46.6%)*

GAS EQUILIBRIA AND THE IDEAL-GAS LAW

12. In the ideal-gas equation, substances, which are not in the gas phase, are also taken into account. *(79.2%)*
13. An increase in pressure results always from a corresponding decrease in volume, in accordance with Boyle's law. *(70.8%)*
14. Under constant volume and temperature, an increase in pressure is due to a decrease in the number of moles. *(73.0%)*

(5: *misconception*) In the case of stoichiometries other than 1:1, errors in the *stoichiometric amounts* of the substances, which react or are produced. Thus 25.0% of students made such errors in solving problem 2 (Appendix 2).

(6: *misconceptio*n) Failure to identify substances, which are present in excess of the stoichiometric amounts: 72.5% of the students gave wrong answers to question 9a (Appendix 1).

(7: *misconception*) The yield of the reaction is estimated from the relative amount of a *reactant*, which has reacted, even in cases when the particular reactant is present in *excess* of the stoichiometric amount. Thus in the case of question 9a (Appendix 1), 70.0% of the students identified the yield with the percentage of reactant that had reacted when equilibrium was established.

Heterogeneous equilibria

(8: *'random' error or misconception*) In the case of *heterogeneous equilibria*, inclusion in the equilibrium-constant expression of "concentrations" of *solids* (in general, of species which are outside the phase in which the reaction occurs). Thus 17.6% of students included solids in the expression for the K_c of the equilibrium $3A(g) + B(s) \rightleftharpoons C(g) + D(s)$ (Question 6c, Appendix 1).

(9: *misconception*) *Le Chatelier's principle* applies in *all systems*, including *heterogeneous-equilibrium systems*.[3] Question 9c (Appendix 1) was about the effect to the position of the equilibrium of adding excess of a solid reactant to a gaseous system at equilibrium; 71.7% of the students applied Le Chatelier's principle and arrived at the wrong conclusion. Here we have a clear misconception which has been reported previously (Wheeler & Kass, 1978; Gorodetsky & Gussarsky, 1986; Banerjee, 1991). Note that a similar finding (70% of twelfth-graders were unsuccessful) was found in the recent study in Spain by Furio *et al.* (2000).

The disturbance of chemical equilibrium

(10: *misconception or random error*) Failure to correctly predict the *direction* of the reaction in the case of *random initial amounts* of reactants and products. Thus, 50.0% of students failed in question 8 (Appendix 1). This prediction is a hard task for many students. In some cases, this error may be caused by an overload of students' working memory ('random error'). Teaching of a systematic procedure, whereby one calculates the reaction quotient Q and compares it to the corresponding K value, may facilitate the solution of such problems: if $Q < K$, the reaction proceeds to the right; if $Q > K$, the reaction proceeds to the left; and if $Q = K$, then we are at equilibrium (Dogguy *et al.*, 1993; Tyson, Treagust, & Bucat, 1999). Note that neither Le Chatelier's (qualitative) principle, nor collision theory (the changes in the rates of the forward and backward reaction) can be of help in answering question 8.

(11: *misconception*) The position of equilibrium *does not change* if *equal numbers of moles* of a *reactant* and a *product* are *added* to a system which is *at equilibrium*. Thus, 46.6% of students were found to hold this misconception in the case of question 8 (Appendix 1). Here we have a misconception caused by the very term *equilibrium*, which contains the word *equal*. The representation of chemical equilibrium in terms of a *static balance* (Gorodetsky & Gussarsky, 1986; Maskill & Cachapuz, 1989) may also be responsible; such a representation then should better be avoided.

Gas equilibria and the ideal-gas law

(12: *'random' error*) In the *ideal-gas equation*, substances, which are not in the gas phase, are also taken into account. This situation arose in the case of question 9b (Appendix 1), where 79.2% of the students included solid substances B and D in the ideal-gas equation. We then have here a very frequent 'random' error, for it is hard to attribute it to a misconception. To avoid this error, it is suggested that students must be practised to always check the validity of the ideal-gas equation (as well as the validity of any equation, Mettes *et al.*, 1980): *"Do I have an ideal gas, or an (ideal) gas mixture? Are all substances in the gas state?"*

(13: *misconception*) An *increase* in *pressure* results always from a corresponding *decrease* in *volume*, in accordance with *Boyle's law*.[4] Thus, 70.8% of students were found to hold this

misconception in the case of question 9d (Appendix 1). [In the recent Spanish study (Furio *et al.*, 2000), 38% of twelfth-graders were unsuccessful in qualitatively predicting the effect on the position of the equilibrium of a pressure increase.] Boyle's law applies only to changes of pressure and/or volume of an (ideal) gas. Here, however, we consider the effect on *chemical equilibrium* of changing the pressure. Thus an increase, say, in pressure is accomplished by proper motion of a piston, so that the volume decreases. The system will respond by tending to reduce pressure, but cannot accomplish this by changing the volume, that is by shifting the piston. The only means of reducing pressure is by reducing the number of particles, through a shift in the position of equilibrium. During this change, the total pressure of the system will be maintained constant externally, by proper adjustment of the position of the piston.

(14: *misconception*) Under *constant volume* and *temperature*, the *increase* in *pressure* is due to the *decrease* in the number of *moles*. Thus, 73.0% of students were found to hold this misconception in the case of question 5 (Appendix 1). This misconception results obviously from a wrong application of Boyle's law - see error # 13: "the decrease in volume can be effected by a corresponding decrease in the number of moles".

DISCUSSION AND IMPLICATIONS FOR INSTRUCTION

Hackling and Garnett (1985) identified four areas in chemical education that present great conceptual difficulties: the mole concept, reaction stoichiometry, oxidation and reduction, and chemical equilibrium. From the four, chemical equilibrium is deemed the most demanding. Now, it is not unusual in schools to go hastily over the basic theoretical concepts of a unit, and then to start solving numerical problems.

Chemical-equilibrium problems involve not only the concepts that are unique to it, but also other concepts such as the mole and reaction stoichiometry, gases and the ideal gas law. It is not then surprising that students encounter numerous difficulties in solving such problems. In stoichiometric calculations, analogical reasoning is involved, and this is an ability lacking or not well developed with some students (Shayer, 1991). In addition, students find it hard to understand that the change in the total number of moles that may occur as a result of a reaction is due to a different grouping of the atoms in the reactants and the products. When gases are involved, we have extra difficulties, apart from the one related to the change of the total volume.

The application of the Chatelier's principle (qualitative statement[3]), although not entirely necessary in problem solving, can be confusing in cases when it is used for the prediction of the direction (forward or backward) of the reaction or for the evaluation of a calculated result. Knox (1985) has provided a useful analysis of the effect of an increase in pressure to the equilibrium of the reaction for the synthesis of ammonia. In that, Boyle's law is not followed quantitatively, while it is demonstrated that Le Chatelier's principle cannot be applied for the partial pressures or for the total pressure, or for concentrations. It is the number of moles and mole fractions for which the principle can be applied. Another related misconception is the application of Le Chatelier's principle for predicting the effect of changing the temperature on the rate of reaction (Tsaparlis, 1985).[1]

Besides Le Chatelier's principle, the dynamic nature of the chemical equilibrium is a hard concept that can be the cause of difficulties in problem solving, especially when dealing with the direction of a reaction or the disturbance of equilibrium. Compartmentalisation of the two sides of the reaction (Johnstone, MacDonald, & Webb 1977; Cachapuz & Maskill, 1989) can also lead to erroneous situations in problem solving. This one-sidedness can be caused by the use of certain analogies and models (Johnstone, MacDonald, & Webb 1977).

Turning to the implications for instruction, one should pay special attention to all concepts (the mole, stoichiometry, gas laws, chemical equilibrium etc.) when dealing with the theory of chemistry. The bibliography of chemistry education is now rich with work that lists students' misconceptions and alternative conceptions with various chemical topics that are related to chemical equilibrium (see the introduction to this paper). In our opinion, special attention should also be paid to the treatment of the changes of gases, and in particular to the effect on partial pressures of the change in the number of moles. On the other hand, one should also consider the alternative suggestion by Niaz (1995), that problem solving should precede conceptual questions, not only because the latter can be more demanding, but also because the practice of algorithms can be conducive to the subsequent concept learning.

Particular attention should be paid to the effect of psychometric factors such as developmental level, working-memory capacity, mental capacity, and degree of field dependence/independence (Tsaparlis, Kousathana, & Niaz, 1998). Consequently, it is recommended that attention should be concentrated on the proper manipulation of the logical structure of these problems and of their mental demand, increasing these gradually, so that to avoid overloading the working memory of many students.

Finally, although the use of algorithms is still at the heart of teaching and learning practice throughout the world, there is consensus among educators that the emphasis should be moved away from learning to use complex algorithms, into activities that require higher-order cognitive skills (Zoller & Tsaparlis, 1997). Conceptual understanding may not be a prerequisite for applying algorithms, but it is very likely that if such understanding does exist, students are more capable of dealing with more demanding problems that require them to have overcome misconceptions and alternative conceptions. As such, it calls for the thorough investigation of the factors affecting it, as well as of the factors that differentiate it from novel problem solving.

CORRESPONDENCE: *Georgios TSAPARLIS, University of Ioannina, Department of Chemistry, GR-451 10 Ioannina, Greece; fax: +30 6510 98798; e-mail: gtseper@cc.uoi.gr*

NOTES

1. In a study of conceptual difficulties in chemistry among upper-secondary (twelfth-grade) students in Greece (Tsaparlis, 1985), students were highly successful in correctly applying Le Chatelier's principle for predicting the change in the yield of a reaction that is due to a change (increase) in temperature [82.4% ($N = 85$) correct answers for the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + q$ (heat) (**Question *a***)] or in total pressure [80.0% correct answers for the equilibrium $SO_2(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$].

What, however, was surprising was the performance in predicting the effect of increasing the temperature to the rate of the reaction $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ (**Question *b***): 45.9% (39 students) correct answers, 48.2% (41 students) wrong answers, 5.9% (5 students) no answer. From 9 students who had answered wrongly in Question b that the rate would decrease, 8 students had also answered (Question a, that time correctly) that the yield of the same reaction would decrease. On the other hand, from 12 students who had answered wrongly that the yield would increase: 6 students had also answered (this time correctly) that the rate would increase; 3 students that it would not change; 1 student that it would decrease; and 2 students did not answer. Finally, from 70 students who had answered correctly that the

yield would decrease: 31 students answered also correctly that the rate would increase; 27 students that it would not change; 8 students that it would decrease; and 4 students did not answer.

It is observed that many students in our Greek sample, of the early 80s, failed to grasp the fact that reaction yield and reaction rate are different concepts that are not directly related to each other. [Indirectly there is a link: for instance, in an exothermic reaction, the heat that is 'evolved', unless 'absorbed' by (transferred to) a heat reservoir, increases the rate of the further reaction.] Note that the misconception "*Rate of reaction means the same as extent of reaction*" is among those mentioned in the review by Griffiths (1994).

More specifically, in our 1985 study, we found the following misconception:

"*Le Chatelier's principle is applied to reaction rates too*".

This misconception is made clearer if we observe that the mere neglect in the chemical equation of the reaction heat (the $+q$ in our case: compare **Questions *a*** and ***b***) is interpreted by many students to mean that the reaction is thermoneutral (neither endothermic nor exothermic), therefore … "the reaction rate is not affected by a change in temperature, in accordance (apparently) with Le Chatelier's principle". We may have here then another hidden misconception: "*heat is evolved or absorbed only in the cases that heat is explicitly involved (that is, shown) in the chemical equation ('thermochemical' equation)*".

2. A first presentation of the results of this work was made at the 3rd ECRICE (Tsaparlis & Kousathana, 1995).

3. The principle of Le Chatelier is a useful principle which however has many qualitative as well as quantitative statements (Solaz & Quilez, 2001, and references therein). In Pauling and Pauling (1975, p. 338) the principle is stated qualitatively as follows: "*if the conditions of a system, initially, at a equilibrium, are changed, the equilibrium will shift in such a direction as to tend to restore the original conditions, if such a shift is possible*". The students of our sample were taught the following qualitative statement of this principle: "*Every change of one of the factors of chemical equilibrium (temperature, pressure, concentration) causes a shift in the equilibrium of the system in the direction which tends to cancel the change being made*" (Sakellarides, 1992, p. 30, translated from Greek).

4. Boyle's law states that with temperature constant and number of moles constant: $PV =$ constant. Applied to two states of a system, initial 1 and final 2, this law becomes $P_1V_1 = P_2V_2$.

APPENDIX 1: THE TEST USED IN THE STUDY

1) How many moles are a) 0.64 g CH_3OH; b) 336 L $COCl_2$ (in stp)?
2) How many moles of oxygen gas are contained in a 4 L vessel at 727^oC and at a pressure of 16.4 atm?
3) In a vessel, 10 moles of a gas mixture are contained, consisting of N_2, O_2, and NO in proportions 1:2:2. Calculate the moles of O_2 present.
4) N_2 reacts with H_2 according to the reaction: $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$. Calculate the moles of N_2 and H_2 that must react for 10 mol NH_3 to be formed.
5) In a vessel of volume 10 L, 5 mol PCl_5, 3 mol PCl_3, plus 2 mol Cl_2 are introduced at 1000 K. A manometer shows a gradual increase of pressure. Explain the reason for the observed increase in pressure. [The equilibrium is: $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.]
6) Write the expressions for the equilibrium constant K_c for the following equilibria:
   $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$;
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$;
   $3A(g) + B(s) \rightleftharpoons C(g) + D(s)$.
7) In a vessel of volume 10 L, 10 mol NH_3, 2 mol N_2, and 1 mol H_2 are present at equilibrium. Calculate the value of the equilibrium constant K_c for the equilibrium
   $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.
8) In a vessel of volume 1 L, 3 mol $COCl_2$, 2 mol CO, and 1 mol Cl_2 are present at equilibrium: $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$. If 1 mol $COCl_2$ plus 1 mol CO are added in the vessel, what will happen to the amount of Cl_2 in the vessel: Will it increase or decrease? Explain.
9) Consider the following (exothermic in the forward direction) equilibrium: $3A(g) + 4B(s) \rightleftharpoons 2C(g) + D(s) + heat (q)$. Initially, 3 mol A and 3 mole B are placed in the reaction vessel. When equilibrium has been established, it is found that 0.3 mol A has reacted.
   a) Calculate the yield of the reaction;
   b) given that the volume of the vessel is $V = 10$ L and the temperature is kept constant at 1000 K, calculate the pressure at equilibrium;
   c) if a considerable amount of B is added at equilibrium, how the equilibrium is going to shift?
   d) if we increase the pressure at equilibrium, how the equilibrium is going to shift?
   e) if we increase the temperature at equilibrium, how this is going to affect the yield of the reaction?

APPENDIX 2: EXAMPLES OF PROBLEMS USED IN THE STUDY

1. In a vessel of fixed volume $V = 4.5$ L, 198 g $COCl_2$ plus 44.8 L CO (in stp) are introduced. The mixture is heated to 1000^oC, and let to reach the equilibrium: $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$. Calculate the equilibrium constant K_c, taking into account that at equilibrium the total pressure of the gas mixture is 82 atm, at 1000^oC.

2. In a vessel of fixed volume $V = 10$ L, an undetermined amount of NH_3, plus 9 mol of a mixture of N_2 plus H_2 at the ratio 1:2 are introduced. The temperature is maintained constant at 1000^oC. An increase in the total pressure in the vessel is observed, until the total pressure becomes stable at 155.8 atm. At this time, 6 mol NH_3 are present in the vessel. To this equilibrium mixture, 1 mol H_2 plus 2 mol NH_3 are added. Examine whether the amount of N_2 in the vessel will increase or decrease, in comparison with its amount at the previous equilibrium condition. Calculate also the initial amount of NH_3.

REFERENCES

Banerjee, A. C. (1991). Misconceptions of students and teachers in chemical equilibrium. *International Journal of Science Education, 13*, 487-494.

Cachapuz, A.F.C. & Maskill, R. (1989). Using word association in formative classroom tests: Following the learning of Le Chatelier's principle. *International Journal of Science Education, 11*, 235-246.

Camacho, M., & Good, R. (1989). Problem solving and chemical equilibrium: Successful versus unsuccessful performance. *Journal of Research in Science Teaching, 26*, 251-272.

Dogguy, L. Mayrargue Kodja, A., & Boujlel, K. (1993). Une approche concrète pour mieux faire assimiler les notions d' évolution et d' équilibre. *Actes de 1st ECRICE, Le Bulletin du CIFEC*, Numéro Hors Série, *Vol. II*, 26-31. Montpellier, France: Centre International Francophone pour l' Education en Chimie.

Furio, C., Calatayud, M.L., Barcenas, S.I., & Padilla, O.M. (2000). Functional fixedness and functional reduction as common sense reasonings in chemical equilibrium and in geometry and polarity of molecules. *Science Education, 84*, 545-565.

Gabel, D.L., Sherwood, R.D., & Enochs, L. (1984). Problem-solving skills of high school chemistry students. *Journal of Research in Science Teaching, 21*, 211-233.

Garnett, Pamela, J., Garnett, Patrick J., & Hackling, M.W. (1995). Students' alternative conceptions in chemistry: A review of research and implications for teaching and learning. *Studies in Science Education, 25*, 69-95.

Gorodetsky, M. & Gussarsky, E. (1986). Misconceptions of the chemical equilibrium concept as revealed by different evaluation methods. *European Journal of Science Education, 8*, 427-441.

Griffiths, A.K. (1994). A critical analysis and synthesis of research on students' chemistry misconceptions. In: H.-J. Schmidt (Ed.), *Problem solving and misconceptions in chemistry and physics*, p.p. 70-99. ICASE.

Gussarsky, E. & Gorodetsky, M. (1988). On the chemical equilibrium concept. Constrained word association and conception. *Journal of Research in Science Teaching, 25*, 319-333.

Hackling, M.W. & Garnett, P. (1985). Misconceptions of chemical equilibrium. *European Journal of Science Education, 7*, 205-214.

Johnstone, A. H., MacDonald, J. J., & Webb, G. (1977). Chemical equilibrium and its conceptual difficulties. *Education in Chemistry, 14*, 169-171.

Kempa, R.F. (1991). Students' learning difficulties in science: Causes and possible reasons. *Ensenanza de las Ciencias*, *9*, 119-128.

Knox, K. (1985). Le Chatelier's principle. *Journal of Chemical Education, 62,* 863.

Maskill, R. & Cachapuz, A.F.C. (1989). Learning about the chemistry topic of equilibrium: The use of word-association tests to detect developing conceptualisations. *International Journal of Science Education, 11*, 57-69.

Mettes, C.T.C.W., Pilot, A., Roosink, H.J., & Kramers-Pals, H. (1980). Teaching and learning problem solving in science. Part I. A general strategy. *Journal of Chemical Education, 57*, 882-885.

Niaz, M. (1995). Relationship between student performance on conceptual and computational problems of chemical equilibrium. *International Journal of Science Education, 17*, 343-355.

Niaz, M. (2001). Response to contradiction: Conflict resolution strategies used by students in solving problems of chemical equilibrium. *Journal of Science Education and Technology, 10*, 205-211.

Pauling, L. & Pauling P. (1975). *Chemistry*. San Francisco: Freeman and Company.

Pedrosa, M.A. & Dias, M.H. (2000). Chemistry textbook approaches to chemical equilibrium and student alternative conceptions. *Chemistry Education: Research and Practice in Europe (CERAPIE), 1*, 227-236. [http://www.uoi.gr/conf_sem/cerapie]

Quilez-Pardo, J. & Solaz-Portoles, J.J. (1995). Students' and teachers' misapplication of Le Chatelier's principle: Implication for the teaching of chemical equilibrium. *Journal of Research in Science Teaching, 32*, 937-957.

Sakellarides, P.O. (1985). Chemistry for 3rd grade upper secondary school (in Greek). Athens: The Eugenides Foundation ("Eugenideion Hidryma").

Shayer, M. (1991). Improving standards and the national curriculum. *School Science Review, 72* (260), 15-24.

Solaz, J.J. & Juan Quilez, J. (2001). Changes of extent of reaction in open chemical equlibria. *Chemistry Education: Research and Practice in Europe* (*CERAPIE*), *2*, 303-312. [http://www.uoi.gr/conf_sem/cerapie]

Tsaparlis, G. (1985). Some of the difficulties of chemistry in upper secondary school (in Greek). *Synchroni Ekpaideusi*, No. 24, 40-48.

Tsaparlis, G. & Kousathana, M. (1995a). Students' common errors and misconceptions in solving molecular-equilibrium problems. In R.M. Janiuk (ed.), *Proceedings of IIIrd European Conference on Research in Chemical Education* (3rd ECRICE), pp. 309-313. Lublin-Kazimierz, Poland: Maria Curie-Sklodowska University.

Tsaparlis, G. & Kousathana, M. (1995b). Manipulation of the logical structure and of the M-demand of molecular-equilibrium problems. In R.M. Janiuk (ed.), *Proceedings of IIIrd European Conference on Research in Chemical Education* (3rd ECRICE), pp. 305-308. Lublin-Kazimierz, Poland: Maria Curie-Sklodowska University.

Tsaparlis, G., Kousathana, M., & Niaz, M. (1998*).* Molecular-equilibrium problems: Manipulation of the logical structure and of *M*-demand, and their effect on student performance. *Science Education*. *82*, 437-454.

Tyson, L., Treagust, D.F., & Bucat, R.B. (1999). The complexity of teaching and learning chemical equilibrium. *Journal of Chemical Education, 76*, 554-558.

Van Driel, J.H., De Vos, W., & Verloop, N. (1998). Relating students' reasoning to the history of science: The case of chemical equilibrium. *Research in Science Education*, *28*, 187-1198.

Voska, K.W. & Heikkinen, H.W. (2000). Identification and analysis of student conceptions used to solve chemical equilibrium problems. *Journal of Research in Science Teaching, 37*, 160-176.

Wheller, A.E. & Kass, H. (1978). Student misconceptions in chemical equilibrium. *Science Education, 62*, 223-232.

Wilson, J.M. (1994). Network representations of knowledge about chemical equilibrium. *Journal of Research in Science Teaching, 31*, 1133-1147.

Zoller, U. & Tsaparlis, G. (1997). Higher and lower-order cognitive skills: The case of chemistry. *Research in Science Education, 27*, 117-130.