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## TEACHERS' MISCONCEPTIONS ABOUT THE EFFECTS OF ADDITION OF MORE REACTANTS OR PRODUCTS ON CHEMICAL EQUILIBRIUM

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**ABSTRACT.** The importance of research on misconceptions about chemical equilibrium is well recognized by educators, but in the past, researchers' interest has centered on student misconceptions and has neglected teacher misconceptions. Focusing on the effects of adding more reactants or products on chemical equilibrium, this article discusses the various misconceptions held by high school teachers. A misconception test was administered to two samples of chemistry teachers in Nanjing, China. Of the 109 teachers who participated in the test, only one understood that adding more CS<sub>2</sub> gas to the equilibrium system  $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) = \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$  at constant pressure and temperature can shift the equilibrium to the reactant or product side, depending upon the amount of CS<sub>2</sub> in the initial equilibrium system. Most of the teachers relied on Le Châtelier's principle and thus made erroneous predictions. The misconception test also revealed that those teachers who managed to compute equilibrium constants had a limited conceptual understanding of chemical equilibrium. Implications of these findings for teacher education and chemistry curriculum development are discussed.

**KEY WORDS:** chemical equilibrium, Le Châtelier's principle, teacher knowledge, teacher misconceptions

### INTRODUCTION

A deep understanding of how various factors affect a chemical system at equilibrium is important. Altering the positions of chemical equilibria in industrial processes is one of the key tasks carried out by chemical engineers, who attempt to produce more of the desired products efficiently and economically by manipulating the conditions under which the chemical equilibria occur. For example, the Haber process is used to manufacture ammonia fertilizers from hydrogen and nitrogen. Under less than desirable conditions, only about 10% yield of ammonia is obtained at equilibrium.

Unfortunately, most high school and college chemistry textbooks rely on Le Châtelier's principle (LCP) to predict the direction in which a chemical equilibrium will shift when it is disturbed. In the USA, for example, two textbooks present the following misleading information

about the effects of adding more reactants or products to a chemical system, initially at equilibrium:

Le Châtelier's principle states that the shift will be in the direction that minimizes or reduces that effect of the change. Therefore, *if a chemical system is at equilibrium and we add a substance (either a reactant or a product), the reaction will shift so as to reestablish equilibrium by consuming part of the added substance. Conversely, removing a substance will cause the reaction to move in the direction that forms more of that substance* (Brown, LeMay, Bursten & Murphy, 2006, p. 650; emphasis in original).

So another way of stating Le Châtelier's principle is to say that *if a component (reactant or product) is added to a reaction system at equilibrium (at constant  $T$  and  $P$  or constant  $T$  and  $V$ ), the equilibrium position will shift in the direction that lowers the concentration of that component. If a component is removed, the opposite effect occurs* (Zumdahl & Zumdahl, 2007, p. 606; emphasis in original).

It is important to note that the above predictions based on LCP may conflict with experimental facts. If the amount of products formed by a reversible chemical reaction is not equal to the amount of reactants, adding more reactant at constant pressure and temperature may shift a gaseous chemical equilibrium to the reactant rather than the product side (Cheung, 2004). LCP fails to predict such an equilibrium shift. Actually, chemistry education researchers and chemists have known of the scientific inadequacies of LCP for about 100 years (Allsop & George, 1984; Bridgart & Kemp, 1985; Canagaratna, 2003; De Heer, 1957, 1958; Ehrenfest, 1911; Epstein, 1937; Gold & Gold, 1984, 1985; Katz, 1961; Lacy, 2005; Levine, 2002; Posthumus, 1933; Quílez, 2004; Raveau, 1909; Sandler, 1999; Solaz & Quílez, 2001; Solaz-Portolés & Quílez-Pardo, 1995; Torres, 2007; Uline & Corti, 2006; Wright, 1969). They have shown how apparently reasonable applications of LCP can lead to incorrect predictions about the effects of changes in concentration, volume, pressure, or temperature on chemical systems at equilibrium. Yet textbook writers are generally unaware of the inadequacies of LCP.

Because most teachers use textbooks as their major source of information to prepare classroom teaching, our concern is that the misleading ideas presented by textbook writers such as Brown, LeMay, Bursten & Murphy (2006) and Zumdahl & Zumdahl (2007) may cause teachers to hold misconceptions about chemical equilibrium. This is critically important because chemistry teachers cannot help students understand what they themselves do not understand. They should be knowledgeable about the key chemical-equilibrium concepts and the strategies for teaching them. Gess-Newsome (1999) reviewed the

literature on teachers' subject matter knowledge and summarized its effects on student learning as follows:

For instance, from this review, teachers having low levels of subject matter knowledge often teach for factual knowledge, involve students in lessons primarily through low-level questions, are bound to content and course structures found in textbooks, have difficulty identifying student misconceptions, and decrease student opportunities to freely explore the content either through manipulatives or active discussion (pp. 82–83).

Although chemical equilibrium is a very important topic in the high school or college chemistry curriculum, both practicing and prospective teachers are generally weak in their subject matter knowledge (Banerjee, 1991; Ganaras, Dumon & Larcher, 2008; Özmen, 2008; Quílez, 2004; Quílez-Pardo & Solaz-Portolés, 1995). How well do high school chemistry teachers understand the effects of adding more reactants or products on the position of equilibrium? What are the major misconceptions held by high school chemistry teachers? Research into these questions is not abundant. To our knowledge, only five previous studies (Banerjee, 1991; Özmen, 2008; Piquette & Heikkinen, 2005; Quílez, 2004; Quílez-Pardo & Solaz-Portolés, 1995) assessed how LCP affects teacher understanding of the effects of addition of more reactants or products on chemical equilibrium. Although these five studies are useful, they have not documented and discussed the nature of teachers' misconceptions in detail. The aim of the present study was to probe teachers' misconceptions concerning the effects of addition of more reactants or products on chemical equilibrium. This article is organized in four parts. First, the relevant literature is reviewed to synthesize the findings obtained in previous research, focusing on empirical studies conducted to assess teachers' misconceptions about chemical equilibrium. Second, we describe our method used to investigate the misconceptions held by high school chemistry teachers in Nanjing, China. Third, we present and discuss the results. Finally, the article concludes with a discussion of the implications of our findings for teacher education and chemistry curriculum development.

#### PREVIOUS RESEARCH

In India, Banerjee (1991) constructed several multiple-choice items to assess teachers' misuse of LCP to predict equilibrium shifts concerning the reversible reaction  $\text{CO(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{COCl}_2\text{(g)}$ . The items were administered to 40 secondary school chemistry teachers with B Sc and B

Ed degrees in chemistry and to 29 senior secondary chemistry teachers with M Sc and B Ed degrees in chemistry. Widespread misconceptions among teachers were found by Banerjee. For example, one of the items asked the 69 teachers to predict the change in mass of CO if some  $\text{Cl}_2$  is removed from the equilibrium system  $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$  at constant volume and temperature. Only 49% of the teachers understood that when the equilibrium is reestablished, the mass of CO will be greater than that in the initial equilibrium state. However, Banerjee did not delineate the nature of the misconceptions held by those teachers who had failed to predict the equilibrium shift correctly.

In Spain, Quílez-Pardo & Solaz-Portolés (1995) assessed 40 chemistry teachers (23 from high school and 17 from university). All of the teachers had at least 5 years of teaching experience in chemistry. The assessment consisted of three questions about addition of more reactant or product to the heterogeneous equilibrium system  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ . The numbers of moles of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  in the equilibrium system were  $1.65 \times 10^{-2}$  mol and  $1.10 \times 10^{-2}$  mol, respectively. The first question required the teachers to explain how the position of equilibrium would be changed by adding  $\text{H}_2\text{S}$  gas at constant pressure and temperature. A total of 80% of the teachers predicted a shift of the equilibrium to the reactant side, and 40% of the teachers applied LCP to explain the shift. Actually, the application of LCP results in two opposite equilibrium shifts as the partial pressure of  $\text{H}_2\text{S}$  increases but the partial pressure of  $\text{NH}_3$  decreases. Only 15% of the teachers indicated that the position of equilibrium can be shifted to the reactant or product side. The second question asked the teachers to explain how the position of equilibrium would be changed by adding solid  $\text{NH}_4\text{HS}$  at constant pressure and temperature. A total of 95% of the teachers were able to answer correctly (i.e., no change in the position of equilibrium). The third question asked the teachers to solve a chemical equilibrium problem quantitatively. They needed to find out the new equilibrium composition of the gaseous mixture after  $1.35 \times 10^{-2}$  mol of  $\text{H}_2\text{S}$  is added to  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$  at constant pressure and temperature. Eighty percent of the teachers appeared to use LCP as their basis of reasoning, saying that the increased amount of  $\text{H}_2\text{S}$  would increase its concentration or partial pressure, which in turn would decrease by producing more solid  $\text{NH}_4\text{HS}$ . Only one teacher (2.5%) managed to solve this equilibrium problem successfully using the equilibrium constant expression, and only four teachers (10%) reported that the results were inconsistent with those predicted by LCP. Thus, Quílez-Pardo and Solaz-Portolés concluded that teachers and students had similar misconceptions about LCP and students' misapplication of LCP may have resulted from their teachers' instructions.

Using an open-ended question, Quílez (2004) assessed the ability of 31 in-service Spanish chemistry teachers and 20 pre-service Spanish chemistry teachers to explain how the partial pressure of HBr would be changed if  $\text{NH}_3$  is added to the heterogeneous equilibrium system,  $\text{NH}_4\text{Br}(s) \rightleftharpoons \text{NH}_3(g) + \text{HBr}(g)$ , at a constant volume and temperature. The in-service teachers had at least 5 years of teaching experience in chemistry. Quílez found that 71% of the in-service teachers and 50% of the pre-service teachers answered correctly (i.e., the partial pressure of HBr is lower than the initial value when the equilibrium is reestablished). Quílez also reported that 58% of the in-service teachers and 55% of the pre-service teachers applied LCP to make their predictions.

In the USA, Piquette & Heikkinen (2005) assessed the ability of general chemistry instructors to predict changes in chemical equilibrium when more reactant or product is added. Their sample consisted of 52 general chemistry instructors from 50 colleges and universities. They devised two questions with hypothetical responses written by general-chemistry students. The 52 chemistry instructors were invited to evaluate the correctness of these hypothetical responses. The first question focused on the heterogeneous equilibrium system  $\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$ , which required students to predict any change in the concentration of barium ions when solid barium sulfate is added to the system at a constant temperature. The hypothetical student response constructed by Piquette and Heikkinen was: "Eventually the concentration of barium ions will increase because Le Châtelier's Principle says that if you put a stress on a system at equilibrium, it will shift to compensate. The extra solid barium sulfate causes the reaction to shift to the right and produce more of each ion and a new equilibrium" (p. 1129). Piquette and Heikkinen found that none of the 52 instructors failed to recognize the error in the hypothetical student response. The second question involved the homogeneous chemical equilibrium  $\text{PCl}_5(g) \rightleftharpoons \text{PCl}_3(g) + \text{Cl}_2(g)$ , which required students to predict any change in the value of the equilibrium constant,  $K_c$ , if more chlorine gas is added to the system at a constant volume and temperature. The hypothetical student's response devised by Piquette & Heikkinen was: "The value of  $K_c$  will not change because equilibrium constants are always the same value for a particular system under various conditions" (p. 1131). Fifty of the instructors understood the constancy of the equilibrium constant at constant temperature. Only two instructors incorrectly evaluated the hypothetical student's answer and Piquette and Heikkinen thought that these two instructors may have misread the question. Thus, they concluded that the instructors possessed adequate chemical-equilibrium content knowledge.

Recently, Özmen (2008) used multiple-choice items to assess 90 Turkish prospective teachers' understanding of chemical equilibrium. One item was about the effect of removing some solid  $\text{CaCO}_3$  from the system  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$ . A total of 75.5% of teachers understood that the equilibrium will not be disturbed. Another item also focused on the same system but asked teachers to predict the change in the equilibrium concentration of carbon dioxide when an extra solid,  $\text{CaCO}_3$  is added to the system. Özmen reported that 78.8% of teachers got the correct answer (i.e., the concentration remains unchanged).

In summary, the results of the above five previous studies (Banerjee, 1991; Özmen, 2008; Piquette & Heikkinen, 2005; Quílez, 2004; Quílez-Pardo & Solaz-Portolés, 1995) indicated that chemistry teachers generally understand that if more solid reactant is added to a heterogeneous equilibrium system, LCP should not be applied to predict the change in concentration of a chemical species. Similarly, LCP should not be applied to predict the effects of removing some solid reactant from a heterogeneous equilibrium system. Most teachers also understand that adding more products to a gaseous equilibrium system at a constant volume and temperature will not change the value of the equilibrium constant. However, teachers generally do not understand that if the amount of gaseous products formed by a reversible chemical reaction is not equal to the amount of gaseous reactants, the following two chemical concepts are important:

- Adding more reactants to a chemical equilibrium at a constant pressure and temperature may shift the equilibrium position to the reactant rather than the product side, but LCP fails to predict such an equilibrium shift.
- Adding more products to a chemical equilibrium at a constant pressure and temperature may shift the equilibrium position to the product rather than the reactant side, but LCP fails to predict such an equilibrium shift.

## METHOD

### *The Context*

This study was conducted in Nanjing located in the Jiangsu Province of China. It is a city 1,100 km away from Beijing, which is the capital city of China. The population in Nanjing is about 7 million. There are about 100 high schools in Nanjing. Secondary schooling consists of 6 years (Secondary 1–6), and chemistry is offered as a separate subject to Secondary 3–6 year students (approximately 15–18 years of age). The

principles of chemical equilibrium are taught by teachers in the Secondary year 5. Most of the high school chemistry teachers have a B Sc degree with a major in chemistry education.

### *Samples, Instrument, and Data Collection*

In October 2007, we invited a convenience sample of 59 high school chemistry teachers to respond to the following equilibrium problem when they participated in some in-service professional development activities at a high school in Nanjing. The aim of the test was to assess whether they understood the effect of adding more reactant on the position of equilibrium. The test lasted for 10 min. The problem was in Chinese and adapted from Cheung (2004). It has been translated into English for reader information.

#### Problem #1.

The reaction  $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$  is at equilibrium in a vessel fitted with a movable piston. If a small amount of  $\text{CS}_2(\text{g})$  is suddenly added to the equilibrium mixture at constant temperature and pressure, what will happen to the number of  $\text{CH}_4(\text{g})$  molecules when equilibrium is reestablished? Give reasons for your answer.

After the first survey, we expanded the scope of the misconception test by including a question used in the study conducted by Quílez-Pardo & Solaz-Portolés (1995). Answers to both problems #1 and #2 were collected in November 2007 when 50 chemistry teachers who had not participated in the first survey attended an in-service workshop at a high school in Nanjing. The second test lasted for 15 min. Therefore, a total of 109 teachers responded to problem #1, while 50 teachers responded to problem #2. The teaching experiences of the 109 chemistry teachers ranged from 2 to 41 years, with a mean equal to 12.0 years.

#### Problem #2.

The reaction  $\text{NH}_4\text{HS}(\text{s}) \rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$  is at equilibrium in a vessel fitted with a movable piston. The numbers of moles of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  in the equilibrium mixture are  $1.10 \times 10^{-2}$  mol and  $1.65 \times 10^{-2}$  mol, respectively. The total volume of the gaseous mixture is 1.0 L. What will happen if  $1.35 \times 10^{-2}$  mol of  $\text{H}_2\text{S}$  gas is suddenly added to the equilibrium system at constant temperature and pressure? Clearly show your calculations.

### *Data Analysis*

The answers given by the 109 chemistry teachers were content analyzed, focusing on the different types of explanations offered by the teachers when they responded to each equilibrium problem. The different types of



explanations formed the coding categories in the present study. The first and third authors coded the teacher responses together. For each answer sheet, we compared and discussed the allocation of codes until a consensus was reached.

## RESULTS AND DISCUSSION

### *Teacher Responses to Problem #1*

Analysis of the content of teachers' answer sheets revealed that only one out of the 109 teachers correctly stated that the number of  $\text{CH}_4$  molecules in the new equilibrium state is affected by the amount of  $\text{CS}_2$  in the initial equilibrium mixture. A total of 64 teachers expected the number of  $\text{CH}_4$  molecules to increase, 25 teachers indicated a decrease in the number of  $\text{CH}_4$  molecules, 18 teachers thought that the number of  $\text{CH}_4$  molecules is not predictable, and one teacher did not comment on the change in the amount of molecules.

The finding that only one teacher solved problem #1 correctly is alarming in view of the supposedly strong knowledge base of chemistry teachers in Nanjing, China. But our finding is consistent with those obtained by Quílez-Pardo & Solaz-Portolés (1995) in Spain. We found that few of the 109 teachers had applied the equilibrium law or the concept of reaction quotient to tackle problem #1: the majority of teachers reasoned in terms of the 'stress-then-counteract' logic of LCP even though many teachers did not explicitly put down LCP in their answers. One possible explanation is that textbook writers (e.g., Ash & Hill, 2008; Irwin, Farrelly, Vitlin & Garnett, 2006; Van Kessel, Jenkins, Davies, Plumb, Di Giuseppe, Lantz & Tompkins, 2003) often do not apply the equilibrium law and reaction quotient to analyze how equilibria respond to changes in pressure, volume, or concentration of reactants and products. For example, the textbook written by Irwin et al. (2006) introduces both LCP and reaction quotient. Yet it gives a four-page discussion of the use of LCP to predict how changes in pressure, volume, and concentration affect equilibrium position without mentioning reaction quotient. This wastes the opportunities to demonstrate the usefulness of reaction quotient. The fundamental concepts of chemical equilibrium are thus neglected in favor of LCP.

Owing to a limitation of space, we cannot describe all the teachers' misconceptions in detail here. Instead, we have focused on those major misconceptions held by at least six teachers. Table 1 shows the correct



TABLE 1  
Coded responses to the first problem

Code	Teacher response	No. of teachers
IA1	The $K_c$ expression is applied correctly to predict the equilibrium shift. The number of $\text{CH}_4$ molecules may increase or decrease, depending upon the amount of $\text{CS}_2$ in the initial equilibrium mixture.	1
IB1	LCP predicts that the equilibrium will shift to the right to minimize the effect of the addition of $\text{CS}_2$ . The number of $\text{CH}_4$ molecules will increase.	2
IB2	Because the amount of $\text{CS}_2$ is increased, the equilibrium will shift to the right to oppose such a change.	3
IB3	The number of $\text{CH}_4$ molecules will increase. Because $[\text{CS}_2]$ is increased, the equilibrium will shift to the right to minimize the impact. The number of $\text{CH}_4$ molecules will increase.	15
IB4	The equilibrium shifts to the right. The number of $\text{CH}_4$ molecules will increase. No further explanation.	24
IB5	Two changes are involved: addition of $\text{CS}_2$ , and an increase in volume. The overall shift is to the right. The number of $\text{CH}_4$ molecules will increase.	5
IB6	Because the volume is increased, the equilibrium will shift to reduce the volume. The number of $\text{CH}_4$ molecules will increase.	3
IC1	The volume is increased. $[\text{H}_2]$ is decreased. LCP predicts that the equilibrium will shift to the left. The number of $\text{CH}_4$ molecules will decrease.	5
IC2	The volume is increased. The equilibrium will shift to the left. The number of $\text{CH}_4$ molecules will decrease.	5
IC3	$[\text{CS}_2]$ and the total volume are increased. $K_c = \frac{[\text{CH}_4][\text{H}_2\text{S}]^2}{[\text{CS}_2][\text{H}_2]^4}$ . Because the exponent of $\text{H}_2$ in $[\text{H}_2]^4$ is 4, the value of $[\text{H}_2]^4$ is significantly reduced. Thus, the equilibrium will shift to the left to increase $[\text{H}_2]$ . The number of $\text{CH}_4$ molecules will decrease.	6
ID1	LCP predicts two opposite equilibrium shifts. Thus, the number of $\text{CH}_4$ molecules is not predictable.	11

answer to problem #1 and the prevalent misconceptions held by teachers. This section presents and discusses excerpts from teachers' written responses to illustrate the solution path as well as the nature of misconceptions.

*Correct Answer.* As can be seen in Table 1, only one teacher (Code 1A1) applied reaction quotient,  $Q_c$ , successfully to give an acceptable answer to problem #1. The teacher set up the  $Q_c$  expression for  $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$  as follows:

$$Q_c = \frac{[\text{CH}_4][\text{H}_2\text{S}]^2}{[\text{CS}_2][\text{H}_2]^4} = \frac{\left(\frac{n_{\text{CH}_4}}{V}\right)\left(\frac{n_{\text{H}_2\text{S}}}{V}\right)^2}{\left(\frac{n_{\text{CS}_2}}{V}\right)\left(\frac{n_{\text{H}_2}}{V}\right)^4} = \frac{(n_{\text{CH}_4})(n_{\text{H}_2\text{S}})^2(V)^2}{(n_{\text{CS}_2})(n_{\text{H}_2})^4}$$

where  $V$  is the total volume of the gaseous mixture,  $n_{\text{CH}_4}$  is the number of moles of  $\text{CH}_4$ , and so on. If a small amount of  $\text{CS}_2$  gas is added at constant pressure and temperature, both the number of moles of  $\text{CS}_2$  and the total volume must increase. Therefore, the new position of equilibrium will depend upon the ratio,  $V^2/n_{\text{CS}_2}$ , in the above  $Q_c$  expression. The teacher specified the conditions clearly. If the new ratio,  $V^2/n_{\text{CS}_2}$ , is greater than the original ratio in the  $K_c$  expression, then  $Q_c$  is greater than  $K_c$  and the equilibrium must shift to the left. Conversely, if the new ratio is less than the original ratio, then  $Q_c$  is less than  $K_c$  and the equilibrium must shift to the right. Thus, the equilibrium can shift to the left or right, depending on the amount of  $\text{CS}_2$  in the initial equilibrium mixture. The reader may refer to Cheung (2004) and Silverstein (2005) for more information about the usefulness of reaction quotient.

*Misconception Coded 1B3.* Fifteen teachers held this misconception. They explicitly indicated that something must be done to minimize the impact of the increase in concentration of  $\text{CS}_2$  and this could be achieved by shifting the equilibrium  $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$  to the right. Thus, the misconception coded 1B3 is caused by the reliance on the logic of LCP. Also, those teachers with the misconception coded 1B3 tended to focus their attention on the variable whose change is most evident. This is a way of thinking found in many students who have misconceptions in science (Talanquer, 2002). Our data showed that, like their students, some chemistry teachers also possessed this kind of narrow thinking when solving problem #1. In addition to a change in the concentration of  $\text{CS}_2$  molecules, they should have noted that the concentrations of  $\text{H}_2$ ,  $\text{CH}_4$ , and  $\text{H}_2\text{S}$  are also changed when the equilibrium system is disturbed at constant pressure and temperature. Excerpts of three

teachers' written responses are shown below. Each teacher was coded with a number when the data were content-analyzed.

$$K = \frac{[CH_4][H_2S]^2}{[CS_2][H_2]^4}$$

Adding a small amount of CS<sub>2</sub> increases [CS<sub>2</sub>], but the concentrations of other gases are momentarily unchanged. To keep the K constant, the concentrations of products must increase and [H<sub>2</sub>] must decrease. (Teacher 66)

The number of CH<sub>4</sub> molecules will increase.

At constant total pressure, adding CS<sub>2</sub> will speed up the reaction with H<sub>2</sub>. Momentarily, the partial pressure of CH<sub>4</sub> and the partial pressure of H<sub>2</sub>S will decrease, but the partial pressure of CS<sub>2</sub> will increase. This is equivalent to an increase in the concentration of CS<sub>2</sub>. The equilibrium shifts to the right (Teacher 70).

The number of CH<sub>4</sub> molecules will increase.

Adding CS<sub>2</sub> will increase the volume.

Two factors have to be considered: (1) The concentration of CS<sub>2</sub> increases and thus the equilibrium shifts to the right: this is the main effect. (2) The volume is increased and thus the equilibrium shifts to the left, but this is the minor effect (Teacher 73).

The teacher coded 66 did try to solve problem #1 by applying the equilibrium constant expression but mistakenly assumed that the total volume of the gaseous mixture did not increase momentarily. Although the teacher coded 70 recognized that the partial pressure of hydrogen gas will be reduced, he/she believed that it was due to the reaction with methane rather than the expansion of the total volume of the gaseous system. Like the teacher coded 70, the teacher coded 73 argued that the equilibrium should shift to the right to counteract the increase in the concentration of CS<sub>2</sub> gas. In addition, the teacher coded 73 conceptualized the increase in volume as a minor effect on the chemical equilibrium and applied LCP-type logic to predict a shift of the equilibrium to the left.

*The Misconception Coded 1B4.* Twenty-four teachers predicted that the equilibrium must shift to the right. As a result, they concluded that the number of CH<sub>4</sub> molecules would increase. However, they did not provide further explanations. Three typical responses written by teachers are shown below.

At constant temperature and pressure, if a small amount of CS<sub>2</sub> is added, the equilibrium must shift to the right. The number of CH<sub>4</sub> molecules will increase (Teacher 52).

Increase. The pressure inside the vessel is kept constant: the equilibrium will shift to the right. (Teacher 96)

The number of CH<sub>4</sub> molecules is increased. Because CS<sub>2</sub> is added to the vessel at constant pressure, the equilibrium shifts to the right (Teacher 107).

The misconception coded 1B4 is less specific than the misconception coded 1B3. Why did these 24 teachers predict that the equilibrium system must shift to the right? Perhaps the logic of LCP had affected their problem solving. According to LCP, the addition of more reactants will favor the formation of products. Thus, these teachers may have thought that adding more CS<sub>2</sub> to the system  $\text{CS}_2(\text{g}) + 4\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g})$  must shift the equilibrium to the right. Because problem #1 appeared to be a trivial question that requires simple recall of knowledge of LCP, they did not bother about thinking over the equilibrium law or writing down the equilibrium constant expression to check the changes in concentrations of the four gases. They also did not bother about the change in total gas volume.

*The Misconception Coded 1C3.* Six teachers held this misconception. These teachers were unique in the fact that they did try to apply the equilibrium constant expression but erroneously focused on the concentration of hydrogen gas. They argued that since the exponent of [H<sub>2</sub>] in the K<sub>c</sub> expression is 4, the value of [H<sub>2</sub>]<sup>4</sup> will be significantly reduced. To increase the concentration of H<sub>2</sub>, the equilibrium must shift to the left. As a result, the number of CH<sub>4</sub> molecules will decrease in the new equilibrium state. Obviously, their thinking was affected by the ‘stress-then-counteract’ logic of LCP. Below are two typical written responses from those teachers with the misconception coded 1C3.

Adding CS<sub>2</sub> increases the volume of the gaseous mixture when the equilibrium is reestablished. The concentration of CS<sub>2</sub> should become higher in the new equilibrium state. But the concentration of H<sub>2</sub> will become lower.

$$K = \frac{[\text{CH}_4][\text{H}_2\text{S}]^2}{[\text{CS}_2][\text{H}_2]^4}$$

Because the value of [H<sub>2</sub>]<sup>4</sup> will be significantly reduced, the equilibrium shifts to the left, forming less CH<sub>4</sub> molecules (Teacher 64).

Decrease.

Adding  $\text{CS}_2$  will increase the volume of the chemical system.  $[\text{CS}_2]$  will increase, but the decrease in the  $[\text{H}_2]$  is even more significant. The equilibrium should shift to the left to increase  $[\text{H}_2]$  (Teacher 67).

*The Misconception Coded 1D1.* Eleven teachers mistakenly thought that the number of methane molecules is not predictable because adding  $\text{CS}_2$  to the equilibrium mixture will result in two opposite shifts. Their predictions were based on LCP-type reasoning. Also, these 11 teachers thought that the disturbance could be conceptualized as two independent changes. The two following teachers' responses demonstrate the nature of the misconception coded 1D1.

First, assume that the piston is not movable: adding  $\text{CS}_2$  shifts the equilibrium to the right. As a result, the number of  $\text{CH}_4$  increases. Then, assume that the total pressure is reduced to restore to the initial value. The equilibrium shifts to the left to counteract the decrease in pressure, and the number of  $\text{CH}_4$  decreases. Therefore, the overall change in the number of  $\text{CH}_4$  molecules depends upon which effect is the major factor (Teacher 32).

Momentarily, adding  $\text{CS}_2$  does not change the volume. The equilibrium should shift to the right. But this shift will reduce the total number of molecules in the vessel and the volume will become smaller. The change in concentration should be considered. According to Le Châtelier's principle, the direction of equilibrium shift is to minimize but not to cancel the change, to increase the total number of molecules (Teacher 48).

### *Teacher Responses to Problem #2*

Analysis of the content of the 50 teachers' answer sheets found that two teachers left the problem blank and one teacher provided ideas, which were irrelevant to the problem. Of the remaining 47 teachers, 13 applied the  $K_c$  and  $Q_c$  expressions to give a correct answer to problem #2; one teacher used the  $K_p$  expression to give an acceptable answer; seven teachers expected the equilibrium to shift to the right but calculated the value of  $K_c$  or  $Q_c$  incorrectly; nine teachers expected the equilibrium to shift to the left; 15 teachers did not put down any conclusive statements on the equilibrium shift; one teacher thought that the equilibrium first shifts to the left and then to the right, and one teacher believed that adding  $\text{H}_2\text{S}$  gas to the system has no effect on the equilibrium position. Table 2 displays the coded correct answers and other common responses.

*Correct Answers.* A total of 13 teachers (Code 2A1) correctly calculated the values of  $K_c$  and  $Q_c$  for the system  $\text{NH}_4\text{HS}(s) \rightleftharpoons$

TABLE 2  
Codes responses to the second problem

<i>Code</i>	<i>Teacher response</i>	<i>No. of teachers</i>
2A1	The $K_c$ and $Q_c$ expressions are correct. $Q_c < K_c$ . The equilibrium will shift to the right.	13
2A2	The $K_p$ expression is correct. The new $K_p <$ the original $K_p$ . The equilibrium will shift to the right.	1
2B1	The $K_c$ and $Q_c$ expressions are correct, but the value of $K_c$ or $Q_c$ is incorrect. $Q_c < K_c$ . The equilibrium will shift to the right.	3
2B2	The $K_c$ and $Q_c$ expressions are correct. But the teacher did not draw any conclusion.	3
2C1	The $K_c$ expression is correct. But the $Q_c$ expression does not take the volume change into account. The equilibrium will shift to the left.	7
2C2	The equilibrium will be affected. The $K_c$ expression is correct. But the teacher did not indicate the direction of equilibrium shift.	4
2C3	Calculations are not shown or incomplete.	11

$\text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ . A typical solution path used by these teachers is shown below.

$$K_c = [\text{H}_2\text{S}][\text{NH}_3] = \left(\frac{n_{\text{H}_2\text{S}}}{V}\right)\left(\frac{n_{\text{NH}_3}}{V}\right) = \left(\frac{1.65 \times 10^{-2}}{1.0}\right)\left(\frac{1.10 \times 10^{-2}}{1.0}\right)$$

$$= 1.82 \times 10^{-4}$$

In the initial equilibrium state, 1.0 L contains  $(1.65 \times 10^{-2} + 1.10 \times 10^{-2}) = 2.75 \times 10^{-2}$  mol of gaseous molecules.

After  $\text{H}_2\text{S}$  is added, the vessel momentarily contains  $(2.75 \times 10^{-2} + 1.35 \times 10^{-2}) = 4.10 \times 10^{-2}$  mol of gaseous molecules. And the total volume momentarily becomes  $4.10/2.75 = 1.49$  L.

$$Q_c = [\text{H}_2\text{S}][\text{NH}_3] = \left(\frac{n_{\text{H}_2\text{S}}}{V}\right)\left(\frac{n_{\text{NH}_3}}{V}\right) = \left(\frac{1.65 \times 10^{-2} + 1.35 \times 10^{-2}}{1.49}\right)\left(\frac{1.10 \times 10^{-2}}{1.49}\right)$$

$$= 1.49 \times 10^{-4}$$

Therefore,  $Q_c < K_c$ , and the equilibrium must shift to the right.

Alternatively, a simpler way to solve problem #2 is to compute the ratio,  $\frac{n_{\text{H}_2\text{S}}}{V^2}$ , because the number of moles of  $\text{NH}_3$  molecules remains unchanged when the equilibrium is disturbed.

In the initial equilibrium state,  $\frac{n_{\text{H}_2\text{S}}}{V^2} = \frac{1.65 \times 10^{-2}}{(1.0)^2} = 1.65 \times 10^{-2}$

After adding  $\text{H}_2\text{S}$ , the new ratio becomes  $\frac{n_{\text{H}_2\text{S}}}{V^2} = \frac{1.65 \times 10^{-2} + 1.35 \times 10^{-2}}{(1.49)^2} = 1.35 \times 10^{-2}$

Therefore, new ratio is smaller than the initial ratio, indicating that  $Q_c$  is less than  $K_c$  and the equilibrium must shift to the right.

A teacher (Code 2A2) correctly answered problem #2 by using the  $K_p$  expression. His/her calculations are shown below:

In the initial equilibrium state:  $P(\text{NH}_3) = \frac{1.10}{2.75} \times P_0$  and  $P(\text{H}_2\text{S}) = \frac{1.65}{2.75} \times P_0$

$$K = P(\text{NH}_3) \times P(\text{H}_2\text{S}) = \frac{1.10 \times 1.65}{(2.75)^2} \times (P_0)^2 = 0.24 P_0^2$$



If  $\text{H}_2\text{S}$  is added to the system:  $P(\text{NH}_3) = \frac{1.10}{4.10}xP_0$  and  $P(\text{H}_2\text{S}) = \frac{3.00}{4.10}xP_0$

$$K^1 = P(\text{NH}_3) \times P(\text{H}_2\text{S}) = \frac{1.10 \times 3.00}{(4.10)^2} x(P_0)^2 = 0.196P_0^2$$

Therefore,  $K > K^1$ , and the equilibrium shifts to the right.

However, although a total of 14 teachers (codes 2A1 and 2A2) managed to solve problem #2, none of them pointed out that the shift in equilibrium position is not consistent with that predicted on the basis of LCP. The results of problem #2 give some cause for concern as these teachers were supposed to be experienced rather than novice problem solvers in chemical equilibrium. As was discussed earlier, only one of the 109 teachers applied the equilibrium law to solve problem #1 successfully. Our concern is that none of the 14 teachers correctly answered both problem #1 and problem #2. This implies that those teachers who managed to calculate the correct values of equilibrium constants actually had an inadequate conceptual understanding of the effect of the addition of more reactants on chemical equilibrium.

Students are typically asked to solve computational equilibrium problems, which are readily solved by the application of an algorithm memorized through repeated drill (Bergquist & Heikinen, 1990). For example, they can perform the calculation of equilibrium constants by rote. Our data indicated that, like their students, some chemistry teachers in the second sample may have used the  $K_c$  or  $Q_c$  expression algorithmically rather than understanding the underlying chemical-equilibrium concepts.

*The Misconception Coded 2C1.* This is the most common misconception about the effect of addition of more  $\text{H}_2\text{S}$  gas to the equilibrium  $\text{NH}_4\text{HS}(\text{s}) = \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$ . Seven teachers (code 2C1) thought that the total gas volume did not change and thus computed the value of  $Q$  incorrectly. For example, the following teacher did not pay any attention to the volume change and concluded that the equilibrium will shift to the left because  $Q_c$  is larger than  $K_c$ .

$$K_c = 1.10 \times 10^{-2} \times 1.65 \times 10^{-2}$$

$$\text{But } [\text{H}_2\text{S}] \times [\text{NH}_3] = (1.65 + 1.35) \times 10^{-2} \times 1.10 \times 10^{-2} > K_c$$

Therefore, the equilibrium will shift to the left. (Teacher 78)

The above teacher forgot to consider the change in total gas volume. One possible reason is that in gaseous equilibrium systems, the equilibrium law is often expressed as  $K_p$  rather than  $K_c$  in many chemistry textbooks. The teacher may not have recognized that the concentrations of  $H_2S$  gas and  $NH_3$  gas can be expressed as mol/L; that is, the moles of gaseous species per liter occupied. Another possible reason why the teacher did not consider the total volume of the gaseous system is that he/she did not recognize that the conditions under which the system is disturbed are important (i.e., the piston is movable and the addition of  $H_2S$  gas is made at constant pressure and temperature). In fact, many chemistry textbooks (e.g., Ash & Hill, 2008; Irwin et al., 2006; Wong & Wong, 2005) do not specify the variables to be kept constant when an equilibrium mixture is disturbed.

Similarly, the following teacher did not consider the volume change when solving problem #2. Even worse, he/she assumed that the equilibrium must shift to the left when setting up the reaction quotient expression and let the unknown,  $X$ , be the amount of  $H_2S$  gas converted to solid  $NH_4HS$ . Possibly the prediction was made on the basis of the logic of LCP. It should be noted that this error was not a careless mistake: it is a misconception about chemical equilibrium. Also, the teacher did not understand that the purpose of calculating the values of  $K$  and  $Q$  is to compare them to determine the direction in which the reversible reaction will proceed to reestablish equilibrium.

$$K = [NH_3][H_2S] = (1.10 \times 10^{-2})(1.65 \times 10^{-2}) = 1.815 \times 10^{-4}$$

The equilibrium position shifts to the left.

$$(3 \times 10^{-2} - X)(1.1 \times 10^{-2} - X) = 1.815 \times 10^{-4}$$

$$3.3 \times 10^{-4} - 4.1 \times 10^{-2}X + X^2 = 1.815 \times 10^{-4} \text{ (Teacher 100)}$$

Overall, only 14 teachers were able to apply the equilibrium law quantitatively to solve problem #2. Our data showed that 11 teachers (code 2C3) did not complete their calculations while solving the problem. This indicates a limitation of the use of a paper-and-pencil test to collect the teacher data. As experienced solver problems in chemical equilibrium, some teachers tended to skip steps while writing their responses on the answer sheets. Sometimes we needed to reconstruct teachers' cognitive

processes based on insufficient data. Therefore, the most obvious follow-up to this research study would be to improve the method of data gathering by using techniques such as the think-aloud method (Van Someren, Barnard & Sandberg, 1994). Recently, five high school chemistry teachers in Hong Kong were individually interviewed by Cheung (2008). They were asked to think aloud about how addition of more nitrogen gas at constant pressure and temperature would affect the Haber process,  $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ . Analysis of the protocols showed that none of the five experienced teachers were able to solve the Haber problem correctly due to reliance on LCP. Further research is planned to invite more chemistry teachers to participate in think-aloud interviews so as to investigate how LCP adversely affects teachers' ability to solve other types of equilibrium problems.

#### CONCLUSION AND IMPLICATIONS

The importance of research on misconceptions in chemical equilibrium is well recognized by educators. However, in the past, researchers' interest has centered on student misconceptions (see, for example, Bergquist & Heikkinen, 1990; Hackling & Garnett, 1985; Johnstone, MacDonald & Webb, 1977; Thomas & Schwenz, 1998; Van Driel, De Vos, Verloop & Dekkers, 1998; Voska & Heikkinen, 2000) and has neglected teacher misconceptions. The results of the present study lend support to the conclusion that high school chemistry teachers in Nanjing generally hold misconceptions about the effects of adding more reactants or products to a chemical equilibrium system at constant pressure and temperature and the major source of such misconceptions is the reliance on the 'stress-then-counteract' logic of LCP. Regardless of teachers' teaching experiences, all but one of the 109 teachers failed to solve problem #1 due to their use of LCP or LCP-type reasoning. They did not understand that if the amount of products formed by a reversible chemical reaction is not equal to the amount of reactants, adding more reactant at constant pressure and temperature may shift a gaseous chemical equilibrium to the reactant rather than the product side. Although 14 of the 50 teachers in the second survey were able to solve problem #2 quantitatively, they failed to solve problem #1, indicating that they may have relied on algorithms and did not understand the underlying chemical equilibrium concepts fully.

Without question, the most important implications of the research reported in this article have to do with teacher education. If high school teachers continue to rely on LCP to teach the effects of changing

conditions on chemical equilibria, there is little hope for students to develop a deep understanding of chemical equilibrium. It is important to note that effective teaching cannot exist without good subject matter knowledge and pedagogical content knowledge (Abell, 2007; Bucat, 2004; De Jong, Veal & Van Driel, 2002; Gess-Newsome & Lederman, 1999; Van Driel, De Jong & Verloop, 2002). Pedagogical content knowledge is topic-specific and is highly context-dependent. It can empower a chemistry teacher to transform his or her understanding of chemistry into teachable and learnable content in the classroom, under particular conditions and constraints. Some chemistry educators have promoted pedagogical suggestions about methods of teaching LCP. Examples are Berger & Mellon (1996), Grant (1984), Last & Slade (1997), and Russell (1988). However, the limitations of LCP are well documented in the literature (Allsop & George, 1984; Bridgart & Kemp, 1985; Canagaratna, 2003; Cheung, 2004; De Heer, 1957, 1958; Ehrenfest, 1911; Epstein, 1937; Gold & Gold, 1984, 1985; Katz, 1961; Lacy, 2005; Levine, 2002; Posthumus, 1933; Quílez, 2004; Raveau, 1909; Sandler, 1999; Solaz & Quílez, 2001; Solaz-Portolés & Quílez-Pardo, 1995; Torres, 2007; Uline & Corti, 2006; Wright, 1969). Any attempt to teach LCP in high school is, in our opinion, a waste of time.

To improve chemistry education, we recommend that chemistry-teacher educators discuss the scientific inadequacies of LCP explicitly in their teaching methods courses to empower student teachers to identify which basic principles of chemical equilibrium should be taught in high schools. Opportunities should be given to both student teachers and practicing teachers to reflect upon why LCP is an inappropriate tool for analyzing problems in chemical equilibrium. Hewson's (2007) review of professional development in science found that continuing support for teachers is important in order to make changes in their teaching. Thus, we have developed supplementary teaching and learning materials to support school teachers to delete LCP from the chemistry curriculum, which can be downloaded at <http://www3.fed.cuhk.edu.hk/chemistry/>. Research is underway to investigate how school teachers in China feel about the use of these supplementary materials in their classroom teaching.

Furthermore, the results of this study should prompt curriculum developers, textbook writers, and examination authorities to assess the value of LCP in school chemistry. LCP, if indeed it is a principle, serves only to increase the difficulties in understanding chemical equilibrium as it can lead to incorrect predictions and cause both teachers and students to hold misconceptions about chemical equilibrium. The present study has provided solid evidence of its adverse effects on chemistry teachers'

understanding of chemical equilibrium. The remarks given by the following educators are worth quoting:

However, it is questionable whether Le Châtelier's principle is at all necessary in A-level courses and whether it is of anything but historical interest. Changes in pressure or volume of a system at equilibrium, and changes in mass or concentration of 'reactants' or 'products' are, in fact, all related to concentration changes... Hence changes in any of the factors will result in changes within an equilibrium system which may be predicted by using the equilibrium law expression (Allsop & George, 1984, p. 54).

Allsop and George entitled their paper 'Le Châtelier – a redundant principle?' We emphatically agree with their point of view, and would go even further: the question mark at the end of their title is also redundant!... Knowledge of Le Châtelier's Principle cannot be a pre-requisite to a deeper understanding of chemical equilibrium. Its inclusion in more elementary teaching can therefore be justified only if it provides an easier and conceptually simpler introduction.... A simple and correct introduction to the principles of chemical equilibrium, suitable for school teaching, is to be found in the work of van't Hoff.... Thus, the scientific inadequacy of Le Châtelier's principle has long been appreciated by experts in the field (Gold & Gold, 1985, p. 82).

We concur with Allsop & George (1984) that in high schools, LCP has no value for chemistry teachers and students other than historical interest. To conceptually understand chemical equilibrium, curriculum developers, textbook writers, and examination authorities should encourage teachers and students to utilize the equilibrium law, reaction quotient, and a simplified version of the van't Hoff equation when analyzing factors affecting an equilibrium position (Allsop & George, 1984; Cheung, 2004; Katz, 1961; Kemp, 1987; Miller, 1954; Quílez, 2004; Silverstein, 2005; Solaz-Portolés & Quílez-Pardo, 1995). Unfortunately, many textbook writers just introduce these three concepts superficially. In Canada, for example, Van Kessel et al. (2003) discuss reaction quotient in their textbook but it is not applied to predict the effects of changing conditions on chemical equilibria. Also, in many countries, the chemistry syllabuses prepared by curriculum developers or examination authorities require high school teachers to teach LCP only (e.g., Board of Studies, 2002). Thus, educating chemistry educators worldwide on the scientific inadequacies of LCP should be a high priority.

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