CE-1

A BRIEF REVIEW OF THE COMPLEXITIES OF TEACHING AND LEARNING CHEMICAL EQUILIBRIUM WITH SPECIFIC REFERENCE TO MALAYSIA

[1]A.L. Chandrasegaran, [1]David F. Treagust, [2]Mauro Mocerino, [1]Mihye Won & [3]Mageswary Karpudewan,

[1]Science and Mathematics Education Centre, Curtin University, Perth, Australia; [2]Chemistry Department, Curtin University, Perth, Australia; [3]School of Education, Universiti Sains Penang, Malaysia

Abstract

The purpose of this study was to review the extant literature on chemical equilibrium research in high school chemistry. The review involved understanding of the nature of chemical equilibrium, particularly about chemical reactions not going to completion, the reversibility of chemical reactions and the idea of *dynamic equilibrium*. Associated with these understandings was the derivation of the Equilibrium Law and the significance of the equilibrium constant followed by the use of Le Chatelier's Principle including the limitations of this principle. The review then focused on the common alternative conceptions associated with the chemical equilibrium concept. The study next considered these features in the Malaysian context. For this purpose, the researchers formulated an instructional program relevant to the Malaysian Higher School Certificate curriculum that was implemented over 11 hours with 56 high-achieving students in Year 12 from a private secondary school. To evaluate students' understanding of chemical equilibrium concepts after instruction the *Chemical Equilibrium Conceptual Test-1* (*CECT-1*) was administered after instruction. The test consisted of 10 two-tier multiple-choice items that were adapted from previously developed questionnaires. The results indicated very limited understanding of the relevant concepts. The total scores in the *CECT-1* ranged from 0 to 9 (out of a maximum score of 10) with a mean score of 5.04. Less than 50% of students correctly answered five of the 10 items. The findings suggest the need for teachers to address students' preconceptions about chemical equilibrium concepts and use appropriate strategies to enable students to acquire scientifically acceptable understandings.

Keywords: Chemical equilibrium; dynamic equilibrium; Le Chatelier's Principle; reversibility of chemical reactions

Introduction

The topic of chemical equilibrium has been widely researched in several countries (Cheung, 2009; Özmen, 2008; Piquette & Heikkinen, 2005; Quilez-Pardo & Solaz-Portoles, 1995; Tyson, Treagust & Bucat, 1999). Chemical equilibrium is one of the key concepts in chemistry (van Driel & Gräber, 2002) that is important for the understanding of several other concepts in chemistry like, redox reactions, phase changes, weak and strong acids and solubility. This study summarises a brief review of studies that have been conducted on the teaching and learning of chemical equilibrium and will provide valuable guidelines to teachers when planning their instruction on chemical equilibrium by focusing on the complex issues associated with understanding the related concepts.

Literature review

Traditionally, chemical equilibrium has been taught using a kinetic approach that is based on the assumption that at equilibrium, the two opposing reactions occur at the same rate. For the equilibrium system aB + bB ↔ cC + dD, $K_{eq} = k_f / k_r = [C]^c.[D]^d / [A]^a.[B]^b$, (where k_f and k_r are rate constants for the two opposing reactions). However, this derivation is incorrect (too simplistic) because for the reaction aA + bB → products, it is not always correct that $r = k.[A]^a.[B]^b$ (van Driel & Gräber, 2002). More correctly, it is common to introduce chemical equilibrium qualitatively based on the idea of *dynamic equilibrium* using the Equilibrium Law, $K_{eq} = [C]^c.[D]^d / [A]^a.[B]^b$ (Tyson, Treagust & Bucat, 1999). The Equilibrium Law is derived not from kinetic information, but as an empirical law for ideal equilibrium systems (very dilute solutions and gases at low pressures).

Students generally encounter problems understanding chemical equilibrium concepts. When they first learn about chemical reactions, they associate reactions with observable macroscopic changes like colour changes, heat changes, gas evolution and precipitate formation. Their observations confirm that reactions proceed to completion in one direction. However, when they learn about chemical equilibrium, they find that many chemical reactions are reversible, and may not go to completion, i.e., all the reactants and products are present in the equilibrium system. In addition, students are expected to know that all macroscopic properties are constant in an equilibrium system, yet due to the dynamic nature of chemical equilibrium, two opposite reactions are taking place at equal rates so that there is no observable effect. Hence, students are expected to revise their understanding about chemical reactions.

Several studies over the past three decades or so are documented in the extant research literature that suggest that high school students (e.g. Gussarksy & Gorodetsky, 1990; Hackling & Garnett, 1985), university students (e.g., Thomas & Schwenz, 1998) as well as teachers (Banerjee, 1991) have difficulty understanding chemical equilibrium concepts.

As a result of the difficulties that students experience with chemical equilibrium concepts, they display several alternative conceptions such as (1) at equilibrium no reaction is taking place (Griffiths, 1994) indicating failure to understand the dynamic nature of chemical equilibrium, (2) equilibrium is like oscillations of a pendulum (Van Driel et al., 1998), (3) both sides (‘left’ and ‘right’) of a chemical equilibrium system can act independently of one another (Wheeler & Kass, 1978), (4) inability to distinguish between *rate* and *extent* of a chemical reaction (Johnstone, MacDonald & Webb, 1977), (5) there is a simple arithmetic relation between concentrations of reactants and products at equilibrium (Hackling & Garnett, 1985; Huddle & Pillay, 1996), (6) the concentrations of the reactants are equal to the concentrations of the products (Hackling & Garnett, 1985; Huddle & Pillay, 1996), and (7) when a reactant is added to an equilibrium system, the rate of the forward reaction increases with time until equilibrium is established (Hackling & Garnett, 1985).

Several strategies have been suggested in the research literature to help students overcome these alternative conceptions. In one example, in a study involving grade 10 students (15-16 year-olds), van Driel, De Voss, Verloop and Dekkers (1998) successfully used conceptual change strategies to challenge the students’ conceptions about chemical equilibrium by creating cognitive dissonance about their understandings. As a result, the students were able to accept the “incompleteness of a chemical conversion as an empirical fact” (p. 389). By doing so, they introduced the idea of *dynamic equilibrium* to account for the reversibility of chemical reactions and for the reactions not going to completion.

To further help students with understanding the concept of *dynamic equilibrium*, several instructional strategies involving the use of simulations and analogies are discussed in the research literature (van Driel & Gräber, 2002).

Concerns have also been raised about the inadequacy of Le Chatelier’s Principle (LCP) (Quilez-Pardo, 1995), often stated as “*When a stress is applied to a system, the system responds in a way to try to relieve the stress*” (van Driel & Gräber, 2002; p. 279). Students tend to learn the principle by heart and often apply it without understanding (Furió, Catalayud, Barcenas & Padilla, 2000). Students have the tendency to apply LCP outside the area of validity of the principle. Examples include the addition to or removal of solids from heterogeneous equilibrium systems, and the addition of non-reacting substances like water and an inert gas to equilibrium systems (Tyson et al., 1999; Voska & Heikkinen, 2000). Also, when the temperature of an equilibrium system was changed, students believed that the effect could be predicted without knowing whether the reaction was exothermic or endothermic (Voska & Heikkinen, 2000). Furthermore, the principle breaks down by not being specific about the conditions under which a gaseous system is in equilibrium (Lacy, 2005), like for example, whether the equilibrium is at constant temperature or pressure. Especially in gaseous systems, it is important that the conditions of equilibrium are unequivocally stated.

The simplistic definition of LCP that is used by students is likely to cause serious errors in its application to equilibrium systems. The over-simplification in the use of LCP is illustrated in particular when there is a change in the number of moles in a gaseous reaction like the dissociation of dinitrogen tetroxide, $N_2O_4(g) \leftrightarrow 2NO_2(g)$. Assume for example, that the system is in equilibrium in a syringe with a movable piston and an inert gas say argon is added to the mixture at constant temperature and pressure. Using LCP, some teachers and textbooks suggest a blanket explanation that the equilibrium is not disturbed because argon does not take part in either reaction. However, when the reaction quotient (Q) expression for the equilibrium is considered, the total volume of the system appears in the denominator. When the inert gas argon is added, the total volume increases and Q becomes less than K_{eq}. Therefore, the equilibrium moves to the right producing more NO_2. In another example, involving the ammonia equilibrium, Cheung (2009) has shown how the application of LCP breaks down for gaseous chemical equilibrium systems in which there is a change in the number of moles.

As noted by Cheung, Ma and Young (2009), purely relying on LCP to make predictions of the effects of disturbing an equilibrium system often leads to erroneous predictions. Earlier, a multi-faceted approach suggested by Tyson et al. (1999) involved using in addition to LCP, the equilibrium law and using collision theory to analyse the forward and reverse reactions. However we have not identified any research on teaching using this approach.

Rationale of the study in the Malaysian context and research question

Chemical equilibrium is widely included in several secondary school chemistry and tertiary curricula (Cheung, Ma & Yang, 2009; Kousathana & Tsaparlis, 2002; Özmen, 2008; Tyson, et al., 1999; Voska & Heikkinen, 2000). In Malaysia, the topic is introduced in Years 11-12 and includes understanding of reversible reactions, dynamic equilibrium, equilibrium law, equilibrium constant, heterogeneous equilibria, effects of changing concentrations of reactants & products, addition of inert gas, addition of catalyst, and Le Chatelier's Principle. In view of the extensive difficulties faced by students that have been documented in the research literature as previously discussed, this study was conducted with a sample of Malaysian students' to elucidate their understanding of chemical equilibrium concepts and thereby to highlight the complexities associated with the teaching and learning of chemical equilibrium concepts.

Based on this rationale, the research question that was posed was: What is the understanding of a sample of Year 12 high-achieving students about chemical equilibrium? The findings of this study will benefit chemistry teachers by helping them plan more effective instruction to facilitate more appropriate understandings of the complex issues associated with the teaching and learning of chemical equilibrium concepts.

Methodology

Research design

A mixed methods design (Cohen, Manion & Morrison, 2011) using a treatment group was used in this study. As the purpose of the study was merely to evaluate students' understandings of chemical equilibrium concepts and not to evaluate the effectiveness of the instructional program, it was decided not to include a control group.

Research sample

The last author liaised with the chemistry teacher from a private secondary school who had agreed to participate in the study. Two classes consisting of 56 Year 12 students were involved in the study. The same teacher taught both classes, thus ensuring consistency in instruction in both classes.

Instructional program

The instructional program was developed by the authors based on several propositional content knowledge statements (see Figure 1) related to the chemistry syllabus. Lessons were conducted in eight lessons over 11 hours during a period of four weeks.

Research instrument

The *Chemical Equilibrium Conceptual Test-1* (*CECT-1*) that consisted of 10 two-tier multiple-choice items was adapted from previous studies (Cheung, 2009; Özmen, 2008). A summary of the items is provided in Figure 2, and an example of an item is given in Figure 3. The complete instrument may be obtained from the first author. Eight of the items (except Items 7 and 10) were adapted from Özmen (2008). All these eight items were not specific about the conditions under which the chemical equilibrium systems were established or the responses in one or both tiers were not sufficiently clear. Consequently, these items were improved to avoid the shortcomings that are mentioned in the literature review. Conditions like equilibrium systems in a closed container or at constant temperature or pressure were not indicated in the original items. Item 7 about the addition of a catalyst to the $2CO(g) + O_2(g) \leftrightarrow 2CO_2(g)$ equilibrium system was developed by the authors. Item 10 about the effect of adding an inert gas to the gaseous equilibrium system $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$, was adapted from Cheung (2009). However, his item was a multiple-choice item. So, the authors developed the second tier of reasons. The instrument had a Cronbach's alpha reliability of 0.63 that was above the threshold value of 0.5 for two-tier multiple-choice items (Nunally & Bernstein, 1994).

---

1. Beginning with the reactants, as a reaction mixture approaches equilibrium, the concentrations of the reactants decrease while those of the products increase.
2. Beginning with the reactants, as a reaction mixture approaches equilibrium, the rate of the forward reaction decreases and the rate of the reverse reaction increases.
3. When equilibrium has been established, the concentrations of all the reactants and products remain constant.
4. Once equilibrium has been established, the forward and reverse reactions continue to occur (i.e. the equilibrium system is a dynamic one, not static), at the same rate.
5. At equilibrium, the concentrations of the reactants and products are related by the equilibrium law, where K_c and K_p are the equilibrium constants based on concentrations and partial pressures, respectively. For the hypothetical system $2A(g) + B(g) \leftrightarrow 3C(g)$,

   $$K_c = \frac{[C]^3}{[A]^2\,[B]} \quad \text{and} \quad K_p = \frac{(p_C)^3}{(p_A)^2\,(p_B)}$$

6. A large value of K_c indicates that the concentration of the products is relatively greater than that of the reactants, and vice versa.
7. According to Le Chatelier's Principle, when some change is made to an equilibrium system, the system reacts to partially counteract the imposed change and re-establish equilibrium.

8. When a *catalyst* is added to an equilibrium system, the rates of the forward and the reverse reactions increase to the same extent.
9. The concentrations of the reactants and the products remain unchanged when a catalyst is added to an equilibrium system.
10. In the presence of a catalyst, the value of the equilibrium constant, K_c, remains the same as in the initial equilibrium system.
11. When an inert gas like helium is introduced at constant volume, the total pressure of the system increases, but does not change the partial pressures (or the concentrations) of the reactants. Therefore, it has no effect on the system.
12. In a heterogeneous equilibrium system the equilibrium constant, K_c, does not include substances in the solid state.
13. There is no effect on the addition or removal of some solid reactant or product to a heterogeneous equilibrium system; LCP is not applicable in this case.

Figure 1 Major propositional content knowledge statements defining instruction on chemical equilibrium

No.	Description of items
1.	Establishing equilibrium: $CO(g) + 3H_2(g) \leftrightarrow CH_4(g) + H_2O(g)$
2.	Establishing equilibrium: $PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g)$
3.	LCP-changing concentration in aqueous solution: $2CrO_4^{2-}(aq) + 2H^+(aq) \leftrightarrow Cr_2O_7^{2-}(aq) + H_2O(l)$
4.	LCP-changing temperature in gaseous system: $N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g)$, $\Delta H = -92.4\ kJmol^{-1}$
5.	Equilibrium constant, K_{eq}: $4NH_3(g) + 5O_2(g) \leftrightarrow 4NO(g) + 6H_2O(g)$, $\Delta H = -905.6\ kJmol^{-1}$
6.	Equilibrium constant, K_{eq}: $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$
7.	Addition of a catalyst: $2SO_2(g) + O_2(g) \leftrightarrow 2SO_3(g)$, $\Delta H = -197.78\ kJmol^{-1}$
8.	Addition of a catalyst: $2CO(g) + O_2(g) \leftrightarrow 2CO_2(g)$, $\Delta H = -556.0\ kJmol^{-1}$
9.	Heterogeneous equilibrium: $CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$
10.	Addition of inert gas: $CO(g) + 2H_2(g) \leftrightarrow CH_3OH(g)$

Figure 2 Summary of items in *CECT-1*

Item 3: Suppose that 0.30 mol PCl_5 is placed in a **closed reaction vessel** of volume 1000mL and allowed to reach equilibrium with its decomposition products, phosphorus trichloride and chlorine at 250° C, according to the equation below:

$$PCl_5(g) \leftrightarrow PCl_3(g) + Cl_2(g).$$

What can we say about the concentrations of PCl_3 gas and Cl_2 gas at equilibrium?

A Equal to 0.15 $molL^{-1}$
*B Lower than 0.30 $molL^{-1}$
C Equal to 0.30 $molL^{-1}$

The reason for my answer is:

1 The concentrations of all species in the reaction mixture are equal at equilibrium.
2 All of the phosphorus pentachloride decomposes into the products.
3 Half of the phosphorus pentachloride decomposes into products.
*4 Some of the phosphorus pentachloride decomposes into products.

(* correct response)

Figure 3 Example of an item in *CECT-1*

Data analyses techniques
The data obtained from the *CECT-1* were analysed using SPSS software package (version 21). The responses to the first tier of the items were first recorded as A, B, C, etc. while the combined tiers responses were recorded as A1, A2, .., B1, B2, ..C1, C2, … etc. The combined tier responses were then coded 1 if correct and 0 if wrong. These codes were then used in the analyses. The maximum score was therefore 10.

Results and discussion
CECT-1 responses
The overall correct response to each of the items was not very encouraging (see Table 1). Less than 50% of students provided correct responses to four of the 10 items. The total score achieved by the students ranged from 0 to 9 (out of a maximum score of 10) with a mean score of 5.04. Figure 4 summarises the distribution of the total scores achieved by the students in the *CECT-1*.

Table 1 Frequency of correct responses to both tiers of each item in the *CECT-1* (N = 56) (% in parentheses)

Item no.	Combined tiers frequency	Item no.	Combined tiers frequency
1	50 (89.3)	6	33 (58.9)
2	31 (55.4)	7	34 (60.7)
3	7 (12.5)	8	36 (64.3)
4	39 (69.6)	9	14 (25.0)
5	23 (41.1)	10	15 (26.8)

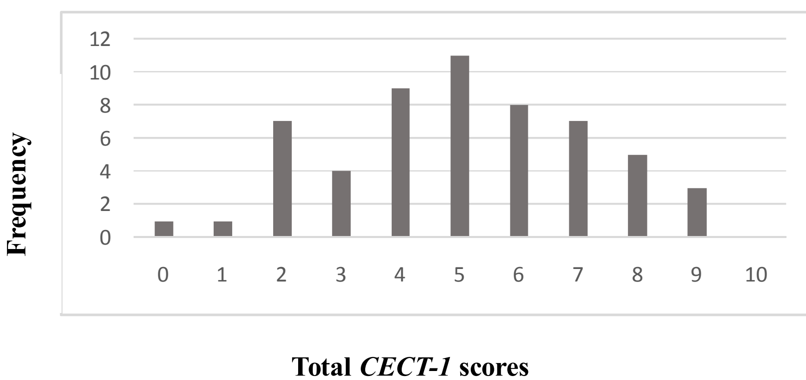

Figure 4 Distribution of Total *CECT-1* Scores (N = 56)

Conclusion and recommendations
The review of the research literature that was conducted as part of this study highlights several deficiencies in students' understanding about chemical equilibrium concepts. It is important that teachers themselves are aware of the misunderstandings that students tend to develop and therefore are able to take measures to develop scientifically acceptable understandings about chemical equilibrium concepts.

This research study has shown that similar to the studies that have been discussed in the literature review, the Year 12 Malaysian students possessed limited understanding about several chemical equilibrium concepts like, the reversibility of chemical reactions leading to establishing a state of equilibrium, the use of LCP in predicting changes in an equilibrium system resulting from perturbations to the system, and the effects of a catalyst or an inert gas on an equilibrium system. When using LCP in particular, it is important to be aware of the conditions under which the system concerned is being disturbed.

One major source of concern is in the inappropriate interpretation of LCP when referring to equilibrium systems involving the addition of an inert gas or when adding or removing a solid from a heterogeneous equilibrium system. Limited understanding about the influence of solids in equilibrium systems was reflected in Item 9 in the *CECT-1* involving the decomposition of solid $CaCO_3$ in a closed container; as many as 46.4% of students inappropriately applied LCP and suggested that addition of more solid $CaCO_3$ to the equilibrium system resulted in the production of more CaO and CO_2.

It is important therefore, that high school students have a firm foundation about the basic concepts of chemical equilibrium in preparation for more advanced study at university. Educators in preservice teaching programs need first to be made aware of students' misconceptions so that they are able to take appropriate measures to convey the correct ideas about chemical equilibrium concepts to their student teachers. At the same time, well-coordinated professional development courses need to be considered for inservice teachers.

References

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

Cheung, D. (2009). The adverse effects of Le Chatelier's principle on teacher understanding of chemical equilibrium. *Journal of Chemical Education, 86*(4), 514-518.

Cheung, D., Ma, H.-J., & Yang, J. (2009). Teachers' misconceptions about the effects of addition of more reactants or products on chemical equilibrium. *International Journal of Science and Mathematics Education, 7*(6), 1111-1133.

Cohen L., Manion L, and Morrison K., (2011), *Research methods in education* (7th ed.). Oxford, UK: Routledge.

Furió, C., Catalayud, M. L., Barcenas, S. L., & 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.

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* (pp. 70-99). Proceedings of the 1994 International Seminar, University of Dortmund, Germany. Dortmund: ICASE.

Gussarsky, E., & Gorodetsky, M. (1990). On the concept 'chemical equilibrium': The associative framework. *Journal of Research in Science Teaching, 27*, 197-204.

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

Huddle, P. A., & Pillay, A. E. (1996). An in-depth study of misconceptions in stoichiometry and chemical equilibrium at a South African university. *Journal of Research in Science Teaching, 33*, 65-78.

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

Kousathana, M., & Tsaparlis, G. (2002). Students' errors in solving numerical chemical equilibrium problems. *Chemistry Education Research & Practice, 3*(1), 5-17.

Lacy, J. E. (2005). Equilibria that shift left upon addition of more reactant. *Journal of Chemical Education, 82*(8), 1192-1193.

Nunally, J. C. & Bernstein, I. H. (1994). *Psychometric theory* (3rd. ed.). New York: McGraw-Hill.

Özmen, H. (2008). Determination of students' alternative conceptions about chemical equilibrium: A review of research and the case of Turkey. *Chemistry Education Research & Practice, 9*(3), 225-223.

Piquette, J. S., & Heikkinen, H. W. (2005). Strategies reported used by instructors to address student alternative conceptions in chemical equilibrium. *Journal of Research in Science Teaching, 42*(10), 1112-1134.

Quílez-Pardo, J. (1995). Students' and teachers' misapplications of Le Chatelier's Principle: Implications for the teaching of chemical equilibrium. *Journal of Research in Science Teaching, 32*(9), 939-957.

Quilez-Pardo, J., & Solaz-Portoles, J. (1995). Students' and teachers' misapplications of Le Chatelier's Principle: Implications for the teaching of chemical equilibrium. *Journal of Research in Science Teaching,* 32(9), 939-957.

Thomas, P. L., & Schwenz, R. W. (1998). College physical chemistry students' conceptions of equilibrium and fundamental thermodynamics. *Journal of Research in Science Teaching, 35*, 1151-1160.

Tyson, L., Treagust, D. F., & Bucat, R. (1999). The complexity of teaching and learning chemical equilibrium. *Journal of Chemical Education, 76*(4), 554-558.

Van Driel, J. H., & Gräber, W. (2002). The teaching and learning of chemical equilibrium. In J. K. Gilbert, O. D. Jong, R. Justi, D. F. Treagust & J. H. van Driel (Eds.). *Chemical education: Towards research-based practice* (pp. 271-292). Dordrecht, The Netherlands: Kluwer Academic Publishers.

Van Driel, J. H., De Vos, W., Verloop, N., & Dekkers, H. (1998). Developing secondary students' conceptions of chemical reactions: The introduction of chemical equilibrium. *International Journal of Science Education, 20,* 4, 379-392.

Voska, K. W., & Heikinnen, H. W. (2000). Identification and analysis of student conceptions used to solve chemical equilibrium problems. *Journal of Research in Science Teaching, 37*(2), 160-176.

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