Research article

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Understanding Le Châtelier's principle fundamentals: five key questions

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Abstract: The well-known Le Châtelier's principle is almost always mentioned when dealing with chemical equilibrium. Nevertheless, although a must in most general chemistry courses starting from the secondary level, when students face questions about it, some major misconceptions are often highlighted; to avoid this, a somewhat challenging problem is now presented. It can be deemed a very useful tool for a full understanding of this principle and chemical equilibrium as a whole. A generic chemical reaction at equilibrium is subject to different types of perturbation, and the student is required – in each case – to identify the new position of equilibrium among a number of proposals. The correct answers are finally provided along with the corresponding explanations.

Keywords: chemical equilibrium; key questions; Le Châtelier's Principle; misconceptions; problem solving.

Introduction

Le Châtelier's principle (Chang & Goldsby, 2015; Novak, 2018; Petrucci & Herring, 2016) is a useful tool to predict what happens when the conditions are changed in a chemical reaction in dynamic equilibrium. Nevertheless, its proper application often gives rise to doubts among 12th graders and freshmen (first-year students at the university). Here is an interesting proposal to check if they understand the fundamentals of this principle and also to avoid some frequent misconceptions (Cheung, 2009; Hackling & Garnett, 1985; Satriana, Yamtinah, & Ashadi Indriyanti, 2018), which may be summarized as follows: (a) incorrect control of the different variables involved; (b) scarce use of the equilibrium constant to predict shifts in equilibrium; (c) failure in the application of this principle to heterogeneous chemical equilibria; (d) poor explanations of the changes in equilibrium position. These misconceptions are often a consequence of the utilization of rote-learning and algorithmic procedures.

Let us consider the following endothermic ($\Delta H° > 0$) reaction:

$$2\,A(g) \rightleftharpoons B(g)$$

It is allowed to come to equilibrium inside a closed container. The equilibrium system can be depicted as shown in Figure 1.

It undergoes different changes thereafter, the corresponding new possible equilibrium systems being represented in the following numbered containers (Figure 2).

Students are then required to choose – in each of the following cases – the container which best describes the new position of equilibrium and provide a reasoned explanation for their answers. To analyze frequent misconceptions, this five-question test was administered to 74 first-year university chemistry students.

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Figure 1: Scheme of the equilibrium system.

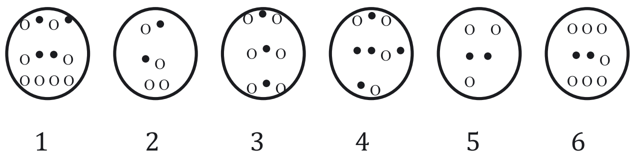

Figure 2: New positions of the equilibrium system.

a) The pressure of the system at equilibrium was decreased at constant temperature.
b) The temperature of the system at equilibrium was increased at constant pressure.
c) A defined amount of O was added to the system at equilibrium at constant volume.
d) A certain amount of an inert gas is added to the system at equilibrium. It must be assumed that this process takes place with no volume change.
e) A small amount of a catalyst is added to the system at equilibrium.

Correct answers

a) If the pressure is decreased, the equilibrium will shift in such a way that the pressure is increased again. This can be achieved by moving the position of equilibrium to the side with more moles of gas molecules, *i.e.*, to the left in this case. If this happens, the amount of reactant will increase whereas the amount of product will decrease, and therefore the ratio of ●s to Os will become lower than the original ratio (3:6). This situation only corresponds to the last container (ratio 2:7). *The correct answer is six.*
b) In an endothermic reaction, increasing temperature will result in a higher value of the equilibrium constant, since equilibrium will shift to the right. This also implies a greater ratio of ●s to Os. Taking into account that the sum of Os and ●s should be equal to the original amount (6 + 3 = 9), these two conditions are only met in container 4. *The correct answer is four.*
c) The original equilibrium system consisted of six Os and three ●s. The addition of a certain amount of A makes the equilibrium shift to the right (some of the Os will be transformed into ●s) until the equilibrium ratio ●/O is again reached. This is achieved in containers 1 and 3, but the latter has the initial amount of Os and ●s, which would not reflect the addition of some Os. *The correct answer is one.*
d) The addition of an inert gas into this equilibrium (gas phase) at constant volume does not cause any shift, since it does not change the partial pressures of O and ● in the container. Although the total pressure of the system increases, it does not affect the equilibrium constant. *The correct answer is three.* Nevertheless, it would also be interesting to consider what happens if the volume is allowed to increase in the process; in that case, the partial pressures of all gases would be decreased, resulting in a shift towards the side with more moles of gas molecules, *i.e.*, to the left. Under these conditions, the situation would be similar to the one described in (a), six being the correct answer.
e) The addition of a catalyst makes absolutely no difference to the position of equilibrium. The catalyst speeds up both the forward and back reaction to exactly the same extent, what means that their relative rates remain the same. *The correct answer is then three.*

Conclusions

The correct application of Le Châtelier’s Principle, *i.e.*, an accurate prediction about the evolution of a chemical equilibrium mixture that has been disturbed, is often undermined by its vague and ambiguous formulation as well as by the fact that many students consider each one of this Principle's qualitative statements as an easy rule that can infallibly be applied, whatever the case may be. For them, this rule is a concept that should be considered "mechanically", as it was demonstrated when the above mentioned five questions were raised among the sample of undergraduate students: On average, only 34.6% of the responding students (out of 74) answered all the questions correctly. The detailed results were the following:

(a) 67 correct answers (90.5%)
(b) 65 correct answers (87.8%)
(c) 65 correct answers (87.8%)
(d) 27 correct answers (36.5%)
(e) 59 correct answers (79.7%)

All in all, I believe that better results could be obtained if both chemical equilibrium concepts and the limited usefulness of Le Châtelier's principle would be taken into account. Teachers (and students) should never go beyond its range of applicability; otherwise, problems will be the order of the day.

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