Escher: The Waterfall and Chemical Equilibrium. An Analogy Derived From Art for Chemistry

Armando Marín-Becerra[†], Andoni Garritz*,[†] and Andrés Raviolo[‡]

†*Facultad de Química, Universidad Nacional Autónoma de México, México D.F. 04510, México,* ‡*Universidad Nacional de Río Negro y Universidad Nacional del Comahue, Bariloche, Río Negro, 8400, Argentina,* andoni@unam.mx

Abstract: The use of analogies is widely recognised as an effective teaching strategy that helps students to engage with difficult scientific concepts through a more familiar domain. Chemical equilibrium is a subject that students often find difficult to understand and, in an effort to address this problem, a simple analogy, inspired by "The Waterfall" picture by M. C. Escher, is proposed. This analogy, which is derived from art for chemistry, can be presented as a simple blackboard drawing or as an easy-to-build practical model. Both of these approaches would help to illustrate the dynamic nature of the chemical equilibrium and the controversial Le Châtelier´s principle.

Introduction

Many undergraduate students find it difficult to understand the concept of the chemical equilibrium, probably due to the image that many students may have about the term: *i.e.* as a perfectly balanced scale. This image is rather unfortunate, however, because a chemical equilibrium is neither static nor "balanced". Furthermore, when equilibrium is attained, the concentrations of the species involved no longer change and, in spite of its apparent static nature, we have to convince students that the forward and reverse reactions are actually taking place.

Chemical equilibrium has long been associated with difficulties in the learning process [1] and it is therefore not surprising that students often generate a variety of misconceptions about this topic [2–4]. As chemical equilibrium is the cornerstone of many other subjects – such as acid-base behaviour, catalysis, precipitation and solubility – it is very important to be aware of the alternative interpretations that students may have developed and attempt to overcome these and achieve conceptual change. Several proposals to help in the teaching and learning of this concept have recently been published [5–13].

It has long been recognised [1, 14] that three key aspects need to be appreciated to understand this concept properly:

(a) All reactions must be viewed as 'incomplete', *i.e.* reactants are never completely consumed in a reaction.
(b) The rate of the forward reaction decreases as reactants are consumed, whilst the rate of the reverse reaction increases with the concentration of the products. At equilibrium both rates are equal.
(c) Changes in the conditions of a system at equilibrium cause the extent of the reactions to change until a new equilibrium state is re-established.

The aim of this work is to describe a blackboard analogy (or an easy-to-build practical model) that can help to illustrate the concepts outlined above.

The use of analogies as a teaching tool has been reported to be one of the four successful strategies for learning about chemical equilibrium [4] and, over the years, different sorts of analogies have been proposed [15–20]. The analogy described here is not the first one in which chemical equilibrium is illustrated by transferring water between two containers. Since this idea was first described by N. Rakestraw [21], various 'hydraulic' analogies have been reported and these involve the transfer of water either manually [22–25] or mechanically [26, 27]. Nevertheless, we believe that the proposal described here is useful as the analogy can be developed from a simple blackboard drawing and, due to its resemblance to a well-known piece of art, in our experience it helps students to grasp the concepts being illustrated.

Description of the Analogy

Target and Analogue. The analogue must be a familiar domain whereas the target is an unknown field and there must be a set of relationships, maps or processes established between them [28]. In this case, the analogue is a system of two interconnected containers, in which the rate of water flowing into and out from them can be easily mapped to the forward and reverse rates of a reversible chemical reaction.

$$A + B \rightleftharpoons C + D$$
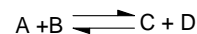
This analogy was conceived while considering "The Waterfall" drawing by M. C. Escher (Figure 1) and the blackboard analogy resembles this picture. First, it is important to make students aware of the fact that such perpetual motion machines are thermodynamically impossible.

---

* Address correspondence to this author.
† Universidad Nacional Autónoma de México.
‡ Universidad Nacional de Río Negro

Figure 1. M. C. Escher, The Waterfall (1961).

For a generic chemical reaction, $A + B \rightarrow$ products, the rate of the reaction can be described by the rate law: $V = -d[A]/dt = k\,[A]\,[B]$. Making $[A]\,[B] = R$ (where R = overall concentration of reactants), then equation 1 applies:

$$V = kR \qquad (1)$$

(This simplification can also be considered for reactions of higher order: $R = [A]^x[B]^y$).

This equation is similar to the one that describes the rate of water flowing from a container, such as those shown in Figure 2, in which the flux of water that comes through tube 'T' is directly proportional to both the height of the liquid and width of the tube. This situation can be described by equation 2:

$$V = qh \qquad (2)$$

where V is the rate of water coming out through tube 'T', h is the height of the liquid in the container and q is a constant related to the cross-section of the tube; *i.e.* the wider the tube, the larger the value of q.

In this case, equations (1) and (2) are very similar and the relationships that can be established between the two systems are straightforward: The overall concentration of reactants (R) can be related to the height of the liquid (h), and the rate constant (k) is related to the cross-section of the side tubing (related to q). The latter relationship will be fully understood when temperature changes are included in our analogy.

It is quite likely that many students would already be familiar with these types of containers and also with the following three facts on which the current analogy is based:

1. When a fully filled container is drained, the volume of water released per second will be at its highest rate at the beginning of the experiment and will steadily decrease as the water level decreases.
2. When a container is drained and filled simultaneously and if water drains at the same rate as it is added, the amount of water in the container will remain constant.
3. When comparing the rate of draining of two equally filled containers (Figure 2), container 'P' will drain faster than container 'R' because tube 'T' is wider in the former one.

As mentioned earlier, the targets are a pair of simultaneous reactions interrelated by a chemical equilibrium:

$$A + B \rightleftharpoons C + D$$
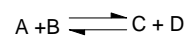
In order to represent these simultaneous reactions with containers such as those shown in Figure 2, it is required that container 'R' drains into container 'P' at the same time as container 'P' drains into container 'R'.

Clearly, this could not happen in the real world but, at the blackboard, two Escher-type hoses can be depicted (Figure 3).

If container 'R' is initially filled with water (at height h_0 in Figure 3) and container 'P' is initially empty, the rate at which the water starts flowing *from* container 'R' is at its maximum and will continuously decrease (as h_R decreases). Also, the rate at which the water flows *into* container 'R' starts at its minimum (zero) and will continuously increase (as h_P increases).

Eventually, both containers will be filled and drained at the same rate and therefore the state of equilibrium will be reached. From this point onwards, the amount of water in each container will remain constant.

Relations Between Analogue and Target

The relationships between the analogue and the target (chemical equilibrium) are very simple:

1. If the reaction initially starts from reactants it will develop forwards, beginning at its maximum rate and steadily decreasing. The rate at which products are converted to reactants will start at zero and will steadily increase.
2. Eventually, both rates (forward and reverse) will become equal, attaining chemical equilibrium in which the concentrations of reactants and products will no longer change.

In the blackboard analogue, equilibrium is attained when $q_R h_R = q_P h_P$, and as q_R and q_P are constants, so is their ratio $q_R/q_P = h_P/h_R$. Although the equilibrium values of h_P and h_R will depend on the amount of water used, their ratio h_P / h_R will not. Furthermore, for a fixed amount of water, equilibrium values of h_P and h_R will be constant regardless of which container was originally filled.

These properties and behaviour can easily be mapped to those observed in a chemical equilibrium in which concentrations at equilibrium will vary if the initial concentrations are modified but their ratio, the equilibrium constant (K_{eq}), remains constant as long as the temperature is kept constant.

This analogy suffers from the compartmentalised alternative conception of equilibrium, which is a common misconception that is present in several other analogies, where reactants and products are expressed in separate vessels or processes [29–31]. Nevertheless, as long as the attributes and limitations of the analogies used are highlighted and discussed with students, this approach certainly represents a valuable teaching strategy [32, 33].

Le Châtelier´s Principle

Several papers have been published that criticize the teaching of Le Châtelier´s principle [34–39]. For example, the
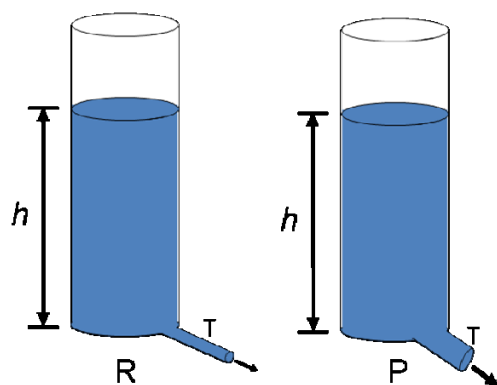
Figure 2. The two analogue containers with the same amount of water, showing that container 'P' drains water faster than 'R' because it has a wider draining tube.
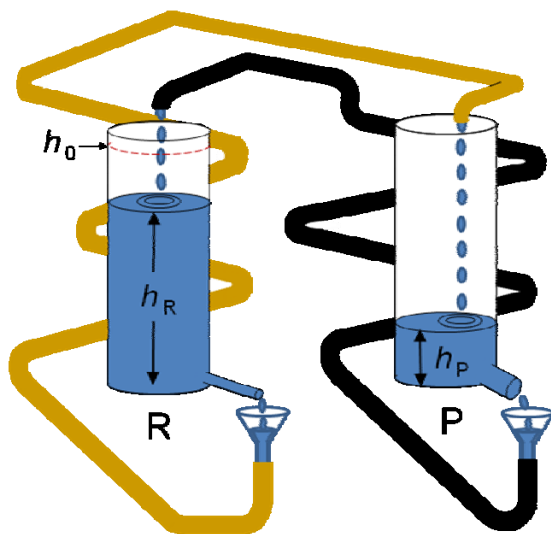

Figure 3. Representation of two interrelated containers using two "Escher hoses" in which the equilibrium is reached at certain values of h_R and h_P.

latter reference states that: "this paper presents evidence, both theoretical and empirical, to conclude that Le Châtelier's rules should be abandoned completely in chemical education". Nevertheless, the principle has acquired sufficient prominence in its usual vague and ambiguous form or in its correct one [34]. As a result, it could be convenient to take this principle into account, bearing in mind that its alleged universal validity is illusory and it suffers from pitfalls with changes of pressure, the addition of water or an inert gas or solid [5]. In the discussion below, the two main effects of the principle (perturbations of concentration and temperature) are developed in relation to the Waterfall Analogy:

> The sudden addition or removal of water from any of these containers will illustrate the effect that modifying the concentration of reactants (or products) has on a system at equilibrium:

Once the equilibrium is reached, if water is added or removed from one of the containers, the speed of draining of this container will be abruptly changed, therefore affecting the balance of draining and filling of both containers and the system will be consequently shifted from equilibrium. For example, the sudden addition of water to a container will cause

the speed of draining in that vessel to be higher than the speed of filling. As a result, the level of water in this vessel will steadily decrease while the level in the other will increase.

Eventually, a new equilibrium state will be reached in which the changes introduced will be partially counteracted. Thus the analogue conveniently illustrates the underlying processes that govern the Law of Mass Action.

> An increase or decrease in the diameter of the draining tube illustrates the effect of increasing or decreasing the temperature of a system at equilibrium.

Numerous textbooks, when dealing with temperature-induced changes, use an approach similar to the law of mass action: For instance, in the case of an exothermic process, heat can be seen as a "product" of the reaction and therefore increasing temperature (applying 'heat' to the reaction) will cause a shift towards reactants. Unfortunately, this approach does not explain, but only predicts, the consequence of temperature changes. The current analogy illustrates the changes that take place when temperature is modified.

As previously stated, the rate of a chemical reaction (A + B → products) is described by $V = k\,[A]\,[B]$, where k is the rate constant, which varies with temperature as described by the Arrhenius equation: $k = A\,\exp\{-E_a/RT\}$. The rate of any chemical reaction will therefore increase if the temperature increases and decrease if the temperature decreases. As there are two interrelated reactions in a chemical equilibrium, if the temperature is modified both reaction rates will be affected in the same way, but not to the same extent. This uneven shifting of k causes K_{eq} to be modified with temperature.

In the Arrhenius equation both E_a and A (activation energy and pre-exponential factor, respectively) are usually considered as constants that are not modified by temperature [40], therefore the relative change in k can be described by equation 3:

$$\Delta k(\%) = \left\{\frac{k(T_2)}{k(T_1)} - 1\right\} \times 100 = \left[\exp\left\{\frac{E_a}{R} x \frac{\Delta T}{T_1 T_2}\right\} - 1\right] \times 100 \quad (3)$$

With

$$\Delta T = T_2 - T_1$$

Consequently, the rate constant of the reaction with the largest activation energy will be the most affected. If we consider an endothermic equilibrium, a decrease in the temperature will lead to decreases in both rate constants, but as E_a of the forward reaction is larger than that of the reverse one, the rate constant of the former will decrease more markedly than that of the latter. Thus, a sudden drop in temperature will slow down both processes, but initially the forward reaction will be slower than the reverse one and, therefore, the reactants will be produced faster than they are consumed and their concentration will slowly increase until the two reactions rates once again become equal. Using the current analogy it is possible to illustrate this behaviour. In the analogue, the rate constant k is represented by the cross-section of the draining tube. Therefore in order to illustrate the effect of temperature two draining tubes could be depicted in each container, as shown in Figure 4.
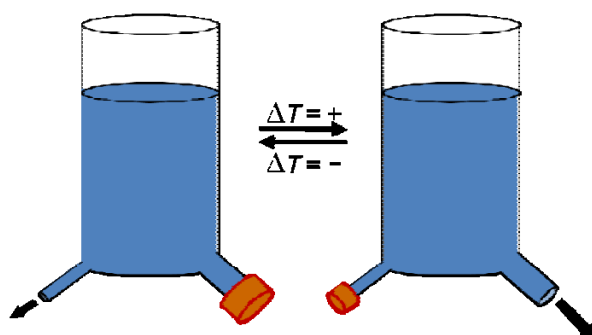
Figure 4. An increase or decrease in temperature can be illustrated by changing the draining tube used.
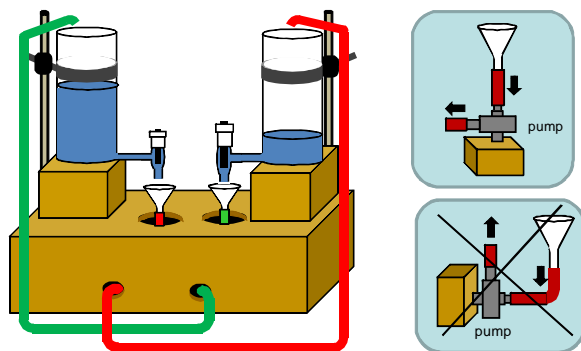

Figure 5. Suggested apparatus to illustrate the dynamic nature of a chemical equilibrium. The lower-right insert shows a configuration that is not recommended as air bubbles can be trapped within the feeding tube, a situation that would prevent water from flowing freely.

Suggested Apparatus

It has been mentioned that this analogy can be expressed as a simple blackboard drawing and/or as an easy-to-build practical model. The second alternative is represented in Figure 5 without, of course, thinking in terms of the impossible Escher hoses.

This apparatus requires two small pumps and the device will work as required as long as the maximum capacities (ft³/min) of the pumps are larger than the maximum draining speed of the containers. If the apparatus is built, it is important to make sure that the pumps are not directly connected to the containers, as this would invalidate the analogy; in this case the speed of draining would be seriously disrupted by the pumps. Also, as fine flux control is required (if temperature changes are to be demonstrated), it is suggested that needle valves are used as these are more suitable than common stopcocks. It is also desirable to leave a gap between the valve and the funnel so that students can clearly appreciate changes in the flux of water.

The effect of temperature in a chemical equilibrium may be illustrated more effectively in the apparatus. In such a case, the water flux can be modified using valves. It is important to mention that the constant 'q' would be related to the bore size of the valve (if they are fully open) and not to the diameter of tube 'T'. Therefore, the bore sizes of the valves should be different from each other, so that when both are fully opened and equilibrium is reached, h_R will be different from h_P.

It is also worth mentioning that modification of the water flux (by partially opening or closing valves) would change the original ratio h_P/h_P observed at equilibrium. This illustrates

that K_{eq} is modified by temperature because k_f and k_r do not change in the same proportion (where k_f and k_r are the rate constants of the forward and reverse processes, respectively). On the other hand, if the water flux is modified by the addition or removal of water from any of the containers, although the new equilibrium is reached according to Le Châtelier´s principle, the ratio h_P/h_P is not held constant (it varies by up to 10%) so we do not recommend the use of this practical model to illustrate the invariant value of K_{eq}.

Conclusions

A simple analogy is presented to illustrate both the dynamic nature of the chemical equilibrium and Le Châtelier's principle. Although this is not the first example of a hydraulic analogy, the approach proposed here allows one to highlight that the underlying reasons for Le Châtelier's principle are the kinetics of the forward and reverse processes. It is important to stress that, regardless of which of these arguments is preferred (the "mechanical" approach of Le Châtelier's principle or the kinetic argument), both approaches lead to the same conclusion. The current proposal is also a good pretext to introduce a relationship between chemistry and art.

References and Notes

1.   Maia, P. F.; Justi, R. *Int. J. Sci. Educ.* **2009**, *31*, 603–630.
2.   Garnett, P. J.; Garnett, P. J.; Hackling, M. W. *Stud. Sci. Educ.* **1995**, *25*, 69–95.
3.   Raviolo, A.; Martínez Aznar, M. *Educ. Quím.* **2003**, *14*, 159–165
4.   Piquette, J. S.; Heikkinnen H. W. *J. Res. Sci. Teach.* **2005**, *42*, 1112–1134.
5.   Tyson, L.; Treagust, D. F.; Bucat, R. B. *J. Chem. Educ.* **1999**, *76*, 554–558.
6.   Raviolo, A. *J. Chem. Educ.* **2001**, *78*, 629–631.
7.   Thomas, G. P.; McRobbie, C. J. *Int. J. Sci. Educ.* **2002**, *24*, 405–423
8.   Akkus, H.; Kadayifci, H.; Atasoy, B.; Geban, O. *Res. Sci. Technol. Educ.* **2003**, *21*, 209–227.
9.   Stieff, M.; Wilensky, U. *J. Sci. Educ. Technol.* **2003**, *12*, 285–302.
10.   Bilgin, I. *Int. J. Sci. Math. Educ.* **2006**, *4*, 467–484.
11.   Bilgin, I.; Geban, Ö. *J. Sci. Educ. Technol.* **2006**, *15*, 31–46.
12.   Rollnick, M.; Bennett, J.; Rhemtula, M.; Dharsey, N.; Ndlovu, T. *Int. J. Sci. Educ.* **2008**, *30*, 1365–1387.
13.   Raviolo, A.; Martínez Aznar, M., *J. Sci. Educ.* **2010**, *11*, 80–84.
14.   Justi, R.; Gilbert, J. K.; Ferreira, P. F. In Gilbert, J. K.; Treagust, D. (Eds.), *Multiple Representations in Chemical Education*; Springer: New Jersey, **2009**, 285–307.
15.   Dickinson, P.; Erhardt, W. *J. Chem. Educ.* **1991**, *68*, 930–931.
16.   Donati, E.; Jubert, A.; Andrade, G. *J. Anu. Latinoam. Educ. Quí.* **1992**, *2*, 259.
17.   Desser, D. *Sci. Teach.* **1996**, *63*, 40–43.
18.   Harrison J.; Buckley P. *J. Chem. Educ.* **2000**, *77*, 1013.
19.   Hanson R. M. *J. Chem. Educ.* **2003**, *80*, 1271–1274.
20.   Raviolo, A.; Garritz, A. *Chem. Educ. Res. Pract.* **2009**, *10*, 5–13.
21.   Rakestraw, N. *J. Chem. Educ.* **1926**, *3*, 450–451.
22.   Sorum, C. H. *J. Chem. Educ.* **1948**, *25*, 489–490.
23.   Hansen, R. C. *J. Chem. Educ.* **1984**, *61*, 804.
24.   Russell, J. M. *J. Chem. Educ.* **1988**, *65*, 871–872.
25.   Laurita, W. *J. Chem. Educ.* **1990**, *67*, 598.
26.   Karns, G. *J. Chem. Educ.* **1927**, *4*, 1431–1433.

27. Weigang O. *J. Chem. Educ.* **1962**, *39*, 146–147.

28. Orgill, M. K.; Bodner, G. In Pienta, N. J.; Cooper M. M.; Greenbowe, T. J. (Eds.); *Chemists' Guide to Effective Teaching*; Prentice-Hall: Upper Saddle River, New York; **2005**, 90–105.

29. Johnstone, A. H.; MacDonald, J. J.; Webb, G. *Educ. Chem.* **1977**, *14*, 169–171.

30. Gorodetsky, M.; Gussarsky, E. *Eur. J. Sci. Educ.* **1986**, *8*, 427–44.

31. Van Driel, J.; Gräber, W. In Gilbert et al. (Eds.); *Chemical Education: Towards Research-based Practice*; Springer: Netherlands; **2003**, 271–292.

32. Glynn, S. M. In: Glynn, S. M.; Yeany, R. H.; Britton, B. K. (Eds.); *The Psychology of Learning Science*; Hillsdale: New Jersey; **1991**, 219–240.

33. Harrison, A.; Coll, R. (Eds.) *Using Analogies in Middle and Secondary Science Classrooms*; Corwin Press: California; **2008**.

34. De Heer, J. *J. Chem. Educ.* **1957**, *34*, 375–380.

35. De Heer, J. *J. Chem. Educ.* **1958**, *35*, 133–136.

36. Allsop, R. T.; George, N. H. *Educ. Chem.* **1984**, *21*, 54–56.

37. Quílez, J.; Solaz, J. J. *J. Res. Sci. Teach.* **1995**, *32*, 939–957.

38. Furió, C.; Calatayud, M. L.; Barcenas, S. L.; Padilla, O. M. *Sci. Educ.* **2000**, *84*, 545–565.

39. Quílez, J. *Chem. Educ. Res. Pract.* **2004**, *5*, 281–300.

40. Leenson, I. A. *J. Chem. Educ.* **1999**, *76*, 1459–1460.