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A HISTORICAL APPROACH TO THE DEVELOPMENT OF CHEMICAL EQUILIBRIUM THROUGH THE EVOLUTION OF THE AFFINITY CONCEPT: SOME EDUCATIONAL SUGGESTIONS

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ABSTRACT: Three basic ideas should be considered when teaching and learning chemical equilibrium: incomplete reaction, reversibility and dynamics. In this study, we concentrate on how these three ideas have eventually defined the chemical equilibrium concept. To this end, we analyse the contexts of scientific inquiry that have allowed the growth of chemical equilibrium from the first ideas of *chemical affinity*. At the beginning of the 18th century, chemists began the construction of different affinity tables, based on the concept of elective affinities. Berthollet reworked this idea, considering that the amount of the substances involved in a reaction was a key factor accounting for the chemical forces. Guldberg and Waage attempted to measure those forces, formulating the first affinity mathematical equations. Finally, the first ideas providing a molecular interpretation of the macroscopic properties of equilibrium reactions were presented. The historical approach of the first key ideas may serve as a basis for an appropriate sequencing of the teaching and learning of chemical equilibrium. Finally, the paper aims also to encourage teachers to introduce historical and philosophical issues in their chemistry classrooms. [*Chem. Educ. Res. Pract.*: 2004, 5, 69-87]

KEY WORDS: *history; philosophy; student conceptions; affinity; chemical equilibrium; chemical forces; incomplete reaction; reversibility; dynamics; teaching/learning*

INTRODUCTION

History and philosophy of chemistry and chemistry education

Among science research educators there is an emergent consensus about the incorporation of the history of science into the curriculum. Matthews (1992) has eloquently argued about the advantages of using the history of science in science classes. Monk and Osborne (1997) discussed how such a proposal can be implemented.

A historical research on the development of chemistry should give explanatory clues about the processes involving the evolution of chemical concepts. In this way, one can focus on the problems which arose and how they were tackled. Thus, history of chemistry can be used by the teacher to get a *metadisciplinary* analysis of the didactic topics (Sánchez & Martín, 2003).

Historical knowledge of chemistry may contribute to the understanding by the teachers of students' difficulties and alternative conceptions, enabling them to address the

issues of instruction; that is, to formulate general chemical problems as well as didactic learning sequences that eventually may facilitate the apprenticeship of the related concepts. In this way, teachers can utilise a well-founded conceptualisation of the history of chemistry in order to design teaching strategies to promote students' conceptual restructuring of their early beliefs (Níaz, 1998a). On the other hand, historical knowledge may help students in their understanding of the nature of chemistry, clarifying different aspects of scientific inquiry and, therefore, enhancing students' capacities for critical thinking.

Research studies have shown the existence of similarities between some of the alternative conceptions held by students on science topics and the ideas of early scientists (Leite, 2002). The insight into that parallelism has led to suggestions about how the history of science can be used to promote conceptual change. Campanario (2002) suggested that the history of science can be used with a *metacognitive* dimension: "...this implies taking advantage of episodes of resistance to conceptual change in the history of science in order to stimulate students intellectual curiosity and make them more conscientious of their own misconceptions that result in resistance to change". Yet, obviously, the contexts in which contemporary students learn are different from those in which scientists of the past worked. Therefore, Gauld (1991) argued that, to be effective in the classroom, historical material must also take into account the significant differences between the ideas of modern day school students and the ones of early scientists.

Although compelling and preponderant research evidence for the inclusion of the history of chemistry into the chemistry curriculum may be missing or scattered (Duschl, 1994), there is enough supporting evidence to justify further attempts to do so (Wandersee & Griffard, 2002). Furthermore, Erduran (2001) has focused her attention on the philosophy of chemistry as a missing point in the curriculum, for many epistemological and ontological studies have been reduced to physics. Moreover, she has highlighted the importance of chemical epistemology/ontology in chemical education. Scerri (2001) has also claimed that chemical educators need to be introduced to the study of the nature of chemistry.

Despite the extensive suggestions on improving chemistry education through insights from the history and philosophy of science (HPS), the proposal has not been received with great enthusiasm by authors of science textbooks (Brackenridge, 1989; Níaz 1998b; Knain, 2001; Rodríguez & Níaz, 2002). A study based on seven high school chemistry textbooks concluded: "*All of the chemistry textbooks deemphasize science as a way of thinking. Their authors do not stress the importance of how chemists discover ideas and experiment, the historical development of chemistry concepts, cause-and-effect relationships, evidence and proof, and self-examination of one's thinking in the pursuit of knowledge*" (Chiappetta, Sethna & Fillman, 1991).

According to Níaz (2000), the inadequate way in which history of science is dealt with in textbooks is not due to limitations of space but rather to a lack of a HPS framework. Therefore, one of the key aspects that contributes to the aforementioned obstacle in the implementation of HPS issues seems to be lack of an epistemological perspective in the teachers' background (Kauffman, 1989; Blanco & Níaz, 1998) as well as with teachers' attitudes (Lederman, 1999). Thus, a necessary initial condition for an effective introduction of the HPS in the science curriculum implies the elaboration of available works that teachers may find helpful in the reconstruction of some essential concepts. From seminal works such as the one by Conant (1948), many authors have focused on this issue. But there is still a lot of work to be done, particularly in the case of chemistry. The challenge seems to be to develop new material using the history and philosophy of chemistry in order to help chemical educators to promote learning in chemistry (Paixao & Cachapuz, 2000). Bearing this aim in mind, one key point to be focused on is giving clues about the development in the knowledge

of the concept of chemical reaction. Many works have been devoted to Lavoisier as well as to the chemical revolution. A recent paper (Justi & Gilbert, 1999) has tried to broaden our knowledge of the chemical reaction in the case of models of chemical kinetics.

With this paper, our main aim is to contribute to the realisation of the chemical reactivity concept, tracing the evolution of the concept of chemical affinity that eventually supported the concept of chemical equilibrium. In addition, the paper aims to promote teachers' philosophical/historical chemical knowledge. Hence, it may contribute to familiarise teachers with how chemical knowledge growth occurs, which, in short, would allow them to develop the necessary capability of transforming subject matter into teachable content.

The introduction of chemical equilibrium in the classroom

The problems associated with a proper understanding of chemical equilibrium concepts have been reviewed by several authors (Griffiths, 1994; Garnett, Garnett, & Hacking, 1995; Quílez & Solaz, 1995; Van Driel & Gräber, 2002; Raviolo & Martínez, 2003). In introductory chemistry lessons, chemical reactions are presented as proceeding to completion, taking place in one direction. Yet, in the case of chemical equilibrium, three basic ideas should be considered (Van Driel, de Vos, Verloop, & Dekkers, 1998): *incomplete reaction*, *reversibility* and *dynamics*. These three concepts are difficult for the students to grasp, for when they begin the study of chemical equilibrium, they are aware that *all* reactions take place in only one sense, and that a chemical reaction stops when one of the reactants disappears. As a consequence, students face several cognitive conflicts when dealing with chemical equilibrium reactions. The most observed misunderstandings emerging from those conflicts can be summarised as follows:

1. Students (Driscoll, 1960; Wheeler & Kass, 1978; Hackling & Garnett, 1985; Banerjee, 1991):
 - often do not discriminate between reactions that go to completion and reversible reactions;
 - may believe that the forward reaction goes to completion before the reverse reaction commences;
 - may fail to distinguish between rate (how fast) and extent (how far);
 - often think that the rate of the forward reaction increases with time from the mixing of reactants until the equilibrium is established.
2. Students often fail to understand the dynamic nature of a system in a state of chemical equilibrium. Instead, many of them hold a static conception, for they believe that 'nothing happens' in that state (Godoretsky & Gussarsky, 1986; Thomas & Schwenz, 1998).
3. Students often conceptualise equilibrium as oscillating like a pendulum (Bergquist & Heilkkinen, 1990; Van Driel et al., 1998).
4. Students may have a compartmentalised view of equilibrium (Johnstone, MacDonald & Webb, 1977; Furió & Ortiz, 1983; Cachapuz & Maskill, 1989; Stavridou & Solomonidou, 2000).
5. Students may believe that mass and concentration mean the same thing for substances in equilibrium systems (Wheeler & Kass, 1978; Quílez & Solaz, 1995; Quílez, 2004).
6. Students may believe that the concentrations of the reactants at equilibrium equal the concentrations of the products (Hackling & Garnett, 1985; Huddle & Pillay, 1996).
7. Students may find difficulties in understanding and using many of the terms (*e.g.* equilibrium, displacement, shift, stress, balanced, reversible, etc) used in chemical equilibrium lessons (Évrard, Huynen & De Bueger-Vander Broght, 1998; Pedrosa & Dias, 2000; Quílez, 2004).

THE HISTORICAL DEVELOPMENT OF CHEMICAL EQUILIBRIUM

The historical development of chemical equilibrium has been analysed in several educational studies (Van Driel, 1990; Quílez, 1995; Ganaras, 1998), which produced insights into some key ideas in the evolution of the concepts related with the study of equilibrium systems, that is, reporting the problems that arose and how 19th-century scientist coped with them. It was expected that each of those historical analyses would contribute to teachers' understanding of students' reasoning and conceptual difficulties related to chemical equilibrium.

As it has been stated before, the first and main aim of this work is to contribute to the historical reconstruction of the concepts involved in the study of chemical equilibrium, accounting for the different early interpretations given in the context of the study of incomplete reactions. Thus, we will concentrate on how these three key basic ideas: *incomplete reaction*, *reversibility* and *dynamics* have eventually defined the chemical equilibrium concept. Keeping all this in mind, we will try to analyse the contexts of scientific inquiry that have allowed the growth of chemical equilibrium from the first ideas of *chemical affinity*. This requires searching for answers to the following questions/problems:

- which were the theoretical frames that supported it;
- how the first ideas have been accepted or rejected;
- which were the problems faced and why;
- what knowledge counted and why;
- what were the different meanings of it; and, therefore,
- how this concept has evolved through time.

The starting point of this historical reconstruction will be the state of the art in the construction of the first affinity tables during the 18th century. We will show that those studies were the origin to the understanding of chemical equilibrium systems. Abandoning the Aristotelian conception of matter as well as the first attempts at measuring relative affinities enabled scientists to provide new explanatory ideas for chemical reactions.

Monitoring the historical development of chemical affinity will let us grasp the fundamentals of a process that has allowed the construction of the current background to the facts and concepts involved when dealing with chemical equilibrium reactions. The study will help us in the understanding of the searching for the first mathematical laws, based on previous empirical studies, in which scientists tried to find which were the factors that allowed a chemical reaction to take place.

Despite the fact that the concept of *affinity* was the key idea for the development of the chemical equilibrium concept during the last quarter of the 18th century and the 19th century, we will show that this concept was not given a precise definition. To its vague and ambiguous meanings we must add its polysemy. All of these features have determined the structure of the following discussion. Consequently, our historical analysis will be focused on these three main points: a) its different meanings (Goupil, 1991); b) the searching for finding the factors it depended on (Holmes, 1962); c) the proposal for quantifying this property of chemicals (Lemoine, 1882).

Affinity tables

The oldest tradition that explained why chemicals reacted was based on an anthropomorphic view of nature, for it established that chemical reactions were due to the

concepts of sympathy and antipathy between substances, and might be traced back ultimately to Empedocles's principles of 'love and strife' (Duncan, 1970). The first idea of affinity, as a term expressing the tendency of substances to react, was introduced by Albertus Magnus. This concept stated that "the greater the affinity (resemblance, similarity or relationship) between two chemicals, the greater is the tendency of these substances to react". This view of the interaction between bodies occurring most easily between closely related substances ('like assorts with like') is an idea that goes back to Hippocrates (Partington, 1970).

In the early years of the 18th century, Newton tried to address a theoretical explanation about why some substances reacted with others. In the thirty-first Query of his book *Optics*, he considered that in chemistry there would be forces similar to the gravitational ones. These forces were manifested only at a very short distance, and it was assumed that the extent of those forces depended on the type of substances involved. As a consequence, some scientists tried to give account of the measure of these 'elective affinities'. Within this theoretical basis, Newton introduced a mechanical view for chemistry.

The chemists of the 18th century, either under the Newtonian paradigm or with the aim of systematising all the known chemical behaviour, began the construction of the first affinity tables. It was, essentially, an attempt at giving a quantitative approach in order to measure the differences in the reactivity of bodies. The earliest affinity table was published by E.F. Geoffroy in 1718. This table consists of sixteen columns. At the head of each column there is the traditional symbol of a substance (or a group of substances to which it refers). Below it, the symbols for the substances with which it reacts are arranged in order of their affinity for it. Therefore, each substance will displace from combination any of those lower down the column. Although it is difficult to prove an influence of Newtonian matter theory on Geoffroy's table (Klein, 1995), it can be asserted that the device of this table initiated a tradition that tried to formulate empirical laws that would make chemistry respectable and might even be expressible mathematically (Duncan, 1970). In accordance with this purpose, several authors attempted to determine quantitatively the magnitude of the force of affinity or chemical attraction. Wenzel, Kirwan, Guyton de Morveau, and Fourcroy are some of the most remarkable chemists that adhered to this tradition (Duncan, 1996).

Among the many chemists who contributed to the elaboration of tables of chemical affinities, the Swedish chemist T.O. Bergman made the most extensive studies of displacement reactions. He published in 1775 'De Attractionibus Electivis'. This table, as well as those that followed till 1784, was made keeping in mind the aim of studying all the possible reactions, and was founded on the Newtonian interpretation of chemical affinities. Thus, this conceptual framework established that chemical combinations were the result of the *elective affinities*, which solely depended on the nature of the substances involved in the reaction. The determination of the affinities gave a relative order, which accounted for the interpretation of displacement reactions. For example, if a substance A reacted with another substance BC, producing two new substances AB and C, it was concluded that the affinity of A over B was greater than the one of C. This framework was of applicability to reactions between acids, bases and salts. Therefore, an acid replaced another one if its affinity over a base was greater than the one initially combined with the base. Another field of application was the interpretation of the reactions of metals in solution.

Bergman considered that all chemical reactions were complete and took place only in one sense. However, he was aware of other factors that also affected chemical reactions: the possibility of formation of gases depending on the temperature, the different solubility of substances or the influence of the mass of the substances over the course of the reaction. But Bergman did not believe that any influence other than heat could mask the forces of affinities. Therefore, he felt that few remaining anomalous reactions resulted from inadequate

data, believing that further and careful experimentation would enable chemists to fit all reactions into ordered displacement affinity series without inconsistencies (Holmes, 1962). On the contrary, new anomalies (due to the initial amounts of the reactants, the solubility of substances or their volatility) were reported, although they were initially considered as external factors that could compensate the true relative order of affinities.

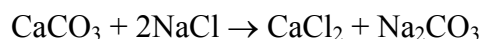
Berthollet and the importance of the mass of the reactants

At the end of the 18th century, the concept of affinity was consolidated as a coherent system when trying to explain chemical reactions. It was assumed that affinity was a constant property of the substances and that it manifested itself in an elective way.

Berthollet, who was a professor of Chemistry at the *École Normale*, initially adhered to the paradigm of elective affinities. According to this theoretical framework, it was assumed impossible that a reaction whose direction was determined by the relative order of affinities could be reversed. Chemical reversibility was thus theoretically forbidden. But, as we will extensively discuss later, the social demand of pure nitre as well as the teaching program which Berthollet developed at the *École Normale*, prompted him to a revision of the concept of elective affinities (Grapí & Izquierdo, 1997).

We must place the work of Berthollet in the socio-political context that followed the *French Revolution*. In 1789 he faced the problem of the invariability of affinities when trying to find a reliable test for the determination of the purity of nitre. The anomalies he found when dealing with this problem reappeared four years later when he was appointed director of a refinery of nitre for the production of gunpowder. The obtaining of pure KNO_3 required some recrystallizations and Berthollet took into account that as the concentration of nitrate increased in the solution, the solution decreased its capacity for dissolving a new amount of nitrate. He interpreted this anomaly stating that the affinity responsible in the process of dissolution was not an absolute force; therefore, in this phenomenon there would be an equilibrium between antagonistic forces.

Berthollet had to organise all this new knowledge for his classes at the *École Normale*. The effect of the proportions of substances was not an anomaly anymore. It challenged the previous theory, for the result of the amount of substances was irreconcilable with the principles of elective affinities. Berthollet's ideas, which were developed from experiences with chemical reactions on a large scale, had a new frame of implementation thanks to the trip he made to Egypt in 1798, during Napoleon's expedition. He observed the continuous formation of sodium carbonate on the edge of 'sodium lakes'. We can represent this reaction as follows:



This reaction was the inverse of the reaction predicted by the theory of elective affinities. Berthollet accounted for it by means of the great quantities of sodium chloride and calcium carbonate present and the continuous removal of the products: in point of fact, sodium carbonate formed a crust around the edges of the lake, and the deliquescent calcium chloride seeped into the ground.

When Berthollet returned to France, he published his findings in several journals and in his book *Essai de Statique Chimique* (1803). He did not deny the action of affinities in chemical reactions, but called attention to the mass as one of the factors affecting the result of a reaction (Holmes, 1962). That is, the mass of the reactants could reverse the reaction predicted by the scale of relative affinities. Thus, if two substances are competing to combine

with a third substance for which they have unequal affinities, a relative large quantity of the substance with weaker affinity may exert a force that can surpass the force of the substance with greater affinity.

Berthollet adhered to the Newtonian concept of force in order to explain chemical reactions. Consequently, chemical affinity was a kind of gravitational force, for the force of affinity was proportional to the mass of the reactant. Thus, any displacement reaction was never complete: there was an equilibrium state between opposite affinity forces. The strength of these forces, therefore, depended on two factors: the difference in their relative affinities and the quantitative proportion. The achieved equilibrium state was, in an analogous manner as in mechanics, static. Moreover, the extent of a chemical reaction was determined by the physical state of the reactants because it might affect the degree to which the affinities could play a role. Many reactions take place in solution, so if a product is an insoluble solid or a gas, it cannot exert its affinity in the solution, for as it leaves the solution its active mass decreases. This explanation accounted for the fact that many reactions continue to take place until at least one of the reactants exhausts.

The new conception improved the previous idea of *elective affinity*, and deprived it of the leading role that it had played during the 18th century. The leading role was now assigned to the concept of *chemical action*, understood as the tendency between two different substances to form a new combination, exerted according to both their relative affinity and their proportional amounts. Thus, the consideration of the mass of the reactants as a key factor allowed the explanation of incomplete reactions as well as of the fact that both the direct reaction (permitted on the basis of the theoretical frame of elective affinities) and the inverse one (forbidden on the same basis) could occur. The sense in which a reaction took place was determined by the quantitative proportion of the chemicals involved in the reaction.

Berthollet's theory was not exempt from both flaws and difficulties. Lemoine (1882) remarked as facts that contradicted Berthollet's laws the reactions in which soluble salts were formed from insoluble ones, as well as the decomposition of substances by the action of gaseous acids and bases. Moreover, the difficulties that Berthollet's ideas faced can be summarised in the following aspects:

- a) The high level of acceptance of the theory of elective affinities among his contemporary chemists; this theory persisted during some decades as a theoretical support of the experimental investigations.
- b) The inherent difficulty of the new ideas, which made it difficult to be fully understood.
- c) The emergence of Dalton's atomic theory as well as of Berzelius' electrochemical theory (Levere, 1971).

Berthollet's conception of affinity had an important corollary: since affinities were a manifestation of universal attraction, all particles exerted an attraction toward all others, tending to unite them in chemical combination. Hence, combinations between particles in variable proportion were likely. This last assertion confronted with Dalton's new atomic theory, which established the principle of definite proportions as a suitable theoretical basis. As a consequence, the interest and success in the determination of atomic weights, and in the examination of the composition of chemical compounds impeded a proper development of Berthollet's theory. In addition, textbooks did not transmit properly the theoretical basis suggested by Berthollet, while his ideas had to compete with the influence of Fourcroy and his school (which supported the theory of elective affinities) in the textbook market (Grapí, 2001).

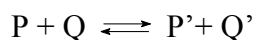
Berthollet hoped that, eventually, his theory would supplant Bergman's determinations of affinities. But after his method had proven to be invalid, it was thought that affinities could not be measured at all (Holmes, 1862). However, at the beginning of the second half of the 19th century the interpretation of new experimental facts allowed the reformulation of his ideas. The new theory had a mathematical support, which, as their authors stated, finally allowed the quantification of the chemical affinities.

The first mathematical formulation of chemical equilibria: the work of Guldberg and Waage

In 1862, two French chemists, Berthelot and Saint-Gilles, gave a new experimental approach to the study of the reactions in dissolution. They thought that the reactions between acids, bases and salts were not appropriate in the study of chemical equilibria because they were so fast that any analytical technique broke the equilibrium. These disadvantages were overcome when they decided to turn to the study of esterification reactions, for their rates were slow enough, and thus facilitated their study. Besides, the amounts of each chemical in the equilibrium position were always high enough to be easily measured.

Berthelot's and Saint-Gilles' experimental findings were the starting point for the investigations performed by two Norwegian scientists: Guldberg and Waage. They tried to find a general mathematical equation that would account for the experimental data. Their aim was to find a theory that could reconcile the earlier ideas of Bergman and of Berthollet or that would overcome them. In their first work of 1864 (Waage & Guldberg, 1986), they took into account mechanics as paradigm, and focused on the measurement of what was responsible for the, as they called them, *chemical forces*. Convinced that chemistry should become, like mechanics, a science of forces and their effects, Waage's and Guldberg's purpose was the development of a mathematical theory of chemical affinity. For example, for a process that they called simple (which nowadays we represent as $A \rightleftharpoons B + C$), Guldberg and Waage stated: "... *two forces assert themselves, either a composing or a decomposing, or an acting and a reacting, and we view it as unavoidably necessary to regard these forces together if one is to find any quantitative expression of these forces.*"

Unlike Berthollet, Guldberg and Waage assumed that chemical forces were not proportional to the amounts of the substances involved in the reaction, but to the *active masses* (concentrations). For each substance, its active mass was the concentration raised to a power that they determined by experiment. Thus, for a process that nowadays we represent as

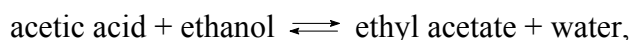


they argued as follows:

If one begins with the general system which contains the four active substances in a variable relationship and designates the amounts of these substances, reduced to the same volume, by p , q , p' , and q' , then, when the equilibrium state has occurred, a certain amount x of the two first substances will be transformed. The amounts of P , Q , P' , and Q' which keep each other in equilibrium will be consequently $p - x$, $q - x$, $p' + x$, and $q' + x$ respectively. According to the law of mass action, the action force for the first two substances is $\alpha(p - x)^a(q - x)^b$ and that for the last two is $\alpha'(p' + x)^a(q' + x)^b$ [where α and α' were proportion constants and a and b exponents, all to be determined by experiment]. At the equilibrium state the following equality should apply:

$$\alpha(p - x)^a(q - x)^b = \alpha'(p' + x)^a(q' + x)^b$$

Applying this approach to the equilibrium



they obtained the following results: $a = 1$, $b = 0.786$; $a' = 0.846$; $b' = 0.807$; $\alpha/\alpha' = 0.502$.

The above equation was indeed the first equation that approximates the mathematical expression of what we call nowadays *equilibrium constant*. But we must notice that they obtained an equation that represented a balance between two *chemical forces*. Although they later argued in terms of the *rates* of reactions in forward and reverse directions, initially they did it in terms of *forces*. Besides, the exponents were determined empirically and, thus, they bore no relationship to the stoichiometry. Only in a later paper appeared in 1879 did Guldberg and Waage obtain an equation similar to the equilibrium constant (Guldberg & Waage, 1879). In it, the exponents were the stoichiometric coefficients in the chemical equation that represents the equilibrium system.

Laidler (1995) stated that in spite of the fact that this was the correct relationship, they had not arrived at it in anything like a satisfactory way. Neither did they make any contribution to kinetics, since they worked in terms of forces and not of rates, although they did tentatively suggest that the rates might be proportional to the forces. However, the first equation obtained by Guldberg and Waage represented a promising starting point in the search for a quantitative determination of chemical affinities (Lindauer, 1962). The consideration of the concentrations of the substances involved in the equilibrium system, instead of their amounts, was a key factor that accounted for the evolution of the chemical equilibrium reactions.

At the end of their first article, Guldberg and Waage made reference to the former theories of chemical affinity of both Bergman and Berthollet. They pointed out that Bergman's theory had been refuted by many chemical processes and that it was totally in conflict with the theory presented by them. In contrast, they stated that they had adopted part of Berthollet's theory. However, they had refuted that the affinity was always proportional to the mass. Eventually, Guldberg and Waage resolved the dispute which had lasted for sixty years by showing that Bergman's complete reactions were a limiting case of Berthollet's partial reactions, both accounted for by a single equation (Holmes, 1962).

As Servos (1990) pointed out, Guldberg's and Waage's work did not produce an immediate interest in the study of the *law of mass action*. The main reason was that affinity studies did not represent a coherent set of problems, nor did they draw the attention of a network of scientists in close communication with one another. In the case of the two Norwegian scientists, their geographical and linguistic isolation, as well as their personal styles, did little to foster productive contacts. On the other hand, initially, only a small number of applications of the law were found, and, as Guldberg and Waage stated, chemists were concerned with finding new compounds, rather than with dealing with tedious and less rewarding investigations. Besides, the isolation of chemists from physics did not contribute to the development of these first ideas.

About dynamics in chemical equilibrium

In the ancient and medieval times, a rapid change meant an easy one, that is, the more readily one substance is transformed into another, the quicker this process occurs (Mierzecki, 1991). This view pertained to observations related to physical changes and changes of inorganic compounds.

The first systematic idea about time in chemical reactions was formulated by Wenzel (Farber, 1961). In 1777 he published the “*Theory of the affinities of substances*”, in which he described some measurements of the rates of the dissolution of metals in acids. He found that the rate at which metals were dissolved was influenced by the concentration of the acid as well as by the nature of the acid. As his goal was to estimate chemical affinities, he concluded that the affinity of substances to a common solvent was inverse to the time of dissolution. But Wenzel’s findings did not attract the attention of contemporaries, and his work was forgotten (Lindauer, 1962). As stated above, the chemists of the time were primarily concerned with discovering new compounds, and had not much interest in interpreting chemical behaviour in terms of any kind of conceptual theory. Despite this, new experiments made it possible to gain a better insight into the role of the time variable.

The birth of chemical kinetics is often considered to have occurred in 1850, when the German chemist Wilhelmy studied quantitatively the rate of inversion of sucrose (Laidler, 1985). Wilhelmy’s work was unnoticed until Ostwald drew attention to it. Other scientists such as Williamson, Berthelot and Saint Gilles, Guldberg and Waage, and Hartcut and Esson developed new quantitative studies of the factors upon which the rate of reaction depended (Partington, 1970; Laidler, 1995). All these contributions to the mathematical implementation of chemical kinetics constituted an important milestone in the development of chemical equilibrium, for chemists became aware of mass action as an important factor in the outcome of chemical reactions.

In 1850, Williamson (1851-1854), studying the incomplete esterification reactions, was the first scientist to propose a submicroscopic model in order to explain the ‘static’ state of chemical equilibrium. He did not consider this equilibrium as a situation in which nothing happens; on the contrary, he assumed that two reactions run simultaneously, each in opposite direction. Thus, ‘reactants’ as well as ‘products’ were constantly forming and decomposing in a way that the amount of all the substances involved remains constant. This dynamic balance was achieved assuming an interchanging of atoms, equal in absolute number in each moment of time, taking place in opposite direction. Consequently, the relative velocity of transfer of analogous atoms in each of the two directions was not the same, for it was greater for the substances whose quantity was less.

A new attempt to explain the molecular changes that take place in an equilibrium state was due to Pfaundler (Lemoine, 1882; Lund, 1965, 1968; Snelders, 1977; Berger, 1997). In 1867, he wrote an article which treated a chemical reaction in terms of the kinetic theory developed by Clausius and Maxwell. Later, Berthelot, in his *Essai de mécanique chimique* (1879), performed a qualitative discussion that was similar to the one given by Pfaundler. Eventually, Guldberg and Waage (1879), in their third and last article on chemical affinity referred to Pfaundler’s theory in their argumentation. But, before accounting for this theory, we must refer to its foundation.

In order to trace back Pfaundler’s theory, we must consider that in the middle of the 19th century, thermodynamics was boosted by dramatic developments. Taking into account Clausius’s ideas about the nature of heat, some authors tried to explain both physical and chemical processes in terms of molecular kinetics. In 1857 Clausius published an article entitled ‘On the kind of motion which we call heat’ in which he explained the partial evaporation of liquids in closed systems. He assumed that in liquids the individual molecules might have velocities which deviate from the mean within wide limits. Only the molecules with enough high kinetic energy were able to overcome the forces of cohesion in the liquid. Thus, a previously evacuated space above the liquid would be filled with an increasing number of molecules, which behaved as a gas, colliding with the walls of the vessel as well as the surface of the liquid phase. Therefore, some molecules from the gas would be captured

in their collision with the liquid surface. Eventually, the vapour pressure does not increase and remains constant, which was assumed as a dynamic equilibrium because it implied a state in which both evaporation and condensation simultaneously happened, exchanging equal number of molecules.

Ten years after Clausius's paper on the kinetic theory of evaporation, Pfaundler applied these previous physical ideas to develop a theory of chemical dissociation. In the case of partial decomposition of a gas, Pfaundler reasoned assuming that at a given temperature equal amounts of molecules decompose and unite by collision. That explanation required that not all molecules were in the same state of motion at a given temperature, for only a small amount of collisions were effective to produce chemical reaction both in the decomposition and in the formation senses. Eventually, a balanced molecular chemical equilibrium was achieved. Pfaundler applied his ideas not only to dissociation phenomena, but also to chemical equilibria and to the law of mass action. Arguing this way, he disagreed with Williamson's idea that there was a continuous exchange of elements in a molecular aggregate, finding his own ideas about distribution of motion over the individual molecules to provide a better explanation, which had turned into a more generally applicable theory.

EDUCATIONAL IMPLICATIONS AND SUGGESTIONS

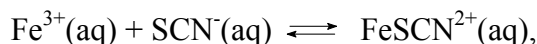
The historical approach of the first key ideas regarding the concept of chemical equilibrium may serve as a basis for an appropriate sequence of learning in the introduction and development of this topic. The historical reconstruction of the concept of chemical affinity allows teachers to challenge the first student ideas regarding chemical reactions: that is, these processes are produced always in one sense and continue to take place until at least one of the reactants is consumed. A critical reflection about those conceptions may facilitate the construction of two of the basic ideas of chemical equilibrium reactions: reversibility and incompleteness.

It is possible to develop such a historical reconstruction in parallel with an experimental approach, by selecting a set of challenging chemical equilibrium reactions. The study of these reactions should, in its first stage, focus only on macroscopic changes, and not on their explanation using a kinetic model of reaction. (The dynamics of chemical equilibrium reactions could be developed in a second stage - see below.) In this way, the selected reactions may contribute not only to the questioning of the first ideas, but also they may enhance those ideas, employing conceptual thinking in a process of conceptual change (Wandersee, Mintzes, & Novak, 1994). The procedural and motivational issues inherent to this practical discussion are likely to attract students' interest and ensure a warm environment in the process of evolution of ideas.

This first stage can culminate with an empirical introduction of the Equilibrium Law, that is, the mathematical expressions for K_c and K_p will be presented through a mathematical interpretation of empirical data. This can be implemented in the laboratory by means of the determination of the value of K_c for a esterification reaction (Hill & Holman, 1995). The empirical derivation of the Equilibrium Law allows students to realise that, at a given temperature, there is not a unique position of equilibrium. On the contrary, there are a lot of values of amounts (*i.e.* concentrations) that agree with the value of the equilibrium constant when they are introduced appropriately into the corresponding mathematical expression. Those sets of equilibrium values can be achieved starting from several amounts of 'reactants' or 'products' or both. Furthermore, this mathematical emphasis is the basis for a further treatment of systems that are not in chemical equilibrium, in order to predict their evolution,

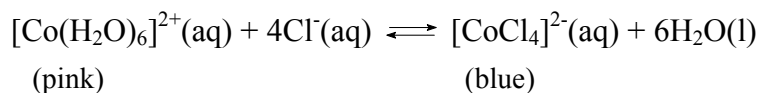
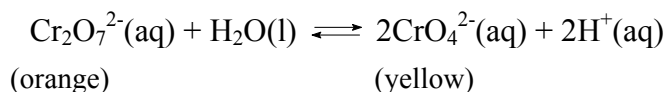
which is an alternative to the traditional use of the qualitative statements of Le Chatelier's principle (Quílez & Solaz, 1995; Quílez, 2004).

The idea of *incompleteness* (that is, once the equilibrium is achieved, the concentrations of all the substances involved remain constant) may be introduced as a challenging problem. The equilibrium reaction



that was studied by Gladstone (1855) in the 19th century, may serve as an excellent example in order to develop in the laboratory this concept (Van Driel, de Vos & Verlop, 1998). Also, some other discrepant event laboratory activities, such as the ones discussed by DeMeo (2002), may contribute to change students' previous notions of complete chemical reactions. Thus, limiting-excess stoichiometry may be used to introduce equilibrium reactions through the qualitative investigation of two precipitation reactions: (i) the formation of lead carbonate from aqueous solutions of lead nitrate and of sodium carbonate; and (ii) the formation of lead iodide from aqueous solutions of lead nitrate and of potassium iodide.

The concept of the *reversibility* of chemical reactions can be studied experimentally by means of changing the concentrations of reactants or products in the following equilibrium reactions, by observing and explaining the changes in colour:



(The second reaction can also be reversed by changing the temperature.) In each of the two above reactions, gradual transitions in the colour of the solution can be performed; for example, in the chromate-dichromate solution, gradual colour transitions red - to orange - to yellow can be worked out. Further examples can be performed using indicators in acid-base reactions (Connor, 1991). The interpretation of these events may help students to anchor the concepts of incompleteness and reversibility.

Once the equilibrium law and the concepts of reversibility and incompleteness have been introduced, it is time to explain all those aspects using a chemical model of reaction. The explanation of why a chemical reaction advances till a certain point without consuming completely the reactants can be given with the help of a kinetic theory. Van Driel et al (1998) have suggested that rather than making the dynamic model of chemical equilibrium accessible for students through analogies and simulations, it could be better to introduce the dynamic model as a plausible or attractive explanation accounting for the key macroscopic characteristics of chemical equilibrium reactions.

This interpretation can also be developed bearing in mind its first historical explanations. That is, starting with Clausius's ideas of evaporation and condensation in a closed vessel, and enlarging them with Pfaundler's ideas about incomplete chemical reactions, it could be possible to develop an explanatory sequence that may help students in the construction of the concept of dynamism in chemical equilibrium, that is, by accounting by means of statistical notions the two opposite reactions that are taking place simultaneously. This approach may help to avoid or change ideas related with oscillating reactions in parallel with the behaviour of a pendulum (Bergquist & Heikkinen, 1990; Van Driel, de Vos, Verlop, & Dekkers, 1998). The two reactions that are taking place

simultaneously and at the same rate are necessary to explain the fact that there are no macroscopic changes with time. This requires consideration of students' ideas (Van Driel, de Vos, & Verlop, 1999). Yet, this explanation must take into account the differences between physical and chemical equilibria, for if it is not the case we can reinforce alternative conceptions such as left and right sidedness (Johnstone, MacDonald, & Webb, 1977), as well as the existence of unique (or 'saturation') values of concentrations (or partial pressures, in the case of gases) of the chemicals involved in the equilibrium reaction (Tyson et al., 1999).

Finally, we would like to remark that the kinetic introduction of chemical equilibrium has been popular in general chemistry textbooks. Moreover, the deduction of the Law of Mass Action, claiming erroneously a historical foundation on the kinetic grounds used by Guldberg and Waage, still remains very popular among teachers of chemistry. In our opinion, this approach should be avoided. In most of the cases, it is a declarative general previous assumption that allows to write the mathematical expression of the equilibrium constant. Apart from that, this introduction is questionable from pedagogical and epistemological frames (Otero, 1985; Strube, 1989). It is an example of obtaining a correct result (equilibrium constant) using an improper procedure that writes down two rate equations based on the stoichiometry of the reaction. Although the aim of this study is not to treat this last topic in depth, it can be useful to remember the didactic errors that emerge when using this kinetic approach (Guggenheim, 1956; Mysells, 1956; Ashmore, 1965; Oldham, 1965; Wright, 1965), as well as the misconceptions that arise as a consequence (Johnstone, MacDonald, & Webb, 1977; Hacking & Garnet, 1985). On the other hand, many simulations and analogies have been designed attempting to make the dynamic character of chemical equilibrium accessible or comprehensible for students (Van Driel & Gräber, 2002). But many of them may reinforce the aforementioned students' difficulties; moreover, they do not usually account for an explanation of the macroscopic characteristics of chemical equilibrium reactions.

A rigorous deduction of the mathematical expression of the equilibrium constant is based on thermodynamic grounds (Banerjee & Power, 1991; Banerjee, 1995), but it exceeds an introductory course. Therefore, an advanced approach to teaching equilibrium may serve as a post-hoc justification of the equilibrium law which students have studied previously (Van Driel & Gräber, 2002).

The nature of scientific knowledge and the implementation of the HPS approach

A remarkable potentiality of our historical-philosophical approximation is that it allows teachers to exemplify many of the aspects of the nature of scientific knowledge:

- the problems faced;
- the theoretical frames from which they are formulated;
- the interpretation of experimental facts from different conceptions, as well as the treatment in textbooks;
- the evolution in the meaning of concepts and the process associated in that change;
- the role of the scientific community or the controversial issues;
- the importance of social and economic factors in the construction of scientific concepts.

The method also offers the opportunity to show the central role that models play in the growth of chemical knowledge (Justi & Gilbert, 2002). It may be achieved by engaging students in a process of generation, evaluation, revision and development of models. Keeping all this in mind, we can both avoid the image of science as it is presented by many textbooks

(Novak, 1984; Stinner, 1989; Sutton, 1989) and show the circumstances in which the concept of chemical equilibrium emerged in a process of inquiry around the evolution of the affinity ideas.

Eventually, this paper has the potentiality to encourage teachers to implement HPS issues in the chemistry classroom. The following summary tries to give teachers insight into teaching chemical equilibrium within an HPS framework:

1. Students may develop a better understanding of the nature of chemistry (Monk & Osborne 1997; Woody & Glymour, 2000; Níaz & Rodríguez 2001; Campanario 2002; Justi & Gilbert 2002):
 - (a) The historical sequence: elective affinities (forces) → affinities/mass of reactants/static equilibrium → concentration of reactants/static equilibrium (forces) → dynamics/rates of forward and reverse reactions in equilibrium may be the basis for a teaching sequence. This aim may be fulfilled by keeping in mind a holistic context of epistemological justification, that is, by facing students with *how* we know *what* we know, thus, trying to understand both the struggle between rival frameworks and how a new model overcame explanatory shortcomings of its predecessor or competitor, accounting for scientists' resistance to new ideas.
 - (b) The different meanings of *affinity* may illustrate the necessity of reaching an agreement about definitions, principles, laws and theories.
 - (c) Scientists' reluctance to abandon a theory on the basis of anomalous reactions alone illustrates that although experimental details are important, the theoretical rationale in which the experiments are both conducted and interpreted is even more important.
 - (d) Affinity tables assisted prediction via an orderly repository of a large number of chemical reaction types. Chemistry is a discipline whose very subject matter requires extensive organisation and classification. Furthermore, qualitative and comparative modes of reasoning have been highly productive for chemical inquiry.
 - (e) All of the above epistemological issues may help students to see chemistry as a collective activity that is constructed and progresses via consensus of the scientific community in a historical and cultural context rather than through the work of great minds in isolation.
2. Teachers have additional conceptual tools in order to understand students' ideas as well as in the comprehension of their resistance to change. Some of the misunderstandings that students hold when dealing with chemical equilibrium parallel some of the ideas of 19th century scientists (Níaz, 1995; van Driel, de Vos & Verloop, 1998).
3. Teachers may use the history of chemical equilibrium to encourage students' conceptual change. It means that students may be helped by the teacher in order to challenge early models of chemical reaction and, ultimately, their own conceptions. Hence, students may become more conscientious about their own misunderstandings that result in resistance to change. Moreover, this historical dimension can be used to achieve determined affective objectives, because, as Campanario (2002) has suggested: 'The episodes of resistance to conceptual change in science clearly show that even well-known scientists can be mistaken. Knowing these facts could minimise the impact of negative affective consequences once students discover that they were also unintentionally holding misconceptions and wrong beliefs'.

4. The laboratory can be used to replicate some 19th-century chemical equilibrium experiments (e.g. the study of incomplete reactions such as the ones carried out by Gladstone, and the determination of K_c , as Guldberg and Waage did in the case of esterification reactions) and, thus, to challenge student previous ideas, as it has been stated previously.
5. The historical reconstruction of chemical equilibrium may serve as a basis to design historical case studies (Wandersee & Griffard 2002). Apart from helping to fulfill the above HPS issues, these studies can motivate and encourage students to read more about chemistry and chemists.

Finally, we would like to stress that all the above potentialities should be addressed within the implementation of programs for teacher education that produce teachers who will have a sound knowledge of the content of chemistry, focusing not only on its pedagogical content, but also on its history and philosophy.

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