Theories in the Evolution of Chemical Equilibrium: Implications for its Teaching and Learning

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This study is divided into two main but related parts. Firstly, a brief historical account is presented of the role of theories of chemical equilibria that evolved around different research programs concerning the attempts at measuring chemical affinities; and secondly, how this may be used as a base for an appropriate sequencing for the teaching and learning of chemical equilibrium. In particular, the background to the four basic chemical equilibrium concepts, namely, 'incomplete reaction', 'reversibility', 'equilibrium constant' and 'molecular dynamics' and suggestions about how teachers may translate such understandings into classroom practice.

Introduction

Despite the fact that 'affinity' was the key concept in the development of the idea of chemical equilibrium during the last quarter of the 18th century and the early 19th century, the concept was not at the time given a precise definition (1, 2). This paper traces the evolution of theories of chemical equilibria grounded on the different research programs concerning chemical affinities. How scientists tried to determine the factors affecting affinity and measure this property of chemicals will be discussed. This led eventually to both mathematical reasoning and molecular dynamics as key theoretical tools in the explanation of equilibrium reactions. The starting point of this historical account is the state of the art in the construction of the first affinity tables. Berthollet re-worked this first theory, 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 mathematical affinity equations. Next, the first ideas providing a molecular interpretation of the macroscopic properties of equilibrium reactions will be presented. Lastly, how theoretical chemists integrated the previous findings, into a new field, that of physical chemistry will be outlined (3).

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Affinity Tables

The earliest affinity table was that published by E.F. Geoffroy in 1718 (4). 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). Below it, the symbols for the substances with which it reacts are arranged in order of their affinity. Therefore, each substance will displace from a combination any of those lower down the column. The affinity table visually represented the relationships between chemical substances determined in the laboratory. The table had two intended uses: to 'discover or explain' what went on in the mixtures of several bodies and to 'predict' what had to result from particular mixtures (5).

In the early years of the 18th century, Newton tried to find a theoretical explanation for 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. Within this theoretical basis, Newton introduced a mechanical view for chemistry. As a consequence, some scientists tried to give account of the measure of these 'elective affinities.' Buffon, Guyton de Morveau, and Bergman were some of the eighteenth-century chemists who supposed that chemical affinity was merely a gravitational attraction (6). The Swedish chemist T.O. Bergman made most extensive studies of displacement reactions. In 1775 he published *De Attractionibus Electivis*. The table in this book, as well as those that followed, up until 1784, was constructed with the aim of studying all the possible reactions. Bergman's theoretical goal was to discover, by experiment, the order of the varying attractions between different particles. This attraction, following very different laws from the gravitational forces, depended on the positions and "figures" of the particles. 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 explained displacement reactions.

Bergman considered all reactions as being complete and taking place only in one direction. According to his conceptual framework, chemical reversibility was forbidden because it was assumed impossible that a reaction whose direction was determined by the relative order of affinities could be reversed. However, Bergman was aware of other factors that also affected chemical transformations, such as the influence of the mass of the substances over the course of the reaction. He felt that the few remaining anomalous reactions resulted from inadequate data, believing that further and more careful experimentation would enable chemists to fit all reactions into an ordered displacement affinity series without any inconsistencies (7).

Geoffroy's affinity table (1718).

Berthollet and the Importance of the Amounts of the Reactants

The problem of incomplete and reversible reactions was already known to chemists before the French Revolution. At the beginning of 19th century, these unusual reactions were given a new explanation by the French chemist C. L. Berthollet. His ideas developed from experiences with chemical reactions carried out on a large scale. He faced the problem of the variability of affinities when trying to obtain pure KNO_3 because the process required some recrystallizations and Berthollet noted that as the concentration of nitrate increased, the capacity of the solution for dissolving additional nitrate decreased. He interpreted this anomaly by stating that the affinity responsible for dissolution was not an absolute force; therefore, in this phenomenon there would be equilibrium between antagonistic forces. These ideas found a new frame of implementation thanks to the trip he made in 1798, when he accompanied Napoleon's expedition to Egypt (8). He observed the continuous formation of sodium carbonate on the edge of 'natron lakes.' This reaction can be represented as follows:

$$CaCO_3 + 2\ NaCl \rightarrow CaCl_2 + Na_2CO_3.$$

This reaction was the reverse of that 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. The sodium carbonate formed a crust around the edge of the lake, and the deliquescent calcium chloride seeped into the ground.

Berthollet objected to the perception that elective affinity was an absolute, constant force that always determined the outcome of displacement reactions. He added the effect of quantity on chemical action, for the mass of the reactants could reverse the reaction predicted by the scale of relative affinities. That is, if two substances were competing to combine with a third substance for which they had unequal affinities, a relative large quantity of the substance with weaker affinity might exert a force that could surpass the force of the substance with greater affinity. Eventually, Berthollet considered that any displacement reaction was never complete but that 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, "All substances which tend to enter in combination act by reason of their affinity and their quantity" (9). The equilibrium state was, in a manner analogous to mechanics, static. Thus, the consideration of the mass of the reactants as a key factor provided a rationalisation for incomplete reactions. It also explained why both the "direct" (forward) reaction (permitted, according to elective affinities) and the reverse one (forbidden by that theory) could occur.

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 proportions were likely to occur. This last assertion was inconsistent with Dalton's new atomic theory, which established the principle of definite proportions.

The First Mathematical Formulation of Chemical Equilibria by Guldberg and Waage

Early investigations of chemical affinity focused primarily on acid/base and metal/acid reactions. In 1862 Berthelot and Saint-Gilles's laboratory, redefined affinity studies by focusing on organic equilibria (*i.e.*, esterification reactions). Their experimental findings were the starting point for the investigations performed by two Norwegian scientists, C. M. Guldberg and P. Waage. They tried to

formulate a general mathematical equation to account for the experimental data, with the aim of devising a theory that could reconcile the earlier ideas of Bergman and of Berthollet. In their first publication of 1864 (10), they took into account mechanics as a paradigm, and focused on the measurement of what was responsible for what they called "chemical forces". Convinced that chemistry should become, like mechanics, a science of forces and their effects, Waage and Guldberg aspired to develop a mathematical theory of chemical affinity. For a process they called simple (such as A = B + C), they stated (11):

…two forces assert themselves, either a composing or a decomposing, or acting and 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 had a power they determined by experiment. Thus, for the following: P + Q = P'+ Q', they argued as follows (12):

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 force for the first two substances is $\alpha(p - x)^a(q - x)^b$ and the action force 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]. Since there is equilibrium

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

For the equilibrium: acetic acid + ethanol = ethyl acetate + water, they obtained the following results: a = 1; b = 0.786; a' = 0.846; b' = 0.807; α/α' = 0.502.

The above formula received confirmation from previously published data of Berthelot and Saint-Gilles. Moreover, the accuracy of that equation was tested by Thomsen in 1869 and later by Ostwald in 1876 (13). It was indeed the first equation that approximates the mathematical expression of what we call nowadays an "equilibrium constant".

The consideration of the concentrations of the substances involved in the equilibrium system, instead of their amounts (*i.e.* masses), was a key factor that account-

ed for the understanding of the evolution of chemical equilibrium. Moreover, the vital step neglected by Berthelot and St. Giles, that of the reverse reaction, was taken into account by Guldberg and Waage, eventually allowing them to formulate the condition for chemical equilibria, when the net rate of reaction is zero (14).

Finally, it should be stressed that Gulberg's and Waage's new approach led the way in the application of mathematical reasoning to the facts of chemical science. The search for an exact equation between the concentrations of the substances involved in equilibrium represented a promising starting point in the search for the quantitative determination of chemical affinities.

Molecular Dynamics in Chemical Equilibrium

In the preceding section attention was drawn to the first attempt at the derivation of mathematical equations representing systems in chemical equilibrium. The brief account that follows here is intended to convey the early interpretations as to how the equilibrium comes about.

In 1839 Gay-Lussac (15) imagined the equilibrium condition as a dynamic process of continuous interchange of acids and bases, which he described as a "pell-mell." In 1850 Williamson (16), studying 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 ran simultaneously, each in opposite directions. Thus, reactants as well as products were constantly forming and decomposing in such a way that the amounts of all the substances involved remain constant. This dynamic balance was achieved by 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, but it was greater for the substances of lower quantity.

A later attempt to explain the molecular changes taking place in an equilibrium state was due to Pfaundler. In 1867 he described a chemical reaction in terms of the kinetic theory developed by Clausius and Maxwell. Pfaundler's approach was the first attempt to apply the mechanical theory of heat to chemical reactions by using Clausius's kinetic theory of evaporation in the development of a qualitative theory of chemical dissociation (17, 18).

Pfaundler was the first scientist who gave a correct account of partial dissociation. He hypothesised that dissociation varies in different molecules: a fraction of them is completely dissociated, and another fraction is unchanged. In the case of partial decomposition of a gas, Pfaundler assumed that at constant temperature and pressure 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. That is, it was assumed that some of the molecules regularly diverged more or less widely from the average state, for only a small number of collisions were effective to produce chemical reaction both in the sense of decomposition and formation. Eventually, a balanced molecular chemical equilibrium between decomposition and recombination was achieved.

In their last paper, Guldberg and Waage (19) took into account molecular kinetics and energy considerations. This was an attempt to explain the molecular changes taking place in an equilibrium state in the terms previously stated by Pfaundler in 1867.

Kinetics and Thermodynamics in the Study of Chemical Equilibrium Reactions: van't Hoff

 The first systematic idea about time in chemical reactions was formulated by C. F. Wenzel (20), whose aim was to search for a method of measurement of chemical affinities. By analogy to mechanics, he chose to measure chemical forces by the velocities with which they affected analogous processes.

 In the summer 1864 Guldberg and Waage presented a paper in which they argued in terms of the velocities of reactions in forward and reverse directions. They derived the following rate equation for the forward reaction (21):

$$v = \frac{dx}{dt} = k(p - x)^a (q - x)^b$$

where v is the velocity of reaction, x is the quantity transformed in the time t, and k a constant depending on the nature of the system, including the temperature. Similarly, they also considered the rate equation for the reverse reaction. The rate of the net reaction was considered to be the difference of the two velocities,

$v_{net} = v_{forward} - v_{reverse}$. They thus defined the equilibrium condition as $v_{net} = 0$. Although Guldberg and Waage later argued in terms of the "rates" of reactions in forward and reverse directions, initially they did it in terms of "forces". Guldberg's

and Waage's theoretical framework was criticised by Ostwald, Guggenheim and Laidler (22).

Eventually, a theoretical explanation of Guldberg's and Waage's equations came mainly from the work of van't Hoff (23) after he turned his attention to the question of how the equilibrium state was reached. Thus, his interest was no longer on the static analysis of forces, but on the dynamics of rates of reversible reactions. The starting point of his deduction was that the equilibrium is to be regarded as a result of two processes taking place with the same velocity in opposite directions. This kinetic approach allowed him the deduction of the mathematical equation representing the equilibrium constant.

In 1885, van't Hoff published one of his most remarkable contributions to the development of physical chemistry, *i.e.* the theory of dilute solutions (24). One of his aims was to derive the law for the equilibrium at constant temperature in a dilute state (*viz.* the equilibrium constant, K), based on thermodynamics. van't Hoff expressed the variation of the equilibrium constant with temperature as follows;

$$\frac{d \log K}{dT} = \frac{q}{R T^2}$$

stating his mobile equilibrium principle (25): 'Every system between two conditions of matter (systems) is displaced by lowering the temperature, at constant volume, toward that system the formation of which evolves heat'.

The Introduction of Chemical Equilibrium in the Chemistry Classroom

In introductory chemistry lessons, chemical reactions are normally presented as proceeding to completion, taking place in one direction only. However, in the case of chemical equilibrium, four basic ideas have to be considered (26):

> – incomplete reaction;
> – reversibility;
> – dynamics;
> – equilibrium constant.

Chemical equilibrium reactions are incomplete and can take place in both directions. The state of chemical equilibrium is characterised by a quantity, the equilibrium constant. These concepts are explained at a molecular level with the help of the dynamics concept. These four ideas are difficult for students to grasp. As a consequence, there are many misconceptions and difficulties about chemical equilibrium (27). For example students:

- 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),
- frequently think that after the reaction has started, the rate of the forward reaction increases with time and that of the reverse reaction decreases, until the equilibrium is reached,
- tend to misrepresent the changes that occur in chemical equilibrium reactions due to a variation in the temperature,
- often lack of mathematical tools and reasoning, which often leads to a poor understanding of the equilibrium law,
- may believe that mass and concentration mean the same thing for substances in equilibrium systems,
- often find difficulties in defining chemical equilibrium. Therefore, they frequently fail to understand the dynamic nature of a system in a state of chemical equilibrium. Instead, many students hold a static conception, for they believe that 'nothing happens' in that state,
- may find difficult to understand the proper meaning of words and concepts such as stress, balance, displacement, shift, equilibrium, etc.

Some of those misunderstandings and difficulties are regrettably reinforced in the chemistry classroom by (28):

Methodology:

- students are exposed to the answers before the problems have been stated (*e.g.* dynamics is usually presented as a fact rather than as an explanation),

- the popular kinetic introduction of chemical equilibrium, in which unsound kinetic assumptions are presented.

These teaching methods may explain some of the student misunderstandings related with the dynamic nature of equilibrium.

Algorithmic chemical equilibrium problems

The mastery of chemical equilibrium seems to be related with the solving of algorithmic chemical equilibrium problems, which neglects the promotion of conceptual reasoning on students.

Teachers who also hold misconceptions that are transmitted to their students.

To avoid those problems a novel curriculum has been developed that facilitates student understanding, based on appropriate uses of the history of chemical equilibrium, as explained in the following section.

The Nature of Scientific Knowledge and the Implementation of the HPS Approach: Suggestions for Teaching Chemical Equilibrium

Among science education researchers there is an emerging consensus about the incorporation of a sound treatment of the history and philosophy of science (HPS) into the curriculum (29). Many authors have eloquently argued about the advantages of using the history and philosophy of science in science classes. The discussion of using the history of chemistry in the chemistry classroom can be focussed on four main points:

– A historical research on the development of chemistry should give explanatory clues about the processes involving the evolution of chemical concepts (*i.e.* to focus on the problems which arose and how they were tackled). That is, to give clues about the important epistemological question 'how we know'.
– The historical knowledge of chemistry may help in understanding of the difficulties and alternative concepts held by students.
– The history of chemistry teaches students about the nature of chemistry.
– All of the above enables teachers to address the issues of instruction, which means:

a) to formulate general chemical problems; b) to design effective learning sequences.

Many science textbooks present an unsound image of science and many teachers lack a proper background of the HPS issue. Thus, the implementation of programs for teacher education that produce teachers that have a sound knowledge of the content of chemistry, focusing not only on its pedagogical content, but also on its history and philosophy would seem to be essential. In this context, the historical-philosophical reconstruction of key chemical concepts may allow teachers to exemplify many of the key aspects of the nature of scientific knowledge such as:

– the kind of problems that are addressed;
– the theoretical frames from which they are formulated;
– the hypothetical, tentative character of the process of inquiry;
– the interpretation of experimental facts from different concepts, as well as its treatment in textbooks;

– the role played by imagination and creativity;
– the limitations of models and theories;
– the evolution in the meaning of concepts and the process associated with that change;
– the unsolved problems;
– the role of the scientific community;
– the controversial issues;
– the importance of social and economic factors in the construction of scientific concepts.

Listed below are (1) some advantages that accrue to students from the translation of HPS understanding into classroom practice, in particular insight into teaching chemical equilibrium within a HPS framework, (2) key points to be considered and (3) some advantages that are of benefit to teachers.

1. Students may develop a better understanding of the nature of science:

– The importance of classification in chemistry (*e.g.* affinity tables).
– Scientists' reluctance to abandon a theory on the basis of anomalous reactions alone (*e.g.* Bergman's affinity).
– Rival theories coexist many years (*e.g.* Bergman's and Berthollet's theories).
– The construction of chemistry may be viewed as a human endeavour (*e.g.* the outcome of chemical equilibrium theory was due to the contribution of several individuals, most of them contemporaries of each other).
– Scientific argumentation (*e.g.* to consider the evidence for and against each model).
– Language (*e.g.* different meanings of affinity).
– Controversial issues (*e.g.* Berthollet's theory/Proust law and Dalton's theory).

2. The historical reconstruction sequence as a basis for teaching the introduction and development of the main chemical equilibrium concepts:

– The kinetic introduction of chemical equilibrium is questionable from an epistemological point of view (*i.e.* students are exposed to the answers before having given the question).
– Challenging student's previous ideas about chemical reactions in order to develop the concepts of incompleteness [*e.g.* $Fe^{3+}(aq) + SCN^-(aq) \Leftrightarrow FeSCN^{2+}(aq)$] and reversibility [*e.g.* $Cr_2O_7^{2-}(aq) + H_2O(\ell) \rightleftharpoons 2\ CrO_4^{2-}(aq) + 2\ H^+(aq)$]

– Explaining chemical equilibrium reactions (why is it that the reaction 'stops' when there are still reactants in the vessel of reaction?). Then, dynamism comes as an explanatory concept.

– The traditional textbook kinetic deduction of the equilibrium law has many flaws. Then, is seems appropriate the empirical derivation of the equilibrium constant, leaving to advanced levels the rigorous deduction of K, based on thermodynamic grounds.

3. Teachers' understanding of students' ideas and their resistance to change: teaching implications:

– To note that some of the misunderstandings that students hold when dealing with chemical equilibrium parallels some of the ideas of 19th century scientists.
– 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.
– The historical dimension can be used to achieve determined affective objectives because the episodes of resistance to conceptual change in science clearly show that even well-known scientists can be mistaken. Thus, it is comforting to perceive that others have thought in a similar manner-that to hold such thoughts are not guilty of mere stupidity.
– The laboratory can be used to replicate some 19th century chemical equilibrium experiments.
– The historical dimension may add fundamental insights when planning alternative teaching approaches to questioned/controversial educational issues (*e.g.* Le Chatelier's principle may be reshaped on the grounds of the equilibrium law).

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