

THE ROLE OF THEORIES IN EARLY STUDIES OF CHEMICAL EQUILIBRIA

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This work traces the role of theories of chemical equilibria that evolved around different research programs concerning the attempts at measuring chemical affinities. We will concentrate on searching for the theoretical grounds of four basic chemical equilibrium concepts: 'incomplete reaction,' 'reversibility,' 'equilibrium constant,' and 'molecular dynamics.'

Despite the fact that 'affinity' was the key concept for the development of the chemical equilibrium idea during the last quarter of the 18th century and 19th century (1), we will show that the concept was not given a precise definition. To its vague and ambiguous meanings we must add its polysemy (2). Kim (3) has noted that "the concept of affinity was rendered in many different ways, depending on the particular kind of practice that the chemist was engaged in." Therefore, we will discuss how scientists tried to determine the factors affecting affinity and how they tried to measure this property of chemicals, all of which led eventually to both mathematical reasoning and molecular dynamics as key theoretical tools in the explanations given to equilibrium reactions.

Affinity Tables

The oldest tradition that explained why bodies or substances 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, possibly being traced back ultimately to

Empedocles's principles of 'love and strife' (4). 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 bodies, the greater is their tendency 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 (5).

In the early years of the 18th century, Newton tried to address 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. 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. 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 gravitational attraction, modified by the shapes of the small particles of the reacting bodies (6).

The chemists of the 18th century, either under the Newtonian paradigm or with the aim of systematizing all the known chemical behavior, began the construction of the first affinity tables. It was, essentially, an attempt at estimating the comparative differences in the

reactivity of bodies. The earliest affinity table ('Table des rapports') was published by E. F. Geoffroy in 1718 (7). This table consists of sixteen columns. At the head of each column is the traditional symbol of a substance (or a group of substances to which it refers). Below it are the symbols of the substances with which it reacts, arranged in decreasing order of their affinity. Therefore, each substance will displace from combination any of those below it (8):

Whenever two substances which have some disposition to unite, the one with the other, are united together and a third which has more rapport for one of the two is added, the third will unite with one of these, separating it from the other.

Geoffroy intended his table as a place where one could see at glance the different relationships between the principal materials with which one is accustomed to work in chemistry. He wrote (9):

I have believed that it would be very useful to mark those relations which the substances commonly met with in chemistry show to each other and to construct a table where at a glance one could see the different relations which substances have for one another.

The affinity table then visually represented the relationships between chemical substances determined in the laboratory. That is, it had two intended uses: to 'discover' what went on in the mixtures of several bodies and to 'predict' what had to result from them (10). Thus, the table represented a helpful device to both beginners and experienced chemists (11):

By this table those who are beginning to learn chemistry may form in a short time an adequate idea of the rapports which exist between different substances, and the chemists will there find an easy method to determine what takes place in many of their operations which are difficult to disentangle and to predict what should result when they mix different bodies.

It is interesting to note how Geoffroy organized his table (12). At the top of the left half of it, he listed three mineral acids and four different kinds of alkalis that produced a variety of middle salts with the substances below each of them; column 8 showed the reactions of metallic substances with individual mineral acids. Columns on the right half of Geoffroy's table were headed by sulfur, mercury, lead, copper, silver, iron, antimony, and water. Klein (13) has explained that this section of the table derived largely from the age-old metallurgical practices which dealt with metallic sulfides (column 9), amalgams (column 10), and alloys (columns 11-15).

There are conflicting interpretations of this first affinity table. Although some authors consider that Geoffroy's table embodied Newtonian philosophy, it is difficult to prove any influence of Newtonian matter theory on the table (14). Holmes (15) suggested the (mysterious) term 'rapports' was a convenient device to avoid the complications of the 'ad hoc' mechanistic images held by other members of the 'Academy of Sciences.' This does not mean, however, that the table was a nontheoretical, merely empirical, theory-neutral 'art' rather than science. Kim (10) reported a historiographical analysis confronting that empiricist assumption. Holmes (16) has identified salts as the main subject of theoretical investigation in eighteenth-century chemistry and placed Geoffroy's affinity table in the midst of it. Not only did the table depict middle salts as combinations of acids and bases, but it rested on the premise that chemical composition was determined by rapports of affinities. Also, the selective displacement of metals in acids emerged as a central question in theoretical chemistry. Holmes has stressed that the table of rapports was not simply a classification of experimental evidence, summarizing chemical reactions and predicting others, for it represented ways to view and to organize that knowledge and to set priorities for further investigation. Moreover, Klein (17) has argued that the modern concept of the chemical compound provided the conceptual framework for Geoffroy's table.

Geoffroy employed in his table the term 'rapport' to indicate the 'dispositions' of substances to unite (18), in contrast to the meaning of 'affinity,' which carried a somewhat ambiguous connotation of kinship and analogy. Still, this early meaning as the cause of chemical combination was gradually replaced by the words 'affinity' and 'attraction' in the late eighteenth century. In practice, affinity and attraction were virtually identical, signifying the 'tendency to combine,' which meant that 'affinity' gradually lost its connotation of cousinly relationship; and, likewise, 'attraction' lost any implication of a particular kind of mechanical explanation (19).

Thus, Kim suggested that chemical affinity developed as a viable investigative program because of its function in guiding laboratory practice, rather than because its claim embodied Newtonian philosophy. She stated (20):

Geoffroy's 'rapports' served on the one hand to classify chemical substances and on the other hand as an umbrella term referring to the cause of chemical combination. His table of 'rapports' recorded the observed relations between chemical substances

without the speculation on the indivisible principles or particles that supposedly underlay the phenomena. Such avoidance of metaphysical speculations was closely linked to the formulation of affinity chemistry as a laboratory science.

During the decades after 1720 Geoffroy's conceptual structure began to expand, as chemists applied it and the solution methods with growing power to discover new combinations within each of the categories of acid, alkali, alkaline earth, and metal (21). Although many chemists 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 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 accounted for the interpretation of displacement reactions. He stated (22):

Suppose *A* is a substance for which other different substances *a*, *b*, *c* have an attraction; suppose further, *A* combined with *c* to saturation, (this union I shall call *Ac*), should upon the addition of *b*, tend to unite with it to the exclusion of *c*, *A* is then said to attract *b* more strongly than *c*, or to have stronger elective attraction for it; lastly, let the union of *Ab*, on the addition of *a*, be broken and let *b* be rejected, and *a* chosen in its place, it will follow, that *a* exceeds *b* in attractive power, and we shall have a series, *a*, *b*, *c*, in respect of efficacy. What I here call attraction, others denominate affinity.

Therefore, an acid replaced another one if its affinity toward a base were greater than the one initially combined with the base. Another field of application was the interpretation of the dissolution of metals.

Bergman considered all reactions as being complete and taking place in only one direction. However, he was aware of other factors that also affected chemical transformations: the possibility of evolution of gases depending on the temperature; the varying solubility of substances; and the influence of the mass of the substances over the course of the reaction. 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 (23). On the contrary, new anomalies, the result of the initial amounts of the reactants, solubility of substances, or their volatility, were reported, although they were initially considered as external factors that could counteract the true relative order of affinities.

Eventually, affinity tables summarised visually the reactions between substances and thus allowed a certain degree of prediction; the table served as the theory. Hence, it can be asserted that the device of Geoffroy's table initiated a tradition from which to formulate empirical laws that would make chemistry respectable and might eventually even be expressible mathematically. Bergman, in his *Dissertation on Elective Attractions*, stated (24):

In this dissertation I shall endeavour to determine the order of attractions according to their respective force; but a more accurate measure of each, which might be expressed in numbers and which would throw great light on the whole of this doctrine, is as yet a desideratum.

In accordance with this purpose, several authors attempted to determine the magnitude of the force of affinity or chemical attraction. Wenzel, Kirwan, Guyton de Morveau, and Fourcroy were some of the most prominent chemists who adhered to this tradition (25). Wenzel believed that the order of affinity of metals for a solvent that would dissolve them bore an inverse relationship to the time required for their dissolution. In other words, affinity was regarded as a force and the body acted upon as a resistance; thus, the velocity of dissolution was considered to be proportional to the force and inversely proportional to the resistance. Fourcroy rejected the idea that the velocity of combination was the measure of affinity, for the time needed for a combination could not express the force. Kirwan concluded that the weights of bases required to saturate a determinate weight of an acid were in direct relation to the affinities of the acid for the bases. Guyton de Morveau attempted to measure the attractions between metals and mercury by the force required to detach metal discs floating on mercury.

Berthollet and the Importance of the Amounts of the Reactants

At the end of the 18th century, the concept of affinity was consolidated as a coherent system for explaining chemi-

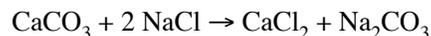
cal reactions. It was assumed that affinity was a constant property of the substances and that it manifested itself in an elective way. According to this conceptual framework, chemical reversibility was forbidden because it was assumed impossible that a reaction whose direction was determined by the relative order of affinities could be reversed. Those reactions which, under some particular conditions, deviated from the order established by the table became anomalous problems, somehow to be integrated into the theoretical framework of elective affinities (26). Indeed, the problem of incomplete and reversible reactions was already known to chemists before the French Revolution. At the beginning of the 19th century, those unusual reverse reactions were given a new explanation by the French chemist C. L. Berthollet.

Berthollet, who was a professor of Chemistry at the École Normale, initially adhered to the paradigm of elective affinities, although he was aware that some decades earlier Macquer, Kirwan, and Guyton de Morveau had extensively discussed and puzzled over the reactions that contradicted the invariability of affinities (27). From this previous knowledge, the social demand for pure nitre, and the teaching program Berthollet had developed at the École Normale, he was prompted to revise the concept of elective affinities (28).

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 in dealing with this problem reappeared four years later when he was appointed director of a refinery of nitre for the production of gunpowder. To obtain pure KNO₃ required some recrystallizations and Berthollet took into account 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 an equilibrium between antagonistic forces.

Berthollet had to organize 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. Moreover, Berthollet's ideas, which were developed from experiences with chemical reactions on a large scale (29), had a new frame of implementation thanks to the trip he made in 1798,

when he accompanied Napoleon's expedition to Egypt (30). He observed the continuous formation of sodium carbonate on the edge of 'sodium lakes.' This reaction can be represented as follows:



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: in point of fact, the sodium carbonate formed a crust around the edge of the lake, and the deliquescent calcium chloride seeped into the ground.

When he returned to France, Berthollet published his findings in several journals and in two books: *Recherches sur les lois affinités chimiques* (1801) and *Essai de Statique Chimique* (1803). Berthollet's aim was to refute the notion of elective affinity, although he did not deny the action of affinities as the cause of chemical combination (31):

The immediate effect of the affinity which a substance exerts is always a combination, so that all the effects which are produced by chemical action are a consequence of the formation of some combination.

He called attention, however, to the mass as one of the factors affecting the result of a reaction (32):

All substances which tend to enter in combination act by reason of their affinity and their quantity.

That is, Berthollet objected to the sense of false absolute-ness that the notion of elective affinity conveyed, adding the effect of quantity on chemical action, for 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 relatively large quantity of the substance with weaker affinity may exert a force that can surpass the force of the substance with greater affinity. Hence, Berthollet objected to the perception that elective affinity was an absolute, constant force that always determined the outcome of displacement reactions. He wrote (33):

The doctrine of Bergman is founded entirely on the supposition that elective affinity is an invariable force and of such a nature, that a body which expels another from its combination, cannot possibly be separated from the same by the body which it eliminated. Such was the certainty with which elective affinity has been considered as a uniform force, that celebrated chemists have endeavoured to represent by numbers, the comparative elective affinities of different substances,

independently of any difference in the proportion of their quantities.

It is my purpose to prove that elective affinity, in general, does not act as a determinate force, by which one body separates completely another from combination; but that, in all the compositions and decompositions produced by elective affinity, there takes place a partition of the base, or the subject of combination, between the two bodies whose actions are opposed; and that the proportions of this partition are determined, not solely by the difference of energy in the affinities, but also by the difference of the quantities of the bodies; so that an excess of quantity of the body whose affinity is weaker compensates for the weakness of the affinity.

If I can prove that a weaker degree of affinity can be compensated by an increase of quantity, it will follow, that the action of any body is proportionate to the quantity of it which is necessary to produce a certain degree of saturation. This quantity, which is the measure of the capacity of saturation of different bodies, I shall call *mass*.

Hence it follows, that in estimating the comparative affinities of bodies, their absolute weights are to be considered, and ought to be equal; but in comparing their actions, which depend on their affinities and mutual proportions, the mass of each is to be considered.

Moreover, in a recent study, Kim has focused her attention on the central goal of Berthollet's *Recherches*. She has stressed that (34):

For Berthollet chemical affinity possessed a mechanical component, for the force of affinity was proportional to the mass of the reactant.

He stated (35):

The forces which produce chemical phenomena are all derived from the mutual attraction between the molecules of the bodies and have been given the name *affinity*, to distinguish it from astronomical attraction. ...the effects of chemical attraction, or affinity, are affected by particular conditions, often indeterminate, that a general principle cannot be deduced....However, since it is very probable that affinity does not differ in its origin from general attraction, it should equally be subject to the laws which mechanics has determined for the phenomena due to the action of mass, and it is natural to think that the more the principles to which the chemical theories apply have generality, the more they have analogy with those of mechanics; but it is only by observation that they can reach that degree which they are already able to indicate.

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. The equilibrium state was, in a manner analogous to 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 over the dissolution, because its active mass decreases as it leaves the solution. This explanation accounted for the fact that many reactions continue to take place until at least one of the reactants is depleted.

The new conception modified the previous idea of elective affinity and deprived it of the leading role that it had played during the 18th century. The emphasis was now redirected to the concept of 'chemical action,' understood as the tendency between two substances to form a new combination, exerted according both to their relative affinity and their proportional amounts. Thus, the consideration of the mass of the reactants as a key factor provided a rationalization 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 theory was not free of flaws and difficulties. M.G. Lemoine (36) drew attention to facts that contradicted Berthollet's laws such as the reactions in which soluble salts were formed from insoluble ones and the decomposition of substances by the action of gaseous acids and bases. The difficulties that Berthollet's ideas faced can be summarized as follows:

- a) The high level of acceptance of the theory of elective affinities among his contemporary chemists; this theory persisted during some decades as theoretical support for experimental investigations (37).
- b) The inherent difficulty of the new ideas, which meant that they could not be fully understood (38).
- c) The emergence of the atomic theory of Dalton and the electrochemical theory of Berzelius (39).

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 was inconsistent

with Dalton's new atomic theory, which established the principle of definite proportions. As a consequence, the attention directed toward the determination of atomic weights and the composition of chemical compounds impeded a proper development of Berthollet's theory. In addition, textbooks did not tend to present the theoretical basis suggested by Berthollet, and his ideas had to compete with the influence of Fourcroy and his school, which supported the theory of elective affinities (40).

Berthollet's measure of chemical action was "chemical mass," defined as the product of the quantity of the substance with the strength of its affinity. He stated (41):

I consider that each of the acids which compete for an alkaline base acts in proportion to its mass [that is, quantity multiplied by affinity]. In order to determine the masses, I compare the capacities of saturation, whether of all the acids with one base, or of all the bases with one acid.

The "strength of affinity" was equivalent to the "power of saturation" (42): that is, the smaller the amount of acid required to neutralize a given quantity of base, the greater the affinity. But, it must be noted that this is nothing more than the equivalent weight. Hence, Berthollet measured chemical action by dividing the amount of the substance by the equivalent weight, this quotient representing the number of equivalents of the substance taking part in the reaction. Berthollet hoped that his method would establish the relative affinities of acids and bases and thus that his theory eventually would supplant Bergman's determinations of affinities. Once his method had been shown to be invalid, it was thought that affinities could not be measured at all (43). However, at the beginning of the second half of the 19th century the interpretation of new experimental observations allowed the reformulation of his ideas. The new theory had mathematical support, which, its authors stated, finally allowed for the quantification of chemical affinities.

The First Mathematical Formulation of Chemical Equilibria: The Work of Guldberg and Waage

Between the time of publication of Berthollet's *Essai* and the year 1864 the problem of the affinity had not developed substantially (44). Only in the last third of the nineteenth century did chemists turn their attention to the theory of affinity, which could then evolve in the light of new kinetic and thermodynamic ideas (45).

As discussed above, early investigations of chemical affinity focused primarily on acid/base and metal/acid reactions. Berthollet's laboratory practice redefined affinity studies by focusing on organic equilibrium systems and slow reactions. In 1862 Berthollet and Saint-Gilles used a new experimental approach to the study of reactions in solution. They thought that reactions between acids, bases, and salts were not appropriate in the study of chemical equilibria because they were so fast that any analytical technique upset the equilibrium. These disadvantages were overcome by turning to the study of esterification reactions, whose rates were sufficiently slow. Besides, the amounts of each component at equilibrium were always high enough to be easily measured. Berthollet and Saint-Gilles had established that the amount of ester formed at any instant was proportional to the product of the reacting substances (*i.e.* alcohol and acid) and inversely proportional to the volume. They also found that the reaction did not reach completion but progressively approached a limiting situation (*i.e.* equilibrium), where all four substances were present simultaneously. Berthollet and Saint-Gilles devised a mathematical formulation of the phenomenon but failed to take into account the reverse reaction between ester and water.

Berthollet's and Saint-Gilles's experimental findings were the starting point for the investigations performed by two Norwegian scientists, C. M. Guldberg and P. Waage. Their own experimental work was concerned with a heterogeneous system, the reaction between solid barium sulfate and a solution of potassium carbonate, together with the reverse reaction between solid barium carbonate and potassium sulfate solution. 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 work of 1864 (46), taking into account mechanics as a paradigm, they 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 (which we can represent as $A = B + C$), they stated (47):

...two forces assert themselves, either a composing or a decomposing, or an 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:

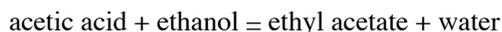


they argued as follows (48):

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]. Hence, the equilibrium is expressed as:

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

For the equilibrium :



they obtained the following results:

$$a = 1; b = 0.786; a' = 0.846; b' = 0.807; \alpha/\alpha' = 0.502.$$

We must stress that Guldberg and Waage obtained an equilibrium equation that represented a balance between two "chemical forces." In their memoir of 1867 (49), for the reaction $A + B = A' + B'$ they expressed the force as $k \cdot p \cdot q$, where k is the coefficient of affinity and p and q are the active masses of A and B . Similarly, they expressed the force which produced A and B from A' and B' as $k' \cdot p' \cdot q'$, where p' and q' are the active masses of A' and B' . When the two forces are in equilibrium, the active masses remain unchanged, and $k \cdot p \cdot q = k' \cdot p' \cdot q'$. They reasoned as follows:

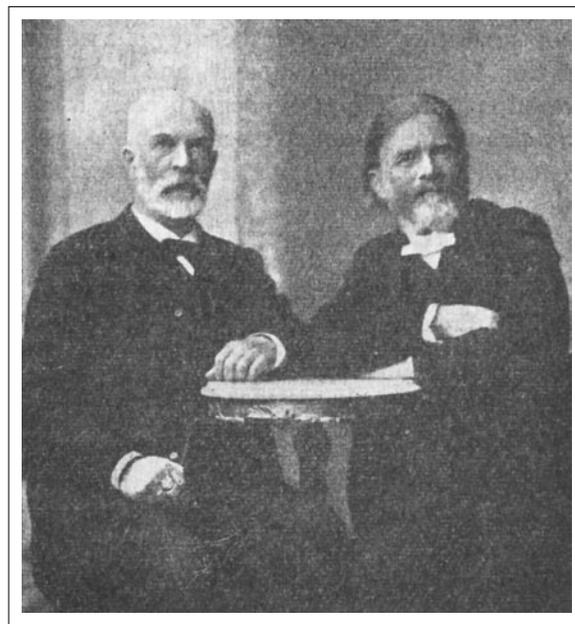
If the number of molecules A , B , A' and B' before of the reaction be represented by P , Q , P' and Q' , and if x be the number of molecules of A and B transformed into A' and B' , then, supposing the total volume to remain constant during the reaction, we have

$$p = \frac{P - x}{V}, q = \frac{Q - x}{V}, p' = \frac{P' + x}{V}, q' = \frac{Q' + x}{V}$$

and by substituting these values in the equation of equilibrium and multiplying by V^2 , we get the general equation

$$(P - x)(Q - x) = \frac{k'}{k}(P' + x)(Q' + x)$$

This formula received confirmation from previously published research by Berthelot and Saint-Gilles. Moreover, the accuracy of the above equation was tested by Thomsen in 1869 and later by Ostwald in 1876 (50). Also, Guldberg and Waage's mathematical treatment enabled determinations to be made of the ratio k'/k ; that is, of the relative affinities of two substances for a third with which both interact, and more particularly of the relative affinities of two acids for the same base, and of two



Only known image of Guldberg (l) and Waage (r).
See Ref. 5, Vol. 4, 1964, p 588

bases for the same acid. This idea was further developed experimentally by Ostwald (51).

Dynamic Equilibrium

In 1753 the *Encyclopédie* contained the article "Chymie" written by G. F. Venel. His purpose was to liberate chemistry from the yoke of physics (52). Venel's discussion demarcated the chemical side of the boundary between chemistry and physics. To achieve this end he devised

an adynamical theory of reaction. This theory supposed that reactions were instantaneous and thus they lacked the temporal element of Newtonian mechanics. Therefore, the program embodied in Newtonian affinities stood in opposition to the legacy of Venel's efforts to root dynamics out of chemistry.

The first systematic idea about time in chemical reactions was formulated by C. F. Wenzel (53), 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 his 1777 book on affinity, entitled *Theory of the Affinities of Substances*, 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 inversely related to the time of dissolution. Hence, he concluded that the quicker the action of the solvent the greater was the degree of its affinity.

In the summer of 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 (54):

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

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 (*i.e.* $v_{\text{net}} = v_{\text{forward}} - v_{\text{reverse}}$). And, thus, they defined the equilibrium condition: $v_{\text{net}} = 0$. 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." This assumption can be found in the eighth section of their second publication (55):

When two substances A and B are changed into two new substances A' and B', we call the quantity of A' + B' which is formed in unit time the *velocity* of the reaction, and we establish the *law that the velocity is proportional to the total force of A and B*. Assuming that the new substances A' and B' do not react on one another, we shall have

$$v = \phi T,$$

where v is the velocity, T is the total force, and ϕ is a coefficient which we call *coefficient of velocity*. The velocity represents the *total force* and we can determine this force in the reactions we can measure the velocity. Representing by x the quantities of A' and B' which are produced in the time t , it will be possible to express the total force, T , as a function of x , and noting that

$$v = \frac{dx}{dt},$$

it will be possible to determine x as a function of t . The equation which is found between x and t will serve to determine the *coefficients of affinity* and the *coefficients of action*.

When A and B react to give A' and B', and, at the same time A' and B' react to give A and B, the quantities of A' and B' formed in unit time are proportional to the difference of the two total forces. Consequently, the velocity is expressed by the equation

$$v = \phi (T - T')$$

When $v = 0$, then $T = T'$, thus, the equilibrium is attained.

Laidler (56) stated that, although Guldberg and Waage's theory agreed with experimental data, they had not arrived at their mathematical expressions 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. Guggenheim expressed his strong criticism as follows (57):

...to Guldberg and Waage belongs the credit of being the first to appreciate qualitatively the nature of a balanced reaction. But they did not succeed in formulating a quantitative expression for the equilibrium condition until six years after Horstmann had done so for gases and two years after van't Hoff had done so for the ester hydrolysis. They made no significant contribution either experimentally or theoretically to our knowledge of kinetics.

Ostwald had already remarked that a decisive step in the theory of chemical affinity was achieved only with the clear renunciation of the fiction of chemical forces. He stated (58):

In chemistry, specially, the concept of force has only done damage. As long as one sought to measure chemical 'forces,' the theory of affinity made no progress. Indeed, one still finds the expression in Guldberg and Waage, but only to be soon eliminated. A more general and thorough-going understanding of

the laws of chemical affinity was first achieved when one made chemical energy and its transformation the object of research.

Still, 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 accounted for the understanding of the evolution of chemical equilibrium. Moreover, the vital step neglected by Berthelot and Saint Giles, that of the reverse reaction, was taken into account by Guldberg and Waage, eventually allowing them to formulate the condition for chemical equilibria ($v = 0$). Finally, we would like to stress that the search for an exact mathematical relationship between the concentrations of the substances involved in equilibrium represented a promising starting point in the search for a quantitative determination of chemical affinities. Kim remarked that (59):

The new status of mathematics in chemistry was partly due to its utility as an investigative tool...The evolution of mathematics from an investigative tool to theory was largely due to its utility in organizing numerical results, which otherwise were meaningless. In other words, the status of mathematics as a theoretical structure of physical chemistry developed hand in hand with the nineteenth century penchant for precision measurement.

Hence, in spite of their theoretical flaws, the importance of Guldberg's and Waage's equations has been noted by several authors (60).

As Servos (61) pointed out, Guldberg and Waage's work did not produce an immediate interest in the study of the law of mass action. Some of the publications in the 1870s might have given Guldberg and Waage the impression that their papers of 1864 and 1867 had not been generally known (62). They could have felt the need to write about their ideas in a more widely circulated journal (63). Only in this latter paper did Guldberg and Waage devise an equation similar to the equilibrium constant. In it, the exponents were the stoichiometric coefficients in the chemical equation representing the equilibrium system. Moreover, in this paper they referred to previous works by Thomsen, Ostwald, Horstmann, and van't Hoff (64) as a confirmation of their law of mass action.

During his tenure as professor at the Riga Polytechnicum (1882-1887), Ostwald turned his attention from equilibrium methods to ones based upon the measurement of reaction velocities (65). In 1883 he published a new series of papers on chemical dynamics, which was elaborated in full analogy to mechanics (66). Ostwald's

new research program was grounded on the manipulation of Guldberg's and Waage's dynamical equation to bring out his relative affinities. He stated (67):

From the measurement of the velocities of chemical reactions we are enabled to solve the old problem of measuring the intensity of chemical forces. If two analogous substances (e.g. two acids) occasion under the same conditions analogous processes with different velocities, we shall attribute greater intensity of the chemical forces to the substance generating the greater velocity.

Eventually, a theoretical explanation of Guldberg and Waage's equations (68) came mainly from the works of van't Hoff (69). His ability to combine factors that had seemed unrelated by mixing traditions and manipulating ideas in new ways illustrates how the roles of imagination and creativity are important in the development and evolution of scientific knowledge (70). 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. Van't Hoff's kinetic approach in the derivation of the equilibrium constant is described in his book *Études de dynamique chimique*. This title has two features: its point of difference and its verbal similarity to Berthollet's *Essai de Statique Chimique*. That is, it serves to underline the differences as well as the roots of the new approach. Root-Bernstein (71) pointed out that van't Hoff, rather than worrying about what was formed as the end product at equilibrium as Berthollet had done, turned his attention to how the equilibrium state was reached. Root-Bernstein remarked (72):

Van't Hoff always used experiment to prove an idea rather than in the hopes of discovering new phenomena in need of explanation. Experiment was for him a tool of testing, not a probe for investigating or discovering. For investigating and discovering things about nature, he used his imagination. ..Perhaps the diversity and extent of his teaching load help to explain the emphasis van't Hoff put on deducing the principles that governed chemical phenomena, rather than scrutinising the facts. He had neither the inclination nor the time to get bogged down in the latter. In this way, the demands of pedagogy shaped his research style, and the result was a book of chemical principles.

Molecular Dynamics in Chemical Equilibrium

In the preceding sections attention has been called to the first attempts in the derivation of mathematical equations representing systems of chemical equilibrium. The brief historical account that follows here is intended to convey the early interpretations that accounted for how the equilibrium comes about.

In 1839 Gay-Lussac (73) imagined the equilibrium condition as a dynamic process of continuous interchange of acids and bases, which he described as a "pele-mele." Holmes suggested that this assumption (74):

...probably made it more natural for chemists later to envision the equilibrium itself as a dynamic one involving the constant interchange of acid and base particles among the salt combination.

In the mid-19th century chemists paid increasing attention to the role of time in the course of chemical reactions (75). As mentioned in the previous section, the problem of chemical kinetics was closely linked with that of chemical equilibrium. In the following discussion we are going to enlarge that point on the basis of molecular considerations. In 1850 Williamson (76), 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 such a way that the amount of all the substances involved remains 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 an 1867 article he treated 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 (77). That is, Pfaundler used Clausius's kinetic theory of evaporation for the development of a qualitative theory of chemical dissociation (78). He was concerned with the problems arising when trying to apply Avogadro's

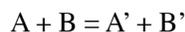
hypothesis to the determination of molecular weights (79). According to that hypothesis there is a simple relation between the relative vapor density and the molecular weight. But this method met with great difficulties when it was applied to the case of ammonium chloride: the value of the vapor density of ammonium chloride was one half of that expected for the formula NH_4Cl . A partial decomposition was suggested in order to account for the experimental data; although most chemists of that time accepted this phenomenon, they could not provide an explanation.

Pfaundler was the first scientist who gave a correct account of partial dissociation. He hypothesized that the change 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 (80) 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. They reasoned as follows (81):

If we consider a chemical process taking place under such circumstances that two substances A and B are converted into two others A' and B', while at the same time the reconversion of A' and B' into the original A and B can also occur, then the mere assumption of attractive forces between the substances of their components is no longer sufficient to explain the reactions, but we must for this purpose take into account the motion of the atoms and molecules.

The equilibrium between two such chemical processes is a mobile equilibrium, for two opposite reactions take place simultaneously – fresh quantities of A' and B' being formed while A and B themselves are being reproduced. When equal quantities of these pairs are formed in unit time, equilibrium results. The chemical reaction for the conversion of A and B into A' and B' is represented by the equation



If the molecule A is composed of the atoms or molecules α and γ , these latter execute their own proper movements within the compound molecules. Owing to these proper movements, α and γ will now approach, now retire from each other, and under certain circumstances their motions will become of such extent as to decompose the molecules A into the two components α and γ . The same holds for β and δ , the components of the molecules B.



Now, as each of the compound molecules A and B is in motion as a whole, it will from time to time come to pass that a molecule A will encounter a molecule B. If this encounter of A and B happens under such circumstances that either α and γ as well as β and δ are completely separated from each other, or at least that the distance between α and γ on the one hand, and between β and δ on the other, has almost reached the boundary of the sphere of action, the chemical forces of attraction between β and δ , and between α and γ can do no other than condition the formation of two new molecules A' and B', where $A' = \alpha + \delta$ and $B' = \beta + \gamma$. In the same way an encounter of two molecules A' and B' may cause the formation of A and B, if the components α and δ , on the one hand, and β and γ , on the other, are either completely separated or so far removed from each other that the attractive forces between α and γ and between β and δ are capable of effecting the formation of new molecules.

The rate of formation of new substances may be determined in the following way. If the number of molecules A and B in unit volume be denoted by p and q, the product pq will represent the frequency of the encounters of these molecules. If now each motion of the various molecules be equally favourable to the formation of new substances, the velocity of the chemical reaction –in other words the quantity transformed in unit time– may be made equal to ϕpq , the coefficient of velocity being supposed dependent on the temperature.

This view, already known from the theory of gaseous dissociation, may now be extended as follows so as to become generally applicable to all states of aggregation.

Amongst the p molecules of A in unit volume, there will be in general only a certain fraction of them, a, in such condition that on encounter with the molecules of B a chemical exchange will take place. Similarly, amongst the q molecules of B contained in unit volume, there will be only a fraction b in the state requisite for chemical exchange with the molecules of A. Thus on the whole there are in unit volume ap molecules of

A and bq molecules of B, which on meeting will be transformed into new substances. Consequently the frequency of encounter of the active molecules will be represented by the product ap·bq, and the rate at which the formation of new substances will proceed is to be expressed thus

$$\phi ap \cdot bq = kpq$$

if for brevity we put $\phi ab = k$.

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