Studies Concerning Affinity

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Translator's Note

This article presents an English translation of "Studies Concerning Affinity" (*1*), Guldberg and Waage's first presentation, in 1864, of the law of mass action. The source of this translation is a facsimile of the Norwegian original that appeared in 1964 as part of the proceedings of a symposium (*2*) commemorating the centennial of the law of mass action. Unfortunately, the figures displaying the experimental data presented in 1864 no longer exist (*3*) and do not appear in the 1964 facsimile.

This lecture to the Academy of Sciences in Christiania (Oslo) was followed by two others in 1864, "Experiments for Determining the Affinity Law" (*4*) and "Concerning the Laws of Chemical Affinity" (*5*). In order to expand their potential audience, Guldberg and Waage published a pamphlet in French, "Studies in Chemical Affinity" (*6*), in 1867. A German paper, "Concerning Chemical Affinity" (*7*), in 1879 concluded their publications on chemical equilibrium.

Although, except for the last publication, these writings are not readily available in American libraries, Abegg's German translations in "Ostwald's Klassiker der Exakten Wissenschaft" (*8*) offer some access to most of them. These include excerpts from the lecture translated in this article and the third 1864 lecture as well as the entire French pamphlet of 1867. Abegg also provides a reprint, with commentary, of the 1879 journal article. An English translation of a portion of the introduction to this article appears in "A Source Book in Chemistry, 1400–1900" (*9*).

The following translation tries to stay as close as possible to the style of the original. Consequently, it presents substances by English names in use in 1864. Brackets containing the modern names appear after each old name at its first use. Suspected misprints in the original are noted with lettered footnotes. Numbered footnotes are those contained in the original publication.

Acknowledgment

I am deeply indebted to Harold Goldwhite for his comments concerning this manuscript and his invaluable assistance regarding nineteenth century nomenclature.

Literature Cited

(1) Waage, P.; Guldberg, C. M. *Forhandlinger: Videnskabs-Selskabet i Christiania* **1864,** 35.
(2) Bastiansen, O., Ed. "The Law of Mass Action, A Centenary Volume"; Universitetsforlaget: Oslo, **1964;** p 7.
(3) Bastiansen, O., Det Norske Videnskaps-Akademi, personal communication, 1986.
(4) Waage, P. *Forhandlinger i Videnskabs-Selskabet i Christiania* **1864,** 92.
(5) Guldberg, C. M. *Forhandlinger i Videnskabs-Selskabet i Christiania* **1864,** 111.
(6) Guldberg, C. M.; Waage, P. "Études sur les affinités chimiques"; Christiania, 1867.
(7) Guldberg, C. M.; Waage, P. *J. prakt. chem.* [2] **1879,** *19,* 69.
(8) "Untersuchungen über die chemischen Affinitäten. Abhandlungen an den Jahren 1864, 1867, 1879 von C. M. Guldberg und P. Waage, Übersetzt und herausgeben von R. Abegg"; No. 104 in "Ostwald's Klassiker der Exakten Wissenschaft"; Englemann: Leipzig, 1899.
(9) Leicester, H. M.; Klickstein, H. S., Eds. "A Source Book in Chemistry, 1400–1900"; Harvard University: Cambridge, 1963; p 468.

The theories which previously prevailed in chemistry regarding the mode of action of the chemical forces are recognized by all chemists to be unsatisfactory. This applies to the electrochemical as well as the thermochemical theories; it must generally be regarded as doubtful that one will ever, with the aid of the electricity and heat evolution which accompany chemical processes, be able to find the laws by which chemical forces operate.

We have therefore sought to find a more direct method for determining the mode of action of these forces, and we believe that, by a quantitative investigation of the mutual interaction of different substances, we have hit upon a way which will most surely and naturally lead to the goal. We should point out that *Mssrs. Berthelot* and *S. Giles* in the summer of 1862 published work concerning etherification [esterification] which, to an important degree, has led us to choose this particular method.

Our work, which was begun in the autumn of 1862 and includes about 300 quantitative investigations, has led us to a definite opinion of chemical processes and to advance a new theory and particular laws which we shall present briefly and demonstrate by experiments, in part our own and in part those of other chemists.

Chemical compounds can, as is known, be divided into two types:

1) *perfect*, which always occur according to particular atomic relationships and

2) *imperfect*, which, within certain limits, can have a haphazard composition.

To the first type belong those, which according to general opinion are called chemical compounds, whose composition can always be expressed either by one of the three major types

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\ \text{[see note}^{a}\text{ below]}$$

$$\left.\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix}\right\}\mathrm{O}_2\ [\mathrm{H_2O}]$$

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[a] This is an apparent misprint; an elemental symbol to the right of the bracket seems to have been omitted.

$$\left.\begin{matrix}H\\H\\H\end{matrix}\right\}N\ [NH_3]$$

or by multiple types of these or, finally, a combination type.

We reckon among the second class alloys, compounds between a dissolved substance and the solvent, individual silicic acid and boric acid compounds, etc.

The imperfect chemical compounds occur under the influence of forces which without a doubt are small in comparison to the forces which come into consideration in the formation and decomposition of the perfect chemical compounds.

In the following work we will consider only the chemical processes[1] which involve perfect chemical compounds. These processes can be divided into:

(A) *Simple*

which always can be classified as one of the two following groups:

(a) direct combination of two molecules to a new molecule (addition) and, in reverse, splitting of a molecule into two others;

(b) a mutual exchange or substitution of the constituent parts of two molecules and, in reverse, regeneration of the original molecule by a backwards substitution. One could call the one action and the other reaction.

(B) *Complex*

which always can be regarded as a sequence of several simple processes.

As an example of addition and cleavage processes, we need only name the formation of sal ammoniac [ammonium chloride] from HCl and NH_3 and, in reverse, its cleavage into HCl and NH_3. Mutual substitution is, without compare, the most frequent process both in inorganic and organic chemistry. It happens, for example, very often when two different salts come together, whether both these and the newly formed salts are soluble, or whether one salt, either before or after the process, is insoluble. A very frequently occurring example of a complex chemical process, where both the simple processes cited above occur simultaneously, is found in the formation of the basic salts. When

$$\left.\begin{matrix}Zn\\Zn\end{matrix}\right\}O_2\ [ZnO]$$

acts on a solution of

$$\left.\begin{matrix}S_2O_4\\Cu_2\end{matrix}\right\}O_4\ [CuSO_4]$$

these are transformed partially to

$$\left.\begin{matrix}Cu\\Cu\end{matrix}\right\}O_2\ [CuO]$$

and

$$\left.\begin{matrix}S_2O_4\\Zn_2\end{matrix}\right\}O_4\ [ZnSO_4]$$

The copper oxide formed and the zinc oxide still unchanged engage in additions, the first to the unchanged vitriol of copper [copper sulfate], and the second to the vitriol of zinc [zinc sulfate] formed, and the result of these two processes is two basic salts. We have emphasized above that for each of two simple chemical processes, 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 for these forces.

In reality, we very often see in chemistry that these two opposing forces simultaneously assert themselves in one and the same chemical process. We need only name the well-known relationship between the action of H_2S_2 [H_2S] on solutions of metal salts and the reverse action of acids on metal sulfides. A further example is the well-known relationship between the cauterizing of the alkalis with lime [calcium oxide], by which caustic potash [potassium hydroxide] can be formed from potash [potassium carbonate] and lime while potash can be formed from caustic potash and carbonate of lime [calcium carbonate]. According to whether one uses diluted or concentrated, hot or cold solutions, one can get the process to go in whichever of the two opposite directions one wishes. If one uses solutions of a suitable temperature and concentration, then under completely identical conditions both the action and reaction will occur, according to whether one begins with one pair of substances or the other.

If processes where either only one or the other direction is apparent seem to occur often in chemistry, it frequently arises from the combining or acting force being either very large or very small in relation to the opposite one under the conditions present. If one modifies the conditions under which the forces operate in one way or the other, then one will either cause the opposing force to become about as strongly effective as the first—and in such a case both directions of the process will be apparent simultaneously—or one will even be able to cause the opposing force to be dominant, so that only the second part of the process appears to occur. As an example of this we shall cite the oxidation of many metals by oxygen in water at a lower or higher temperature and, in reverse, the reduction of the oxides of these metals by hydrogen; for instance *Pebal's* experiment[2] on the formation of sal ammoniac [ammonium chloride] and its cleavage at a higher temperature. Furthermore, mercury is oxidized at a temperature of about 300° [C], but the oxide is cleaved at red heat. There will thus be a temperature interval between 300 and red heat in which the oxide partially cleaves and the metal is partially oxidized.

Also, the well-known phenomenon that salts which are difficult to dissolve very often are easier to dissolve in other salt solutions than in water finds its natural explanation in the occurrence of partial substitution.

In order to determine the size of the chemical forces, we regard it as always necessary to study the chemical processes under such conditions that both its opposite directions are apparent simultaneously. If, under these conditions, one has first found a quantitative expression for the size of these forces for the different substances, the next question is to find the laws by which the exterior circumstances (e.g., temperature and solubility) modify these forces, and only then will one be in a position to be able to calculate in advance the result of the action of the chemical forces for any conditions and substances whatsoever.

If we maintain that for a given chemical process two opposing forces are in effect, one which strives to form new substances and one which strives to restore the original compounds from the new, it is enlightening that, when in the chemical process these forces become equally large, the system is in equilibrium. That the same equilibrium state occurs under the same conditions, whether one goes one way or the other in the process, lies in the nature of the matter.

As we have now hinted how the chemical processes are to be understood according to our view, we will go on to develop the laws by which chemical forces act on the second class of simple chemical processes, which we have named above substitution processes.

Relying partly on earlier experiments carried out by other chemists and partly on our own and guided by the course of chemical processes developed above, we set forth the following two laws, namely *the law of mass action* and *the law of*

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[1] We designate by a chemical process any phenomenon in which the chemical forces bring about a chemical change of the material.

[2] *Annalen der Chemie und Ph*[*arm*]. 123, p. 199 [(1862)].

volume action, from which the *equilibrium condition* for the forces acting in the system is derived.

(1) The Action of Mass

The substitution force, other conditions being equal, is directly proportional to the product of the masses provided each is raised to a particular exponent.

If the quantities of the two substances which act on each other are designated M and N, then the substitution force for these are

$$\alpha(M^aN^b)$$

The coefficients α, a, and b are constants which, other conditions being equal, depend only on the nature of the substances.

(2) The Action of Volume

If the same masses of the interacting substances occur in different volumes, then the action of these masses is inversely proportional to the volume.

If, as above, M and N designate the amount of the two substances, and V and V' the total volume of the system in two different cases, then the substitution force in the one case is expressed by $\alpha(\mathrm{M/V})^a(\mathrm{N/V})^b$ and in the other by $\alpha(\mathrm{M/V'})^a(\mathrm{N/V'})^b$.

(3) The Equilibrium Equation

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, according to the first law 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 which keep each other in equilibrium are consequently $p - x$, $q - x$, and $p' + x$, $q' + x$. According to the law of mass action, the action force for the first two substances is $\alpha(p - x)^a(q - x)^b$ and the reaction force for the last two is $\alpha'(p' + x)^{a'}(q' + x)^{b'}$. Since there is equilibrium

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

From this, x is then found, and one can thus calculate the amounts of the given substances which are changed for any system whatever. As one sees from the equation, only 4 of the 6 coefficients are independent; these remain to be determined by experiment, as one determines the changed amount x for different amounts of the substances when the equilibrium is reached.

That a chemical process, as so often is the case in chemistry, seems to occur in only one direction, so that either complete or no substitution takes place, arises easily from our formula. Since the active forces do not increase proportionally to the masses, but according to a power of the same, the relationship of the exponent does not have to be particularly large before the unchanged or changed amount becomes so small that it does not let itself be revealed by our usual analytical methods. In one of the series of experiments which we shall discuss below, it appears, for example, that even when the relationship between the exponents becomes 1:150, then the changed amount is only 1/1000%; in this case, the experiment naturally shows that no change takes place.

As a rule, the changed amount x can not be determined by a single experiment. Mathematically speaking, the equilibrium state as a rule is not reached until the interaction has lasted an infinitely long time. In the meantime, one will, by determining the changed amounts for the same masses at different times of interaction, be able to see what limiting value this amount approaches. If one chooses the experiments so that one approaches this limit from the two opposite sides, for example both starting with p and q and with p' and q', one obtains even sharper results. This circumstance has made it necessary for us, in our series of experiments, to make a very large number of limit determinations for various stages of the process without yet being in possession of sufficient material to find the laws by which the speed of the process occurs. We have also studied the influence of temperature on the equilibrium state by a large number of experiments. We shall allow ourselves to report the results of these investigations, with which we are still engaged, to the society later.

We can quantitatively establish the laws developed above by the following three series of experiments.

I. Ethyl Alcohol, Acetic Acid, Acetate Ether [Ethyl Acetate] and Water's Mutual Interaction

(Experiments carried out by *Berthelot* and *St. Giles* in 1862)

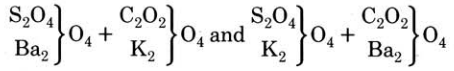
In a series of about 500 experiments, these chemists have studied the interaction of alcohols with a number of organic acids and, conversely, the decomposition of the ether [ester] species by water and demonstrated that, for these groups of organic compounds, the process runs relatively slowly so that the equilibrium state is obtained only after an infinitely long time. Furthermore, they have shown that various equilibrium states occur when various amounts of the four substances interact with each other. However, they expressly point out that they regard these phenomena as peculiar to organic compounds and see a sharp boundary between the ether species on the one hand and inorganic salts on the other. That we, as we have done above, are inclined to apply this view to all simple chemical processes, both in organic and inorganic chemistry, hopefully will appear from what has been developed above and from the following two series of quantitative experiments from inorganic chemistry.

These chemists, in addition, have not derived any law about mass action from their experiments.

We have used our general formulae on the most complete of their series of experiments, the ethyl alcohol-acetic acid series, and the agreement between the calculated and found values is, as one can see from the curves presented (see Fig. I.) completely satisfactory; p = acetic acid, q = alcohol, p' = acetate ether, q' = water (H_2O_2) [H_2O]. The coefficients are $a = 1$; $b = 0.786$; $a' = 0.846$; $b' = 0.807$; $\alpha'/\alpha = 0.502$, volume = 10000.

II.

The second series of experiments includes experiments carried out by us with



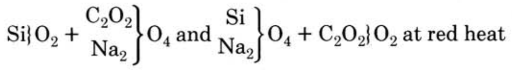
$$\left.\begin{matrix}S_2O_4\\Ba_2\end{matrix}\right\}O_4 + \left.\begin{matrix}C_2O_2\\K_2\end{matrix}\right\}O_4 \text{ and } \left.\begin{matrix}S_2O_4\\K_2\end{matrix}\right\}O_4 + \left.\begin{matrix}C_2O_2\\Ba_2\end{matrix}\right\}O_4$$

$$[BaSO_4 + K_2CO_3 \rightarrow BaCO_3 + K_2SO_4]$$

H. Rose already has published in *Pogg's* Annals [Poggendorff's *Annalen der Physik und Chemie*] for 1855 an investigation of the interaction of potash with sulfate of baryta [barium sulfate] at various temperatures and shown that these substances undergo a partial conversion which approaches completion with larger amounts of potash. Although he has also found that the reverse side of the process occurs under the same conditions he has neither investigated the influence of time nor shown that an equilibrium state occurs, any more than he has derived laws which could explain these phenomena.

We have now studied quantitatively the influence of time, temperature, the amounts of water, and the masses on the mutual action of these 4 substances by a very large number of experiments and by this found that the equilibrium state is first obtained after an infinitely long time; that, as will be seen from the accompanying curves, the effect of potash on sulfate of baryta increases with temperature and decreases with the amount of water, while in reverse, the effect of sulfate of potash on carbonate of baryta [barium carbonate] decreases with temperature and increases with the amount of water. With respect to the mass and volume effect, we have studied these most completely at 100° [C] and used our formulae on these experiments. The agreements are satisfactory, if one takes into account the practical difficulties which stand in the way of the analysis itself. Compare the curves in Fig. II. All experiments are carried out partly in platinum, partly in silver flasks since glass vessels would be attacked by the potash. p = sulfate of baryta, q = potash, p' = carbonate of baryta, q' = sulfate of potash. $a = 1$; $b = 12.480$; $a' + b'$ [see note [b] below] = 10.788; $\log \alpha'/\alpha = 12.494$; Volume = 50000 H_2O_2 [H_2O].

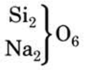
III.



$$\mathrm{Si}\}\mathrm{O_2} + \left.\begin{matrix}\mathrm{C_2O_2}\\ \mathrm{Na_2}\end{matrix}\right\}\mathrm{O_4} \text{ and } \left.\begin{matrix}\mathrm{Si}\\ \mathrm{Na_2}\end{matrix}\right\}\mathrm{O_4} + \mathrm{C_2O_2}\}\mathrm{O_2} \text{ at red heat}$$

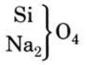
$$[SiO_2 + Na_2CO_3 \rightarrow Na_2SiO_3 + CO_2]$$

In order to determine silicic acid's molecule, *Scherer*[3] has investigated how much carbonic acid is driven off by soda [sodium carbonate] when one heats silicic acid to glowing with various amounts of soda, and therefore wanted to conclude that silicic acid unites with soda in all possible relationships within the limits



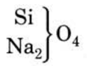
$$\left.\begin{matrix}\mathrm{Si_2}\\ \mathrm{Na_2}\end{matrix}\right\}\mathrm{O_6}$$

and



$$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{Na_2}\end{matrix}\right\}\mathrm{O_4}$$

since all salts lying in between are to be regarded as intermediary silicates consisting of these two. Meanwhile, we have drawn *Scherer's* experiments under our view of the chemical processes, since we assume that silicic acid forms only a single perfect chemical compound with soda, namely



$$\left.\begin{matrix}\mathrm{Si}\\ \mathrm{Na_2}\end{matrix}\right\}\mathrm{O_4}$$

We regard all the others as imperfect chemical compounds equal to metal alloys, and we see an analogy to these compounds in the relationship of the metal oxides to borax and phosphoric salts.

The four active substances which come into consideration here are, on the one side, silicic acid and soda, and on the other side, silicate of soda [sodium silicate] and carbonic acid. The last occurs here in the gaseous form that always surrounds the molten mass when the crucible is in the spirit flame. That the gaseous carbonic acid really is active during such processes surely arises from *Scherer's* experiments, according to which the carbonic acid freshly driven off from the sodium carbonate is taken up again as soon as the temperature falls. The agreement between the results found and the results calculated from our formula is quite striking for this series of experiments. p = silicic acid, q = soda, p' = carbonic acid, q' = silicate of soda, $a = 1$; $b = 0.64$; $a' = 2$; $b' = 0.0632$; $\alpha'/\alpha\ p^{a'} = 62.66$, volume = 1 when $p = q = 300$. See Fig. II.

In conclusion, we should briefly compare our theory with the opinions which have prevailed earlier concerning chemical forces.

The first theory about chemical affinity was advanced by the Swede *Bergman* in 1780, thus at a time when the atomic theory was not yet developed. He assumes that each substance has its particular affinity, whose magnitude is independent of the mass of the substance, toward every other substance. This point of view, which in individual cases appears to be correct, has long since been refuted by many chemical processes and is also totally in conflict with the theory presented by us.

In contrast, *Berthollet* in 1801–1803 developed in his affinity theory the view that affinities of substances, in addition to being dependent on their specific nature, also—and the important thing—are modified by the original amount of the substances as well as by their physical character, for example volatility and insolubility.

As one sees, we have adopted as part of our theory *Berthollet's* theory about the effective chemical forces in a chemical process being dependent on the masses. On the other hand, the law of mass action advanced by *Berthollet*, according to which the affinity is always proportional to the mass, is most decisively refuted by our experiments. Furthermore, our experiments show that *Berthollet's* view of the inactivity of insoluble and volatile substances in chemical processes is incorrect, a view which was already expressed by *Berthelot* concerning organic substances.

One has tried even earlier to apply our view, developed above, of the equilibrium state for every chemical process, although not quantitatively proven it, for a single group of chemical processes, namely for mixtures of two different soluble salts from which no precipitation occurs. One has namely, partly with the help of certain color reactions, partly with the help of the rotation of the plane of polarization (*Gladstone*) and partly with the help of diffusion experiments (*Graham* and *Gladstone*), sought to demonstrate that a partial substitution of the soluble salts occurs.

With respect to the relationship in which our theory stands to the work of *Berthelot* and *St. Giles* on etherification and to *Rose's* experiments with sulfate of baryta and potash, you are directed to that we have presented in experimental series I and II.

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[b] The facsimile shows *b* instead of *b'*, an apparent misprint.

[3] *Annalen der Chemie und Pharm.*, B. 116, 1299 [(1860)].