Cato M. Guldberg and Peter Waage, Researches on Chemical Affinities

Études sur les affinitès chimiques, Brøgger & Christie, Christiania (now known as København/Copenhagen, Denmark), 1867. [1]

When A and B combine with each other by addition, the compound AB has to be considered as resulting from attractions. In the simple substitution according to the formula AB + C = AC + B, the formation of AC is produced mainly by the attractions between A and C; however, other attractions act between the other substances present, and the force that leads to the formation of AC is the resultant of all these attractions. At a given temperature, this force can be considered as constant, and we represent its magnitude by the letter k, which we call the coefficient of affinity of the reaction.

Similarly, in the double decomposition AB + CD = AC + BD, the force producing the new substances is the resultant of all the attractions between A, B, C, D, AB, BC, AC, BD, and the resulting force k is the coefficient of affinity.

In the reaction A + B = A′ + B′, the force leading to A′ and B′ is proportional to the coefficient of affinity, but it also is a function of the masses A and B. From our experiments, we have concluded that the force is proportional to the product of the active masses of A and B. Designating these active masses of A and B by p and q, the force = $k \cdot p \cdot q$.

This force kpq, or the force between A and B, is not the only one effective during the reaction. Other forces tend to retard or accelerate the formation of A′ and B′. Let us, however, assume the other forces do not exist, and let us see how the formulations will look in that case.

Suppose the active masses of A′ and B′ are p' and q' and the coefficient of affinity of the reaction A′ + B′ = A + B is k'; then the force of the regeneration of A and B = $k'p'q'$.

The relationship between K and K′ can be found by experimental measurement of the active masses p, q, p', q'. On the other hand, when the ratio k'/k has been formed, the result of the reaction can be precalculated for any initial state of the four substances.

Action of Insoluble Salts on the Soluble Ones

We have studied mainly the decomposition of barium sulphate and potassium carbonate and the formation of these two salts by the decomposition of barium carbonate with potassium sulphate.

By taking 100 molecules of barium sulphate and 100 molecules of potassium carbonate, a definite limit value is found; for example, 20 molecules of barium carbonate. Starting with 100 molecules of barium carbonate and 100 molecules of potassium sulphate, the end value under the same condition is ξ. It is then very probable that the two end values correspond with each other, so that ξ ought to be 80 = 100 – 20. The experiments do not give exactly this value; ξ is always found to be smaller than 80; however, this is due to special experimental difficulties. ...

Regarding the influence of the masses, we find that the decomposition of barium sulphate is accelerated by increasing the potassium carbonate. Increasing the barium sulphate leads to an analogous result; however, the absolute increase of the end value is much smaller. A complete decomposition of barium sulphate can be achieved by a sufficiently large excess of potassium carbonate, as Heinrich Rose has already observed (1855). Rose also found that the presence of much potassium sulphate completely prevents the action of potassium carbonate upon barium sulphate.

Research in this field is certainly more difficult and time-consuming and less productive than the discovery of new compounds, with which most chemists are now occupied. Nevertheless, in our opinion there is nothing that will bring chemistry more quickly to the rank of a really exact science than the research that is the subject of our work. All our wishes would be fulfilled if we succeeded through this work in directing the attention of chemists to a branch of chemistry that has been too much neglected since the beginning of this century.

[1][Copied from Eduard Farber, Ed., *Milestones of Modern Chemistry*, Basic Books, New York, 1966, pp 147-149. Translation by Farber. Farber gives the source of the translation as *Ostwald's Klassiker der exakten Wissenschaften*, #104 (Leipzig, 1899), which includes papers from 1864, 1867, and 1879. In fact, this excerpt comes exclusively from the 1867 paper cited in the heading. Apparently this translation into English is from the German of the *Klassiker* rather than from the French of the original. —CJG]