

*Marcelin Berthelot and Léon Péan de Saint-Gilles, "Researches on the Affinities of the Formation and Decomposition of Ethers"*

Excerpted from *Annales de Chimie* (3), [Vol. 65 \(1862\), pp. 385-422](#); [Vol. 66 \(1862\), pp. 5-110](#); [Vol. 68 \(1863\), pp. 225-359](#).<sup>1</sup>

Organic chemists have mainly endeavored to obtain new compounds to construct and to study reactions. All of us know how much our science has thereby been enriched through the cumulative labor of three generations of chemists.

Yet, while studying the compounds and the relationships of their formulas and their equivalents, the chemists neglected the general conditions of chemical mechanics which are basic for the formation and decomposition of the compounds, relying instead on the results of mineral chemistry.

However, the study of organic chemistry reveals unexpected facts—almost without any analogy in mineral chemistry—that are of greatest importance for the theory of affinity: the influence of time and the predominant role of certain conditions of equilibrium quite outside of those expressed by Berthollet's laws. These conditions and their effects are perhaps most impressive in the reactions of the ethers, especially their formations and their decompositions.

Ethers represent a new fundamental type that is as characteristic for organic chemistry as the salts are for inorganic. Ethers are formed by the combination of acids with alcohols, and these can be regenerated by decomposition; the similarity with salts formed from bases and acids has often been mentioned. Besides, ethers, like salts, can show double decompositions, at least in some cases, with each other as with salts.

Closer examination shows, however, that the analogy between ethers and salts is only superficial. ... Thus, a volatile alcohol in an ether is not immediately replaced by a solid base, whereas this occurs in a salt with a volatile basis; the volatile alcohol is only slowly and progressively replaced by the base. Also, in soluble or volatile salts that can be formed at the expense of ethers do not occur immediately. For example, calcium chloride

does not directly precipitate an ether of oxalic acid; barium chloride does not immediately form precipitates with the ethyl ethers of sulphuric acid; ethyl chloride, although a gas at room temperature, does not form on contact of an alkali chloride with a solid ether, etc.

Nevertheless, the affinities for the direct combination of acids with alcohols are generally very weak. Ethers are so little stable that not only weak bases, but even water causes decomposition.

The fundamental difference between ethers and salts seems to us to be due to two causes: first, the absence of electrical conductivity of alcohols and ethers; and [secondly] the small heat of reaction between alcohol and acid.

### **The Existence of a Limit**

When an alcohol is brought into contact with an acid, a combination occurs with varying velocities, depending on the physical conditions of the experiment. Acid and alcohol neutralize each other slowly and yield two new products, water and other compounds. As the reaction proceeds, it slows down and gradually approaches a definite limit. This limit does not coincide with a complete saturation of the acid by the alcohol.

When the water is removed, the reaction between acid and alcohol can proceed to the end, like the reaction between an acid and a base. In the presence of water, the formation of ether stops at a definite limit. This limit is almost independent of temperature and pressure so long as the system remains liquid.

Generally speaking, in a system formed of acid, alcohol, neutral ether, and water in any proportions, the limit of the reaction is governed almost completely by the relationship between the equivalents of these substances and is almost independent of their individual nature.

In the mixture of one equivalent of acid with several equivalents of the alcohol, the

amount of ether at first grows with the number of alcohol equivalents, although only one equivalent can enter into the compound. Experiments show that in the presence of excess alcohol, the amount of acid not consumed for forming the compound is in inverse proportion to the total quantity of alcohol.

In the mixture of one equivalent of alcohol with several equivalents of acid, the amount of etherified alcohol grows with the quantity of acid ... and in inverse proportion to the total quantity of the acid.

Let us now consider the role of water in etherification. When one equivalent each of alcohol and acid are mixed with water, ether is formed, but its quantity diminishes as the quantity of water is increased without

becoming zero, however large the excess of water. The decrease is continuous, without jumps, in a progression that changes much more slowly than the equivalents of water added to the system. This shows clearly the influence of the chemical mass of the excess water above the equivalents necessary for the reaction.

We have shown that the quantities of ether formed or remaining in the most varied systems are independent of the individual nature of the constituent acids and alcohols. The ideas of particular individual affinities, usually considered so important in etherification, must therefore yield to a very simple, very general concept mainly based upon the equivalents.

<sup>1</sup>[Copied from Eduard Farber, Ed., *Milestones of Modern Chemistry*, Basic Books, New

York, 1966, pp 143-145. Translation by Farber. —CJG]