

**A STUDY OF THE CONDUCTIVITY
AND DISSOCIATION OF ORGANIC
ACIDS IN AQUEOUS SOLUTION
BETWEEN ZERO AND THIRTY-FIVE
DEGREES: DISSERTATION**

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A Study of the Conductivity and Dissociation of Organic Acids in Aqueous Solution Between Zero and Thirty-Five Degrees: Dissertation by Eugene Pinckney Wightman

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267

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Dissociation of Organic Acids in
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and Thirty-Five Degrees**

DISSERTATION

**SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
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HISTORICAL

White and Jones,¹ in their work on the conductivity and dissociation of organic acids in aqueous solution, give a survey of the data obtained up to that time, and a large amount of the earlier work is discussed in full. It is not necessary to repeat all of this discussion, but a short summary of the results as a whole will be given as an introduction to this work.

One of the first things noticed by early workers was the increase in molecular conductivity with rise in temperature and increasing dilution. It was shown also that this increase is, for most electrolytes in dilute solutions, a parabolic function of the temperature, and the following interpolation formula was deduced and employed by Euler:²

$$\lambda = a + bt - ct^2$$

in which λ is the molecular conductivity at the temperature t , a is the known conductivity at some other temperature, and b and c are constants depending upon the nature of the electrolytes. Extensive use has been made of this formula.

As the dilution increases the rate of increase in conductivity becomes less, and in some cases there is a maximum value of conductivity, as was shown by Grotian,³ Jahn,⁴ Schaller,⁵ and the later workers. As a matter of fact, the maximum occurs for nearly all strong electrolytes at dilutions at which the conductivity can be measured directly.

This is not the case with most of the organic acids, but indirect methods were devised by Ostwald⁶ and by White

¹ Am. Chem. J., **44**, 159 (1910).

² Z. physik. Chem., **21**, 257 (1896).

³ Pogg. Ann., **184**, 215 (1875).

⁴ Z. physik. Chem., **16**, 72 (1895).

⁵ *Ibid.*, **25**, 497 (1898).

⁶ *Ibid.*, **1**, 74, 97 (1887); **2**, 830 (1888).

and Jones,¹ based upon Kohlrausch's law of the independent migration velocities of ions, by means of which μ_{∞} for the acids could be determined.

Ostwald showed that there is a constant difference between μ_v for a given dilution, say thirty-second normal, of the sodium salt of any acid, and the μ_{∞} value of the same, which is found at about ten hundred and twenty-fourth normal. By means of this constant difference he calculated the μ_{∞} values of a large number of sodium salts without direct measurement, and from these it was easy to determine the μ_{∞} values of the acids in question, by subtracting the value for the migration velocity of the sodium ion, and adding the corresponding constant for hydrogen.

A second method suggested by Ostwald was based upon the fact that the velocities of anions of acids containing over twelve atoms in the anion are dependent upon the number of these atoms present—ions with the largest number of atoms having the smallest velocity.

The method of White and Jones (for monobasic acids) is based upon the direct measurement of the μ_{∞} value of the sodium salt of the acid and will be discussed later. The μ_{∞} values of the dibasic acids were determined by a graphic method similar to the second method used by Ostwald.

Just as the molecular conductivity increases at a diminishing rate with dilution, so also it increases at a diminishing rate with rise in temperature, as was brought out by Schaller² and by Noyes.³

Another important fact is the decrease in dissociation with rise in temperature, first noticed by Arrhenius⁴ in the case of phosphoric and hypophosphoric acids, later brought out by Schaller⁵ and a number of others,⁶ and finally thoroughly

¹ *Am. Chem. J.*, **44**, 159 (1910).

² *Z. physik. Chem.*, **15**, 497 (1898).

³ *J. Am. Chem. Soc.*, **24**, 134 (1904); **30**, 335 (1908); **31**, 987 (1909).

⁴ *Z. physik. Chem.*, **4**, 96 (1889).

⁵ *Ibid.*, **25**, 497 (1898).

⁶ Jones and West: *Am. Chem. J.*, **34**, 357 (1905); Jones and Jacobson: *Ibid.*, **40**, 355 (1908); Jones and Clover: *Ibid.*, **43**, 187 (1910); White and Jones: *Ibid.*, **44**, 159 (1910).

established by the work of Noyes¹ at higher temperatures. No entirely satisfactory explanation of this decrease in dissociation has been given; but the results of Noyes in his first work² show that the dissociations of the two salts, sodium chloride and potassium chloride, are nearly identical at all temperatures and concentrations; and he says: "This gives support to the idea that decrease of conductivity and of calculated dissociation with rise in temperature is due to a physical cause (probably in some way to the electrical charges on the ions) and not to specific chemical affinity." More will be said about this in another connection.

It was pointed out by the later workers (Schaller³ was one of the first) that the temperature coefficients of conductivity increase with dilution and decrease with rise in temperature for acids, and increase with temperature for neutral salts. Amino acids are an exception to this, as was shown by White and Jones.⁴ They explain the increase with rise in temperature as "probably due to the formation of inner salts having both acidic and basic groups, which break up with rise in temperature." The decrease of the temperature coefficients for nearly all other acids is explained by them in terms of the theory of hydration.⁵

It was found by White and Jones that the Ostwald dilution law⁶ holds very well for dilute, weak organic acids, with the exception of the amino acids. The law is expressed thus:

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

where $\alpha = \frac{\mu_e}{\mu_{\infty}}$ is the dissociation, V is the volume, and K is a constant. The law is easily deduced from the gas laws and those of osmotic pressure. The discrepancies in the temperature coefficients in the case of amino acids were explained as stated above, viz., as due to the breaking down of the inner salts.

¹ J. Am. Chem. Soc., **26**, 134 (1904); **30**, 355 (1908); **31**, 987 (1909).

² *Ibid.*, **26**, 134 (1904).

³ Z. physik. Chem., **25**, 497 (1898).

⁴ Am. Chem. J., **44**, 159 (1910).

⁵ *Ibid.*, **40**, 402 (1908).

⁶ Z. physik. Chem., **2**, 36 (1888); **3**, 170 (1889). Jahn: *Ibid.*, **22**, 545 (1900).

Strong acids (and also other strong electrolytes) do not conform to the Ostwald law, and a large number of empirical formulae have been suggested,¹ all of which hold fairly well for specific cases, but only a few of which are of general application. These are discussed very thoroughly by Noyes,² who says of the following formulae:

$$\frac{\Delta_0 - \Delta}{C^{1/2}} = K \text{ (Kohlrusch)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^{1/2} C^{3/2}} = K \text{ (Barmwater)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^{3/2} C^{1/2}} = K \text{ (Van't Hoff)}$$

$$\frac{\Delta_0 - \Delta}{\Delta^2 C^{1/2}} = K \text{ (Rudolphi)}$$

"The Kohlrusch formula expresses the results for both salts (potassium and sodium chlorides) at all temperatures without great error, and the same is true of the Barmwater formula except at the highest temperature, where the deviation with both salts is large. The van't Hoff and Rudolphi formulae do not accord at all with the observed values at 306°, the deviations in the case of the latter being especially large; while at the lower temperatures, 140°, 218° and 281°, the van't Hoff formula is far less satisfactory than those of Kohlrusch and Barmwater. On the whole, therefore, the simple Kohlrusch formula furnishes the best representation of the results and the Barmwater next best."

In terms of the Ostwald formula, i. e., using the same notation, these would be:

$$\frac{1 - \alpha}{\sqrt[3]{i} V} = K \text{ (Kohlrusch)}$$

$$\frac{1 - \alpha}{\sqrt[3]{\alpha} V} = K \text{ (Barmwater)}$$

¹ Wied Ann., **26**, 200 (1885); **50**, 394 (1893). MacGregory: *Ibid.*, **51**, 133 (1894). Barmwater: Z. physik. Chem., **28**, 134, 428 (1899). Sabat: *Ibid.*, **41**, 224 (1902). Müller: Compt. rend., **128**, 505 (1899). Kohlrusch: Sitz. preus. Akad., **44**, 1002 (1900). Rudolphi: Z. physik. Chem., **17**, 385 (1895). Van't Hoff: *Ibid.*, **18**, 300 (1895). Kohlrusch: *Ibid.*, **18**, 662 (1895). Storch: *Ibid.*, **19**, 13 (1896). Bancroft: *Ibid.*, **31**, 188 (1899). Jahn: *Ibid.*, **37**, 499 (1901); **41**, 265, 288 (1902). Nernst: *Ibid.*, **38**, 493 (1901).

² J. Am. Chem. Soc., **26**, 162 (1904).