

FREDERICK GEORGE DONNAN AND THE RELATIONSHIP BETWEEN ELECTROLYTIC DISSOCIATION AND LIGHT ABSORPTION

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Donnan's Early Years

Although Frederick George Donnan (Fig. 1) grew up in Northern Ireland, actually he was born in Columbo, Ceylon (now Sri Lanka), on September 5, 1870 (1). He lost the sight of his left eye at the age of nine but did not allow this accident to handicap him. As a schoolboy, his main interest was in mathematics and physical science. He attended the Belfast Royal Academy from 1880 to 1889; and although he received instruction in physics and chemistry, this was confined to theory, because the Academy lacked laboratories. However, Donnan managed to get some practical training by attending evening courses elsewhere.

In 1889 Donnan entered Queen's College, Belfast, where one of his instructors was the organic chemist Edmund Albert Letts (1851-1918). His outstanding ability for chemistry and physics was recognized by the award of several scholarships. In 1893 he was granted an 1851 Exhibition Research Scholarship, which enabled him to study abroad. He went to the



Figure 1. Frederick George Donnan

University of Leipzig and, not surprisingly, studied for a year under Johannes Wislicenus (1835-1902), the professor of organic chemistry. No publication resulted, so the instruction was probably general. Eventually Donnan's natural interests in the physical sciences prevailed, and he decided to turn to physical chemistry.

At that time, this field was rapidly developing under the influence of Wislicenus's colleague, Wilhelm Ostwald (1853-1932), who became Donnan's dissertation advisor. Donnan's assignment was an experimental study of the relationship between dissociation and light absorption in solutions of violuric acid (2).

Physical Chemistry

Texts concerned with the general history of chemistry usually include a section on physical chemistry. An illuminating statement in one of them is (3):

Prior to about 1884 physical chemistry was the study of the physical properties of chemical substances.

There were of course exceptions to this very broad statement. One example was the question of *affinity*, or combining intensity, of

chemical substances. Attempts to measure, or at least to compare, affinities had been in progress since the 17th century. The concept that a reaction need not run to completion and could be reversible eventually led to the experimental formulation of the law of mass action (4). Jacobus Henricus van't Hoff (1852-1911) showed that this law could be deduced theoretically (5). He found that the gas equation, $PV = RT$ could be extended to solutions when osmotic pressure replaces gas pressure, P . However, when the solute is an electrolyte, the gas constant, R , had to be multiplied by an arbitrary factor, i , to make the observations fit the equation.

Early in his career, Ostwald had determined the relative affinities of acids by equilibrium methods and then by kinetic methods that involved catalysis by acids. This enabled him to list various monobasic acids in a numerically decreasing order of affinity. In 1884 Svante Arrhenius (1859-1927) sent a copy of his dissertation to Ostwald. This document contained the germ of the ionic theory, the development of which he described in 1887 (6). Arrhenius had studied the electrical conductivity of electrolyte solutions, and Ostwald realized that conductivity measurements should provide an alternative approach to the assessment of affinities. He found that the equivalent conductivities of his collection of organic acids were nearly proportional to the affinities obtained chemically. If a substance undergoes dissociation, the number of solute particles in the solution is increased, thus accounting for the factor i in van't Hoff's concept. The application of the law of mass action to ionization led to the *Ostwald Dilution Law*:

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

where α is the degree of dissociation into ions at dilution V (*i.e.*, the reciprocal of concentration), and k is a quantity now termed the dissociation constant of the solute (7).

In 1887 Ostwald founded and became the principal editor of the *Zeitschrift für physikalische Chemie*. He thus had a vehicle for the rapid publication of research when he moved to the University of Leipzig in the same year. One of his assistants was Walther Nernst (1864-1941) who, by 1889, had developed the quantitative aspects of the electromotive force of galvanic cells (8). Ostwald kept in close contact with Arrhenius and van't Hoff. All four scientists eventually became Nobel laureates.

The announcement of the ionic theory did not lead to its wide acceptance. In fact, it was strongly opposed by some workers. That the indefinitely stable sodium chloride should break up (*i.e.*, dissociate into ions) when dissolved invited disbelief. Opponents could point out that the dilution law breaks down when applied to solutions of strong electrolytes, *i.e.*, those with equivalent conductivities that are high even in concentrated solutions. Several decades were to pass before the behavior of strong electrolytes in solution could be explained. Despite this anomaly, the theory accounted for some hitherto inexplicable relationships and was strongly supported by Ostwald. Donnan's project, which was to involve optical phenomena instead of those of conductivity, may have been chosen to obtain additional evidence for the validity of the theory. Certainly, developments were at an exciting stage when Donnan arrived in Leipzig.

Background to Donnan's Project

The project was probably initiated by the photometric studies of Gaetano Magnanini (1866-). He obtained his doctorate in 1888 and was assistant at the University of Padua in 1888. After the next year in Leipzig, he became professor of chemistry at the University of Messina. In 1892 he was appointed to simultaneous professorships at the Universities of Bologna and Modena (9). In 1892 Magnanini had claimed that the light-absorbing capacity of a solution of a colored electrolyte is independent of its dissociation but depends solely on the concentration (9). He had found that the light absorption of a solution of CuSO_4 was not changed by the addition of H_2SO_4 . Magnanini believed, as did all his contemporaries, that a salt like CuSO_4 was only partially dissociated in solution, and that the addition of H_2SO_4 would decrease its degree of dissociation. Hence, if Cu^{2+} is the light-absorbing species, a decrease in the absorbance should have occurred. Ostwald had stated that both ion and nondissociated salt were light absorbers, so that the changed ratio of the two species could leave the absorbance unchanged.

Magnanini then began the study of violuric acid (HV) (Fig. 2) and its salts (10). HV exhibits keto-enol tautomerism and acts as a pseudo acid. Magnanini

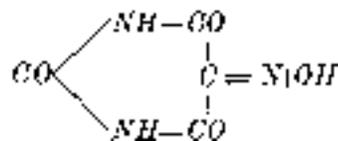


Figure 2. Violuric acid

claimed to have made solutions of HV that were colorless, but conductivity measurements showed the acid was appreciably dissociated. From this, he concluded that violurate ions (V) were colorless, *i.e.*, had practically no absorbance. However, a solution of potassium violurate (KV) is violet in color. He found that although the addition of KNO_3 did not change the light absorbance of such a solution, it considerably decreased the dissociation of KV.

Magnanini also prepared sodium and ammonium violurates. The solids differed in color from that of KV, but the three salts gave solutions of the same color. This could not be due either to the colorless cations or to the violurate ion, which he had stated to be colorless. He therefore assumed that the violet color of the salts depends on what happens to them when they are dissolved in water, or at least on the portions not split into ions.

Ostwald's assistant, Julius Wagner (1857-1924), in commenting on this assumption, stated that the color comes from "dissolved salt molecules," no matter what their state (11). Wagner felt that Magnanini had not correctly interpreted the significance of Ostwald's observation concerning solutions that contain a colored ion as a companion to a colorless one. Wagner then began his own examination of the behavior of HV and its salts. This involved the partial repetition of Magnanini's experiments, some results of which were found to be in conflict with the dissociation theory.

Despite Magnanini's claim, Wagner was unable to prepare a colorless solution of HV. In fact, as a preliminary to his study, Magnanini had obtained HV solutions that showed some color. He attributed this to the presence of alkali, dissolved from the glass-distilled water reservoir. Wagner found that water thus stored and that freshly distilled through a zinc condenser both

gave violet HV solutions, thus invalidating Magnanini's attribution.

Wagner used a colorimeter to compare the absorbance of a solution of HV with one of NaV. He found that the light path lengths required for equal absorbance were inversely related to the calculated concentrations of violurate ions. He then examined the effect of diluting a solution of HV. The intensity of color understandably decreased, but the effect was partially offset by the increased dissociation of HV as the solution became more dilute. Wagner found that, for a given solution and the same diluted fourfold, the color intensity ratio agreed with the ratio of the calculated ionic concentrations of the two solutions. Although he made no measurements, Wagner noted that the addition of HCl to a solution of HV diminishes the color. This can be explained as due to the suppression of the dissociation of HV by the additive. Overall, these experimental results are in harmony with the ionic theory. They show that the color of a solution of HV is due to the presence of the violurate ion. Later, Magnanini gave up his earlier ideas (12). Nevertheless, Donnan made use of Magnanini's conductivity data in his studies.

Donnan's Plan of Research

The first step of Donnan's plan was to determine optically the precise relationship between the concentration of HV and its degree of dissociation. He pointed out that although many others had examined light absorption in solutions, only one, Thomas Ewan (1868-1955), had determined electrolytic dissociation by colorimetric means (13). By use of a refined form of spectrophotometer, Ewan found that his results of the dissociation of dinitrophenol agreed very well with those calculated from conductivity measurements. If his first step was successful, Donnan planned to examine quantitatively the behavior of mixed solutions of HV and another acid.

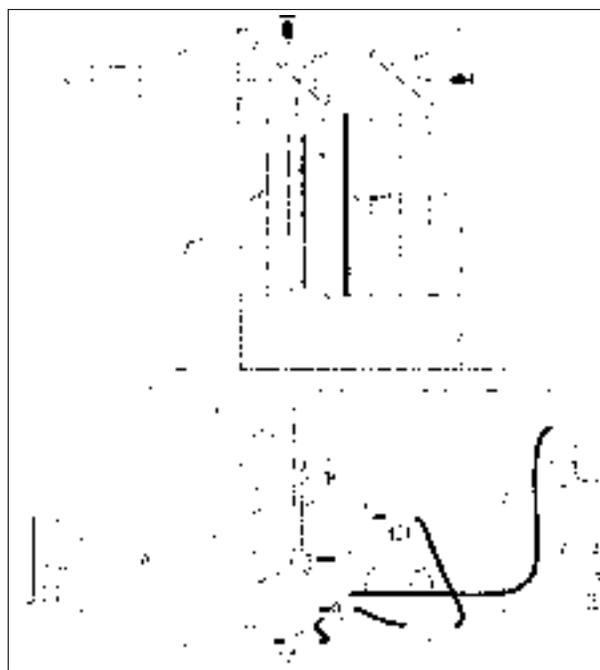


Figure 3. Colorimeter, side view at top, front view at bottom.

Donnan's Apparatus and Results

The simple but effective colorimeter designed by Donnan is shown as a side view at the top of Fig. 3 and as front view at the bottom. Light from the shielded incandescent gas burner *a* passes through tunnel *b* and is reflected upwards by the opal glass plate *c*. This is covered with a piece of frosted glass to diffuse the light, which is directed upwards through the approximately 20-cm high cylindrical cells *d*, *d*, which are shielded from one another by partition *s*. The rear cell (side view) contains a predetermined height of the solution to be examined, while the height of the reference solution in the other cell can be adjusted. After passage through the solutions, the light is reflected forward by mirrors *r*, *r*. An elliptical portion of the silvering of the front mirror is removed, so that light reflected by the rear mirror can pass through. Light from both mirrors passes through light filter cell *t*, which contains a solution of malachite green, of color complementary to the violet color of the solutions in cells *d*, *d* and then to the ocular *e*, which is merely a horizontal brass tube. The observer sees a circle of gray light in a similar background provided by the remainder of the front mirror. When the height of the reference solution is adjusted to achieve balance, *i.e.*, when the same amount of light is emerging from the two cells, the circle appears to have vanished; its illumination is the same as that of the background.

Pump *m* is used to compress the air in the large vessel *l*. Manipulation of cocks *g* and *p* allows the height of the reference column to be raised by air pressure, held constant, or lowered by relief of pressure. The height of the column in the reference cell is determined by reading the scale etched on tube *f*, the lower portion of which is sealed into the cell. Because of capillary action due to the difference in diameters of the cell and of the tube, the two levels are not the same. However, Donnan found that a constant correction could be applied. He also corrected for the fact that light from the rear mirror has to pass through the thickness of the glass of the front mirror, and also corrected for the absorbance caused by water in the differing column heights.

Donnan prepared violuric acid from hydroxylamine "hydrochlorat" and alloxan (14). After careful purification, he used it and carbonate-free NaOH to make the 1/1200-normal NaV that was used as the standard solution. Assuming that the degree of dissociation of NaV would be approximately the same as that found for KV by Magnanini, Donnan calculated that the dissociation

in his standard solution was 98.5%, *i.e.*, is practically complete.

The results obtained by Donnan for HV solutions are listed in Table 1. For each concentration (expressed as a fraction of normality), the percentages of dissociation of HV given are those obtained from conductivity, uncorrected colorimetry, and colorimetry corrected for solvent absorbance, respectively. It is obvious that the correction becomes important with the more dilute solutions. Donnan pointed out that these results were in harmony with the Ostwald dilution law.

TABLE 1

Percentage Dissociation of Violuric Acid in Solution

Concentration	Conductivity	Colorimetry	Colorim., corr.
1/32	2.90	2.89	2.88
1/64	4.08	4.07	4.14
1/128	5.75	5.54	5.74
1/256	8.06	7.61	7.97

Experiments with Violuric Acid Solutions that Contain Other Substances

If a solution of HV is acidified, the degree of dissociation, and hence the color, is decreased. The next section of Donnan's paper dealt with the examination of mixed solutions of HV and another monobasic acid (2). He wished to find out whether the decrease agreed with that indicated by the theory of equilibrium in electrolyte solutions. In such mixtures the concentration, dissociation constant, and degree of dissociation of each of the acids will be involved. The general approach for the calculation of α_1 , the degree of dissociation of HV, involves the solution of a complicated cubic equation. However, there are two cases in which this cubic equation can be simplified to a quadratic, namely, when the second acid is much stronger than HV and when the dissociation constants of the two acids are identical.

In the first case, the simplified equation is:

$$c_1\alpha_1^2 + (c_2 + k_1)\alpha_1 - k_1 = 0 \quad (1)$$

where α_1 is the degree of dissociation of HV at concentration c_1 and c_2 is the concentration of the strong acid.

According to Magnanini, the dissociation constant of HV, k_1 is 0.0000272.

As an example of this case, Donnan used solutions of HV that contained very low concentrations of HCl. He had found that, for 1/32-N HV solution itself, a_1 was 2.90%. However, when this solution was made 0.0003952-N with respect to HCl, a_1 had fallen to 2.47%. A similar experiment with 1/64-N HV gave corresponding percentages of 4.08 and 3.10. These results, along with another obtained at an HCl concentration of 0.0001976-N, agreed fairly well with those predicted by Eq. 1.

In the second case, the relevant equation is:

$$\frac{\alpha_2^1}{1 - \alpha_1} = \frac{k_1}{c_1 + c_2} \quad (2)$$

Donnan chose *p*-hydroxybenzoic acid (PAB, $k = 0.0000286$) and then levulinic acid (LA, $k = 0.0000255$) as solutes with dissociation constants close to that of HV. With PAB, both 1/32 N and 1/64 N HV solutions were used. As an example, a_1 was found to be 2.71% in a 1/32 N solution of HV that was also 0.005128 N with respect to PAB. The effect of PAB on a_1 was thus less than that produced by a much smaller concentration of HCl. Only 1/64 N HV solutions were used in experiments with LA. As an example, a_1 , found to be 4.14% with HV alone, fell to 3.14% when LA was added to a concentration of 0.01182 N. The results obtained with PAB were gratifying, those with LA less so. However, the LA results agreed very satisfactorily with those predicted by the general cubic equation.

This equation had to be used for 1/64 N solutions of HV that contained acetic acid (HA, $k = 0.0000180$), the dissociation constant of which differs considerably from that of HV. As an example, the addition to the HV solution of HA at a concentration of 0.0132 N caused a_1 to fall to 3.27%. Overall, the results were very satisfactory.

Arrhenius had examined the equilibrium in a solution that contained a weak acid and a strong acid, along with their potassium salts (9). He tested the theory by determining the hydrogen ion concentration through its specific effect on the velocity of the inversion of sugar (16). Donnan saw colorimetry as an alternative determinative method for solutions made from HV and a colorless alkali salt of a strong acid, for which he chose NaCl. Viewed on a molecular basis, equilibration will

result in the formation of NaV and of HCl, so that four solutes are involved. Further, these solutes dissociate to degrees that may differ greatly. Naturally, a rigid treatment of the resulting equilibrium state would be very complicated.

Donnan made the following assumptions: (i) the light-absorbing capacities of nondissociated NaV and of the violurate ion are the same; (ii) the concentration, x , of nondissociated NaV and the dissociation constant of HV are small compared with N , the concentration of NaCl. He showed that the concentration of the "light absorbing component" in a volume of V liters is given by:

$$\frac{(1 - x)\alpha_1 + x}{V} \quad (3)$$

Making use of his assumptions, Donnan was able to obtain expressions for a_1 and for x^2 (and hence for x) and could then evaluate expression (3). The considerable disagreement between the calculated values and those determined experimentally, e.g., 0.000688 N and 0.000762 N respectively, could not be explained, but was unlikely to be due to the difference in the light absorbing capacities of NaV and of its anion. Some experiments with mixed solutions of NaV and NaCl appeared to show that NaV was a better absorber than its anion, but the difference was too slight to affect the results.

Finally, Donnan tried his methods on *p*-nitrophenol and "commercial" dinitrophenol, which yield yellow ions. He found that his colorimeter lacked the necessary sensitivity. Ewan had been successful because of his more sophisticated instrumentation (7).

Donnan's Postdoctoral Career

In 1896, Donnan was awarded a Leipzig Ph.D. (*magna cum laude*). He then went to Berlin to work with van't Hoff (1852-1911) on the hydrates of salts and the vapor pressures of their solutions (1). Studying at home for a year, he wrote four papers on various aspects of theoretical physical chemistry. In 1898 he became a senior research student under William Ramsay (1852-1916) at University College, London. At that time, Donnan was the only person in the College who was well acquainted with Arrhenius-Van't Hoff-Ostwald concepts of physical chemistry, and he applied these vigorously to his studies. These led to publications on the Hall effect in electrolytes (17) and on the velocity of the iodide-ferricya-

nide reaction (18). Donnan's appointment as assistant lecturer in 1901 was his first academic post. In 1903 he moved to the Royal College of Science in Dublin, but his stay was short for he had become a leading scientist through his numerous publications on widely ranging physicochemical topics. In 1904 he became the first occupant of the new chair of physical chemistry at the University of Liverpool, where he continued to publish extensively.

His discovery of what is now known as the Donnan membrane equilibrium was announced in 1911 (19). Consider the simplest case: a solution of NaCl that is separated by a membrane from a solution of NaR, the anion R of which cannot pass through the membrane. The chloride ion concentrations become unequal, although the membrane is permeable to this ion. The Donnan effect has many ramifications, especially in biological systems.

Donnan succeeded Ramsay at University College in 1913 and remained there until his retirement in 1937. The outbreak of war in 1914 led him to become greatly involved in the national effort and, at the same time, brought him into close contact with leaders in the chemical industry. Donnan had become nationally and internationally famous, as indicated by his receipt of numerous awards and distinctions. He received eleven honorary doctorates, including those from Princeton and Johns Hopkins. He had been elected as a Fellow of the Royal Society in 1911 and received its Davy Medal in 1928. He was Foreign Secretary of the Chemical Society from 1925 until 1933, when he delivered the Ostwald Memorial Lecture to the Society.

Donnan's final papers, dated 1953, marked the 50th anniversary of the Faraday Society, of which he was a founding member. He died at Sittingbourne, Kent, on December 16, 1956.

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