The Proton

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The interesting anectodotal material describing the series of events which led to the recognition of the proton as a fundamental particle of nature seems worthy of a more prominent place in the teaching of physics and chemistry than currently given it. Modern texts, at best, give only a few of the bare bones that litter the trail of this fundamental particle. Since essentially no uncombined hydrogen nuclei exist in electron donor solvents (1), such as water, it is not surprising that the proton was first perceived in the plasmas of the gas phase reactions which occur at low pressures in electrical discharges.

The roots of this discovery can be traced back to the early works of Michael Faraday (2), who appears to have done the first experiments (3,4) on continuous electrical discharges through rarefied gases. A contemporary of Faraday, William Robert Grove, an experimenter *par excellence*, carried out a series of experiments on electrical discharges through gases, which he described in the *Philosophical Transactions of the Royal Society* in 1852 (5). As a consequence of these experiments, Grove reasoned that anions and cations are formed when an electric discharge proceeds through a tube containing a mixture of rarefied hydrogen and oxygen. To explain the results of his experiments, he applied the von Grotthuss Model of electrical conduction by electrolytes. This was the popular model until the advent of Arrhenius theory. Grove was familiar with this theory and had, in fact, pointed out an inadequacy in the theory when it was applied to his gas battery. Faraday had introduced the terms anion and cation in 1834. Thus, Grove was thinking in terms of hydrogen as a cation as early as 1852. It seems unlikely that Grove could have had a correct vision of the mechanism of proton production, but one should not rule out the tantalizing possibility that his visions were decades ahead of his time. We offer an excerpt from Grove's paper which we believe is the first mention of the hydrogen cation in the gas phase (5).

> As may be gathered from my opening remarks, the experiments above detailed appear to me to furnish a previously deficient link in the chain of analogy connecting dielectric induction with electrolysis. The only satisfactory rationale which I can present to my own mind of these phenomena is the following. The discharges being interrupted . . ., the gaseous medium is polarized anterior to [prior to] each discharge, and

> polarized not merely physically, as is generally admitted, but chemically, the oxygen or anion being determined to [appearing at] the positive terminal or anode, and the hydrogen or cation being determined to [appearing atl the negative terminal or cathode; at the instant preceding discharge there would then be a molecule or superficial layer of oxygen or of electro-negative molecules in contact with the anode, and a similar layer of hydrogen or of electropositive molecules in contact with the cathode, in other words, the electrodes in gas would be polarized as the electrodes in liquid are.

William Robert Grove, who held a professorship in the London Institution, has received only limited attention in the literature. His interesting mix of interests, law and natural philosophy, placed Grove in a position to play pivotal roles in both the experimental and structural sides of the science of his time. His legal talents and training allowed him via shrewd committee service to exercise a powerful behind-the-scenes influence in the restructuring of the Royal Society, thus making it into a formidable organization of scientists. His talents as a scientist brought about the invention of the first fuel cell, which was based on hydrogen and oxygen electrodes, and the construction of one of the most popular voltaic cells of his time.

A contemporary of Faraday and Grove and the vice president of the Royal Society, John P. Gassiot, in his Bakerian Lecture of 1858 reported deflections of the electrical discharges in rarefied gases by both magnetic and electrostatic means, but another contemporary and great experimenter in discharge-tube phenomena, J. Plücker in Germany, is credited with the discovery of cathode rays. However, it was Eugen Goldstein some decades later who gave these rays the name *Kathodenstrahlen* (cathode rays), and it was W. Hittorf, a student of Plücker, who first noted that objects in the path of cathode rays cast shadows (2). Research in this area of discharge tube phenomena was greatly accelerated by the development of the high-voltage transformer by Ruhmkorff (5) and the large-scale capacitor by Despretz (5).

At this stage in the development of the understanding of gaseous discharge phenomena, a dominant intellect entered physics from the field of physiology. This man, Herman Ludwig Ferdinand von Helmholtz, had recently completed his great treatises on physiology and was looking for new fields to conquer. With the death of Gustav Magnus the chair in physics at Berlin was vacated. Helmholtz assumed the chair with the avowed purpose of bringing order into what he characterized as a pathless wilderness of competing theories and mathematical formulas. While his name is not directly associated with the proton, he sponsored both Eugen Goldstein (7,8) and Wilhelm Wien (9), who did the definitive studies on this fundamental particle. In fact, von Helmholtz's name appears on both the 1876 and 1886 papers of Goldstein. Thus he seems to have cast a large and perhaps benevolent shadow over this development.

Eugen Goldstein, who is credited with the discovery of canal rays, after a year (1869-1870) at Breslau joined von Helmholtz at Berlin, where he received the doctorate in 1881. We call attention to two papers by Goldstein in which he described the use of perforated cathodes. The first of these was published in 1876 (7) and the second 10 years later, 1886 (8). Both appeared in the *Monthly Report of the Royal Prussian Academy of Science* at Berlin, and both were sponsored by von Helmholtz. The second is the oft quoted paper on *Kanalstrahlen* (canal rays). One can only wonder if the great intellect of von Helmholtz made a direct input into this research.

Goldstein observed that in a tube fitted with a perforated cathode containing a rarefied gas a sheaf of light rays (canal rays) came through each perforation in a direction opposite the path of the cathode rays (electrons). The relatively weak magnetic fields that he employed did not give a discernible deflection of these light rays. However, the identical magnetic fields strongly deflected the cathode rays. His conclusion was that for the canal rays observed he was dealing with a phenomenon which he could not explain.

These interesting observations of Goldstein lay buried in the monthly reports of the Berlin Academy for nearly 12 years. During the latter part of this 12-year period, Röntgen discovered Röntgen *Strahlen* (X-rays) and published his first two communications. They appeared in the *Monthly Reports of the Würzburger Physics and Medicine Society*, a publication of limited circulation. Georg Wiedemann, a very perceptive editor, sought the permission of Röntgen to republish these two seminal papers in his widely distributed and prestigious *Annalen*. Röntgen, at first, refused permission, but after publishing a third paper in the monthly reports of the Berlin Academy he allowed Wiedemann to republish all three papers (10). In the 64th volume of the *Annalen*, Wiedemann followed Röntgen's three papers with a fourth: namely, the 1866 paper of Goldstein.

It is worth noting that Goldstein's work attracted little attention in the circle of German physicists (10) largely because they considered his research too descriptive. In addition, Goldstein's work seemed to point to an explanation based on the presence of particulate matter. At that time the best opinion in the German circle on the origin of gaseous tube discharge phenomena was based on an electromagnetic concept (10).

We are principally interested in the proton, a canal ray. However, the name *canal ray* came about from a general phenomenon. Goldstein, while experimenting with a number of gases, not hydrogen alone, noted that these strange rays changed their color from gas to gas (8). He suggested calling them canal rays until such time that someone selected a suitable name. His provisional name became the accepted name.

It remained for Wilhelm Wien, who authored his papers as Willy Wien, to recognize that canal rays were positively charged particles. He noted that one could not visually distinguish them from weak cathode rays, but even with a weak horseshoe magnet that the cathode rays could be deflected and the canal rays were not noticeably deflected (9). Finally he noted that electrostatic deflection served as a good means of identifying the canal rays, for the canal rays were deflected to the negative pole of the electrostatic device. He also specifically stated that the positive electricity carried by the canal rays was an identifying characteristic of the rays. Wien designed deflection equipment using potentials up to 30,000 volts and determined e/m ratios for the proton where e is the charge and m is the mass of the particle. His results agree rather well with results obtained by later investigators. From his measurements on discharges through hydrogen he said that one is easily led to the opinion that canal rays were the hydrogen ions themselves. Thus, it appears that to Wien must go the credit for the following: recognition that the canal rays produced in electrical discharges in low pressure hydrogen gas are positively charged particles. recognition that these rays contain hydrogen ions, and the first e/m measurements of the proton.

It is not clear just how the term proton (from the Greek *protos*, first) became associated with the positively charged hydrogen atom. The best source regarding this choice of a name seems to us to be found in a footnote by E. Rutherford that is appended to a paper by O. Masson (11). However, this interesting footnote does not give a definitive answer as to whom the choice of the term should be attributed.

In May 1907, J.J. Thomson followed up on Wien's measurements with a paper entitled "On Rays of Positive Electricity" (12). In these experiments and e/m measurements he used improved apparatus and greater experimental sophistication and observed both the proton and what appears to be the hydrogen molecule cation [H_2^+]. The reader is referred to J.J. Thomson's historic treatise "Conduction of Electricity Through Gases" (13) for further information on the instrumentation, experimental method, mathematical treatment, and additional points of history in the recognition of the proton.

Literature Cited

(1) Bell,R.P.,"Acids andBases—Their Quantitative Behaviour,"JohnWiley and Sons, Inc., New York, **1952**.

(2) Hittorf, W., "Über die Elekricitätsleitung der Gase," *Ann. Phys. Chem.*, **CXXXVI**, 1, (1869).

(3) Faraday, Michael, "Experimental Researches No.'s 1542, 1543, and 1544, **1838**.

(4) Faraday, Michael, "Experimental Researches In Electrochemstry," No. 576 of Everyman's Library, E.P. Dutton and Co., Inc., New York, **1914**.

(5) Grove, W.R., "VII. On the Electro-Chemical Polarity of Gases," *Phil. Trans. Roy. Soc.*, **142**, (I) 87 (1852).

(6) Arrhenius, Svante, "Text-Book of Electrochemistry," Longmans, Green and Co., New York, **1902**.

(7) Goldstein, Eugen, "Vorläufige Mittheilungen über electrishe Entladungen in Verdünnten Gasen," *Berlin Akd. Monatsber.*, 279 (1876).

(8) Goldstein, E., "Über eine noch nicht untersuchte Strahlungsform an der Kathodeinducirter Entladungen," *Berlin Akd. Monatsber.*, **II**, 691 (1886).

(9) Wien, W., "2. Untersuchungen über die electrische Entladung in verdünnten Gasen," *Ann. der Physik* **8**, 244 (1902).

(10) Ruckhardt, E., "Zur Entdeclcung der Kanalstrahlen vor fünfzig Jahren," *Naturwissenschaften*, **30**, 465 (1936).

(11) Glasstone, Samuel, "Source Book on Atomic Energy," D. van Nostrand Company, Inc., New York, **1950**.

(12) Thomson, J.J., "XLVII. On Rays of Positive Electricity," *Phil. Mag.*, **13**, 561 (1907).

(13) Thomson, J.J., and Thomson, G.P., "Conduction of Electricity Through Gases," 3rd. ed., Cambridge University Press, **1928**.