100 Years of Ion Beams: Willy Wien's Canal Rays

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When Goldstein's report on the "positive light" (or what is known as "Kanalstrahlen", canal rays) in gas discharge tubes first appeared in 1886, Willy Wien had just finished his thesis at the Helmholtz Institute in Berlin. Eleven years later he performed his first experiments on canal rays and found that they consisted of inert, charged and neutral particles. The charged component in canal rays could be deflected using electric and magnetic fields, enabling Wien to roughly determine their mass-to-charge ratio. Improving vacuum conditions and detection efficiency, Thomson finally resolved the lightest constituents of canal rays: the hydrogen ions H^+ and H_2^+. This marked the beginning of mass spectrometry. The first mass spectrographs were parabola-image instruments being used by Thomson to discover isotopes. Until about 1923, canal rays became the most common ion source. Also Aston used canal rays as an ion source for the first double focussing mass spectrometer. - Wien continued his work on canal rays up to the end of his life (he died in 1928). He investigated their interaction with matter, i.e. the mean free path of canal rays in gases with respect to charge exchange and atomic excitation. His particular interest was addressed to the physics of light emission by canal rays, such as the line spectrum and the splitting of these lines in magnetic and electric fields, the Doppler effect and lifetimes.

I Introduction: How Wien came to Physics with Canal Rays

In 1886, Goldstein [1] observed that with an electric discharge in low-pressure gases the discharge seemed to continue through a hole in the cathode, i.e. he saw a bright beam behind the cathode. He called these beams canal rays ("Kanalstrahlen"), as they are formed in front of the cathode and pass through canals in the cathode.

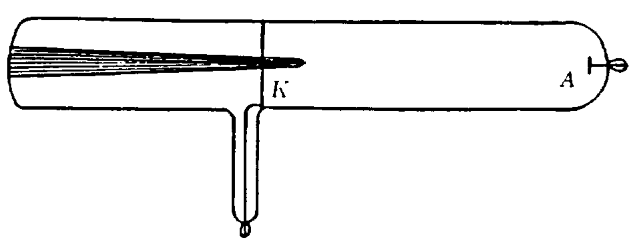


Figure 1. Canal rays in a discharge tube from a sketch by Wien [2]. A = anode, K = cathode.

At that time Willy Wien was 22 years old and had just finished his dissertation on the diffraction of light on sharp edges at the Helmholtz Institute in Berlin. Prior to taking his doctorate, he studied Physics at the universities in Göttingen, Heidelberg and Berlin for only four semesters (two years), an extremely short period of time for the subject of Physics even then. It was perhaps almost too short for he passed his PhD exam with great difficulty. The man who was to be awarded the Nobel prize for his work in theoretical Physics 25 years later almost failed on the math exam.

Figure 2. Willy Wien during his years at the Physikalisch-Technische Reichsanstalt in Berlin (1889-1896).

Willy Wien had a natural inclination and talent for Physics. Nevertheless, for many years he was plagued by doubt as to whether he would be better off following the footsteps of his forefathers. His parents were farmers in East Prussia. They originally worked a large holding near Königsberg, where Willy Wien was born. This was later exchanged for a smaller farmstead following financial difficulties. The new farm proved no easier to cope with and, to add to the Wien's problems, was also heavily damaged during a fire. As Willy was their only child, the Wiens naturally hoped their offspring would take on the farm and carry on their life's work. Willy loved life in the country and was a keen hunter. During his time at university and the years following his PhD, he spent a lot of time on the farm, learning how to farm and helping his father. Yet unfortunately he failed to inherit his father's agricultural skills. Looking back, he wrote: "I felt that farming was not my natural vocation; the technical side became easy for me, but my knowledge of livestock, and especially of horses, was lacking and I would never have trusted myself to buy a horse". Worry about his choice of occupation depressed him for many years until the decision was almost made for him in 1889; "severe drought and a failed harvest" forced his father to sell the holding.

Willy Wien was offered the chance to take up a post as assistant to Helmholtz at the Physikalisch-Technische Reichsanstalt in Berlin. Besides working on experiments to create a new unit of light, Wien investigated a great number of topics in theoretical Physics. These included water waves and cyclones which he treated with hydrodynamics and also with the thermodynamics of thermal radiation, which later produced the Wien displacement law. This work, for which he was awarded the Nobel prize in 1911, was published in 1896 when he was thirty two.

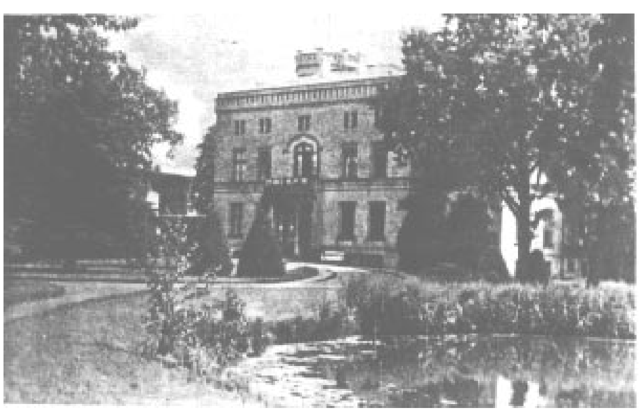


Figure 3. The house where Willy Wien was born on the farm called Gaffken west of Königsberg in East Prussia.

As Helmholtz largely entrusted Wien to carry out his own research, Wien's years in Berlin were relatively undisturbed and extremely productive. When X-rays were discovered in 1895, Wien was given the task of producing these rays. These constituted his first experiments with particle rays in a vacuum. In the autumn of 1896 he accepted a chair as associate professor at the Technische Hochschule in Aachen where he initially devoted himself to the study of cathode rays which were used to produce X-rays. The vacuum apparatus left to him by his predecessor, P. Lenard, proved to be very useful. Lenard had invented the Lenard window, among other devices, through which cathode rays could exit into an adjacent vacuum, as opposed to canal rays, which at the time could not be passed through windows.

II Wien's Experiments with Cathode and Canal Rays in 1897 and 1898

Experimentation with gas discharge started around 1856, when instrument maker Geißler developed a rotating mercury pump which could be used to produce a vacuum pressure of probably 0.1 mm Hg. He developed later a diffusion pump for pressures down to 10^{-5} mm Hg. At these pressures, electric gas discharges could be produced between two electrodes in glass tubes whose brilliant light in particular attracted attention. The light produced depends on the fill gas used; besides band spectra it also produces the line spectrum of this gas and was thus often used as a light source for spectral investigations. Using optical methods, Wien repeatedly studied this light, which also originates from canal rays.

Goldstein's canal rays - also called positive rays because of their propagation direction - were barely heeded until Wien's first experiments in 1897. Goldstein still claimed in 1901 that canal rays could not be deflected neither electrically nor magnetically [3]. Many scientists believed that both cathode rays and canal rays were based on processes in the ether, about which there were only very hypothetical ideas at that time. The ether theory did not permit definite predictions about the behavior of the radiation in electric or magnetic fields, for example. Wien made gas discharges with both types of rays the subject of his first experiments.

Cathode Rays

As early as 1858, Plücker observed a fluorescent glow on the glass wall of discharge tubes near the cathode; in 1869, Hittorf reported on what are known as cathode rays, namely rays which stretch from the cathode towards the anode and can be deflected by electric and magnetic fields. Perrin [4] showed in 1895 that negative electric charge is transfered by or in them - at the same time Röntgen discovered that cathode rays produce X-rays when they collide with metal.

The original aim of Wien's experiments [5, 6] was to decide "if cathode rays are processes in the ether or are moving, electrically-charged, inert masses". Like his English colleagues, Wien favored the latter option, although there were a number of phenomena which did not quite fit the charged particle model. Cathode rays seemed to make their way independent of the path of the current and even passed through thin metal plates without any noticeable drop in velocity. Wien thus had cathode rays pass through an aluminum foil in a tube with an "extreme vacuum", where he monitored the charge by means of an electrometer. He could thus rule out that the charge transfer occurred through the fill gas which had become conductive along the path of the ray. He then determined the velocity of the cathode ray particles and their mass-to-charge ratio with the help of crossed, electric and magnetic fields (Wien filter). In the article he published in Annalen der Physik in 1898 [6] he writes of an m/e value of 5x10^{-8} CGS. In the International System, this is equivalent to 5x10^{-12} kg/C. Today's value is 5.685x10^{-12} kg/C. In spring 1897, J.J. Thomson [7] handed in similar m/e values for publication. He had magnetically deflected the rays in the discharge tube gas and then measured the integral transferred load and energy. Due to this m/e ratio determined for cathode rays, Thomson is generally considered to be the scientist who discovered the electron.

Canal Rays

Following his investigation of cathode rays, in 1897 Wien [5, 6] turned his attentions to "positive light" which he considered *"in its basic nature no different from the processes at the cathode"*. He tried to produce proof of the charge and particle nature of the canal rays using methods similar to those of his cathode ray experiments. He was, however, unable to completely separate the observation area from the discharge area for, despite great effort, he was not successful in finding a substance which the canal rays passed through. It took another 17 years until von Traubenberg [8] observed that canal rays can penetrate a 750 Å thick gold foil.

To start with, Wien used the simple glass tube depicted in Fig. 4 with a cathode "*a*"(a mesh), an anode "*b*" and an electrode "*C*" connected to an electrometer. In order that the discharge area between "*b*" and "*a*" be electrically screened, the tube was placed in a grounded metal box which was connected to cathode "*a*". The canal rays manifested themselves in a positive charging of "*C*", even with a relatively high gas pressure, when a very faint light could just be perceived covering the cathode.

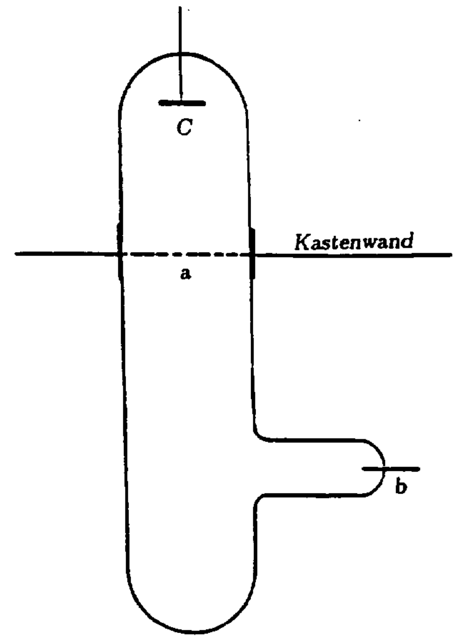


Figure 4. Gas discharge tube with a mesh as the cathode behind which canal rays can be observed. The diagram is taken from an article written by Wien [6]. b = anode, a = cathode, C = electrode connected to an electrometer. The lower section of the tube up to the level of the cathode was placed in a grounded tin box.

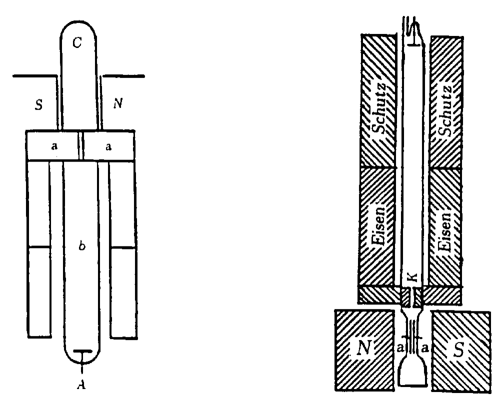


Figure 5. a: Two sets of tube apparatus for investigating canal rays with an electromagnet SN and an electric deflector plate in tube C (not marked). The fields are perpendicular to one another. The canal rays pass from tube b through a hole in the iron screen aa into tube C. A = anode, aa = cathode.
b: A similar setup to the one in Fig. 5a. K = cathode. The electric field between the plates aa is parallel to the magnetic field between the poles N and S. The back wall of the observation tube is within the magnetic field. The equations beside Fig. 8 apply to the deflection of the patch of light. Both diagrams are taken from articles written by Wien [6, 2].

As Goldstein had already claimed, these canal rays did not change when a magnet was brought near them, as long as the magnet itself did not influence the discharge. With an additional electrode, a perforated metal plate placed between "*a*" and "*b*", cathode rays could also be produced if the plate was brought to negative potential relative to "*a*". In this case, mixed canal and cathode rays were emitted through grid "*a*". With higher pressures the charge at "*C*" was negative, i.e. the canal rays - but not the cathode rays - were obviously absorbed in the gas. As described further on in this article, Wien explored later the mean free path of canal rays in gases in detail.

In order to prove that canal rays could be deflected in electric and magnetic fields, the apparatus in Fig. 5a clearly had to be modified. Discharge area and observation area, two glass tubes, were separated by a hole 2 mm wide in an iron plate "*aa*". In addition, the discharge tube was placed in an iron tube with thick sides. In doing so, the discharge area could be screened against the magnetic field, which was created in the observation area "*C*" with the help of an electromagnet SN. Wien tested the residual field of the electromagnet in "*b*" with the aid of the cathode rays, which react sensitively to magnetic fields. A magnetic field in "*b*" of the same strength as the residual field had no effect on the canal rays, which were visible on the back wall of tube "*C*" as a patch of fluorescent green. A magnetic field of 3250 CGS between the pole faces S and N deflected this patch by 6 mm in the opposite direction to the deflection of cathode rays, produced by pole reversal of the electric potential at "*A*" and "*aa*". The canal rays were then also deflected in an electric field, whose direction was perpendicular to that of the magnetic field (the relevant deflector plates in tube "*C*" are not shown in Fig. 5). From these two deflection processes, Wien calculated a velocity of 3.6×10^7 cm/s and an m/e ratio of 3.2×10^{-3} CGS (= 3.2×10^{-7} kg/C) for the canal rays.

"These experiments show that positively-charged particles move in canal rays" [6]. The m/e ratio would have corresponded to the ions of the oxygen molecule - the gas in the tube was probably air - yet the appearance of light in the observation area and the patch of green on the glass wall were extremely diffuse. Wien pointed out in his article in Annalen der Physik [6] that *"canal rays are a mixture of various rays which can be deflected"*. The deflected patch probably looked like a dumbbell with a non-deflected brightness maximum, caused by neutral particles, and an oval maximum, which corresponded to deflected particles up to the hydrogen ion. Wien presumably interpreted the oval patch of light as a mean deflection.

Slow Canal Rays

Following his first m/e ratio for canal rays, Wien went on to observe slow canal rays which transfered positive and negative charge. To this end, he fashioned a discharge tube where the cathode rays could not reach the anode. The area of high voltage drop in front of the cathode (the cathode fall), where the cathode rays are accelerated, is blocked off from the area in front of the anode by a bend in the tube, preventing direct access. The apparatus is shown in Fig. 6, with "*K*" as the cathode and "*a*" as the anode, Wien noticed a very diffuse ray in "*C*", which could easily be deflected both electrically and magnetically and which carried negative charge to the electrometer electrode "*b*". M/e ratios could not be determined due to the strong scattering of the rays in the magnetic field. Their velocity was obviously much lower than that of the positive rays formed around the "*cathodefall*".

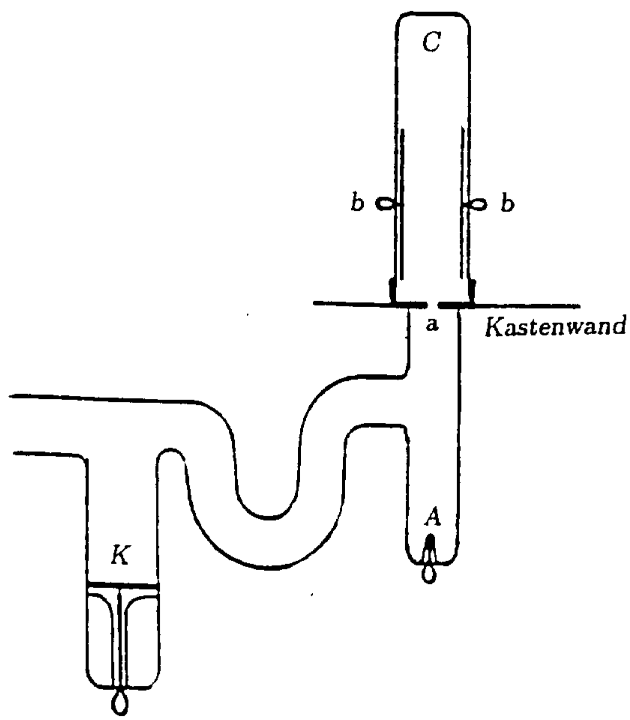


Figure 6. Gas discharge tube with a large bend in the tube between cathode K and anodes a and A; b = electrode connected to an electrometer; C = observation area for negative and positive, slow canal rays. The lower section of the tube up to the level of the anode was placed in a grounded tin box. The diagram is taken from an article written by Wien [6].

Wien thus made electrode "*A*" an anode in addition to anode "*a*" and in doing so gained positive, slow particles which passed through the opening at "*a*" together with the negative particles. The direction of discharge is thus split between "a" and "A". An attempt to explain Wien's baffling observation with regard to our current understanding of the formation of ions would conclude that first negative ions are formed by the capture of electrons from gas atoms and accelerated in the direction of both anodes. This produces the "negative light" behind "a". Then, when these negative ions hit electrode "A", positive secondary ions are formed which fly in the direction of "a" and enter this anode through the canal if the potential of "A" is slightly more positive than the potential at "a". What we can be sure of is that Wien observed slow ions which were formed in the area of low potential drop in front of the anodes.

Wien compared the path of charged particles in a gas discharge with that during electrolysis and established that cathode and canal rays can take paths which deviate from the path of the current, producing further evidence of the inertia of these rays, i.e. their particle nature. He obviously had not enough information at that time to fathom the complex impact and ionization processes taking place in the discharge area, thus providing an explanation for the course of the potential drop between the cathode and anode. In his article in Annalen der Physik from 1898 [6], he concludes that it might be expedient to *"abandon the terms cathod rays, canal rays and positive light and to speak only of positive and negative particles"*.

III The Beginning of Mass Spectrometry

After these first investigations, Wien worked with canal rays during his whole life, - he died in 1928. In numerous monographs he describes his personal experiments on this subject. In addition, his assistants Rüchard and Rau as well as many scientists from Germany and from abroad, who were guests at his institute in Würzburg and later in Munic (after 1920), also contributed to the field. Comprehensive review articles on his "Kanalstrahlen" have been written by him in the handbooks of Radiology [2] and of Experimental Physics [9]. Finally, he denotes with "Kanalstrahlen" all charged and neutral atoms and molecules, which are moving in canal rays. Even such ions, which are produced by thermal processes or by sputtering, are included, - but not the α-rays of the radioactive decay.

At about the same time as Wien, also the English physicist Thomson at Cambridge started his experiments on canal rays. Their attempt to split the bended rays into beams of mass-separated particles fail due to the vacuum conditions in the discharge tube and the observation tube. They connect both tubes by a narrow capillary, through which the canal rays go, and evacuate them by separate pumps. Nevertheless, it was difficult to establish in the discharge tube a pressure sufficiently high for the discharge, and in the observation tube a pressure low enough to allow the rays to reach the back wall. The pressure in the observation tube was probably not lower than 10^{-3} mm Hg. Within the accelaration gap in front of the cathode, but also in the bending fields, the particles experience charge exchange and get accelerated and bended differently. Additionally, the rays are broadened due to scattering in the fill gas or the residual gas. The patch of the bended rays on the observation screen remains diffuse and more or less strutureless.

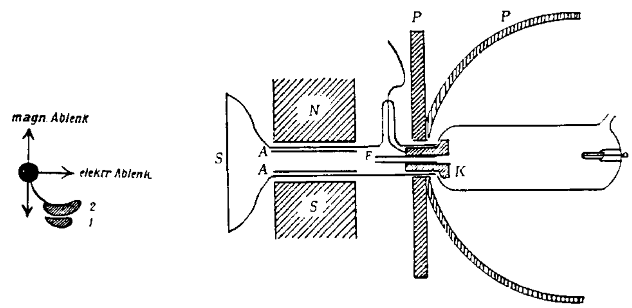
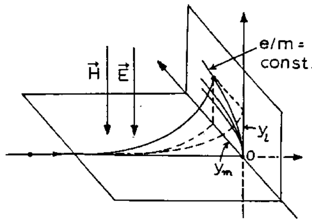


Figure 7. Sketch of a parabola-image spectrograph constructed by Thomson for canal rays in 1897. K cathode, F capillary between discharge and observation tube, S observation screen, AA electric deflection plates, NS magnet, P iron shielding. At the left side of the apparatus, the pattern of the bright patch on S is sketched. Number 1 corresponds to the spot of atomic hydrogen, number 2 to that of molecular hydrogen. Both drawings are taken from the handbook of Radiology [2].

The two bending fields, the electric and the magnetic fields used by Thomson and Wien, are then set parallel. The arrangement used by Wien is sketched in Fig. 5; the spectrograph constructed by Thomson already in 1897 is shown in Fig. 7 copying a drawing of Wien [2]. At the observation screen of these instruments, canal rays of constant mass, but different velocities, should fall on one parabolic strip as it is explained in Fig. 8. The formula for the electric and magnetic deflection have been taken from the handbook of Wien [2]. They apply to the instrumental geometry shown in Fig. 5a. On these parabolas, particles of high velocities are localized close to the spot, where the neutral particles are collected. Particles of different mass form different parabolas, - the atomic hydrogen ion has the widest parabola. Thus, the principle of mass separation by means of parallel fields has been imagined quite early, but it took yet many years until Thomson published a photograph of a bended fluorescent patch, which shows parts of different parabolas.



$$y_e = \frac{V_1}{l}\left(\frac{x_e^2 + 2bx_e}{2v^2}\,\frac{e}{m}\right).$$

$$y_m = \frac{e}{2mv}\,\mathfrak{H}x_m^2.$$

Figure 8. The trajectory of canal rays in parallel electric and magnetic fields. The rays belong to ions of constant mass. The bended rays form a parabolic fluorescent strip at the observation screen. The formula of the deflections y_e and y_m by the electric and magnetic fields, respectively, have been taken from ref. [2]. V_1 = potential at the electric deflection plates, l = distance of these plates, $x_{e,m}$ = distances the ions travel in the two fields, b = distance between the deflection plates and the observation screen, $\vec{H}$ = magnetic field strength, v = ion velocity, m = ion mass and e ion charge.

Wien only saw on the back wall of his observation tube a more or less structureless spot. In 1902, he calculates for the end of the fluorescent strip at a discharge voltage of 30000 Volt an e/m-value of 7545 CGS (see ref. [10]). With respect to the oxygen filling of his discharge tube, this was an unexpected high value. By means of powerful drying agents, the water vapor in the oxygen filling was eliminated. This procedure allowed the high e/m-value, in fact, to almost disappear. Then, Wien obtained e/m = 750 CGS, a value close to that of atomic oxygen (609 CGS).

Thomson improved the method of observation: instead of using the fluorescence of glass, he directed the rays onto Willemit (Zn_2SiO_4), a much brighter shining substance. In addition, he mounted a photo film behind the observation screen, in order to increase sensitivity at long exposure times. He worked at relatively low vacuum pressures, because he added Na, K or Ca to the gas filling, which are easy to ionize. Finally, he was able to observe two oval spots close together as they are sketched in Fig. 7. They agree with the e/m values 10^4 and $0.5\text{x}10^4$ CGS, i.e. the values of the hydrogen ions H^+ and H_2^+ [11].

A characteristic feature of these first e/m measurements by Wien and Thomson was that a large fraction of the canal rays impinging on the observation screen was hydrogen. This was partially attributed to the relatively large range of hydrogen atoms or molecules in the residual gas of the observation tube. Then, Wien supposed that the hydrogen is part of the impurites contained in the fill gas. He backed the vacuum tubes over several days and flooded them with the purified fill gas, in order to remove the hydrogen containing residual gas, - but in most cases without success. The hydrogen patch on the screen seemed to be unavoidable. This led Thomson [12] to assume that the atoms of the canal rays emit a peculiar charged particle, - similar to particle production by the radioactive decay. Many years later, Königsberger and Kutschewski [13] proved with canal rays of mercury vapor that the hydrogen fraction can be completely eliminated.

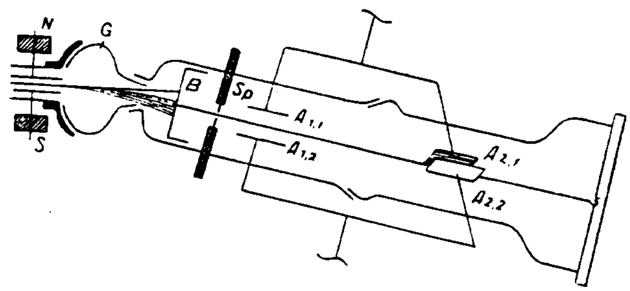


Figure 9. Part of the first time-of-flight spectrometer constructed by Hammer [14] for canal rays. The drawing has been taken from the handbook of Wien [2]. NS = magnet for deflection of the rays being produced in the discharge tube (not shown), B = first observation plane, Sp small aperture, $A_{1,1}$, $A_{1,2}$, $A_{2,1}$, $A_{2,2}$ = electric deflection plates, at the right second observation screen.

These first e/m determinations were the impetous for many further experiments on this subject by means of refined techniques. One method developed by Hammer [14] should be mentioned here, since it employs for the first time a time-of-flight technique to measure the mass of ions.

Hammer added to the usual parabola-image spectrograph a time-of-flight apparatus, in order to measure the velocity of certain ions, which were separated from the bundle of canal-ray particles by the parabola spectrograph. As illustrated in Fig. 9, ions with constant e/m and a narrow velocity range were selected by means of a very small hole drilled in the observation screen of the parabola spectrograph, - i.e. the cross section of the hole covered a small part of one parabolic strip. In order to determine the corresponding e/m value, Hammer measured the electric deflection y_e and the velocity v of the selected ions. Regarding the equation for y_e given in Fig.8, y_e, v, the condensor voltage V_1 and some geometrical quantities are sufficient to evaluate e/m. The velocity v was determined by measuring the time the ions need to pass the distance between two pairs of deflection plates. Both condensers were loaded with help of an oscillating voltage, whose frequency could be precisely tuned. The two electric deflections were perpendicular to each other, - each producing a fluorescent line at the screen, together forming an ellipse. When the ions flight time between the condensers is equal to half of the oscillation period, the ellipse degenerates to a line. The corresponding frequency gives the velocity v. Hammer obtained for the H^+ parabola

$v = 2.8\ 10^8$ cm/s
e/m = 9775 CGS.

Today's e/m-value of H^+ is 9578 CGS, the difference accounts for 2%.

IV Progress of Mass Spectrometry with Canal Rays up until 1920

The pioneering work of Wien and Thomson stimulated many other scientists to experiment with canal rays and to improve the techniques of mass spectrometry. Wien's interest was focussed more on the physics of canal rays. For many years, canal rays generated in discharge tubes became the most important source of ions. Not only ions of different filling gases were studied but also ions of material evaporated inside the discharge tube or produced by sputtering. The canal rays were generally guided through narrow capillaries and apertures into the observation tube. Wien developed a special evacuation device ("Durchströmungsmethode") located between discharge and observation area to control the pressures in both tubes (see Fig. 19). He employed this method to study the interaction of canal rays with various gases. In the following, the development of mass spectrometry based on canal rays will be briefly described.

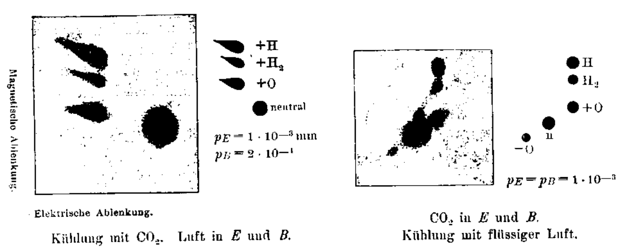


Figure 10. Photographies of canal ray spots taken by Königsberger and Kilching [15] behind a parabola-image spectrograph. Left: discharge and observation tubes contain air (p_E and p_B are the corresponding pressures in mm Hg). Right: the filling is CO_2.

Soon, the visual observation of the patch at the back wall of the obervation tube was replaced by photography, - the photo film was sometimes mounted on the inside of the tube. Two corresponding pictures taken with a parabola-image spectrograph are shown in Fig. 10. The spots of the bended rays are remarkably sharp indicating a narrow velocity range of the particles. Wien was surprised that a carbon spot was not observable, - although the fill gas was CO_2.

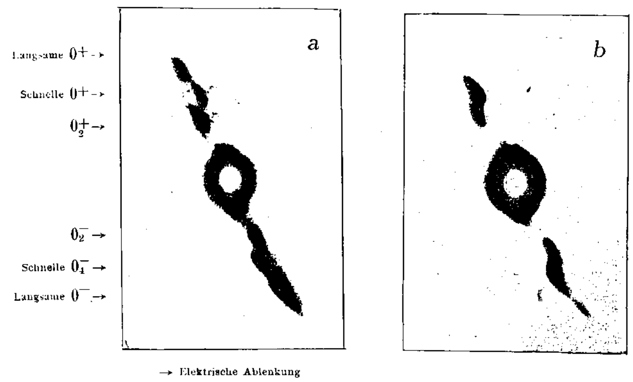


Figure 11. Another example of canal ray spots taken by Retschinsky [16] with oxygen filling. a) the fill gas contains small amounts of mercury vapor. b) half of the fill gas is H_2.

Retschinsky [16] studied the formation of ions in gas mixtures. As can be noticed in Figs. 10a and 10b, sometimes the events of one parabola can accumulate at two different sites, - this means, 'slow' and 'fast' ions of the same e/m-value were present. Small amounts of mercury vapor enhance the intensity of the various oxygen ions. Slow oxygen ions, created outside of the cathode-potential drop, disappear when the oxygen filling is mixed with 50% hydrogen. Supposedly, these intensity variations are associated with the different electron affinities of the gases.

In order to detections of canal rays bended by crossed electric and magnetic fields, Wien [17] used small thermocouples, which were warmed by the impacting particle beam. Measuring the thermovoltage as a function of the magnetic field strength, Wien obtained the "Energiekurve" of the canal rays, i.e. of the ions of the fill gas. He discovered that the ion energy did not correspond to the discharge potential, but was 40-50% smaller, - this means, equal to the cathode-potential drop.

Thomson [18] had already analysed the bended canal rays by means of the 'transported electricity'. He mounted at the position of the observation screen a Faraday cup behind a fine slit. By changing the magnetic field strength he obtained enhanced cup currents, whenever the beam of a certain ion passed the slit. With the help of this method he detected argon ions with charge states up to 3+ and mercury ions up to 7+. An instrument equipped with such a Faraday cup is sketched in Fig. 12. This was built by Dempster [19] in 1916. Substances of interest were evaporated from a glowing wire spiral K. After deflection, the canal rays penetrated the Faraday cup through a parabolically formed slit F. With the help of this spectrometer Dempster was able to observe a strong mass line at m=3u, i.e. the hydrogen ion H_3^+, as illustrated in Fig.13.

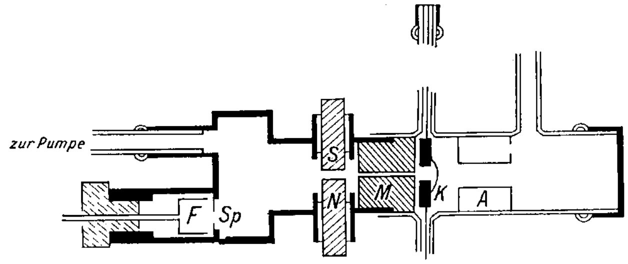


Figure 12. Parabola-image spectrograph equipped with a glowing filament K for evaporation. The apparatus has been constructed by Dempster [19]. The ions are detected by means of a Faraday cup F behind a slit Sp. The poles of the magnet S and N are also the electric deflection plates. M is an iron shielding.

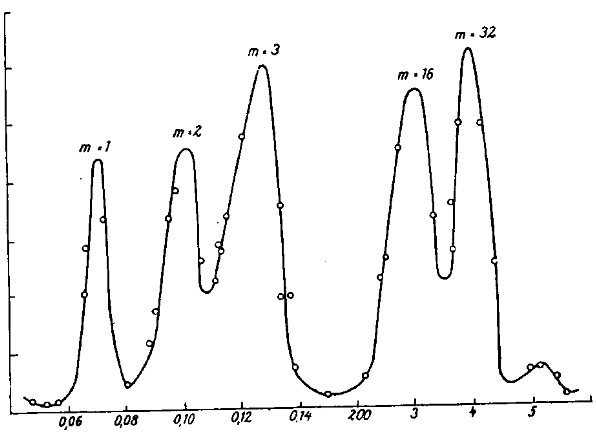


Figure 13. Current of the Faraday cup as a function of the magnetic field strenght. The curve was measured with the spectrograph shown in Fig. 12 at a pressure of 0.01 mm Hg. At this pressure, H_3^+ is the dominant ion of the mass spectrum.

By means of an improved parabola-image spectrograph, Thomson discovered in 1913, amongst destillates of liquid air, particles having the atomic weight 22 u, which he first considered as a new gas. Later, it turned out that the corresponding mass line was associated with an isotope of Neon. This was the first identification of an isotope. Fig. 14 demonstrates that, at these times, mass resolution of parabola-image spectrographs had been sufficiently high to resolve neighbouring masses at about 30 u. The mass spectrum of methane presented in Fig. 14 exhibits, apart from the relatively week CH_4^+ , numerous lighter and heavier ions, which were produced by gas phase reactions in the discharge volume.

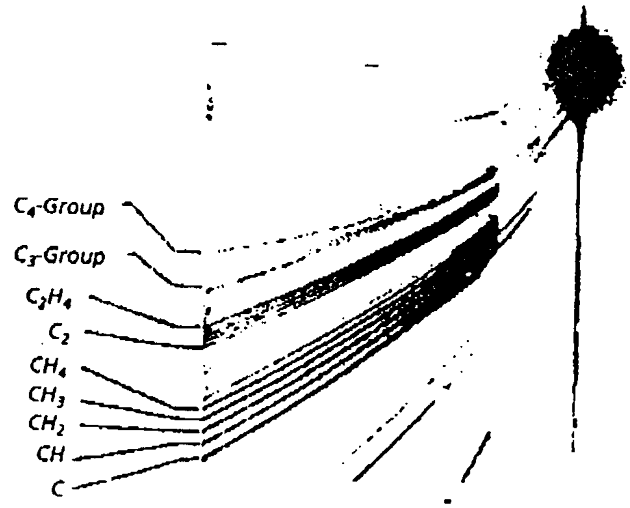


Figure 14. A mass spectrum of positive canal rays of methane measured with an parabola-image spectrograph. The photography has been made by Conrad (see Thomson's book [11]).

Concerning mass resolution, a big step forward was the double focussing spectrograph of Aston, which is explained in Fig. 15 following the handbook of Wien [2]. This instrument also utilizes evaporation of probes inside the discharge tube. The canal rays produced in the right tube of the instrument pass through a small hole in the cathode and a narrow slit in front of the deflection plates, - the latter being the entrance slit of the spectrometer. After traversing the bending magnetic field, which is perpendicular to the electric field, the rays impact onto the photographic film. This film can be turned away to allow visual observation of the canal-ray patch on a Willemit screen through the window F. The accuracy of mass determination was 1/1200, a remarkably high accuracy for ion beams, which have the broad velocity distribution of canal rays. The instrument of Aston compensated the wide energy dispersion in the electric field by the contrary dispersion in the magnetic field. Double focussing requires a certain arrangement of ion source, bending fields and detection device. The functional dependence of the spectrometer parameters has been derived, for instance, by Wien in his handbook [2].

With Aston's instrument, the mass spectrometry of canal rays had reached a culminating point. It seems that, up to 1920, canal rays were plainly the general source of ions. Further improvements of mass resolution required ion sources with more homogeneous ion energies than canal rays can provide. A way out of this dilemma was to apply evaporation of the material of interest leading to a thermal energy spectrum and then to accelerate the thermally generated ions. One of the first spectrometers using such ion sources was that of Dempster [21]. He managed to use only magnetic bending.

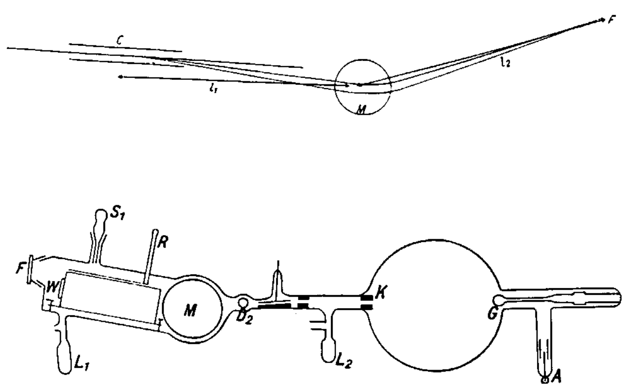


Figure 15. Mass spectrograph of Aston [20]. The upper part of the figure shows the ion trajectories in the electric field between the deflection plates C and in the magnetic field M being perpendicular to the electric field. Ions of the same e/m value but different velocities meet at the focal point F. Theoretical calculations concerning the ion optics of this arrangement can be found in the handbook of Wien [2]. The realization of the spectrograph is sketched in the lower part of the figure. At the right: discharge tube with anode A, cathode K and a beam dump G for the cathode rays. The ions pass in front of the deflection plates and behind them fine slits Sb and D_2 and penetrate then the magnet field M. Before making the photograph, the patch of the canal rays on the screen covered by Willemit W can be observed through the window F. L_1 and L_2 are pumps (liquid air traps).

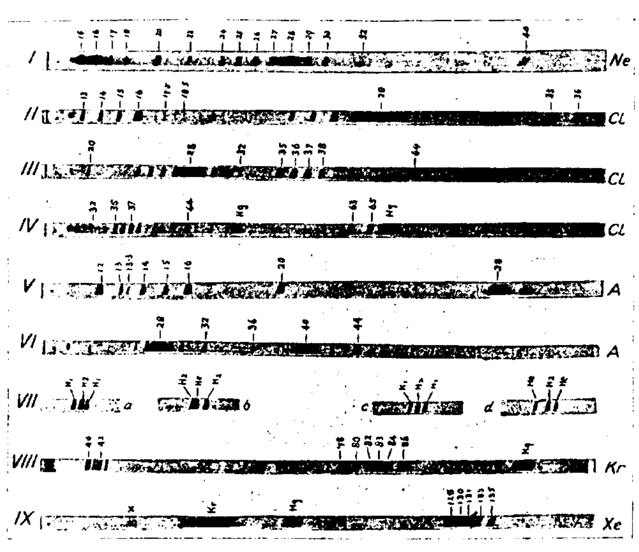


Figure 16. Mass spectra of gases recorded by Aston's double focussing spectrograph. The gases are denoted at the right end of the photographic stripes. The various ions have been marked by their mass or the symbol of the element. Many of these ions are associated with - mostly organic - impurites of the fill gas.

V Experiments on Physics with Canal Rays

V.1 Light Emission

Goldstein had discovered canal rays by the light they emitted when travelling through gases and by the fluorescent patch they produced on the wall of the discharge tube. The study of this light indeed made a major contribution to the understanding of canal rays and how they reacted with matter. It provided information on the nature of the excited atoms. An extremely important discovery made by Stark in 1905 [22] was that of the Doppler shift. In addition to the unshifted lines, broad stripes appeared in the direction of the longer wavelengths which corresponded to the atoms moving towards the observer (see in Fig. 17). The Doppler shift allowed the observer to differentiate moving canal ray ions and neutral particles from static gas atoms excited by canal rays. Wien thus examined the question of whether the light was emitted by charged or uncharged atoms or molecules. In doing so, he studied the light decomposed in spectral lines and emitted from deflectable and non-deflectable rays and found, for example, that the Balmer series of hydrogen came from the neutral atoms and the spark-line of oxygen from the ions. Wien carried out numerous other experiments on light emission; three shall be briefly described in the following section.

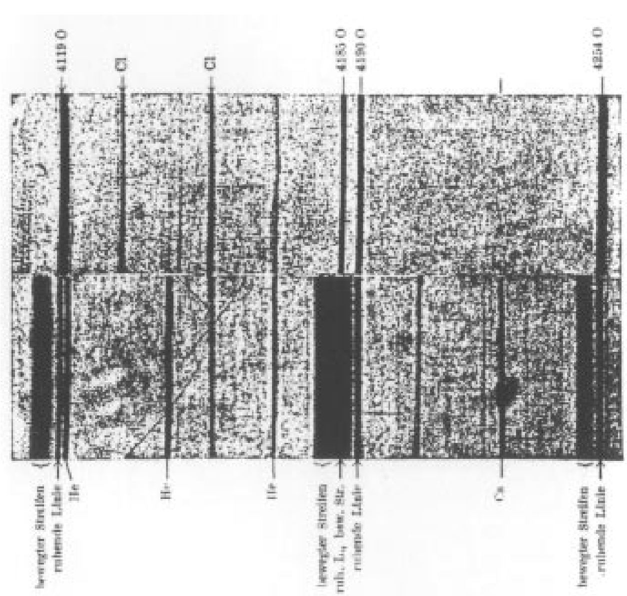


Figure 17. The optical line spectra of O_2 and He measured by Stark [23]. Upper part: spark-spectrum of oxygen, lower part: spectrum of oxygen-canal rays, which move towards the observer. Wavelenght in Å.

a) Mean free path of canal rays in gases

Firstly, Wien [24] used the Doppler effect for measuring the absolute energy of light associated with a single spectral line emitted by canal rays. As it is sketched in Fig. 18, the light of the H_β-line of hydrogen was studied with the help of a high resolution prisma spectrograph. This light was observed behind the cathode in direction of the canal rays and compared with the radiation of a black-body having the same intensity and the same wavelength. Applying the radiation laws, the integral radiation energy was calculated, which accounts for the number of emitted photons. This leads to the number of exciting atomic collisions and subsequently to the cross section for excitation or emission, respectively, of the H_β light. Regarding the atomic excitations by collisions as a statistical process, Wien developed a theory using the mean free path as the basic parameter.

He also employed the concepts of mean free path and cross section to charge exchange processes, i.e. respectively to neutralization of ions and to ionization after neutralization in the plume of canal rays. Such processes were indicated by the fact that a certain fraction of the canal rays experienced a smaller deflection than pure ion beams.

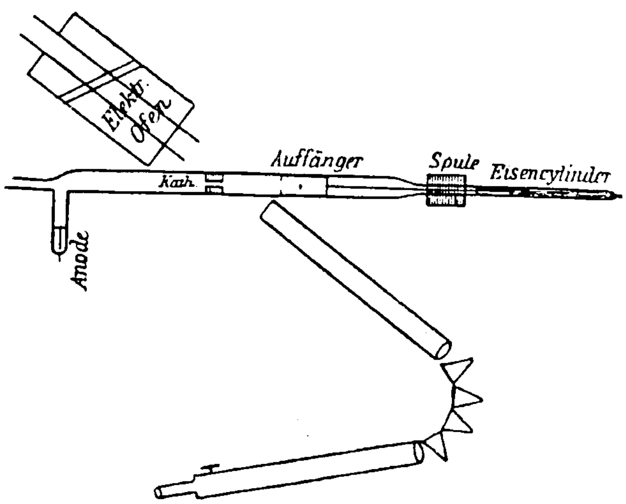


Figure 18. Apparatus constructed by Wien [23] to study light emission from canal rays by means of a high resolution prisma spectrograph. The electric oven was used as a source of black-body radiation.

Wien noticed charge exchange first, when canal rays passed through two subsequent regions with magnetic fields: the first field did not influence the neutral component of the rays. This component, however, turned out to be partially charged, when passing through the second field. Obviously, originally neutral particles were ionized on their way between the two magnets. He recognized that charge exchange depended strongly on the pressure in the observation tube and that also negatively charged particles were formed. To have a better control of the pressures inside the discharge and observation tubes, Wien developed his "Durchflußmethode" being sketched in Fig. 19. It was used, for instance, to fill the two tubes with different gases or to remove water vapor from the canal rays.

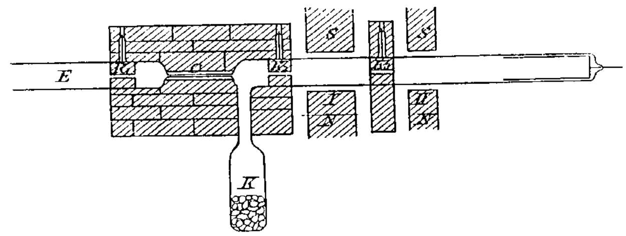


Figure 19. "Durchströmungsmethode" of Wien [26]. E = discharge area, K_1, K_2, K_3 = capillaries, K = adsorbent cooled by liquid air, N-I and N-II = magnets.

In order to prove his theory of collision statistics, Wien built the apparatus shown in Fig. 20. Behind the cathode, the canal rays fly first through the capillary separating discharge and observation area and pass then a series of deflection plates, which remove successively the charged particles from the canal rays. Loading the condensers one after the other, the relative number of particles moving in the straight canal-ray beam was measured by means of a thermocouple T. Thus, it was possible to determine the ratio of charged to neutral particles behind the last loaded condenser. Provided that the velocity of the canal rays remains constant over the series of condensers, this ratio should be independent of the number of loaded condensers. It turned out that reliable results were obtainable only with canal rays being generated in very pure gases with a very narrow velocity distribution. By this method, Wien determined, for instance, the mean free path of hydrogen atoms for charge exchange in 0.01 mm Hg oxygen gas. He got a value of 0.167 cm, which leads to a radius of the "Wirkungssphäre" (cross section) of 1.5 Å. Such results were compared with radii deduced from Bohr's atom model.

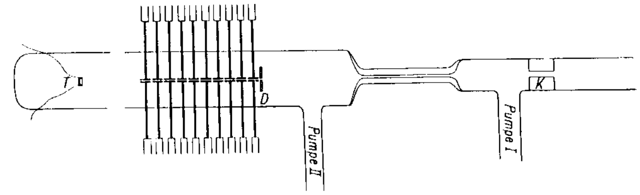


Figure 20. Apparatus constructed by Wien [2] for measuring the mean free path of canal rays for charge exchange in the gas of the observation tube (see text).

b) Life time of excited atomic states

Stark performed numerous optical experiments on canal rays. One of his peculiar findings was that the light of some spectral lines is observable beyond the sharp border of a canal-ray bundle. His interpretation of this phenomenon was that due to thermal motion some gas atoms escape from the bundle still emitting light with decreasing intensity. This did not happen to all spectral lines. An example for decreasing light emission are the lines of the Balmer series. Wien [27] tried to measure the decay constant for these Balmer lines.

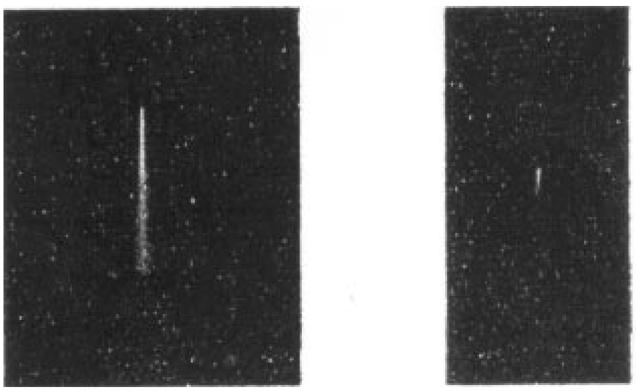


Figure 21. Photographs of a canal ray behind the capillary separating discharge and observation tubes. left: medium vacuum pressure, right: low vacuum pressure ($< 10^{-4}$ mm Hg). See ref. [2].

He let the canal rays penetrate the observation tube through a short, little capillary. The observation tube was evacuated to the lowest possible pressure; this means only a few atomic collisions occurred in the expanding plume. The canal ray bundle was then visible only over a short distance as seen in Fig. 21. The light of this short gleaming strip was split into spectral lines and then used to make a photograph of the strip. The resulting picture was compared with the photographic picture of a slit illuminated by the light of a Geißler tube filled with the same gas as the discharge tube and emitting the same wavelength. A wedge-shaped absorber in front of this slit had weakened the light exponentially over the length of the slit. By tuning the intensity and the exponential decrease of the comparative light, Wien was able to determine the decay constant of the light emitted from the atoms streaming with a certain velocity into the observation tube. The velocity was measured with help of the Doppler effect. For the light of the Balmer series he obtained a decay constant of 6.4 10^7/s. This corresponds to 15.6 ns, the first mean life time of atomic states measured.

c) Electrodynamic splitting of spectral lines

In 1913, Stark [28] made another important discovery concerning light emission of canal rays: he found that many spectral lines - in particular those of hydrogen - split, when the light emitting gas is located in a static electric field. As an example, Fig. 22 shows the splitting of the H_β line of hydrogen. Two series of polarized lines are seen, - one polarized parallel (P) to the field direction, the second one perpendicular (S).

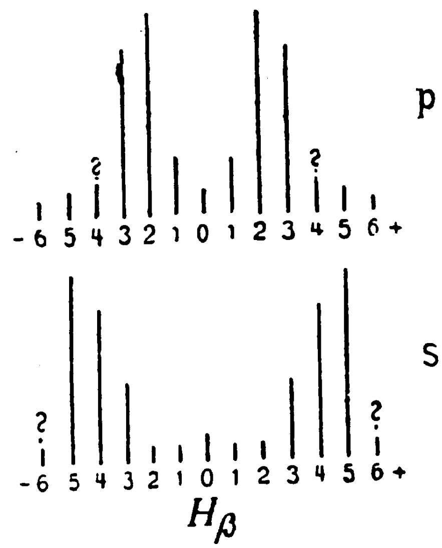


Figure 22. Splitting of the H_β line of hydrogen in an electric field of 104000 V/cm [29]. p = polarized parallel to the electric field, S = polarized perpendicular. The picture was taken from the handbook of Wien [2].

One year after Stark's discovery, Wien [30] tried to prove if the splitting of spectral lines observed in static electric fields occurs in the same way also, when the light emitting atoms move in a magnetic field. Such an effect is predicted by Maxwell's theory taking into account the relativity principle: the field strength affecting an atom moving with velocity $\vec{v}$ in the magnetic field $\vec{H}$ is $\frac{1}{c}[\vec{v} \times \vec{H}]$ with c the velocity of light. The corresponding splitting was compared by Wien with the splitting caused in a static Coulomb field $\vec{E}$. The canal rays used by him had a velocity of 0.5 10^8 cm/s. This corresponds in a magnetic field of 20000 Gauss to an electric field strength of 10000 V/cm as used by Stark. Therefore, Wien could compare his splitting with results obtained by Stark.

Fig. 23 shows the experimental set up used by Wien. The canal rays generated in the discharge tube R fly through the capillary C fixed between the poles of an electromagnet. The canal-ray light emerging from a slit in the capillary is examined through a central hole drilled in one of the magnet poles by means of an optical spectrograph. This means, the direction of observation is perpendicular to the velocity of the canal rays and parallel to the magnetic field and therefore transversal to the electrodynamic field as in case of the experiments performed with the electrostatic field. In order to allow observation of the two differently polarized components, the light passes a lime spar. Wien investigates the H_γ and the H_β lines of hydrogen. The splitting was in fact hardly visible, - probably due to the broad velocity distribution of the hydrogen atoms, - but the width of the patch agreed well with values published by Stark, who applied a static electric field, and also with theoretically expected values. Two years later (1916), Wien succeeded to observe also the actual splitting of the component, which is polarized perpendicularly to the field $\frac{1}{c}[\vec{v} \times \vec{H}]$. Two splitted lines are seen in Fig. 24. This was one of Wien's most beautiful and smartest experiments.

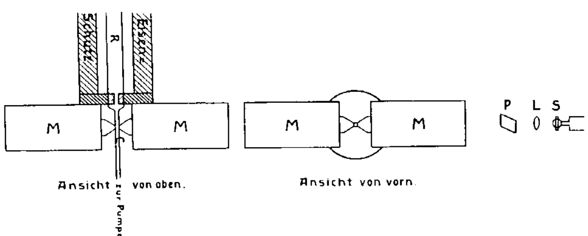


Figure 23. Sketch of the aparatus used by Wien to detect the line splitting in the electyrodynamic field $\frac{1}{c}[\vec{v} \times \vec{H}]$. R= discharge tube, C = capillary, M = electromagnet, P = lime spar, L = condenser lense, S collimator slit of the optical spectrograph.

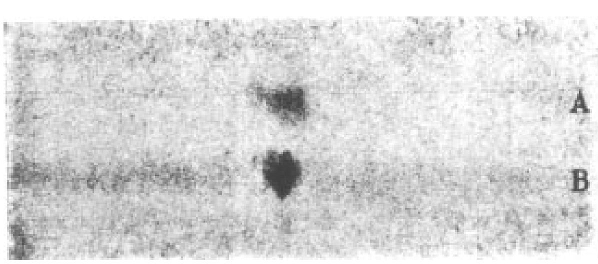


Figure 24. Electrodynamic splitting of the H_γ line of hydrogen. In order to reduce the light emitted by atoms of the residual gas, the magnetic field strength was as high as possible (28000 Gauss) and the velocity of the canal rays correspondingly small (0.36 10^8 cm/s). A: light polarized perpendiculary to $[\vec{v} \times \vec{H}]$. B: corresponding parallel polarized component of the light. In the center of the splitting A, the line of the not moving atoms is visible.

V.2 Sputtering

This phenomenon had been observed by Plücker [31] at the cathode of the gas discharge tube long before canal rays were discovered. Polished metals became rough after the tube had been in use for a certain period. This erosion of the cathode surface has an important effect on the composition of the canal rays, as the sputtered material mixes itself with the rays. Canal rays in the observation area also cause a sputtering of the material they collide with. The amount eroded could be calculated by weighing the cathode, for example. Wien did not carry out any experiments on sputtering himself. A summary was published by Kohlschütter in the 1912 Jahrbuch der Radioaktivität [32].

The various experiments all showed that the sputtered amount is proportional to the voltage of the cathode fall, i.e. to roughly the energy of the canal rays. A dependence such as this corresponds to the sputtering energy dependency observed today of metals in the keV range. Less explicit was the dependency of the atomic numbers and masses of the ions and irradiated metals. A comparison with yields won through application of our contemporary sputtering theory shows that the yields measured then were considerably more dependent on atomic numbers and masses than the sputtering theory would expect.

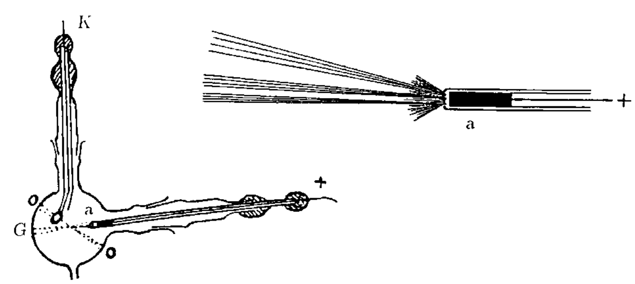


Figure 25. Anode made from alkali halides and graphite. This anode was used in discharge tubes as source of secondary ions [33]. a = anode, K = cathode, G = patch of canal rays at the wall of the discharge tube.

As Wien observed in his first experiments, slow positive ions are emitted by the anode, which are presumably also produced through sputtering with negative ions or electrons which reach the anode from the cathode. This effect was used to produce canal rays of substances which were otherwise difficult to produce in the discharge tube in gas form. Alkaline compounds deposited on the anode are particularly effective. Secondary ion mass spectroscopy (SIMS) was first practiced using an ion source such as this. Fig. 25 depicts a suitable anode where a little graphite has been added to the alkali halides to improve their conductibility. These canal rays, made up of slow particles coming from the anode (see Fig. 6), contain, according to Reichenheim [34], practically no neutral particles.

VI Canal Rays ⟶ Ion Beams?

The work of Wien and his assistants has largely contributed to explaining the nature of canal rays and their cause (electrical discharge in rarefied gases). Wien's experiments always focussed more on their physical aspects and less on the practical application of the information gained through them. This is also expressed in the often very detailed theoretical analyses of his experiments. The diagram of canal rays and their origin Wien sketched out in his handbook on canal rays [2]; it is not, however, the result of a "gas discharge theory". Only certain details of these rays, such as their charge exchange, light emission or the effect of electric and magnetic fields on them, are dealt with theoretically. Attempts to describe in theoretical terms the complicated potential steps in a discharge tube, for example, are summarized in the Handbuch für Physik, Vol. XXII, from 1956, among other sources.

Wien developed the following ideas on the nature of canal rays in his book [2]: *"The place canal rays are formed is what is known as the dark cathode space, where the largest potential difference can be found".* This is where ionization and excitation largely take place by way of electron collision and acceleration of the ionized gas atoms. Negative cathode rays, which move in the opposite direction of the actual canal rays, are chiefly produced as secondary ions at the cathode. They can also produce positive ions, i.e. components of the actual canal rays, through collision with the fill gas or by sputtering of the anode. These are joined by photon-induced ionization processes which are responsible for the "Nebel Strahlen" (fog rays), for example, which clad the actual canal rays. The canal rays behind the cathode mainly consist of neutral, partially-excited atoms or molecules which are formed in front of the cathode or behind it by charge exchange from ions. The gas density in the canal ray is usually so high that charge exchange also occurs behind the cathode. This charge exchange and the wide space in front of the cathode, where ions are accelerated, give rise to a broad spectrum of canal ray particle velocity.

From these characteristics of the canal rays we can deduce that they are not pure ion beams. In order to become so, they must be passed into a vacuum of under 10^{-4} mm Hg and separated from the neutral particles. Ion sources with currents of ca. 0.1 A and several 10 keV of ion energy have actually been built according to this principle. By way of post-acceleration, ion energies were obtained which were sufficient for the first nuclear reaction experiments. As a rule, modern ion sources no longer use canal rays directly, but make use of processes which contribute to these in discharge tubes, such as ionization by electron impact, sputtering, secondary ion emission and ionization through photo-effect. From this, we can conclude that Wien first understood the canal rays to be inert, electrically-charged, atomic particles a hundred years ago were in fact the origin of ion beams.

Acknowledgements

I would like to thank very much Frau Waltraut Wien and Herr Dr. Henning Dwinger, my aunt and my cousin, for the conversations I had with them about their father and grandfather in Munich, where Willy Wien last worked as a professor of Physics. They provided me with a great deal of literature about him, and also with photographs and offprints of his scientific articles. Further material and also an original canal ray apparatus were available at the Deutsches Museum in Munich, whom I would also like to thank for their assistance.

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