large interaction effects in $MnCl_2$ and $FeCl_3$. The crystal structures of these compounds are the same as that of the corresponding metamagnetic chlorides. The only apparent point of difference is that the ground state of these ions is a ^6S state. This would indicate that the exchange interaction is negligible for a ^6S state, even though the electron shell is incomplete.

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Mobilities in Hydrogen at High Current Densities

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The conditions in an investigation of the silent electric discharge from sharp points and fine wires in hydrogen at atmospheric pressure are such that the discharge itself purifies the gas from electron-attaching impurities, so that the conditions of the discharge are productive of free electron conduction. Measurements are made of the generalized coefficient of mobility for the drift of free electrons in hydrogen, and of the mobility of hydrogen positive ions in hydrogen. Past observers have usually had doubts concerning the purity of the gas prepared by chemical means, but the results here reported involve a demonstrably sustained purification during the measurement itself.

WHEN the point is negative in a point-to-plane arrangement of electrodes, it is supposed that the silent discharge is caused by electrons arising at the tip of the point and producing ionizations by collision in avalanches, until the avalanche fronts have moved away from the tip of the point to a place where the electric field is no longer sufficient to support ionizations by collisions. The number of electrons freed by ionizations in an avalanche may be considered to be equal to 2^N where N is the number of ionizations an original electron makes. By considering directions of propagation of an avalanche increasingly removed from the axis of symmetry such as, for example, along the direction of the line, B, in Fig. 1, the electric field is less intense at any given distance from the metal than along a direction such as A, and so the number of ionizations that the original electron can produce is less. For example, if the number of ionizations along a direction A, is 30, while the number along a direction like B, is 20, an avalanche along the direction B will produce less than $1/1000$ as much charge as an avalanche along the direction A (i.e., in the ratio 2^{10}). Thus, ionizations which are responsible for most of the current occur within a region approximating a hemispherical shell, such as CC. The region between the point and the shell and including the shell may be called the "ionizing sheath." In hydrogen, this sheath appears to be about 0.2 cm thick. Such a hemispherical cap is generally observed in this form of discharge.

Stability of Sheath

A rather detailed discussion of the negative point-to-plane discharge in air has been published by Trichel, and by Loeb and Kip.[1]

These observers report on a pulsating character of the negative corona discharge, which they attribute to the attachment of electrons to oxygen molecules to form negative molecular ions, and, due to the much smaller mobility of ions than electrons, the suppression of further ionizations in the sheath until ions have had time to move away. Their supposition is that each step in the sequence: avalanching, electron attaching, movement away of ions, *et seq.* must advance well toward completion before the next step in the sequence can begin.

[1] G. W. Trichel, Phys. Rev. **54**, 1078 (1938); L. B. Loeb and A. F. Kip, J. App. Phys. **10**, 142 (1939).

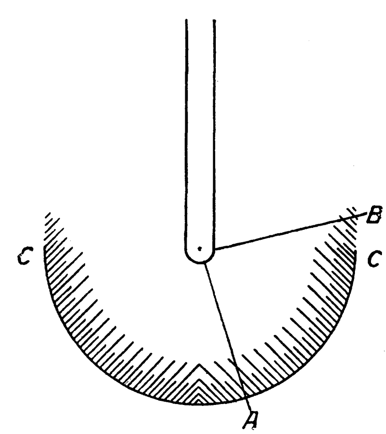
The writer also made a study of the corona discharges in air several years ago, and had observed a pulsating character of the discharge both on the negative and also on the positive polarities.

In our measurements of the negative discharge in hydrogen, observations were made to detect any pulsations which might occur. A circuit similar to Trichel's was used, except that in most of our work both on hydrogen and air, as well as other gases, a higher amplification was available and the signal was taken from a high frequency inductance in series with the discharge circuit. In this way, the bias of the first grid of the amplifier circuit was not thrown off by fluctuations of current during unsteady parts of a characteristic. It was found that a hydrogen discharge initially has more rapid and smaller pulsations than the pulsations in an air discharge, and occasionally these come in regular sequences of pulses. These pulsations gradually disappear with operation, and by the time they have disappeared, the current for any given voltage has risen to much higher values. The steady pulsation-free discharge current in purified hydrogen must be a space charge limited current with the greater density of charge near the ionization sheath at its outer boundary.

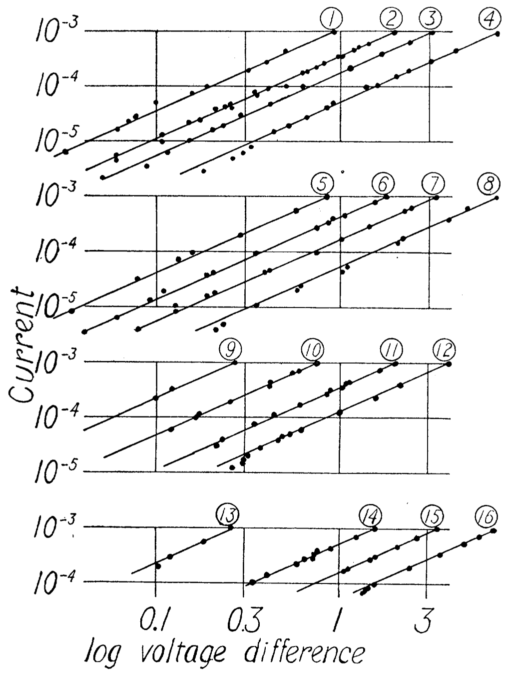
If the tube was allowed to stand idle for a few hours, the reapplication of potential showed that the tube had become partially deconditioned. It was necessary to pass current for a short time before the tube returned to the high current condition which had been attained by sustained operation previously. This reconditioning, however, did not require nearly so long as it did initially. Allowing the tube to stand idle again, the tube again might become deconditioned and if so, it could be reconditioned by operation for a still shorter time. The tube eventually reached a condition such that it remained in the high current condition even when allowed to stand idle. This showed that the deconditioning of the tube was not due to any leak. It was discovered that the initial conditioning of the tube was involved in some way with a sharpening of the tungsten wire ends. Examination with a microscope showed that the end of the tungsten wire was etched into a regular conical shape, and if, for example, a wire 0.0075 cm diameter was being used, the tip of the conical point had a radius of curvature which was less than 0.0010 cm and was usually of the order 0.0005 cm.

It had been observed in our earlier work on the corona discharges in air, that for points having a radius of curvature of 0.0010 cm or less, and of suitable metal to remain with that small a diameter, the pulsating character of the discharge reported by Trichel, Loeb, and Kip[1] did not occur. There were in air, however, some much smaller pulsations of an irregular character which did occur with these extremely sharp points. The fact that the discharge in hydrogen loses its pulsating character with the production of the extremely sharp conical tip, is probably due to the same thing, namely, the very sharp tip of the point. However, this sharpening of the tip of the point does not completely explain the deconditioning with standing, because the tip of the point did not change its shape any simply by turning off the current. It has been well established in high vacuum thermionic investigations[2] that tungsten in the presence of both oxygen and hydrogen acquires a mono-molecular layer of oxygen over which there is a mobile partial second layer of oxygen. The continued operation of the tungsten at an elevated temperature does not remove this oxygen except by the slow formation of tungsten trioxide and all of the oxygen is eliminated from the gas phase by this kind of reaction before the oxygen mono-molecular layer begins to disappear. In other words, this is an extremely quantitative means for eliminating oxygen from the gas phase.

FIG. 1.

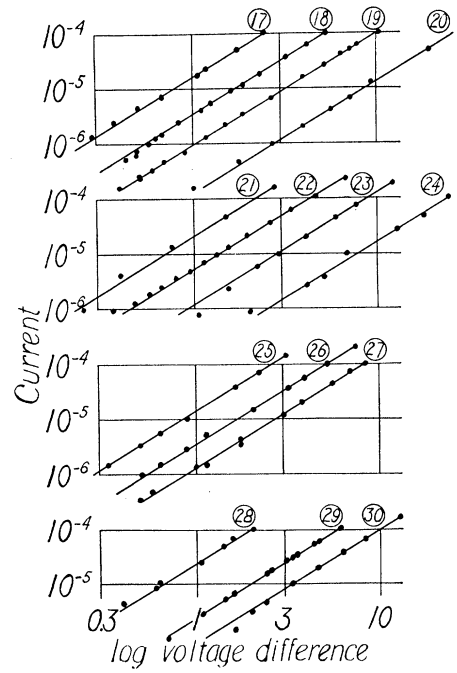


[2] Langmuir, J. Chem. Soc., 511–543 (1940).



Curve	Wire diameter	Distance points to plane	Voltage subtracted
1	0.0010 cm	0.27 cm	520 volts
2		1.18	590
3		3.10	660
4		10.0	810
5	0.0025	0.29	570
6		0.98	645
7		3.00	720
8		10.0	880
9	0.0075	0.38	790
10		1.04	880
11		3.06	970
12		10.0	1170
13	0.020	0.32	1080
14		1.67	1200
15		3.24	1320
16		10.0	1620

FIG. 2. Log-log plots for point negative.



Curve	Wire diameter	Distance points to plane	Voltage subtracted
17	0.0010 cm	0.27 cm	590 volts
18		1.18	690
19		3.10	810
20		10.0	950
21	0.0025	0.29	640
22		0.98	740
23		3.00	860
24		10.0	1100
25	0.0075	0.38	900
26		1.04	1000
27		3.06	1120
28	0.020	0.32	1350
29		1.67	1500
30		3.24	1650

FIG. 3. Log-log plots for point positive.

In the present corona investigations in hydrogen, the faintest trace of oxygen would go to the tungsten wire end, and adhere so as to change the work function of the tip of the point. This change of work function at the tip of the point where field conditions are so extremely critical for the initiation of the avalanches responsible for the conductivity is observed as the conditioning of the tube up to the high current condition (or as explained later, a decrease in potential drop in the ionizing sheath) and so, the high current operation of the tube is really a very sensitive and reliable index of whether the oxygen has been removed from the gas phase. It seems reasonable to suppose that the other electron-attaching impurities should behave more or less like oxygen with respect to adsorption on tungsten, and so the disappearance of pulsations accompanied by the rise of the current to the high current condition is a reliable index of whether the conduction is really free electron conduction. The effects of sharpening of the points by etching are being separated from the effects of work function at the tip in some investigations now being made, and it is expected that a detailed report of these two different effects can be made at a later date.

Brass targets were used in most of this as well as all of the later work with cylinders because it was found that a harder surface sometimes acquired specks of material which gave a back ionization when the wire was negative and this back ionization might produce serious errors in measurements of mobilities.

The Current Voltage Relation

Although the shape of electrodes used in the first half of the work was that of a fine wire discharging toward a plane electrode which does not permit an exact solution for the space charge limited current, a dimensional argument can be used as follows. It will be supposed that the drift velocity of electrons is proportional to the nth power of the electric field intensity.

$$u = KE^n,$$

where u is the drift velocity, E is the electrical field intensity and K is a generalized coefficient of mobility. There is supposed to be a potential drop between the wire and the hemispherical shell V_0 so that the potential difference applied between the shell and the collecting plane equals the total applied voltage V_1, minus the sheath drop V_0.

Between the shell and the plane, the charge satisfies Poisson's equation.

$$\rho = \nabla^2 V / 4\pi.$$

It is supposed that for some value of current and voltage, there exists a solution, $V(x, y, z)$. Multiplying the potential at every point by a constant multiplier λ gives a function $\lambda \cdot V$ which satisfies Poisson's equation and which satisfies boundary conditions where the potential applied between the sheath and the plane is greater by the same constant multiplier, $\lambda(V_1 - V_0)$. The charge density is likewise proportional to V and so is increased by the ratio λ to $\lambda \cdot \rho$.

The total current flowing can be found by integrating the current density over any equipotential surface. If j is the current density so that $j = \rho \cdot u$, the total current is:

$$I = \int\int j \cdot dS = \int\int \rho \cdot u \cdot dS = \int\int \rho \cdot K \cdot E^n dS,$$

which gives the value of the current for the conditions for which it was assumed that there exists a solution. For the circumstances resulting in the potential distribution λV the current is

$$I_\lambda = \int\int \lambda \rho K (\lambda E)^n dS = \lambda^{n+1} \int\int \rho \cdot K \cdot E^n dS.$$

The value of the current when the potential applied across the gap was increased by the factor, λ, is

$$I_\lambda = \lambda^{n+1} I$$

or

$$I = \alpha (V_1 - V_0)^{n+1}$$

gives the current as a function of the applied voltage, where α is a proportionality constant.

Discharge from Sharp Points

The data plotted in Figs. 2 and 3 were taken with tungsten wire in hydrogen after continued operation at 0.1 ma rising to about 1 ma for each set-up, or until pulsations had completely disappeared and the current had reached a steady value. Wires with diameters of 0.001, 0.0025, 0.0075, and 0.02 cm were used at various distances from point to plate, 0.3, 1, 3 and 10 cm. The diameter of the plane target was 15 cm so that the deviation from a point-to-plane arrangement, as well as the erratic effect of charges on the walls, distorts somewhat the observations for the 10 cm distance. It was further observed that the sheath did not present the smooth regular appearance with the 0.02 cm wire that it did with the finer wires. There appeared to be a tendency toward channeling through the sheath at the larger current for the largest wire. The assumption of a substantially constant sheath drop is probably in error for this largest wire.

It will be seen from Fig. 2 that the data generally can be adjusted in a log-log plot to

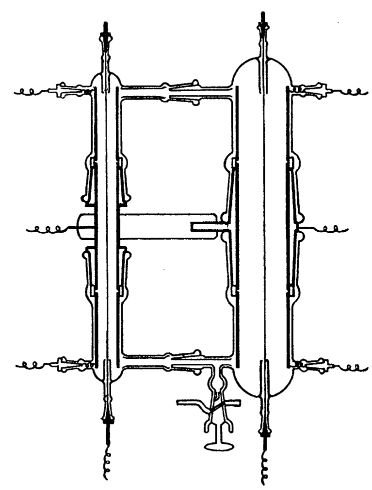


Fig. 4. Diagram of tubes.

straight line relations only by subtracting amounts assumed for the sheath drop which gives slopes of $\frac{3}{2}$. The current voltage relations have the form:

$$I_{-}=\alpha(V_1-V_0)^{\frac{3}{2}}.$$

Observations were also made when the point was positive with respect to the plane, and these data are plotted in Fig. 3. Here the only good fits to straight lines could be obtained by assuming sheath drops yielding slopes of 2. The current voltage relations are

$$I_{+}=\beta(V_1-V_0)^2.$$

These observations show that the conduction in hydrogen which is purified by sustained discharge from negative tungsten points until the pulsations have disappeared, is due to electrical charge whose drift velocity is given by an expression of the form.

$$u=KE^{\frac{1}{2}}$$

and that the discharge when the point is positive is due to charge whose drift velocity is given by an expression of the form:

$$v=CE.$$

It should be noticed that the value of sheath drop changes very little, if at all, for relatively very considerable changes in wire size, and target distance except for the largest size and largest target distance where irregularities of obvious nature can cause very considerable distortions of apparent sheath drop.

Discharge from a Straight Wire

Measurements were made of the negative and positive discharges from 0.0075 cm straight tungsten wires held axially in cylinders as shown in Fig. 4. Guard cylinders were used in order to obtain cylindrical symmetry. Cylinders with two different radii were used in order to separate out the conditions in the ionization sheath from those in the rest of the gap. The two arms of the tube were connected to insure the same composition of hydrogen in the tube for corresponding measurements.

If the ionization sheath, with wire negative, has a radius r_0 the field at the outer surface of the sheath is E_0, the potential drop through the sheath is V_0, and the electrons have a drift velocity in the rest of the gap proportional to the square root of the field:

$$u=KE^{\frac{1}{2}},$$

the current I to a guarded cylinder with radius r and length L, is related to the voltage between the wires and the cylinder by:

$$V-V_0=\left(\frac{2I}{KL}\right)^{\frac{2}{3}}(r-r_0)\left\{1+\frac{1}{3}\left(1-\frac{KLE_0^{\frac{3}{2}}}{2I}\right)\right.$$
$$\left.\times\frac{r_0}{r+(rr_0)^{\frac{1}{2}}}-\frac{1}{18}\left(1-\frac{KLE_0^{\frac{3}{2}}}{ZI}\right)^2\frac{r_0(r_0+r)}{r^2}+\cdots\right\}.$$

For sufficiently large values of current, that is

$$I\gg KLE_0^{\frac{3}{2}},$$

the series is convergent and can be written as

$$V-V_0=(2I/KL)^{\frac{2}{3}}r$$
$$\times\{1-0.722r_0/r-0.333(r_0/r)^{\frac{3}{2}}+\cdots\}.$$

The radius of the larger cylinder used was 2.70 cm, and the smaller cylinder was 1.15 cm in radius. Each guarded section was 15.15 cm long. If the voltage applied to the larger cylinder is V_2 and that to the smaller cylinder V_1, when the same current is passing to the central cylinder of each, I,

Table I. *Values of K calculated from the data.*

I (MA)	V_2 (VOLTS)	V_1 (VOLTS)	V_2-V_1 (VOLTS)	K (E.S.U.)
10	3940	2395	1545	6.8×10^5
8	3660	2330	1330	6.8
7	3540	2290	1250	6.6
6	3360	2265	1095	6.9
5	3160	2200	960	7.0
4	2950	2160	790	7.5
3	2735	2100	635	6.7
2	2600	2010	590	5.8
1	2425	1895	530	3.4
0.6	2300	1830	470	4.1

Table II. *Calculated values of C.*

I (MA)	V_2 (VOLTS)	V_1 (VOLTS)	V_2-V_1 (VOLTS)	C (E.S.U.)
0.5	7750	4115	3635	3.2×10^3
0.4	7100	3900	3200	3.0
0.3	6500	3650	2850	3.2
0.2	5600	3340	2260	3.4
0.1	4725	2990	1735	2.8
0.01	3140	2500	640	2.1

$$V_2 - V_0 = (2I/KL)^{\frac{2}{3}} r_2 \times \{1 - 0.722 r_0/r_2 - 0.333(r_0/r_2)^{\frac{3}{2}} + \cdots\},$$

$$V_1 - V_0 = (2I/KL)^{\frac{2}{3}} r_1 \times \{1 - 0.722 r_0/r_1 - 0.333(r_0/r_1)^{\frac{3}{2}} + \cdots\},$$

so the difference in these voltages is

$$V_2 - V_1 = \left(\frac{2I}{KL}\right)^{\frac{2}{3}} (r_2 - r_1)\left\{1 + \frac{0.333 r_0^{\frac{3}{2}}}{r_2 r_1^{\frac{1}{2}} - r_1 r_2^{\frac{1}{2}}} + \cdots\right\}.$$

The mobility coefficient can be obtained from the data by

$$K = \frac{I}{(V_2 - V_1)^{\frac{3}{2}}} \cdot \frac{2(r_2 - r_1)^{\frac{3}{2}}}{L}\left\{1 + \frac{0.5 r^{\frac{3}{2}}}{r_2 r_1^{\frac{1}{2}} + r_1 r_2^{\frac{1}{2}}} + \cdots\right\},$$

which is relatively insensitive to the assumed value of r_0. Putting an outside limit on r_0 of 0.6 cm,

$$1 + \frac{0.5 r_0^{\frac{3}{2}}}{r_2 r_1^{\frac{1}{2}} + r_1 r_2^{\frac{1}{2}}} \leqslant 1.05.$$

It was observed that the discharge with the 0.0075-cm wire negative was localized in spots, and that increasing the current produced more discharging spots and crowded them more closely together.

Table I shows the data and calculated value of K.

The values for K do not show a monotonous change with decreasing current so it appears that the assumption of I large enough was justified. However, the fluctuations in values of K for the smaller currents is easily understood from the randomness of likelihood that the discharging spots should fall inside the collecting cylinders if near an end. From the data for the five largest current values,

$$K = 6.8 \times 10^5 \text{ e.s.u.}$$

The current with wire positive, limited by space charge where drift velocity is proportional to field ($v = CE$) is related to voltage by

$$V - V_0 = (2I/CL)^{\frac{1}{2}}\{r - 1.542 r_0 + 0.500 r_0(r_0/r) + 0.042 r_0(r_0/r)^3 - \cdots\},$$

if $I \gg CLE_0^2$. Again in terms of voltages for the two cylinders for the same current as before,

$$V_2 - V_1 = \left(\frac{2I}{CL}\right)^{\frac{1}{2}} (r_2 - r_1)\left\{1 - \frac{0.5 r_0^2}{r_1 r_2} + \cdots\right\}.$$

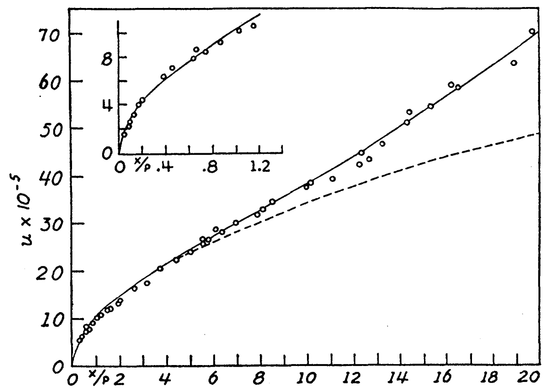


FIG. 5. Comparison of the present value of 6.8×10^5 e.s.u. for the mobility of electrons in hydrogen with the results of Bradbury and Nielsen. The experimental points are from Bradbury and Nielsen. The dotted curve is calculated from the above value of the mobility.

Table II shows the data and calculated values of C.

Discussion

The results for the mobility of electrons in hydrogen may be compared with those of Bradbury and Neilsen[3] as shown in Fig. 5 where the dotted line represents the relation

$$u = 6.8 \times 10^5 E^{\frac{1}{2}} \quad (\text{for } p = 760 \text{ mm}, E \text{ in e.s.u.})$$

or

$$u = 10.8 \times 10^5 (X/p)^{\frac{1}{2}} \quad (\text{in volts/cm and mm})$$

and agrees well with these data for field intensities up to $X/p = 5$.

Larger field strengths than about 4000 volts per centimeter produced arc-over so that a mobility of electrons at greater than about $X/p = 5$ could not be measured.

The result for the mobility of positive ions in hydrogen

$$C = 3.2 \times 10^3 \text{ e.s.u.} = 10.7 \text{ cm/sec. per volt/cm}$$

agrees much better with Bradbury's[4] value of 8.2 rather than with those of Mitchell, which Tyndall[5] notes.

[3] N. E. Bradbury and R. A. Nielsen, Phys. Rev. **49**, 391 (1936).
[4] N. E. Bradbury, Phys. Rev. **40**, 519 (1932).
[5] A. M. Tyndall, *The Mobility of Positive Ions in Gases* (Cambridge University Press, 1938), p. 35.