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THE MOBILITY OF POSITIVE IONS IN FLAMES

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ABSTRACT

Mobility of positive ions of K, Rb and Cs in the Bunsen flame.—The mobility was calculated from measured values of the current density, cathode drop of potential, and the thickness of the layer at the cathode in which the potential varies rapidly. The excess of ionization over recombination in the layer was assumed to be proportional to $(1-x/x_1)^m$, where x is the distance from the cathode, x_1 the thickness of the layer at the cathode, and m is a constant. J. J. Thomson supposed that $m=0$, and P. E. Boucher took $m=1$. The value calculated for the mobility depends on the value assumed for m. The results give, with $m=2$, a value of 1.8; with $m=3$, a value of 1.07 cm/sec. per volt/cm for the mobility. It is found that the mobility is the same for salts of Rb, Cs, and K, and that it does not depend on the concentration of the salt. A small increase of mobility with electric intensity is indicated by the results.

THE mobility of the positive ions has been measured by several physicists[1], and is now believed to be about one cm per sec for one volt per cm; but the possible error of this estimate is very large. The following paper contains an account of a series of experiments the object of which was to determine the mobility of the positive ions in a flame. The method used is similar to that quite recently employed by P. E. Boucher.[2] Boucher observed the variation of the potential near the electrode, and so obtained the thickness of the layer or sheath at the cathode in which the potential varies rapidly. Using a slightly modified form of J. J. Thomson's[3] theory of the variation of the potential in the sheath, the mobility of the positive ions can be calculated in terms of the thickness of the sheath, the current density, and the drop of potential across the sheath.

THEORY

The theory of the variation of the potential between two electrodes in an ionized gas was given by J. J. Thomson. He showed that there was a central region of uniform electric intensity, with a sudden large increase of the electric intensity near both the electrodes. The theory may be deduced from his well known equation $d^2X^2/dx^2=8\pi e(1/k_1+1/k_2)(q-an_1n_2)$, where X is the electric intensity, x the distance from the surface of the positive electrode, k_1 and k_2 are the mobilities of the positive and negative ions respectively, q the number of molecules ionized per cc per sec, a the coefficient of recombination, and n_1 and n_2 the number of positive and negative ions per cc.

Let x_1 and x_2 be the thicknesses of the sheaths at the positive and negative electrodes respectively, and d the distance between the electrodes. J. J.

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[1] H. A. Wilson, Phil. Trans. **216**, 63 (1915); Andrade, Phil. Mag. **23**, 865 (1912); Phil. Mag. **24**, 15 (1912).

[2] P. E. Boucher, Phys. Rev. **31**, 833 (1928).

[3] J. J. Thomson "Conduction of Electricity through Gases," Chaps III and IX.

Thomson assumed that the recombination an_1n_2 was equal to zero from $x=0$ to $x=x_1$, and from $x=d-x_2$ to $x=d$. From $x=x_1$ to $x=d-x_2$, X is constant and $d^2X^2/dx^2=0$; so $q-an_1n_2=0$. Also $dX/dx=4\pi e(n_1-n_2)=0$, and $n_1=n_2=n$, the recombination balancing the ionization.

J. J. Thomson's assumption that there is no recombination in the sheaths makes the value of $q-an_1n_2$ discontinuous at the surface of the sheaths, since he assumes $q-an_1n_2=q$ from $x=0$ to $x=x_1$ and $q-an_1n_2=0$ from $x=x_1$ to $x=d-x_2$. P. E. Boucher therefore assumed $q-an_1n_2$ is equal to $q(1-x/x_1)$ from $x=0$ to $x=x_1$, $q-an_1n_2=0$ from $x=x_1$ to $x=d-x_2$, so avoiding the discontinuity at $x=x_1$. This assumption, however, makes $(d/dx)(q-an_1n_2)$ discontinuous at $x=x_1$. It seems better, therefore, to assume $q-an_1n_2=q(1-x/x_1)^m$, where m is an unknown constant.

Thus $\int_0^{x_1}(q-an_1n_2)dx=q\int_0^{x_1}(1-x/x_1)dx=qx_1/(m+1)$. But $\int_0^{x_1}(q-an_1n_2)dx=nk_1X_0$, where X_0 is the uniform electric intensity between the sheaths. Thus $qx_1/(m+1)=nk_1X_0$. Since i, the current density, is

$$Xe(n_1k_1+n_2k_2),\quad nX_0=i/[e(k_1+k_2)],$$

and

$$qx_1/(m+1)=ik_1/[e(k_1+k_2)].$$

Thus

$$q=ik_1(m+1)/[ex_1(k_1+k_2)],$$

$$d^2X^2/dx^2=8\pi eq(1-x/x_1)^m(1/k_1+1/k_2)$$

$$=8\pi i(m+1)(1-x/x_1)^m/x_1k_2.$$

Integrating, $dX^2/dx=-8\pi i(1-x/x_1)^{m+1}/(k_2)+C_1$. At $x=x_1$, $X=X_0$, and $dX_0^2/dx=0$; so $C_1=0$. Integrating again, $X^2=8\pi ix_1(1-x/x_1)^{m+2}/[k_2(m+2)]+C_2$. At $x=x_1$, $X=X_0$, a small constant quantity. Neglecting it, $X^2=8\pi ix_1(1-x/x_1)^{m+2}/[k_2(m+2)]$.

Let V_1 be the potential drop across the sheath at the positive electrode, and V_2 the drop at the cathode. Then

$$V_1=\int_0^{x_1}Xdx=\{8\pi ix_1/[k_2(m+2)]\}^{1/2}\int_0^{x_1}(1-x/x_1)^{(m+2)/2}dx$$

$$=[2/(m+4)]\{8\pi ix_1^3/[k_2(m+2)]\}^{1/2}$$

In the same way it may be shown that

$$V_2=[2/(m+4)]\{8\pi ix_2^3/k_1(m+2)\}^{1/2}.$$

Thus, if the excess of ionization over recombination inside the sheaths can be represented by $q-an_1n_2=q(1-x/x_1)^m$, the mobility of the positive ions is proportional to ix_2^3/V_2^2, whatever the value of m. The variation of the mobility with the concentration of the salt vapor and with the nature of the metal can therefore be determined.

APPARATUS AND PROCEDURE

The apparatus used is shown in Fig. 1. The flame used was of the Bunsen type, and was obtained by burning a mixture of natural gas, air, and spray from a salt solution. The burner (*B*) consisted of 16 quartz tubes, arranged in three rows and cemented into a brass base. The air and gas were mixed in a Guoy sprayer (*S*). Air came from a compressed air supply, which gave a fairly constant pressure of 10 cm of mercury. To exclude any error that might arise from evaporation of the salt solution the air and gas were bubbled through water in large carboys (*C*). The carboys also served in smoothing out pressure irregularities.

The pressure of the natural gas was held constant by a pressure regulator (*R*) similar to that used by H. A. Wilson.[4] When the gas pressure mounted above the steady value desired, the inverted beaker (*F*) rose, and the mercury in the valve (*D*) closed the supply tube. When the pressure subsided to its normal value the supply tube was again opened. The pressure output of the regulator was adjusted by varying a weight (*W*). The pressure used was 1 cm of water. The salt solution was introduced through a tube in the bottom of the sprayer. In this way the level of the solution inside the sprayer was kept constant.

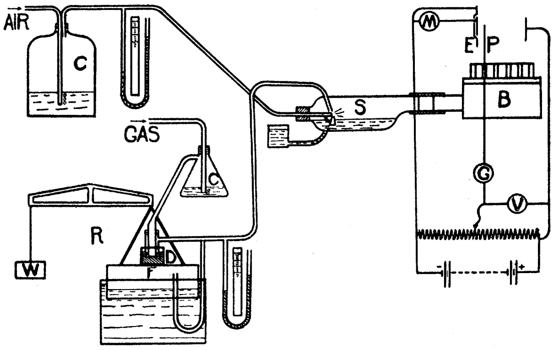

Fig. 1. Diagram of apparatus and electrical connections.

The distribution of potential in the flame was determined by means of a very small platinum-rhodium wire (*P*), encased, except for a tip of about 0.5 mm, in a quartz tube. This tube was drawn down to a very small diameter at the tip, and was mounted on a support with an adjustable vernier scale, not shown in the diagram.

Fig. 1 shows the electrical connections. Here, *M* is a micro-ammeter, *V* a voltmeter, and *G* a high-sensitivity galvanometer shunted by a 0-50000 ohm variable resistance. The negative electrode (*E*) was a circular disk made of sheet platinum of area 1.86 sq. cm. A guard-ring of the same material shielded this electrode at sides and back, so that the current density is given by the ratio of the total current, recorded by the micro-ammeter, to the area of the front of the electrode. The other electrode was a spiral of platinum wire, about 4 cm from the first. An optical pyrometer gave the temperature of the cathode to be 1200°K, and the probe's highest temperature was 1550°K.

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[4] H. A. Wilson, Phys. Rev. **3,** 375 (1914).

The experimental procedure consisted in observing the potential difference between the probe and the anode when the slider carrying the probe was set so that the probe current was zero. The probe is assumed to be at the same potential as the flame gases very near its tip. Thus, with constant potential and current between the two electrodes, the potential of the flame at any distance from the cathode could be obtained. By plotting the probe potential against its distance from the cathode, the thickness of the sheath around the cathode could be obtained. This is x_2; knowing the current and the potential at x_2, k_1 can be calculated.

EXPERIMENTS

I. *Variation of the mobility with the concentration.* Solutions of KCl were sprayed into the flame, and measurements of the current, the sheath thickness, and the potential difference between the electrodes were made. The potential distribution curves for several concentrations are shown in Fig. 2. One volt was taken as the potential at the edge of the sheath, since at about this reading the potential began to increase very rapidly as the probe approached the cathode. The results are shown in Table I; k is the solution concentration, x_2 the sheath thickness, I the total current, and V_2 the potential drop across the sheath.

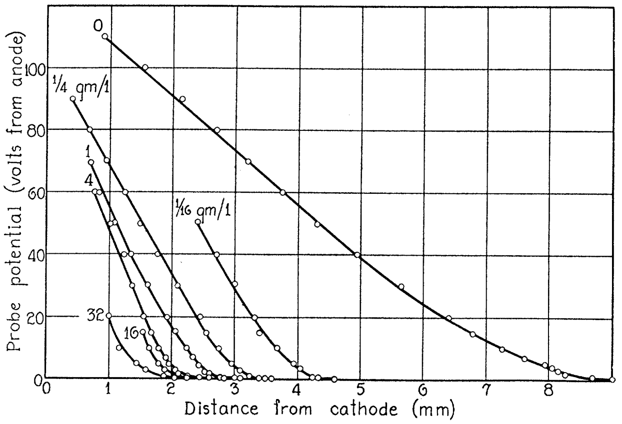

Fig. 2. Potential distribution in flame for several concentrations of KCl.

TABLE I. *Current, sheath thickness and potential difference between electrodes for several concentrations of KCl*

k gm/l	x_2 cm	V_2 volts	$I \times 10^6$ amps	$10^{12} \times I x_2^3 / V_2^2$
0	0.87	132	0.146	5.52
1/16	0.425	139	1.35	5.36
1/4	0.33	130.5	2.7	5.70
1	0.27	132	5.0	5.68
4	0.225	125	8.0	5.83
16	0.21	142	13.0	5.94
32	0.185	142	19.0	5.94

If a value be assumed for m it is possible to calculate k_1, the mobility of the positive ions, from these results. If $m=1$, $k_1=32\pi i x_2^3/(75\,V_2^2)$; i was taken to be the total current divided by the area of the electrode. Thus the mobility of the positive flame ions is 3.5 cm per sec. for one volt per cm (this is for distilled water sprayed into the flame). The mean of the other results, for $k=1/16$ to 32 gms per liter, gives $k_1=3.7$ cm per sec. This difference is well within the range of experimental error, as is all the variation in the mobility with the concentration.

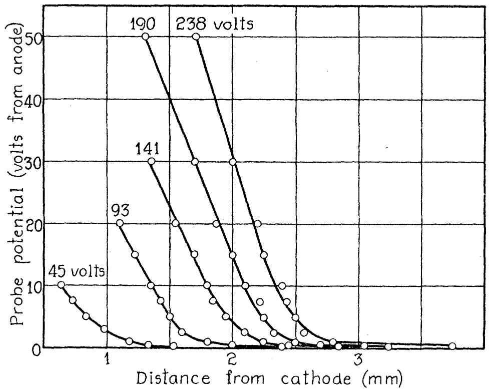

Fig. 3. Potential distribution in flame for several differences of potential between electrodes.

II. *Variation of mobility with potential.* A solution of KCl, concentration 4 gm per liter, was sprayed into the flame, and a set of readings of I, x_2, and V_2 was made for potential differences between the electrodes from 45 to 235 volts. X was obtained as has been explained previously; the potential distribution curves are shown in Fig. 3. The results are shown in Table II.

TABLE II. *Current and sheath thickness for various applied potentials in a KCl flame, concentration 4 gm/liter*

x_2 cm	V_2 volts	$I\times10^6$ amps	$10^{12}\times Ix_2^3/V_2^2$
0.13	44	4.0	4.54
0.19	92	5.7	4.62
0.24	140	7.3	5.15
0.265	188	9.7	5.11
0.29	236	12.5	5.47

In these cases the sheath thicknesses were arrived at by the shapes of the curves; and the total potential less the probe potential at the edge of the sheath was taken as V_2.

The increase of mobility with the potential is shown to be small, if it exists at all. The mobility indicated in each case can be calculated, assuming $m=1$, by the following relation: $k_1=6.4845\times10^{11}\times Ix_2^3/V_2^2$ cm per sec. for one volt per cm. I is in amps, x_2 in cms, and V_2 in volts.

III. *Variation of mobility with nature of salt sprayed.* Solutions of RbCl and CsCl were sprayed into the flame, and their mobilities compared with those obtained for KCl. The results are shown in Table III.

TABLE III. *Sheath thickness and currents for flames sprayed with CsCl and RbCl*

Salt	x_2 cm	$I\times 10^6$ amps	V_2 volts	$10^{12}\times Ix_2^3/V_2^2$
CsCl	0.22	10.0	138	5.59
RbCl	0.265	5.2	139	5.08

The mean value for all the trials for KCl is about $Ix_2^3/V_2^2=5.4$; so there seems no reason to doubt that the positive flame-ions of all these salts have the same mobility.

The value of the calculated mobility depends on m thus: $k_1=32\pi ix_2^3/[(m+4)^2(m+2)V_2^2]$. Taking the mean value of Ix_2^3/V_2^2 equal to 5.4, k_1 was calculated for several values of m. The results are shown in Table IV.

TABLE IV. *Mobility of positive ions of Rb, Cs and K in flames*

m	$(m+4)^2(m+2)$	k_1(cm/sec per volt/cm)
0	32	8.2
1	75	3.5
2	144	1.8
3	245	1.07

It is seen that by taking m equal to 2 or 3, the calculated value of k_1 comes into better agreement with $k_1=1$. For either of these values of m, $q(1-x/x_1)^m=q-an_1n_2$ is continuous at $x=x_1$.

The mean value of the mobility of the positive ions of Rb, Cs, and K salts in flames is about 1.8 cms per sec. for one volt per cm, calculated for $m=2$. It is believed that the value of m is greater than one, for then troublesome discontinuities disappear, and the calculated mobility is in reasonably good agreement with the results of other investigators.

There is some indication that the mobility increases as the electric intensity increases, but the experiments give no proof of a change of mobility with the concentration of the salt.

I wish to thank Dr. H. A. Wilson for suggesting this problem, and Dr. C. W. Heaps for valuable criticisms and suggestions.

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